

Preparation of adsorbents made from sewage sludges for adsorption of organic materials from wastewater

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Abstract

The carbon-bearing adsorbents were prepared from biochemical and surplus sludges by physical activation and chemical activation. The results indicated that the adsorbents made by way of chemical activation were better, with the optimum activator being complex of $ZnCl_2$ and H_2SO_4 . Moreover, the optimum preparation conditions were concentration of two activators 5 mol/L (the ratio of $ZnCl_2$ and H_2SO_4 was 2:1), at the activating temperature of 550 °C, in the proportion of solid to liquid 1:2.5, in a period of 2 h. Contrasting the active carbon, the carbon-bearing adsorbents were characterized by X-ray diffraction (XRD), energy dispersive X-ray spectrometer (EDS), scanning electron microscope (SEM), BET and BJH. By application of those adsorbents to treatment of wastewater of urban, the treatment effect of the carbon-bearing adsorbents were better than the active carbon. On the condition that the concentration was 0.5%, the COD, P and chromaticity color removal rates of carbon-bearing adsorbent made from the biochemical sludge of sewage were higher, which were 79.1, 98.3 and 87.5%, respectively, and the dynamic adsorption capacity was 47.8 mg/g.

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1. Introduction

Growing concerns about the environment have resulted in the development of new environmentally technologies, new materials, and new ways to reduce and minimize wastes [1–4]. One of the wastes produced by contemporary society in abundant quantity is municipal sewage sludge. Activated sludge process is the high class processing technique that deals with wastewater of urban and industry, which produces a great deal of surplus sludge at the same time. Various methods have been used to dispose of or utilize municipal sewage sludge, including incineration, land filling, road surfacing, conversion to fertilizer, compression into building blocks, et al [5–8]. Continuous increase in the quantity of sludge produced, call out for efficient and environmentally friendly approaches to its utilization. One of these is conversion of sewage sludge into adsorbents. Because the biochemical sludges contain the carbon more, can be made into the cheap adsorbents of price through the chemistry path, many

researches focused on making use of sludges to prepare the carbon-bearing adsorbents by different activating ways [9–11], and application of the adsorbents to the removal of organics in the final stages of water cleaning and to the removal of chlorinated organics [12,13]. Sewage-sludge-derived adsorbents have been also tested for their ability to remove acidic gases such as sulfur dioxide and hydrogen sulfide from air streams [14–16]. Physical activation can enhance the adsorbents' pore structure due to a partial oxidation of the carbonized materials by gases such as CO/CO_2 or steam, and it is useful for the formation of micropore structure [17]. Chemical activation involves impregnation of the raw materials with chemicals such as phosphoric acid [18], potassium hydroxide [19], and zinc chloride [20,21]. Corresponding the iodine values of the carbon-bearing adsorbents made by chemical activation and physical activation are about 400 and 10 mg/g, and the specific surface areas are about 100 and 50 m^2/g , respectively.

In this study, three kinds of carbon-bearing adsorbents were prepared by making use of biochemical sludges and surplus sludge as raw materials, characterized with various techniques, and applied of those adsorbents to treatment of wastewater of urban.

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2. Materials and methods

2.1. Preparation of carbon-bearing adsorbents

The materials were biochemical sludge and surplus sludge from the sewage treatment plant (BS and SS), and biochemical sludge from the petrochemistry company (PS). The stainless steel tube was placed in a SK-2-10 electric stove, and the dry sludge was packed to fill quantity about 30 g. The pyrolysis must be protected by the nitrogen atmosphere (the flow was about 20 L/h), heating rate was kept at 5 °C/min. The following activation methods were employed for preparing the carbon-bearing adsorbents.

2.1.1. The physical activation

The sludge sample was first dried at 103 °C for 24 h, then pyrolyzed at 550 °C for 2 h. The carbonization product was opened into the water vapor (the flow was maintained at 12 L/h), the temperature was kept at 550 °C to activate for 2 h. The product was dried at 103 °C for 24 h, crushed and sieved into a uniform size of 1 mm approximately.

2.1.2. The chemical activation

The sludge sample was first dried at 103 °C for 24 h, then the dry sludge was impregnated into activator for 24 h at room temperature, the complex of ZnCl₂ and H₂SO₄ was used as optimum activating agent in different ratios of 3:1, 2:1, 1:1, 1:2 and 1:3 by volume proportions. After the supernatant liquid was removed, it was dried at 103 °C for 24 h and subsequently pyrolyzed at 550 °C for 2 h. Following pyrolysis, the product was washed with 500 mL of 3 mol/L HCl to remove acid-soluble inorganic matter, and then washed with distilled water until the pH of leached solution was 5–6 to remove excess acid, and dried at 103 °C for 24 h, crushed and sieved into a uniform size of 1 mm approximately.

2.1.3. The physical and chemical activation

The chemically activated, dried and crushed sludge was heated for 2 h at 550 °C in a mixture of nitrogen atmosphere and water vapor, then dried for 24 h.

2.2. Analytical methods

The water content were the weight loss of the three sludges by heating at 150 °C for 2 h. The content of volatile matter and ash were evaluated using thermal analysis. The thermal decomposition process of the dry sludges were investigated by simultaneous thermogravimetric and differential thermal analysis (TG-DTA) using a Shimadzu TG-DTA-50 thermal analyzer from room temperature to 800 °C, with a heating rate of 20 °C/min in nitrogen atmosphere, and the elements content of sludges were analyzed by using a Rapid Element analyzer.

A number of authors have used iodine as adsorbate in the characterization of sludge-derived-adsorbent, the iodine value of the carbon-bearing adsorbents and the active carbon (AC) were measured by titrimetric method [22,23]; production rate was calculated by the weight method (weight specific value of

product and experiment dry sludge). The BET surface areas and BJH pore distributions were measured on a Beckman Coulter SA3100 Plus instrument using N₂ adsorption at –196 °C. The scanning electron microscope (SEM) images were obtained on LEO-1530VP scanning electron microscope. X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advance X-ray diffraction using Cu K α radiation. The main elements content were analyzed by energy dispersive X-ray spectrometer (EDS).

The water quality parameters measured were chemical oxygen demand (COD, closed reflux, titrimetric method), total and *ortho*-phosphate *P* (*P*_{tot} and PO₄-*P*, respectively) (ascorbic acid method), and the chromaticity color (colorimetric method). They were tested in accordance with the standard methods [24].

2.3. The wastewater adsorption experiment

The static adsorption experiment was performed to determine the optimum concentration of adsorbents. The adsorbents of 0.1–0.9 g were added to the wastewater of 100 mL relatively, and put to mix quickly on a stirring mixer for 10 min at room temperature. The wastewater was filtrated soon, and the COD and *P* value were measured. The COD, *P* and chromaticity color removal rates were calculated.

The dynamic adsorption test was carried out to evaluate the capacity of adsorbents for organics removal. Adsorbent samples were packed into the glass column (length 23.5 cm, diameter 1.2 cm, bed volume 5 cm³), then wastewater was passed through the column of adsorbents at room temperature with the flow of 40 mL/h. The COD values of different period were measured, and the dynamic breakthrough curves were made. The breakthrough COD value was 60 mg/L, and the adsorption capacities in terms of gram of COD per gram of adsorbent were calculated by integration of the area above the breakthrough curves and from the COD value of the inlet wastewater, flow rate, breakthrough time, and mass of adsorbents.

All adsorption tests were carried out three times, and each figure or table point representing the average of three readings.

3. Results and discussion

3.1. The abilities of the carbon-bearing adsorbents

Table 1 shows the properties of biochemical and surplus sludges. From the Table 1 we can know that the sludges have high water content and low fixed carbon content, and the volatile matter content of biochemical sludges are high. Based on the results of previous studies, the total organic matter in the biochemical sludges are about 60% (wt.%) and the ash are about

Table 1
Properties of different sludges (wt.%)

Sludge	Water	Fixed carbon	Volatile matter	Ash
BS	95.0	17.4	53.5	29.1
PS	84.3	16.0	50.0	34.0
SS	93.0	15.1	34.2	50.7

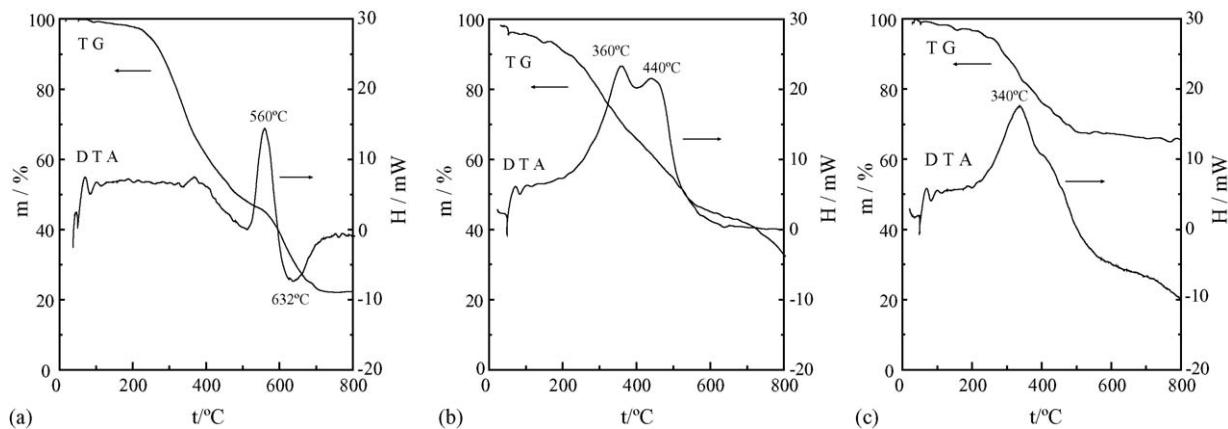


Fig. 1. Thermal analysis curves of (a) BS; (b) PS; (c) SS.

Table 2
Content of N, H and heavy metal elements of different sludges (wt.%)

Sludge	N	H	Ni	Pb	Cr	Cd	Cu
BS	1.08	0.23	0.1	0.04	0.2	0.0004	0.02
PS	1.60	0.63	0.05	0.002	0.06	0.001	0.03
SS	2.72	1.79	0.07	0.005	0.2	0.0005	0.02

30% [25,26], so the fixed carbon content are relatively low. The elements content are shown in Table 2, showing that sludges have lower N, H and heavy metal elements, which is agreement with the previous studies [27].

The result of the thermal analysis of the dry sludges are presented in Fig. 1(a)–(c). The TG and DTA curves show that the stage of weight loss of the three dry sludges occurred at approximately 200–600 °C by TG curves, at the corresponding temperature well-defined exothermal peak in DTA curves, associating with the gradual volatilisation of part of the organic materials contained within the sludges. The residue after heating to 800 °C are the ash, and about 80% of the ash are consist of inorganic oxides such as Al₂O₃, SiO₂, and Fe₂O₃ [28].

Adopt different raw materials of BS, PS, SS and activations to prepare carbon-bearing adsorbents, the iodine values and production rates are shown in Table 3. It is clearly seen that

the abilities of the products prepared by the chemical activation of different sludges are better, and the iodine values of the biochemical-sludges-derived adsorbents are higher.

Under the same conditions (the concentration of activators: 5 mol/L, proportion of solid to liquid: 1 g:2.5 mL, activating temperature: 550 °C, activating time: 2 h), the screening results of different activators are given in Table 4. For

Table 4
The effect of different activators on the adsorbent abilities

Sludge	Activator	Iodine value (mg/g)	Production rate (wt.%)
BS	ZnCl ₂	432.22	45.9
	H ₂ SO ₄	83.50	38.9
	KOH	2.90	31.8
	FeSO ₄	2.34	30.8
PS	ZnCl ₂	403.79	70.8
	H ₂ SO ₄	79.85	65.3
	KOH	1.36	54.1
	FeSO ₄	1.99	50.1
SS	ZnCl ₂	332.09	51.1
	H ₂ SO ₄	53.62	64.3
	KOH	1.20	52.4
	FeSO ₄	2.97	49.8

Table 3
The effect of different raw materials and activations on the adsorbent abilities

Activation	Sludge	Iodine value (mg/g)	Production rate (wt.%)
The carbonization	BS	8.80	42.9
The physical activation		10.39	41.6
The chemical activation		432.22	45.9
The physical and chemical activation		333.81	43.8
The carbonization	PS	6.90	66.3
The physical activation		11.59	62.3
The chemical activation		403.79	70.8
The physical and chemical activation		308.95	68.3
The carbonization	SS	5.50	50.5
The physical activation		13.15	50.4
The chemical activation		332.09	51.1
The physical and chemical activation		277.81	53.8
	AC	473.16	—

Table 5

The effect of the ratio of complex activator on the adsorbent abilities

Sludge	ZnCl ₂ :H ₂ SO ₄ (V:V)	Iodine value (mg/g)	Production rate (wt.%)
BS	3:1	489.64	52.9
	2:1	596.58	51.8
	1:1	349.86	45.9
	1:2	318.31	41.5
	1:3	249.62	38.6
PS	3:1	375.63	68.7
	2:1	438.31	67.5
	1:1	213.56	63.4
	1:2	179.63	60.8
	1:3	123.45	56.8
SS	3:1	309.60	88.1
	2:1	488.02	86.6
	1:1	296.30	76.9
	1:2	238.96	72.4
	1:3	188.28	68.6

all the sludges, the activators of ZnCl₂ and H₂SO₄ are better.

Based on the screening results, 5 mol/L ZnCl₂ and H₂SO₄ of the same concentration reply to go together to activate. Table 5 shows that the abilities of the carbon-bearing adsorbents prepared by complex of ZnCl₂ and H₂SO₄ are better, and the optimum ratio of ZnCl₂ and H₂SO₄ is 2:1.

By taking surplus sludge as raw material, the influential factors on the adsorbents abilities are studied. Orthogonal design of L₉(3⁴) is adopted in the orthogonal experiment. Table 6 shows the result, from the analysis of variance (*R* and *S*) can know that the main influential factor is activating temperature, sub-

sequent is activator concentration, the effect of proportion of solid to liquid and activating time are relatively littler. The optimum preparation conditions are concentration of two activators are 5 mol/L (the ratio of ZnCl₂ and H₂SO₄ is 2:1), activating temperature is 550 °C, the proportion of solid to liquid is 1:2.5, activating time is 2 h. The experiment under the same conditions are repeated for five times, and the iodine values of all the activated products are 480–488 mg/g.

3.2. The characterization of the carbon-bearing adsorbents

The carbon-bearing adsorbents made from BS, PS and SS by the chemical activation with the activator of complex of ZnCl₂ and H₂SO₄ are designated as BSC, PSC and SSC. The specific surface area and pore structure of the carbon-bearing adsorbents

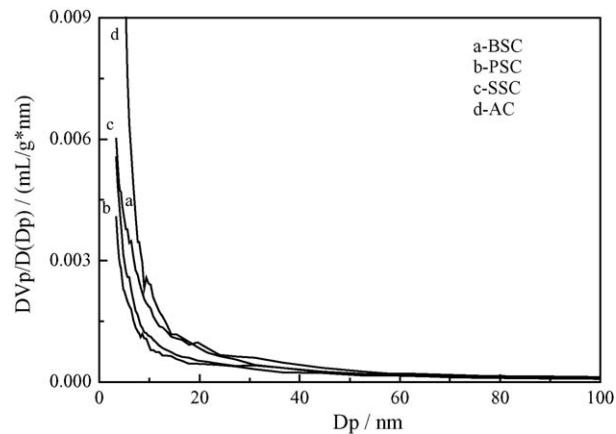


Fig. 2. Pore distribution curves of adsorbents.

Table 6

Orthogonal design of chemical activation

Order number	C (mol/L)	T (°C)	D (1:X)	T (h)	Iodine value (mg/g)
1	3	450	2.5	1	165.17
2	3	550	4.0	2	286.34
3	3	650	5.5	3	282.01
4	5	450	4.0	3	221.18
5	5	550	5.5	1	226.43
6	5	650	2.5	2	347.60
7	7	450	5.5	2	195.37
8	7	550	2.5	3	464.77
9	7	650	4.0	1	431.59
K ₁	244.51	193.91	325.85	274.40	—
K ₂	265.07	325.85	313.04	276.44	—
K ₃	363.91	353.73	234.60	322.65	—
R	119.40	159.82	91.25	48.25	—
S	24449.35	43730.39	14641.23	4468.85	—

Table 7

Pore characteristics of adsorbents

Adsorbent	Pore volume (mL/g)	Micropore volume (mL/g)	Average pore diameter (nm)	Specific surface area (m ² /g)
BSC	0.07	0.02	38.81	114.53
PSC	0.06	0.02	34.89	128.96
SSC	0.05	0.02	32.51	144.47
AC	0.10	0.07	18.27	633.39

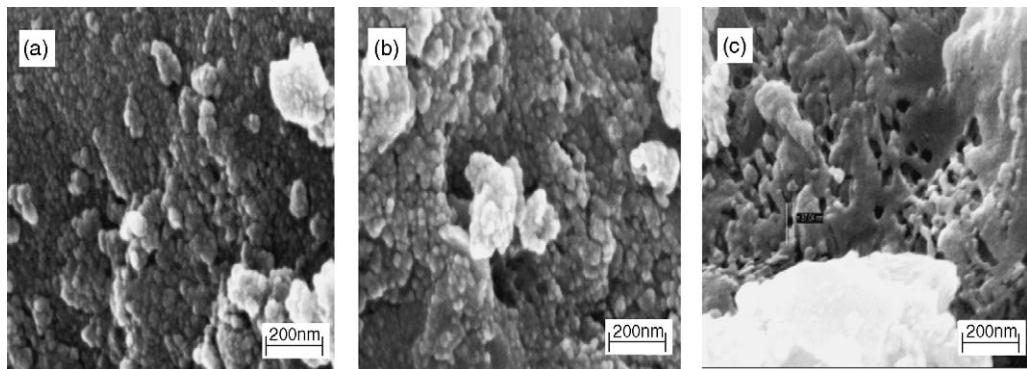


Fig. 3. SEM images of adsorbents of (a) BSC; (b) PSC; (c) SSC.

and the active carbon are measured, as a result seeing the Table 7. Fig. 2(a)–(d) shows the pore path distribute curves. The pore path distribute of the active carbon is more narrow, and is mainly cellular structure. The pore path distribute of the carbon-bearing adsorbents are wider, and are mainly transition pore structure, corresponding the specific surface areas are lower than the active carbon.

Many researches [29,30] have found that the synergistic action of the complex activator accelerates the activation process of dewatering, condensation, wetting and expansion, and making the carbon-bearing chemical compound within the sludges condense to non-volatile carbon. It's activation effect is better than the single activator, and the transition pore structure of the activated products are more flourishing, corresponding the abilities of the carbon-bearing adsorbents increase greatly.

Fig. 3(a)–(c) shows the SEM images of the carbon-bearing adsorbents, and the pore structure of the carbon-bearing adsorbents are heterogeneous, and are mainly transition pore structure. The SEM images are anastomosing with the measurement result of the pore structure.

Fig. 4(a)–(d) shows the X-ray diffraction diagrams of adsorbents, the carbon-bearing adsorbents are all hexagonal crystal structure, and the active carbon is adventitious carbon. The carbon content of BSC and PSC are relatively higher.

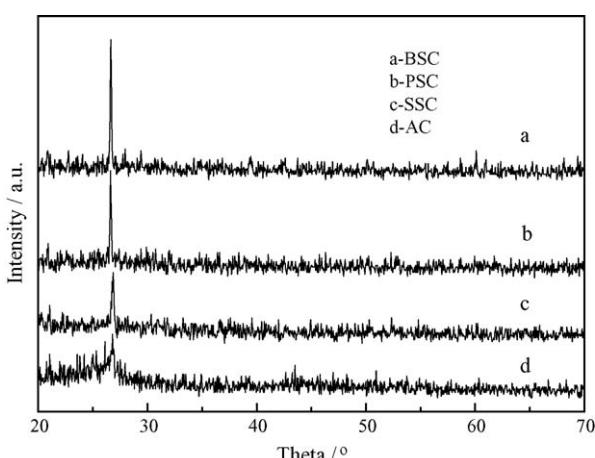


Fig. 4. X-ray diffraction diagrams of adsorbents.

EDS was performed to confirm the composition of the carbon-bearing adsorbents. The images of the three carbon-bearing adsorbents and the active carbon are presented in Fig. 5, and the elements content are shown in Table 8, showing that the carbon-bearing adsorbents are composed of carbon and some inorganic compounds such as zinc and aluminium salts and silica.

3.3. Application in treatment of wastewater of urban

In static adsorption experiment, the effect of concentration of adsorbents sees the Fig. 6. It can be seen that the adsorbents concentration has important effect on the adsorption of the organic substances in wastewater treatment, and the removal rate of COD increase with the rise of the adsorbents concentration, and increase gently after the concentration of 0.5%. On the condition that the carbon-bearing adsorbents concentration is 0.5%, contrast the active carbon and make use of the carbon-bearing adsorbents to treatment of wastewater (pH: 8.5, COD value: 302.4 mg/L, *P* value: 19.7 mg/L), the COD and *P* value of the wastewater of urban are not very high. Table 9 shows that under the same processing condition the adsorption effect to organic materials and *P* and chromaticity color of wastewater of the carbon-bearing adsorbents are better than the active carbon, and the biochemical-sludge-derived adsorbents perform much better than the adsorbent made from surplus sludge.

As indicated elsewhere [31,32], the possibilities of granular activated carbon was normally investigated using a dynamic state experiment. In dynamic adsorption experiment, the breakthrough curves for our samples are shown in Fig. 7. The calculated capacities are summarized in Table 10. It is clearly seen that the capacities of the sludge-derived adsorbents are more than the active carbon, and the breakthrough time of the active carbon decrease greatly comparing to the sludge-derived adsorbents. The treatment effect of adsorbents made from the biochemical sludges are better, which is anastomosing with the result of static adsorption experiment.

Because the sludge-derived adsorbents are mainly transition pore structure, and beneficial to adsorb the big member organic materials, however the active carbon is mainly cellular structure and the velocity of liquid diffusion is slower. The micropore volume of the biochemical-sludges-derived adsorbents are

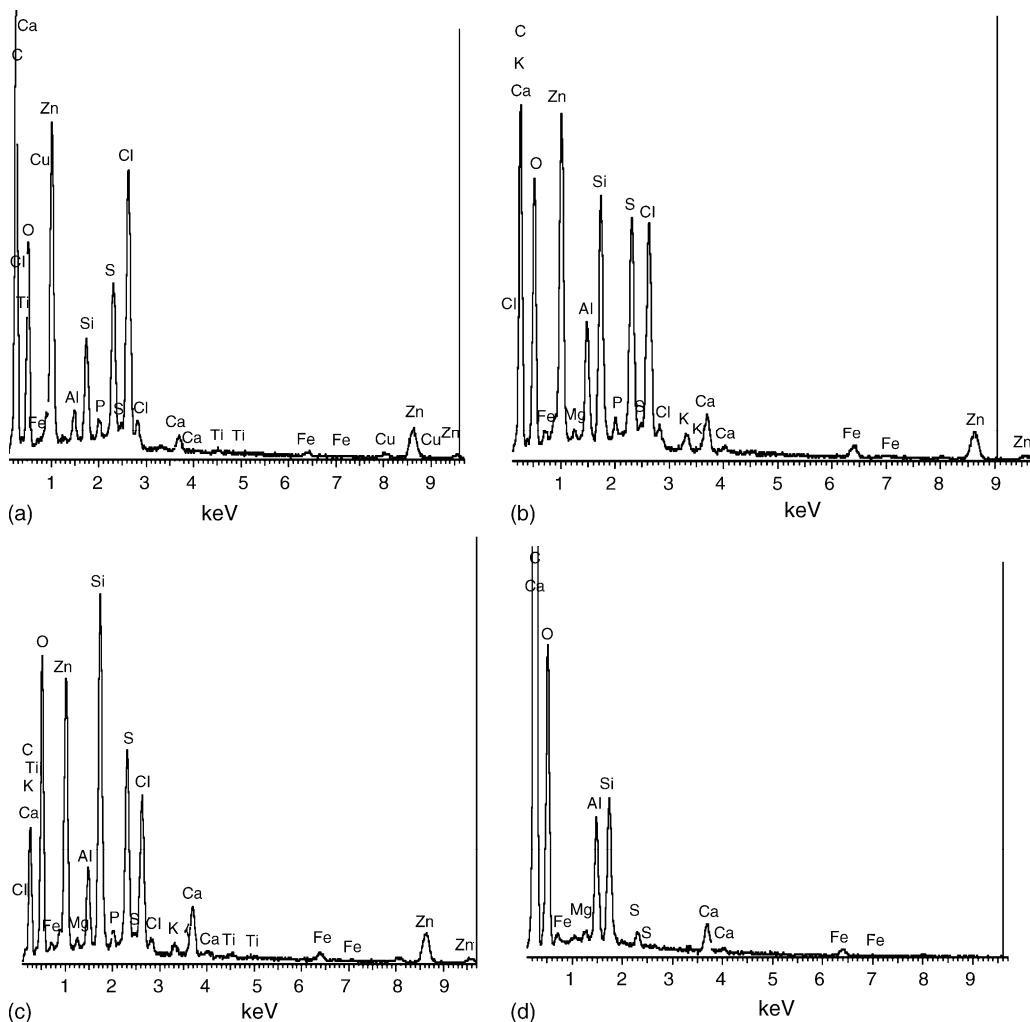


Fig. 5. EDS spectrums of adsorbents of (a) BSC; (b) PSC; (c) SSC; (d) AC.

Table 8
Content of elements of adsorbents (wt.%)

Adsorbent	C	O	Zn	Si	Al	Fe	Ca	Mg	K	Ti	Cl	S	P
BSC	52.5	18.3	12.7	2.1	0.6	0.6	0.6	0	0	0.1	8.1	3.9	0.5
PSC	45.5	20.2	12.5	4.5	2.0	1.5	1.4	0.2	0.5	0	6.1	5.2	0.4
SSC	28.0	27.4	15.1	9.2	1.9	1.4	2.6	0.3	0.5	0.2	6.3	6.5	0.6
AC	70.9	23.0	0	2.2	1.7	0.9	1.0	0.1	0	0	0	0.2	0

Table 9
Treatment effect of adsorbents to wastewater

Adsorbent	BSC	PSC	SSC	AC
pH value	7.1	7.4	7.2	8.7
COD value (mg/L)	63.2	74.2	96.2	178.7
COD removal rate (%)	79.1	75.5	68.2	40.9
P value (mg/L)	0.3	0.3	0.7	17.7
P removal rate (%)	98.3	98.3	96.6	10.2
Chromaticity color removal rate (%)	87.5	87.5	87.5	75.0

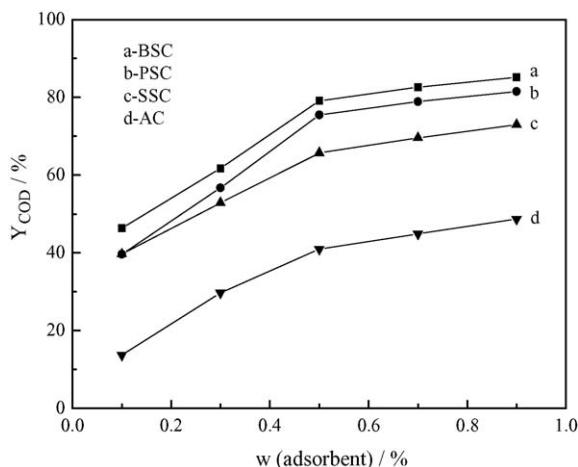


Fig. 6. Effect of the adsorbents concentration to COD removal rate.

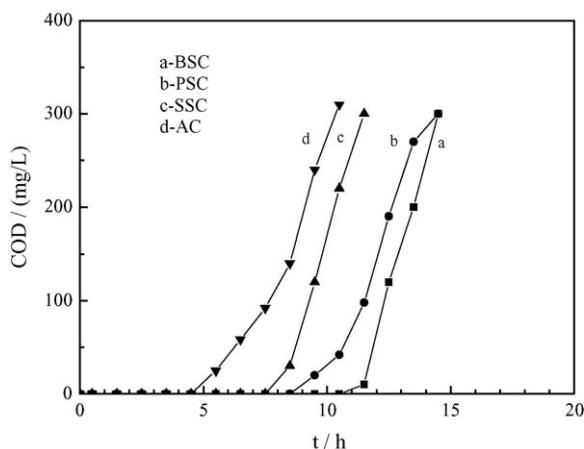


Fig. 7. Breakthrough curves of the adsorbents.

Table 10
The capacity and breakthrough time of adsorbents

Adsorbent	BSC	PSC	SSC	AC
Breakthrough time (h)	12	11	9	6
Adsorption capacity (mg/g)	47.8	45.6	41.2	30.8

lower, corresponding the specific surface areas are lower than the surplus-sludge-derived adsorbent, but the flourishing big and transition pore structure are more favorable to adsorb the organics, in addition the content of carbon are higher, so the treatment effect are better than the surplus-sludge-derived adsorbent.

4. Conclusions

The following conclusions can be made from the present experiment:

- (1) The carbon-bearing adsorbents can be prepared from biochemical and surplus sludges by chemical activation. The optimum activator is complex of $ZnCl_2$ and H_2SO_4 , and the optimum preparation conditions are concentration of two activators 5 mol/L (the ratio of $ZnCl_2$ and H_2SO_4 is 2:1),

at the activating temperature of 550 °C, in the proportion of solid to liquid 1:2.5, in a period of 2 h.

- (2) The pore path distributes of the carbon-bearing adsorbents are wider, and are mainly transition pore structure, corresponding the specific surface areas are lower than the active carbon. They are made of carbon and some inorganic compounds, and are all hexagonal crystal structure.
- (3) In static adsorption, as the concentration of the carbon-bearing adsorbents are 0.5%, the COD removal rates of adsorbents of BSC, PSC, and SSC are 79.1, 75.5, and 68.2%, the removal rates of P are 98.3, 98.3, and 96.6%, respectively, and the chromaticity color removal rates are all 87.5%. The treatment effect to wastewater of the sludge-derived adsorbents are better than the active carbon.
- (4) The treatment effect of the carbon-bearing adsorbents made from the biochemical sludges are better in dynamic adsorption, the adsorption abilities of the sludge-derived adsorbents are better than the active carbon, the adsorption capacities of adsorbents of BSC, PSC, and SSC are 47.8, 45.6, and 41.2 mg/g, respectively.

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References

- [1] L.H. Cecil, M. Peter, N. Juraj, Sludge management in highly urbanized areas, *Water Sci. Technol.* 34 (1996) 517–524.
- [2] S. Jeyaseelan, G.Q. Lu, Development of adsorbent/catalyst from municipal wastewater sludge, *Water Sci. Technol.* 34 (1996) 499–505.
- [3] R.F. Hejazi, T. Husain, F.I. Khan, Landfarming operation of oily sludge in arid region-human health risk assessment, *J. Hazard. Mater.* B99 (2003) 287–302.
- [4] B. Mrayyan, M.N. Battikhi, Biodegradation of total organic carbons (TOC) in Jordanian petroleum sludge, *J. Hazard. Mater.* B120 (2005) 127–134.
- [5] G.B. Willson, D. Dalmat, Sewage sludge composting in the USA, *Bio-cycle* 24 (1983) 20–23.
- [6] N. Goldstein, Biocycle survey sewage sludge composting as a medium amendment for chrysanthemum culture, *J. Am. Soc. Hort. Sci.* 100 (1985) 213–216.
- [7] W.F. Hu, Synthesis of poly(3-hydroxybutyrate-co-hydroxyvalerate) from activated sludge, *Biotechnol. Lett.* 19 (1997) 695–698.
- [8] R.K. Nasrin, C. Marta, S. Giselle, Production of micro-and mesoporous activated carbon from paper mill sludge, *Carbon* 38 (2000) 1905–1915.
- [9] B. Andrey, B. Svetlana, C.L. David, J. Teresa, Sewage sludge-derived materials as efficient adsorbents for removal of hydrogen sulfide, *Environ. Sci. Technol.* 35 (2001) 1537–1543.
- [10] B. Andrey, J.B. Teresa, L. David, Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer, *Carbon* 39 (2001) 1971–1979.
- [11] C. Xiaoge, S. Jeyaseelan, N. Graham, Physical and chemical properties study of the activated carbon made from sewage sludge, *Waste Manag.* 22 (2002) 755–760.
- [12] B. Huasong, Z. Zhongyan, Use of sewage sludge for manufacturing adsorbent, *Environ. Sci.* 20 (1999) 56–59.
- [13] M. Otero, F. Rozada, L.F. Calvo, Elimination of organic water pollutants using adsorbents obtained from sewage sludge, *Dyes Pigments* 57 (2003) 55–65.

- [14] B. Rubio, M.T. Izquierdo, Low cost adsorbents for low temperature cleaning of flue gases, *Fuel* 77 (1998) 631–637.
- [15] B. Andrey, C.L. David, J.B. Teresa, H₂S adsorption/oxidation on adsorbents obtained from pyrolysis of sewage-sludge-derived fertilizer using zinc chloride activation, *Ind. Eng. Chem. Res.* 40 (2001) 3502–3510.
- [16] B. Svetlana, B. Andrey, C.L. David, Adsorption of SO₂ on sewage sludge-derived materials, *Environ. Sci. Technol.* 35 (2001) 3263–3269.
- [17] F. Rodriguez-Reinoso, M. Molina-Sabio, M.T. Gonzalez, The use of stream and CO₂ as activating agents in the preparation of activated carbons, *Carbon* 33 (1995) 15–23.
- [18] M. Molina-Sabio, F. Rodriguez-Reinoso, F. Caturia, M.J. Selles, Porosity in granular carbons activated with phosphoric acid, *Carbon* 33 (1995) 1105–1113.
- [19] W. Fengchen, T. Ruling, J. Rueyshin, Preparation of highly microporous carbons from fir wood by KOH activation for adsorption of dyes and phenols from water, *Sep. Purif. Technol.* 47 (2005) 10–19.
- [20] T.H. Nabarawy, M.R. Mostafa, A.M. Youssef, Activated carbons tailored to remove different pollutants from gas stream and from solution, *Adsorpt. Sci. Technol.* 15 (1997) 61–68.
- [21] M.A. Hourieh, M.N. Alaya, A.M. Youssef, Carbon dioxide adsorption and decolorizing power of activated carbons prepared from pistachio shells, *Adsorpt. Sci. Technol.* 15 (1997) 300–303.
- [22] Z. Yunbo, W. Xianxun, Z. Guangming, Z. Dejian, Z. Kaifeng, Study of adsorbent derived from sewage sludge for the removal of Cd²⁺, Ni²⁺ in aqueous solutions, *Sep. Purif. Technol.* 38 (2004) 191–196.
- [23] Z. Yunbo, W. Xianxun, Z. Guangming, Z. Dejian, Z. Kaifeng, Effects of metallic derivatives in adsorbent derived from sewage sludge on adsorption of sulfur dioxide, *J. Cent. South. Univ. Technol.* 11 (2004) 55–58.
- [24] APHA-AWWA-WEF, Standard Methods for the Examination of Water and Wastewater, 19th Ed., American Public Health Association, Washington, USA, 1995.
- [25] P.C. Chiang, J.H. You, Use of sewage sludge for manufacturing adsorbents, *J. Chem. Eng.* 65 (1987) 922–930.
- [26] G.Q. Lu, D.D. Lau, Characterization of sewage sludge-derived adsorbents for H₂S removal. Part 2. Surface and pore structural evaluation in chemical activation, *Gas Sep. Purif.* 10 (1996) 103–111.
- [27] M. Helena Lopes, P. Abelha, N. Lapa, J.S. Oliveira, I. Cabrita, I. Gulyurtlu, The behaviour of ashes and heavy metals during the co-combustion of sewage sludges in a fluidised bed, *Waste Manag.* 23 (2003) 859–870.
- [28] G.Q. Lu, J.F. Low, C.Y. Liu, Surface area development of sewage sludge during pyrolysis, *Fuel* 74 (1995) 244–248.
- [29] L.F. Calvo, M. Otero, A. Moran, A.I. Garcia, Upgrading sewage sludges for adsorbent preparation by different treatments, *Bioresour. Technol.* 80 (2001) 143–148.
- [30] N. Kojima, A. Mitomo, Y. Itaya, M. Shigekatsu, Y. Shuchi, Adsorption removal of pollutants by active cokes produced from sludge in the energy recycle process of wastes, *Waste Manag.* 22 (2002) 399–404.
- [31] M. Qinglan, W. Zengzhang, L. Minmin, X. Bingshe, Study of activated carbon applied to water treatment, *New Carbon Mater.* 17 (2002) 59–61.
- [32] D.O. Huett, S.G. Morris, G. Smith, N. Hunt, Nitrogen and phosphorus removal from plant nursery runoff in vegetated and unvegetated subsurface flow wetlands, *Water Res.* 39 (2005) 3259–3272.



Removal performance of phosphate from aqueous solution using a high-capacity sewage sludge-based adsorbent

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ABSTRACT

Excessive phosphate always leads to eutrophication in water bodies, which has been paid much attention in recent years. In this work, sewage sludge derived adsorbent was used to remove phosphate from aqueous solutions with the activation of $ZnSO_4 \cdot 7H_2O$ and H_2SO_4 . The suitable dosages of the activation agents with the production of the carbonized sludge were determined. The adsorption performance was evaluated with different initial phosphate concentrations. The kinetics and isotherms were also discussed. Adsorbent characterization was studied by some analysis methods such as X-ray diffraction (XRD) and FTIR to understand the adsorption mechanism. In addition, the effects of pH, temperature, and adsorbent dosage on phosphate removal were investigated. The maximum phosphate adsorption capacity of the adsorbent was 123.46 mg g^{-1} . The sorption kinetic data had excellent fitness of the pseudo-second-order equation, indicating that the removal process belonged to chemisorption. Under the optimal condition (pH 5.0, temperature 35 °C, adsorbent 0.15 g), more than 99% of 65 mg l^{-1} initial phosphate were removed within 0.5 h. The results suggested that $ZnSO_4 \cdot 7H_2O$ and H_2SO_4 enhanced the phosphate adsorption and the adsorbent had the potential to remove phosphate effectively from aqueous solutions.

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1. Introduction

Recent years have seen growing concerns in environmental pollution along with the rapid development of industry, which leads to the improvement of environmental technologies, materials as well as methods of waste disposal [1]. Wastewater treatment as one of the important aspects in environment protection can be carried out by physicochemical and biological methods [2]. There has been wide application of biological treatment processes which always have high removal efficiencies of pollutants as well as low cost [3]. However, a large amount of municipal sewage sludge is generated since they are inevitable by-products from numerous domestic and industrial wastewater treatment systems [4]. This kind of sludge always contains heavy metals, viruses as well as a variety of microorganisms [5]. Without appropriate disposal, surplus sludge will result in secondary pollution to soil, ground water and air [6]. Conventional treatments of sewage sludge are landfill, incineration, farmland utilization, etc. However, these options have severe drawbacks such as land occupation and pollutants emission, which prompt innovations for beneficial utilization of sewage sludge [7]. One approach to reuse the waste sludge is to convert sewage sludge into adsorbents. This method can not only

reduce the amount of excess activated sludge but also achieve resource utilization, which meets both environmental and economic requirements and saves non-renewable natural resources [8].

The production of carbonized sludge has been popular in recent years. Sludge-derived char has been widely used as adsorbents for the treatment of effluents containing various pollutants such as dyes, heavy metals, and phenol [9–11]. Owing to its porous structure, this kind of material showed satisfactory adsorption performance. In order to improve adsorption capacity of sludge-based adsorbents, several methods have been used to change porosity as well as surface area or to modify surface groups [12]. Sludge-based adsorbents can be activated by physical or chemical processes. Physical activation is carried out by partial gasification agents such as steam, CO_2 , and N_2 , the products of which generally have relatively low surface areas [13,14]. For significantly improving adsorption capacity of the sludge-based materials, the carbonized sludge was prepared with several chemical agents. For instance, a kind of carbonized sludge supported by iron oxide was activated with $ZnCl_2$, which had high adsorption capacity and degradation efficiency when treating biologically pretreated coal gasification wastewater [15]. There were also several reports mentioning sludge carbonization activated with acid such as H_3PO_4 [16]. Although these chemical agents employed for sludge activation had different effects, the final products showed better removal ability of pollutants compared with physically activated adsorbents [17].

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Table 1

Chemical composition of dewatered sewage sludge.

Chemical composition	Concentration (wt%)	Chemical composition	Concentration (wt%)
C	39.05	SiO ₂	35.9
O	29.24	Al ₂ O ₃	11.9
N	0.77	Fe ₂ O ₃	4.344
Al	6.297	P ₂ O ₅	2.2
P	0.962	MgO	0.868
K	1.198	CaO	1.2
Fe	3.038		
Ca	0.86		

The discharge of effluents containing high concentrations of phosphorus has received considerable attention since excessive phosphorus causes eutrophication, which does great harm to ecosystems. In this work, a novel sludge-derived adsorbent was used with phosphate as adsorbates. The adsorption performance of the material was evaluated by the variation of several parameters such as initial phosphate concentration, pH value, temperature as well as dose of adsorbents. Moreover, the kinetics, isotherms and properties of adsorbents were investigated for a better understanding of the phosphate adsorption mechanism. The study was expected to provide a promising alternative in phosphate removal from aqueous solution.

2. Material and methods

2.1. Sludge and reagents

The activated sludge used in this study came from the Shahu municipal wastewater treatment plant in Wuhan, Hubei Province, China. The sewage sludge had been dewatered in the wastewater treatment plant before collection. The dewatered raw sludge was treated by using an oven at 105 °C for 48 h to make its weight constant. The principal chemical compositions of the dried sewage sludge are shown in Table 1. The chemical reagents used in this study such as ZnSO₄·7H₂O, KH₂PO₄ were purchased from the National Medicines Corporation Ltd. of China.

2.2. Adsorbent preparation

After crushing of dried raw sludge, the carbonized sludge was prepared by using zinc sulfate. 10.0 g powder sludge was put into 75 ml deionized water supplied with ZnSO₄·7H₂O ranging from 0.05 to 0.25 mol at intervals of 0.05 mol. The mixture was stirred over 12 h to make it homogenous. Subsequently, the sol-gels were dried at 105 °C for several days until the weight was constant. The dried paste was then placed into a programmable electric furnace and heated for 2 h at 500 °C. The biomass was cooled to room temperature followed by ground to reach particle size less than 200 µm. In order to adjust the pH of the products to 7.0, the adsorbents were washed for several times with deionized water before dried at 105 °C. The final products activated by 0.05, 0.10, 0.15, 0.20, and 0.25 mol of ZnSO₄·7H₂O were labeled from CZ1 to CZ5 and tested as adsorbents to remove phosphate from aqueous solution aiming at obtaining the suitable dose of zinc sulfate.

For the sake of improving adsorption capacity of the sludge-based adsorbent, H₂SO₄ with the dose of 0.05, 0.10 and 0.15 mol was added in the sol-gels before mixed to homogenous paste by magnetic stirring apparatus. The other preparation procedures were the same as previous stage. After cooled, washed and dried, the three samples were used to adsorb phosphate and the optimal dose of H₂SO₄ was found. The final products were stored in an airtight container for subsequent tests.

2.3. Adsorption tests

The phosphate adsorption tests were performed in 250 ml flasks. The removal performance of phosphate by carbonized sludge samples with different doses of the two chemicals during adsorbent preparation was evaluated using the following procedure: 0.1 g adsorbents were added in 100 ml aqueous solution with 50 mg l⁻¹ of phosphate. The flasks were subsequently placed in a rotary shaker at 25 °C and 160 rpm for 24 h. The samples were collected during the adsorption process for measuring phosphate concentration. The amount of phosphate removed by the sludge-based char was calculated by

$$q = \frac{C_0 - C_e}{m} \cdot V$$

where C₀ is initial concentrations of adsorbate in contact with the adsorbent (mg l⁻¹), C_e is equilibrium concentrations of adsorbate in solution (mg l⁻¹), V is the volume of phosphate solution (L) and m is the mass of carbonized sludge.

In order to find the optimal parameters of the sludge-derived activated carbon, adsorption conditions were varied in batch tests. 0.1 g adsorbents were added in 100 ml aqueous solution with different phosphate concentration ranging from 50 mg l⁻¹ to 330 mg l⁻¹. The flasks were shaken at 25 °C until the phosphate concentration reached equilibrium. The results were used for fitting isotherms as well as kinetic models. Batch experiments at different pH values were carried out by adjusting the initial pH of the solution in five flasks to 3.0, 5.0, 7.0, 9.0, 11.0, respectively, with supplement of 1 M NaOH and 1 M HCl solution. The effects of temperature and adsorbent dose were investigated by the variation of temperature as well as mass of carbonized sludge ranging from 15 to 45 °C and 0.06 to 0.15 g, respectively. The mixtures were shaken at the speed of 160 rpm during the tests and samples were collected periodically.

2.4. Analytical methods

During the whole experiment, samples were obtained at intervals of 0.5 h. The mixtures were taken from the flasks and filtered immediately by using a 0.45 µm filter. The concentration of phosphate was measured according to the standard methods [18]. The pH values of wastewater in the system were monitored by a pH meter (PHS-3C). All samples were analyzed in triplicate. The analysis of chemical compositions of dried sewage sludge was performed by using X-ray fluorescence spectrometer (XRF, S4 Pioneer, Bruker AXS, Germany). The morphologies of the sludge char in this study were observed by using a scanning electron microscope (SEM, VEGA 3 LMU, TESCAN, Czech Republic). The surface functional groups of the carbonized sludge were determined by a Nicolet 5700 FTIR spectrometer in the range of 4000–400 cm⁻¹. An X-ray diffractometer (X' Pert Pro, PANalytical, Netherlands) was used to record the XRD patterns of the adsorbent samples in the 2θ range of 10–80°.

3. Results and discussion

3.1. Removal performance of phosphate during adsorbent preparation

The adsorption performance of phosphate by different adsorbent samples was investigated and the time courses were shown in Fig. 1. It can be seen from Fig. 1(a) that the phosphate removal rate increased with higher concentration of zinc sulfate. Within the first hour, the concentration of phosphate decreased from 50.19 to 45.24 mg l⁻¹ by using CZ1 while the phosphate concentration reduced to 35.59 mg l⁻¹ when adding CZ2 to the solution. The removal efficiencies of phosphate were 33.90%, 65.55%, and 80.39%,

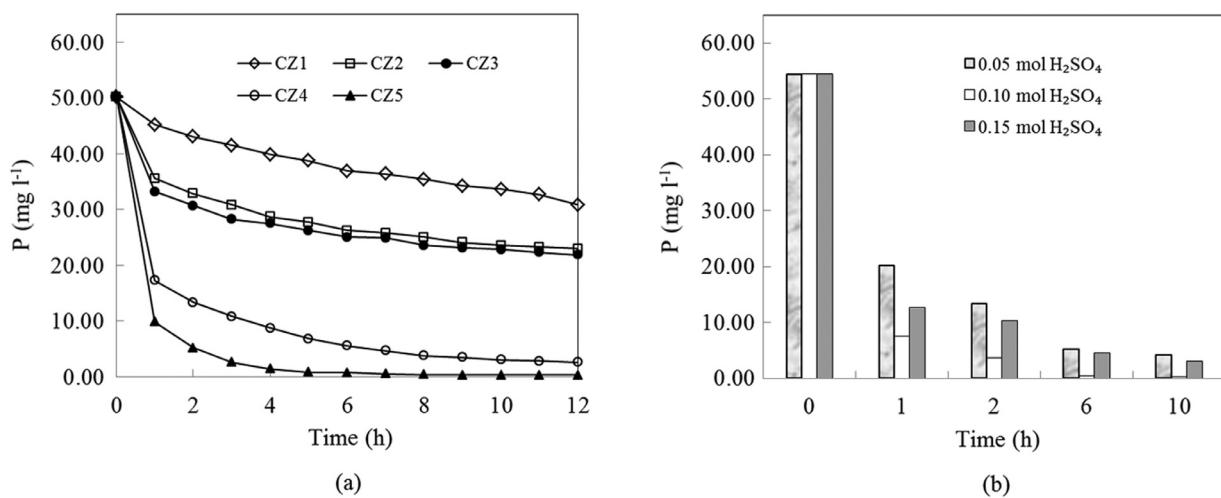


Fig. 1. Phosphate removal performance of sludge-based adsorbents activated with different dosages of ZnSO₄·7H₂O (a) and H₂SO₄ (b).

respectively, when using CZ3, CZ4 and CZ5 after 1 h shaking process. With the same initial concentration of phosphate, the equilibrium concentrations of adsorbate in solution decreased with the increase of zinc sulfate, which meant that the adsorption capacity of the carbonized sludge was improved. This might be due to the higher surface roughness and a greater content of oxygen-containing functional groups in the sludge by zinc salt, which makes it one of the most common inorganic chemical agents for sewage sludge carbonization [19]. When the dosage of zinc sulfate increased from 0.15 to 0.2 mol, the adsorption rate increased significantly and the residual concentration of phosphate was 17.29 mg l⁻¹ after 1-h contact. The adsorption capacity of CZ4 was highly improved in comparison with CZ3. However, further increasing the dosage of zinc sulfate in CZ5 only had slight improvement in phosphate removal when compared the 12 h adsorption process with CZ4. Considering the economic aspect, 0.2 mol of zinc sulfate was suitable. The effect of different dosages of H₂SO₄ on phosphate removal was shown in Fig. 1(b). 0.10 mol was the optimal dosage of H₂SO₄. More than 99% of initial phosphate was able to be removed from aqueous solution within 6 h. However, the removal efficiencies of the other two samples with 0.05 and 0.15 mol of H₂SO₄ were only 90.38% and 91.63%, respectively, during the same period of reaction time. It was found from another report that the Hg(II) adsorption capability was higher with addition of H₃PO₄, H₂SO₄ or ZnCl₂ during char production. Compared with H₃PO₄, H₂SO₄ activated carbon obtained from sewage sludge had higher total pore volumes [20]. In the present work, the addition of 0.10 mol of H₂SO₄ before heating procedure resulted in noticeable increase of phosphate removal rate in contrast with CZ4, indicating that both of the two chemical agents contributed to the improvement of adsorption capacity of the carbonized sludge.

3.2. Adsorption kinetics and isotherms

The initial concentration of phosphate was varied in order to investigate adsorption performance with different dosages of adsorbates. As shown in Fig. 2(a), the adsorption process was divided into two stages. The first stage is rapid adsorption, which mainly happened within the first hour. After that, the residual concentrations of phosphate showed gradually slow drop until the adsorbate reached the equilibrium concentrations. The similar adsorption trend could also be found in removal of many other pollutants by sewage sludge-based adsorbents [21]. The adsorption efficiencies of phosphate in aqueous solutions were 85.17%, 84.59%, 76.86%, 69.76%, and 64.50%, respectively, after 1-h contact with ini-

tial concentration of phosphate ranging from 50 to 90 mg l⁻¹. Although the removal efficiency decreased with the increase of initial phosphate concentration within the same period of reaction time, the higher initial concentration of phosphate led to more adsorption amount during the rapid removal stage. This might be due to the higher driving force provided by more adsorbates in the solution. More than 99% of 60 mg l⁻¹ initial phosphate could be removed from the mixture within 12 h. When initial concentration of phosphate rose to 70, 80, and 90 mg l⁻¹, the residual concentrations of adsorbates were 1.18, 3.29, and 7.29 mg l⁻¹, respectively, in the same period of time. With the lower initial concentration of phosphate, there was lower equilibrium concentration of phosphate in the time course. Less time was also consumed by the adsorbent to make the pollutant in the solution reach equilibrium concentration.

In order to figure out the rate-controlling mechanism of the adsorption process, two of the most common kinetics models, namely pseudo-first-order and pseudo-second-order kinetic models were applied to correlate the data from batch tests. The adsorption data was shown in Table 2. For adsorption results with initial concentration of phosphate ranging from 50 to 90 mg l⁻¹, relatively higher correlation coefficients (R^2) was obtained by using pseudo-second-order kinetic model than that by using pseudo-first-order kinetic model. The excellent fitness of linear forms of the second-order rate model in this work was presented in Fig. 2(b). The calculated q_e values were close to the experimental data, which also suggested that phosphate adsorption could be approximated to the second order rate expression. In many previous reports, this model showed satisfactory correlation for pollutants adsorption by other kinds of sludge-derived char [17,22]. The adsorption isotherms were also investigated to demonstrate the relationship between the phosphate adsorption capacity by the adsorbent under equilibrium status and the equilibrium concentration of phosphate in the solution at a constant temperature. The adsorption data with 90, 130, 170, 210, 250, and 330 mg l⁻¹ of initial phosphate concentration were used to correlate different common adsorption isotherms. It can be found that the adsorption capacity increased when the initial phosphate concentration rose from 90 to 130 mg l⁻¹ and further to 170 mg l⁻¹. After that, with the increase of initial phosphate concentration, the adsorption capacity had no noticeable improvement, indicating the adsorption capacity slowly reached equilibrium (data not shown). The isotherm constants obtained from Langmuir and Freundlich models were presented in Table 3. The data of this work had better fitness to Langmuir model than Freundlich model. The maximum phos-

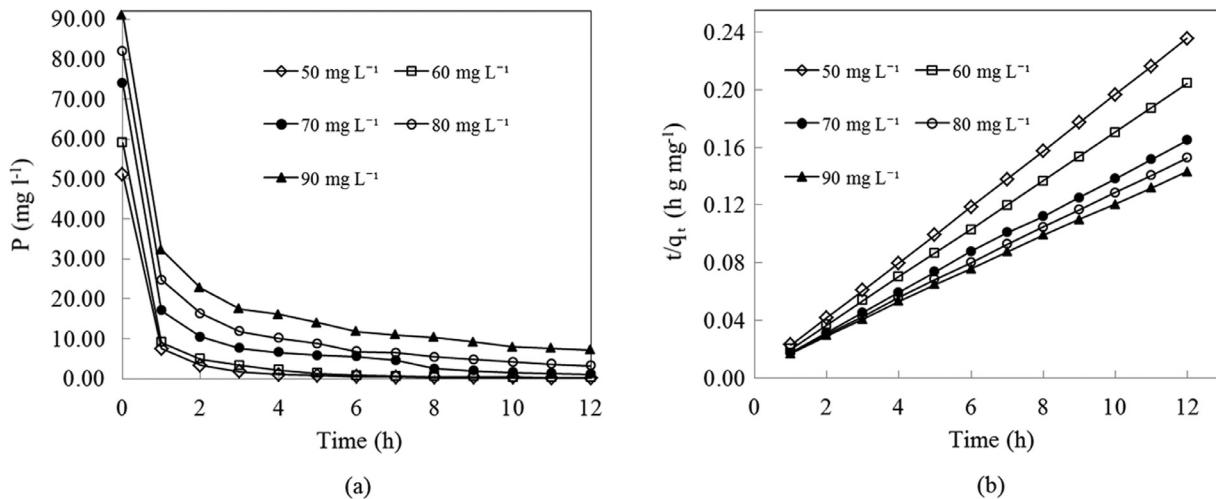


Fig. 2. Phosphate adsorption with variation of initial concentration of adsorbate (a) and linear fitting curves of the pseudo-second-order model (b).

Table 2
Parameters of kinetic models for phosphate adsorption.

Initial concentration (mg l ⁻¹)	Pseudo-first-order model			Pseudo-second-order model		
	q _e (mg g ⁻¹)	k ₁ (h ⁻¹)	R ²	q _e (mg g ⁻¹)	k ₂ (g mg ⁻¹ h ⁻¹)	R ²
50	46.62	0.01	0.522	51.28	0.19	1.000
60	52.78	0.01	0.638	59.52	0.12	1.000
70	60.37	0.02	0.787	74.07	0.04	0.999
80	61.80	0.02	0.739	80.00	0.03	0.999
90	61.70	0.03	0.756	86.21	0.03	0.998

Table 3

Parameters of Langmuir and Freundlich isotherm for phosphate adsorption (T= 298 K).

Isotherm model	Parameter 1	Parameter 2	R ²
Langmuir	q _{max} = 123.46 mg g ⁻¹	K _L = 0.91 L mg ⁻¹	0.999
Freundlich	n = 13.14	K _F = 6.92 (mg g ⁻¹)(1 mg ⁻¹) ^{1/n}	0.913

Table 4

Comparison of adsorption capacities of phosphate with different types of adsorbents.

Type of adsorbent material	P adsorption (mg g ⁻¹)	References
Zirconium (IV) loaded cross-linked chitosan particles	71.68	[32]
Nano-FeOOH composite biomass char	37.3	[33]
lanthanum hydroxide and zeolite synthesized from coal fly ash	66.09	[34]
Oak wood-derived hydrochars	26.6	[35]
Greenhouse waste-derived biochars	18.7	[35]
Municipal waste-derived biochars	14.3	[35]
Pumice	0.10	[36]
CuO nanoparticles	23.90	[37]
Sludge-derived char	123.46	This study

phate adsorption capacity of the char by using Langmuir model in the present study was far better than some other adsorbents such as biochar derived from oak wood, soybean, bamboo wood, maize residue, and peanut shell [23]. The adsorption capacities of phosphate with diverse types of adsorbents were listed in Table 4, which revealed that the adsorbent in the present study had good potential for phosphate removal.

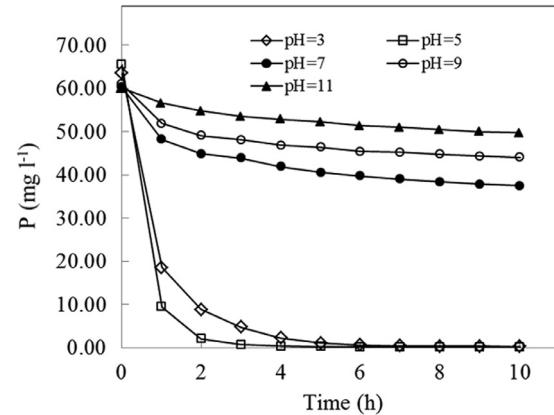


Fig. 3. Time courses of phosphate adsorption on modified adsorbents at different pH values.

3.3. Effect of pH, temperature, and dosage

The adsorption capacity of sludge-derived adsorbent at different pH values was presented in Fig. 3. It can be concluded that the phosphate removal performance varied significantly when pH of solution ranging from 3.0 to 11.0. The optimal pH value was 5.0, at which 96.81% of initial phosphate was removed from the solution within 2 h. There were also relatively high adsorption rates at pH of 3.0. More than 86% of initial phosphate was reduced at this pH level during the same period. When pH increased to 7.0, the removal efficiency decreased notably. Only 25.6% of initial phosphate was adsorbed within 2 h. Further increasing pH value to 9.0 and 11.0 showed lower removal rate of phosphate. The variation of phosphate removal capacity of the sludge-derived adsorbent along with the increase of pH value might be due to the change in sur-

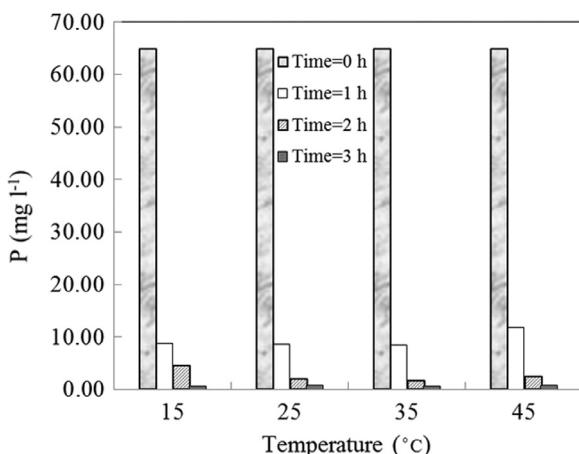


Fig. 4. Effect of temperature on phosphate adsorption process.

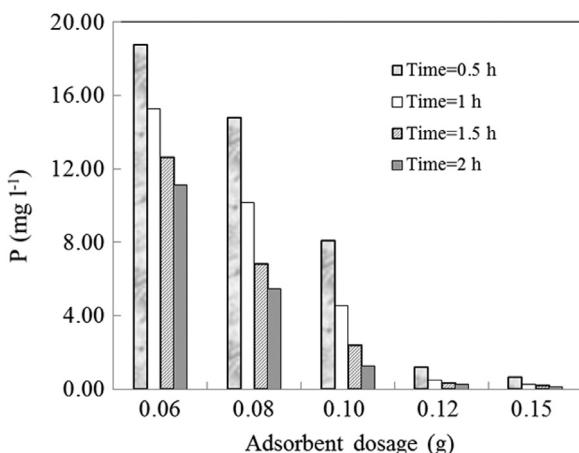


Fig. 5. Phosphate concentration with the change of contact time by different dosages of the adsorbent.

face characteristics. For instance, the pH might affect the surface charges of the sludge. It has been found that electrostatic properties could be changed with the increase of OH⁻ concentration in solution. The charged counter-ion layer might be formed and the active sites could also be occupied [24]. The effect of adsorption temperature on phosphate removal performance was shown in Fig. 4. The variation of temperature led to slighter change in phosphate reduction rate than that of pH value. During the first hour, the reductions of phosphate concentration were 56.07, 56.18, 56.30, and 52.92 mg l⁻¹, respectively, at 15 °C, 25 °C, 35 °C, and 45 °C. After 3-h contact, the residual concentrations of phosphate were all less than 1 mg l⁻¹. The phosphate adsorption rate at 35 °C was moderately higher than that at other three temperature levels, indicating that it was the optimal temperature, which was agreed with the results from the report of Jung et al. [23]. Fig. 5 described the phosphate removal by different dosages of the adsorbent. All these five dosage levels showed good phosphate removal capacity. The increase of adsorbent dosage resulted in higher phosphate adsorption rate. This might be due to more active sites provided with larger amount of the char. It can also be found from further test that over 99% of initial phosphate could be removed when adsorbent dosage was 0.08 g or more within 8 h (data not shown). The high removal rate of phosphate by the small amount of carbonized sludge indicated its effective utilization as an adsorbent material.

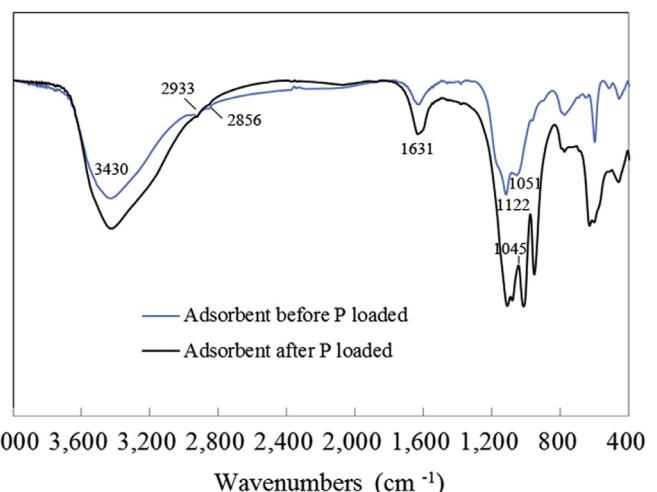


Fig. 6. FTIR spectra of sludge-derived adsorbent before and after phosphate adsorption.

3.4. Adsorption mechanism

It could be found from adsorption tests that the adsorbent could take up the phosphate from the solution efficiently and it had a relatively high maximum adsorption capacity. Therefore, the properties of obtained adsorbent were investigated in order to find the adsorption mechanism. Fig. S1 showed the SEM photograph of the carbonized sludge. The adsorbent had some irregular pores and the surface was rough. It can also be observed that the surface of the carbonized sludge activated by ZnSO₄ and H₂SO₄ had lamellar and crystal structures, which might be due to the production of metal compounds during the sludge preparation [19]. The XRD spectra of both modified sludge-based adsorbents and sludge char without chemical activation were presented in Fig. S2. It was apparent that the unmodified carbonized sludge had an obvious reflection of the crystallized quartz forms ($2\theta = 26.67^\circ$). It can be found from previous reports that quartz was one of the most common crystallized forms in carbonized sludge [25,26]. Compared with sludge char without chemical activation, the modified adsorbent had some more notable peaks representing crystals such as Zinc Sulfate hydroxide ($2\theta = 35.13^\circ$), which was due to the addition of ZnSO₄·7H₂O and H₂SO₄ during the adsorbent preparation.

Considering that the adsorption followed the second-order-rate model, the process might be controlled by chemisorptions. Thus, the surface functional groups of the adsorbent and the prepared samples with P loaded were measured by FTIR spectroscopy. As shown in Fig. 6, the FTIR spectra exhibited several functional groups. For instance, the O-H stretching vibrations of the hydroxyl groups in the layers as well as interlayer water molecules occurred at 3430 cm⁻¹ and the broad band at about 1630 cm⁻¹ was responsible for water deformation [27,28]. The peak at around 2933 cm⁻¹ and 2856 cm⁻¹ was assigned to antisymmetric and symmetric stretching vibration of -CH₂ [29]. Furthermore, there were several bands from 900 to 400 cm⁻¹ on the spectra of adsorbent before P removal. This region was proposed to reveal the stretching vibration and bending vibration of M-O and M-OH [30]. It could also be observed that the spectra of the carbonized sludge after adsorption had intensive bends from 1200 to 800 cm⁻¹, which were associated with structural diagnosis of metal orthophosphate complexes in aqueous solutions [24]. For the sludge-based activated carbon before adsorption, the spectra also peaked around 1122 and 1051 cm⁻¹, which could be attributed to Fe-OH bending bands. However, these two peaks disappeared after adsorption process. Instead, a new bend at around 1045 cm⁻¹ appeared. This intensive

band indicated the asymmetry vibration, which suggested that the surface hydroxyl groups were replaced by the phosphate loaded onto the adsorbent [31].

4. Conclusion

In this study, the sludge-based adsorbent was prepared with the activation of $ZnSO_4 \cdot 7H_2O$ and H_2SO_4 . The suitable dosages of $ZnSO_4 \cdot 7H_2O$ and H_2SO_4 were 0.2 mol and 0.1 mol, respectively. The obtained sewage sludge-derived char showed high removal efficiency of phosphate. More than 99% of 60 mg l^{-1} initial phosphate could be removed from the mixture within 12 h and the maximum adsorption capacity was 123.46 mg g^{-1} . The adsorption data was well described by pseudo-second-order model and Langmuir model. The optimal pH, temperature, and adsorbent dosage were 5.0, 35 °C and 0.15 g, respectively. The results of XRD and FTIR analysis indicated that the relative crystal surface and functional groups played significant roles during adsorption process. The high adsorption capacity of the carbonized sludge makes it an effective sorbent for phosphate removal from aqueous solutions.

Acknowledgments

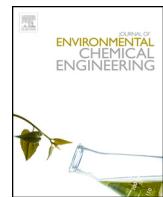
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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.jtice.2017.04.002](https://doi.org/10.1016/j.jtice.2017.04.002).

References

- [1] Yu L, Zhong Q. Preparation of adsorbents made from sewage sludges for adsorption of organic materials from wastewater. *J Hazard Mater* 2006;137:359–66.
- [2] Pal P, Kumar R. Treatment of coke wastewater: a critical review for developing sustainable management strategies. *Sep Purif Rev* 2014;43:89–123.
- [3] Karthik M, Dafale N, Pathé P, Nandy T. Biodegradability enhancement of purified terephthalic acid wastewater by coagulation-flocculation process as pre-treatment. *J Hazard Mater* 2008;154:721–30.
- [4] Chen X, Jeyaseelan S, Graham N. Physical and chemical properties study of the activated carbon made from sewage sludge. *Waste Manage* 2002;22:755–60.
- [5] Qian L, Wang S, Xu D, Guo Y, Tang X, Wang L. Treatment of municipal sewage sludge in supercritical water: a review. *Water Res* 2016;89:118–31.
- [6] Mohamed EF, Andriantsiferana C, Wilhelm AM, Delmas H. Competitive adsorption of phenolic compounds from aqueous solution using sludge-based activated carbon. *Environ Technol* 2011;32:1325–36.
- [7] Sierra I, Iriartevelasco U, Cepeda EA, Camero M, Aguayo AT. Preparation of carbon-based adsorbents from the pyrolysis of sewage sludge with CO_2 . Investigation of the acid washing procedure. *Desalin Water Treat* 2015;1:1–13.
- [8] Martin MJ, Artola A, Balaguer MD, Rigola M. Activated carbons developed from surplus sewage sludge for the removal of dyes from dilute aqueous solutions. *Chem Eng J* 2003;94:231–9.
- [9] Gu L, Zhu N, Zhou P. Preparation of sludge derived magnetic porous carbon and their application in Fenton-like degradation of 1-diazo-2-naphthol-4-sulfonic acid. *Bioresour Technol* 2012;118:638–42.
- [10] Ding WL, Peng WL, Zeng XL, Tian XM. Effects of phosphorus concentration on Cr(VI) sorption onto phosphorus-rich sludge biochar. *Front Env Sci Eng* 2014;8:379–85.
- [11] Qiu M, Huang C. Removal of dyes from aqueous solution by activated carbon from sewage sludge of the municipal wastewater treatment plant. *Desalin Water Treat* 2015;53:3641–8.
- [12] Nielsen L, Bandosz TJ. Analysis of sulfamethoxazole and trimethoprim adsorption on sewage sludge and fish waste derived adsorbents. *Micropor Mesopor Mat* 2016;220:58–72.
- [13] Jindarom C, Meeyoo V, Kitiyanan B, Rirkosomboon T, Rangsuvigit P. Surface characterization and dye adsorptive capacities of char obtained from pyrolysis/gasification of sewage sludge. *Chem Eng J* 2007;133:239–46.
- [14] Marques RRN, Stüber F, Smith KM, Fabregat A, Bengoa C, Font J, Fortuny A, Pullket S, Fowler GD, Graham NJD. Sewage sludge based catalysts for catalytic wet air oxidation of phenol: preparation, characterisation and catalytic performance. *Appl Catal B Environ* 2011;101:306–16.
- [15] Hou B, Han H, Jia S, Zhuang H, Xu P, Li K. Three-dimensional heterogeneous electro-Fenton oxidation of biologically pretreated coal gasification wastewater using sludge derived carbon as catalytic particle electrodes and catalyst. *J Taiwan Inst Chem E* 2016;60:352–60.
- [16] Ros A, Lillo-Rodenas MA, Fuente E, Montes-Morán MA, Martín MJ, Linares-Solano A. High surface area materials prepared from sewage sludge-based precursors. *Chemosphere* 2006;65:132–40.
- [17] Wang X, Liang X, Wang Y, Wang X, Liu M, Yin D, Xia S, Zhao J, Zhang Y. Adsorption of Copper (II) onto activated carbons from sewage sludge by microwave-induced phosphoric acid and zinc chloride activation. *Desalination* 2011;278:231–7.
- [18] APHA. Standard methods for the examination of water and wastewater. 21st ed., Washington, D.C., USA. 2005.
- [19] Zhu W, Yao W, Zhan Y, Gu Y. Phenol removal from aqueous solution by adsorption onto solidified landfill sewage sludge and its modified sludges. *J Mater Cycles Waste* 2015;17:798–807.
- [20] Zhang F, Nriagu JO, Itoh H. Mercury removal from water using activated carbons derived from organic sewage sludge. *Water Res* 2005;39:389–95.
- [21] Nekooghadirli R, Taghizadeh M, Mahmoudi Alami F. Adsorption of Pb(II) and Ni(II) from aqueous solution by a high-capacity industrial sewage sludge-based adsorbent. *J Disper Sci Technol* 2016;37:786–98.
- [22] Gökçe CE, Arayici S. Adsorption of 17 β -estradiol and estrone by activated carbon derived from sewage sludge. *Desalin Water Treat* 2016;57:2503–14.
- [23] Jung KW, Hwang MJ, Ahn KH, Ok YS. Kinetic study on phosphate removal from aqueous solution by biochar derived from peanut shell as renewable adsorbent media. *Int J Environ Sci Technol* 2015;12:3363–72.
- [24] Yang Y, Zhao Y, Babatunde A, Wang L, Ren Y, Han Y. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. *Sep Purif Technol* 2006;51:193–200.
- [25] Gu L, Zhu N, Zhang D, Lou Z, Yuan H, Zhou P. A comparative study of aerobically digested and undigested sludge in preparation of magnetic chars and their application in 1-diazo-2-naphthol-4-sulfonic acid adsorption. *Bioresour Technol* 2013;136:719–24.
- [26] Gupta A, Garg A. Primary sewage sludge-derived activated carbon: characterisation and application in wastewater treatment. *Clean Technol Environ Policy* 2015;17:1619–31.
- [27] Tongamp W, Zhang Q, Saito F. Preparation of meixnerite ($Mg-Al-OH$) type layered double hydroxide by a mechanochemical route. *J Mater Sci* 2007;42:9210–15.
- [28] Robalds A, Dreijalte L, Bikovens O, Klavins M. A novel peat-based biosorbent for the removal of phosphate from synthetic and real wastewater and possible utilization of spent sorbent in land application. *Desalin Water Treat* 2016;57:13285–94.
- [29] Chen J, Yan L, Yu H, Li S, Qin L, Liu G, Li Y, Du B. Efficient removal of phosphate by facile prepared magnetic diatomite and illite clay from aqueous solution. *Chem Eng J* 2016;287:162–72.
- [30] Lü J, Liu H, Liu R, Zhao X, Sun L, Qu J. Adsorptive removal of phosphate by a nanostructured Fe-Al-Mn trimetal oxide adsorbent. *Powder Technol* 2013;233:146–54.
- [31] Zhang G, Liu H, Liu R, Qu J. Removal of phosphate from water by a Fe-Mn binary oxide adsorbent. *J Colloid Interf Sci* 2009;335:168–74.
- [32] Liu Q, Hu P, Wang J, Zhang L, Huang R. Phosphate adsorption from aqueous solutions by Zirconium (IV) loaded cross-linked chitosan particles. *J Taiwan Inst Chem E* 2016;59:311–19.
- [33] Zhou H, Jiang Z, Wei S. Equilibrium and kinetic studies of phosphate adsorption onto corn straw char supported nano Ferric Oxide composite. *Sci Adv Mater* 2015;7:1822–9.
- [34] Xie J, Lai L, Lin L, Wu D, Zhang Z, Kong H. Phosphate removal from water by a novel zeolite/lanthanum hydroxide hybrid material prepared from coal fly ash. *J Environ Sci Health, Part A* 2015;50:1298–305.
- [35] Takaya CA, Fletcher LA, Singh S, Anyikude KU, Ross AB. Phosphate and ammonium sorption capacity of biochar and hydrochar from different wastes. *Chemosphere* 2016;145:518–27.
- [36] Kim JY, Balathanigaimani MS, Moon H. Adsorptive removal of nitrate and phosphate using MCM-48, SBA-15, chitosan, and volcanic pumice. *Water Air Soil Pollut* 2015;226:431.
- [37] Mahdavi S, Akhzari D. The removal of phosphate from aqueous solutions using two nano-structures: copper oxide and carbon tubes. *Clean Technol Environ Policy* 2016;18:817–27.



Review

Coal-based adsorbents for water and wastewater treatment

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ABSTRACT

Coal, just like other fossil fuels such as oil and natural gas, is mainly used as a non-renewable source of energy. It is a physically unique mineral resource almost totally composed of organic matter (carbon), and a smaller percentage of elements such as hydrogen, oxygen, sulphur, and nitrogen. It is believed that underground coal deposits formed about 250–300 million years ago, when much of the Earth was a swamp covered with thick forest and plant growth. This review explores the use of coal, not as an energy source used for generating electricity, but as a low cost adsorbent in water and wastewater treatment processes. In fact, today, coal-based adsorbents still attract considerable interest in their usage. The review critically analyses the chemical composition, ion-exchange and sorption properties of coal. The use of the as-received coals, demineralized coals, sulphonated coals, calcium-loaded coals, chitosan-doped coals, activated carbon, coal fly ash, and coal fly ash derived-zeolite has also been extensively discussed. It is evident from this review that although the pollutant exchange capacities of various types of coal-based adsorbents are significantly lower in comparison to other forms of adsorbents, the substantially lower cost of coal shows a great potential for the utilization of coal as a means to remove a range of pollutants from water and wastewater effluents. However, due to the scarcity of consistent cost information, cost comparisons are difficult to make, and consequently, in this review, such comparisons were not done for the coal-based adsorbents.

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1. Introduction

Coal has the longest history of use amongst the fossil fuels, with its use as a fuel dating back to 3000 BC in China and Wales [1], and undoubtedly, it still remains the largest and cheapest source of solid fuel across the globe [2]; and there is an estimated 861 billion tonnes of coal reserves worldwide [3]. Broadly speaking, coal is a complex combustible sedimentary rock, composed chiefly, but not exclusively, of helophytic (\pm aquatic) plant debris and plant derivatives [4]. It is predominantly made of carbon, but also features other elements such as hydrogen, oxygen, sulphur and nitrogen [5]. In other words, coal is a very heterogeneous organic rock in which organic matter has inclusions of mineral matter [6]. In fact, organic material typically represents 85–95% (wt/wt) of a dry coal [7].

In recent past, various types of coal have been increasingly used not only as fuels, but also as valuable materials in several remediation and pollution control processes [8,9]. This is because besides being inexpensive and abundant in many countries, coal possesses very exciting characteristics that make it an effective adsorbent for the removal of various organic and inorganic pollutants. In this regard, this review paper critically analyses the use of coal-based adsorbents in the treatment of water and wastewater. In terms of the paper organization, following this introductory section, Section 2 briefly discusses the classification and composition of coal. This is followed by the surface characteristics of coal in Section 3. The analyses of production and activation of some of coal-based adsorbents are discussed in Section 4. Subsequently, Section 5 discusses applications of coal-based adsorbents. Finally, Section 6 summarises the paper and highlights future prospects of the usage of coal as an adsorbent.

2. Classification and composition of coal

Coal is an extremely complex and a heterogeneous combustible sedimentary rock [4,7,10]. In a broader sense, coal is essentially composed of plant remains, which are coalified organic matter formed by exposure to high temperature and pressure during burial [11]. Three main parameters are considered when classifying coals, i.e., type, rank, and grade [10]. Coal types typically fall into two categories: humic coals, developed from peat, and sapropelic coals, developed from organic mud [4]. Either type may be allochthonous or autochthonous, and within the different types, further refinement of depositional environment can also be made [4]. Coal rank refers to the level of maturity in coal [12]. Broadly speaking, coal rank refers to the changes in geochemistry and resultant changes in reflectance caused by increasing thermal maturity of the coal, thus providing an overprint of maturity on existing coal types [4]. In other words, during coalification, physico-chemical changes occur under conditions of high temperature and

pressure over time, thereby giving rise to the process of maturation and metamorphism (changes) in the various plant fragments (macerals). For example, the high temperatures and pressures result in the transformation of the original peat swamp plant materials through progressive stages of brown coal (lignite), sub-bituminous and bituminous coals to anthracite and meta-anthracite [4,13]. The end-point of this continuum is graphite, which occurs only rarely in nature as a result of intense pressure and temperature in some coalfields of the world [13]. In summary, the level to which a coal has reached in this coalification series is referred to as rank or level of maturity [13]. On the other hand, coal grade refers to the amount of inorganic matter content [10].

3. Surface characteristics of coal

It is known that the surface properties of coal, such as surface area, pore volume, and surface chemical structure, affect the physico-chemical behaviour of coal in many applications [14] including adsorption. In fact, it is on the surface of coal where it initially interacts with the rest of the world, and under many circumstances, the initial contact is totally controlled by the area, geometry, and chemical nature of the surface [15]. Therefore, this particular section explains the general physical and chemical characteristics of the surface of coal and why they are important.

Coal particles are extremely heterogeneous, comprising of various heteroatoms and functional groups along with inorganic impurities within the hydrocarbon matrix [6]. These surface sites exhibit various characteristics, which all contribute to the overall adsorption capacity of coal. For example, coal surface electro-chemical properties stem from the presence of oxygenated surface functionalities, such as carboxylic acid and phenolic groups [16]. There are also other forms of oxygen that are buried as heteroatoms in aromatic or naphthenic rings or as bridges between the nuclei as ethers or, to a lesser extent, as esters [7]. All these types of oxygen functional groups strongly influence coal reactivity [7,17], and their relative numbers vary significantly as a function of coal rank [7,18]. Furthermore, chemically, coals become progressively more aromatic with increasing coal rank, and the cross-link density in the macromolecular system is considered to decrease with increasing coal rank to coals of about 87 wt% of carbon and then progressively to increase again to the most mature anthracites [19].

In aqueous solution, the acidic protons on the oxygenated surface functional groups on coal dissociate, leaving negatively charged sites on the coal surface [16]. The dissociation is enhanced in basic solution, whereas the surface groups are protonated in strongly acidic solution, reducing the negative charge density and the surface can even become positively charged in highly acidic solution. Positively charged sites can also develop from proton adsorption by chromene and pyrone-type structures on coal [16].

Table 1

Properties of activated carbon from various material sources.

Raw material	% carbon	% volatile	% ash	Density (kg/L)	Texture	Surface area (m ² /g)	Application	Reference
wood	40–45	55–60	0.3–1.2	0.4–0.8	Soft, large pore volume	240–500	Aqueous phase adsorption	[41,45]
Coconut shells	40–45	55–60	0.5–0.6	1.4	Hard, large micropore volume	700–2500	Vapor phase adsorption	[41,43]
Bituminous coal	65–80	25–30	2.12	1.25–1.50	Medium hard, medium micropore volume	400–1300	Waste water treatment	[41,42]
Anthracite coal	85–95	5–10	2.15	1.5–1.8	Hard, large pore volume	500–2300	Industrial water purification and chemical recovery	[41,44,47]
Lignite	55–70	25–40	5–6	1.00–1.35	Hard, small pore volume	280–400	Waste water treatment, gas vapour adsorption	[41,46]

In fact, the formation of coal surface charge in aqueous solution through the ionisation or protonation of the surface carboxylic and hydroxyl groups has been well established [20].

One other structural element of coal, and perhaps its most distinctive feature when compared to other solid fossil fuel sources like petroleum and oil shale, is an extensive network of pores which give coal a high surface area (e.g., >100 m²/g for bituminous, sub-bituminous coals, and lignites) and an appreciable volume of pore space [7]. In other words, coal is a high surface area material previously thought to have a network of slitlike pores interconnected by narrow capillary constrictions [15,19,21]. However, a more realistic model postulates that pores in coals are closed-isolated bubbles that are only reachable by diffusion through the solid coal [15]. In other words, coal is a porous material in which pores are not open to the surface, but can only be reached by diffusion through the solid coal [15].

The size of the pores in coal determines what fraction of the pore volume is accessible to the adsorbate [22]. As a result, it is found that the pore structure of coal plays an important role in the behaviour of coal during mining, beneficiation, utilization, conversion to synthetic fuels, etc [23,24] and adsorption of impurities. Indeed, the porosity plays a key role in all aspects of coal utilization, such as extraction of methane from coal seams,

gasification, combustions, liquefaction, production of metallurgical coke, and activated carbon as well as geological sequestration of CO₂ [25]. Essentially, there are three categories of the pore structure of coal [23,24,26]: macropores (>300 Å in diameter), mesopores or transitional pores (12–300 Å in diameter), and micropores (<12 Å in diameter). Since the bulk of coal porosity is in the micropores (from 40% in lignites to 70% in anthracites), rates of reactions are limited by rates of diffusion through the micropore structure [24].

4. Production and activation of coal-based adsorbents

As already discussed in Section 3, surface functional groups strongly influence coal reactivity. Furthermore, the adsorption capacities of coal strongly depend on their porosity and surface area. Therefore, the interest in the preparation of coal-based adsorbents with special surface characteristics (e.g., functional groups, surface area, and porosity) is warranted. This section seeks to review the principal methods by which coal-based adsorbents are produced, with an emphasis on the following: (1) char production, (2) techniques for production and activation of activated carbon, (3) coal fly ash, and (4) synthesis of zeolite from coal fly ash. However, it must be noted that some studies have used

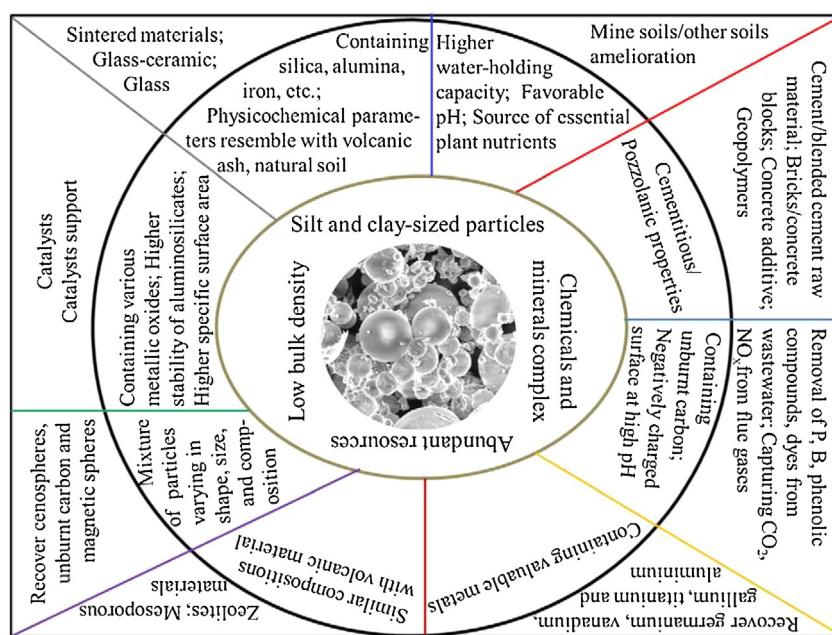


Fig. 1. Various applications of coal fly ash [54].

coal-based adsorbents in their as-received states without any pre-treatment (e.g., Cullen et al., [27]).

4.1. Char production

When coal is heated, its inherent moisture evaporates, and then coal gas comprising hydrogen, carbon monoxide, methane, carbon dioxide, and acetylene is generated by the pyrolysis of its volatile matter [28]. During the pyrolysis stage, coal is devolatilized when it is heated to elevated temperatures. The remaining residue matter formed after the removal of the volatile components or any other carbonaceous material, is called char [29,30]. The pyrolysis of coal is a complex process involving various physical and chemical subprocesses, which include gas transportation across boundary layers surrounding particles, gas transportation through pores inside particles, reactions that occur on carbonaceous surfaces and, surface area evolution that occurs during char conversion [31]. The release of volatile matter during pyrolysis of coal brings about a development of internal porosity, which results directly from one or more of the following [32]: (1) opening of previously closed pores; (2) creation of new pores; and (3) enlargement of preexisting and/or newly developed pores. The development of porosity gives rise to changes in pore structural parameters such as densities, specific surface areas, pore-size distributions, total open-pore volumes and porosities, and average pore diameter. In turn, the nature of the pore structure in a particular coal and char produced determines, to a large degree, the level of its reactivity during its use as an adsorbent. A study by Hobday et al. [33] showed that the relatively high surface areas and pore volumes of coal chars suggest that they may be reasonably efficient adsorbents, so that in some applications it may be possible to replace activated carbons with cheaper coal chars.

4.2. Production of activated carbon

Activated carbon is the generic term used to describe a family of carbonaceous adsorbents with an extensively developed internal pore structure [34]. Furthermore, although it is now recognized that the pore structure is the most important property of activated carbon, it was formerly believed that the carbon had to be activated by means of chemical and heat treatment before it could remove colour, hence the name “activated carbon” [30]. Generally, activated carbons are mainly microporous, but in addition to micropores they contain mesopores and macropores, which are very important in facilitating access of the adsorbate molecules to the interior of carbon particles [35,36]. Basically, almost any carbonaceous material can be converted into activated carbon [36–38]. However, the final properties of the activated carbon depend on the nature of the source material [36,39] and the treatment process [36]. Essentially, the raw material from which a given activated carbon is produced often has a large effect on its porosity distribution, total surface area, carbon density, particle size distribution and adsorptive capacity [40]. As a result, activated carbons produced from different raw materials may have different adsorbent qualities. Table 1 gives a comparison of the properties of coal-based activated carbon with those of activated carbon made from other precursor raw materials [41–47]. The Table also gives the various applications of the resultant activated carbon, clearly indicating that the application is largely depended on the characteristics of carbon, which in turn depends on the source material.

As stated earlier, the treatment process or method of activation is another aspect that may influence the final properties of activated carbon. In principle, there are two different processes for the preparation of activated carbon: physical and chemical activation [48]. Physical activation involves carbonization of a

carbonaceous precursor followed by activation of the resulting char in the presence of some activating agents such as carbon dioxide or steam [48]. In other words, preparation of activated carbon with physical activation involves carbonization of a carbonaceous precursor followed by burnoff of the resulting char in the presence of some mildly oxidizing gases such as carbon dioxide or steam [30,36,41]. Chemical activation, on the other hand, is a single step method of preparing activated carbon, i.e., the carbonization of the precursor in the presence of chemical reagents. In physical activation, elimination of a large amount of internal carbon mass is necessary to obtain a well-developed carbon structure, whereas in the chemical activation process all the chemical reagents used are dehydrating agents that influence pyrolytic decomposition and inhibit formation of tar, thus enhancing the yield of carbon [48,49]. Comparing these two processes, physical activation is favoured when the environmental contamination and equipment corrosion caused by the chemical agents are considered as important drawbacks for chemical activation processes [36]. However, because the temperatures used in chemical activation are lower than those used in the physical activation process, the development of a porous structure is better in the case of the chemical process [48].

4.3. Coal fly ash

Coal fly ash, a by-product of coal combustion, has been regarded as a problematic solid waste [50,51], mainly due to the presence of potentially toxic trace elements (e.g. Cd, Cr, Ni, Pb) and organic compounds (e.g., polychlorinated biphenyls, polycyclic aromatic hydrocarbons) [52]. Its utilization has received a great deal of attention over the past years as more sustainable solutions to waste problems are being sought [53]. A recent review by Yao et al. [54] gives a comprehensive discussion of the applications of coal fly ash as illustrated in Fig. 1. However, this paper reviews studies that investigated the direct use of coal fly ash as an adsorbent in water and wastewater treatment (see Section 5.1.7). A potential advantage of using coal fly ash in water and wastewater treatment is that it could easily be solidified after the metals are adsorbed because it contains pozzolanic particles that react with lime in the presence of water, forming cementitious calcium-silicate hydrates [55]. There is an obvious benefit of using coal fly ash directly, but this may come at the expense of effectiveness. For example, despite coal fly ash being used directly as a soil amelioration agent, there are issues regarding potentially mobile toxic elements being applied to soil which is being used to grow crops; in this case pre-treatment steps have been considered [56]. The variability in chemistry, mineralogy, and morphology of different coal fly ash samples also hinders its direct use. Nevertheless, the indirect applications of coal fly ash usually combine a series of chemical, thermal, and/or mechanical activation methods in order to produce the required formulation [53] as is the case in the synthesis of zeolite from coal fly ash.

4.4. Synthesis of zeolite from coal fly ash

Since the realization of compositional similarity between coal fly ash and some volcanic material, the precursor of natural zeolites, by Höller and Wirsching [57], a number of hydrothermal activation methods have been proposed to synthesize different zeolites from coal fly ash. Basically, coal fly ash is one of the inorganic residues arising from coal combustion processes, whereas zeolites are crystalline aluminum-silicates, with group I or II elements (from the periodic table) as counterions [58]. The structure of zeolite is made up of a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra linked to each other at the corners by sharing their oxygens as shown in Fig. 2 [58]. The tetrahedra make up a

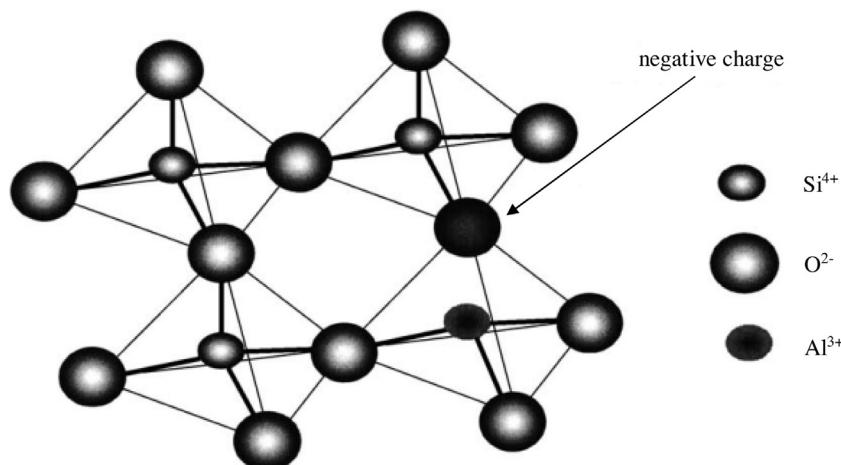


Fig. 2. Idealized structure of zeolite framework of tetrahedral $[SiO_4]^{4-}$ with a Si/Al substitution ($[AlO_4]^{5-}$) yielding a negative charge, and consequently a cation exchange capacity [58].

three-dimensional network, with lots of voids and open spaces. It is these voids that define the many special properties of zeolites, such as cation exchange, molecular sieving, catalysis, and sorption [58,59]. Furthermore, the peculiar structural properties of zeolites enable the adsorbents to have other broad range of industrial applications, mainly based on [58,60]: (1) gas adsorption which involves selective absorption of specific gas molecules, and (2) water adsorption which involves reversible adsorption of water without any desorption chemical or physical change in the zeolite matrix.

As already stated, since the initial studies reported by Holler and Wirsching [57], many different hydrothermal activation methods have been proposed to synthesize different types of zeolite from coal fly ash as discussed in a review article by Querol et al. [58]. All the methodologies developed are based on the dissolution of Al-Si-bearing coal fly ash phases with alkaline solutions (mainly NaOH and KOH solutions) and the subsequent precipitation of zeolitic material [58,61]. In fact, the classic alkaline conversion of fly ash employs the combination of different alkaline solution/fly ash ratios with alkali concentration, temperature, and reaction time to obtain different zeolite species [61]. Table 2 shows the zeolite types that have been synthesized from coal fly ash by different studies [58]. It must be noted that the potential industrial application of these zeolitic materials varies.

Table 2

Zeolites and other neomorphic phases synthesized from fly ash and Joint Committee of Powder Diffraction Standard (JCPDS) codes for XRD identification [5,81].

Zeolitic product	Chemical formula	JCPDS
NaP1 zeolite	$Na_6Al_6Si_{10}O_{32}\cdot 12H_2O$	39-0219
Phillipsite	$K_2Al_2Si_3O_{10}\cdot H_2O$	30-0902
K-Chabazite	$K_2Al_2SiO_6\cdot H_2O$	12-0194
Zeolite F linde	$KAISiO_4\cdot 1.5H_2O$	25-0619
Herschelite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}\cdot 1.8H_2O$	31-1271
Faujasite	$Na_2Al_2Si_{3.3}O_{8.8}\cdot 6.7H_2O$	12-0228
Zeolite A	$NaAlSi_{1.1}O_{4.2}\cdot 2.225H_2O$	43-0142
Zeolite X	$NaAlSi_{1.23}O_{4.46}\cdot 3.07H_2O$	39-0218
Zeolite Y	$NaAlSi_{2.43}O_{6.86}\cdot 4.46H_2O$	38-0239
Perlite	$K_9NaCaAl_{12}Si_{24}O_{72}\cdot 15H_2O$	38-0395
Analcime	$NaAlSi_2O_6\cdot H_2O$	19-1180
Hydroxy-sodalite	$Na_{1.08}Al_2Si_{1.68}O_{7.44}\cdot 1.8H_2O$	31-1271
Hydroxy-cancrinite	$Na_{14}Al_{12}Si_{13}O_{51}\cdot 6H_2O$	28-1036
Kalsilite	$KAISiO_4$	33-0988
Tobermorite	$Ca_5(OH)_2Si_6O_{16}\cdot 4H_2O$	19-1364

5. Applications of coal-based adsorbents

Surface water, ground water, and industrial or household wastewater contain many different types of metallic, inorganic and organic compounds that are hazardous to human beings, animals and plants [59]. Therefore, the removal or degradation of hazardous materials and contaminants from wastewater, ground and surface water is a significant global priority [62]. This section explores recent applications of coal-based adsorbents for removal of various pollutants from water and wastewater. In particular, the section focuses on the use of different forms of coal-based adsorbents such as the as-received coals, demineralized coals, sulphonated coals, calcium-loaded coals, activated carbon chitosan-doped coals, coal fly ash and coal fly ash derived-zeolite. The section comprises three sub-sections, vis-à-vis, removal of heavy metals, removal of metalloids, and removal of organic pollutants.

5.1. Heavy metal ions

Enormous quantities of heavy metals released in the environment from various natural and anthropogenic activities are known to cause severe water pollution [63,64] leading to serious implications on human health [64]. For example, elevated concentrations of heavy metals may, (1) accumulate in vital organs and glands of humans and animals where they disrupt their important functions, and (2) inhibit the absorption, interfere with or displace the vital nutritional minerals from their original place, thereby, hindering their biological functions [64,65]. This is exacerbated by the fact that heavy metals do not undergo biodegradation thus can accumulate in the environment [66]. Therefore, it is fundamentally important that even trace amounts of heavy metals are removed from water and wastewaters.

A summary of some of the heavy metals and their effects on human health together with permissible limits is presented in Table 3 [67–69].

5.1.1. As-received coals

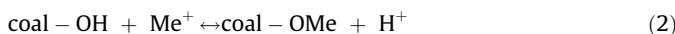
One interesting aspect of low rank coals is their ability to form stable complexes with several heavy metal ions [70] because of the presence of carboxylic and phenolic groups that are attached to a highly cross-linked aromatic structure [71,72]. The carboxylic or phenolic groups are able to take part in ion-exchange reactions as shown in Eqs. (1) and (2), respectively [66,73].



Table 3

Heavy metals and their effects on human health together with permissible limits [67–69].

Heavy metal	Effect	Permissible level (mg/L)
Arsenic	Bronchitis, dermatitis, poisoning	0.02
Cadmium	Renal dysfunction, lung disease, lung cancer, bone defects, increased blood pressure, kidney damage, bronchitis, bone marrow cancer, gastrointestinal disorder	0.06
Lead	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness, liver, kidney, and gastrointestinal damage, acute or chronic damage to the nervous system, epilepticus	0.10
Manganese	Inhalation or contact causes damage to nervous central system	0.26
Mercury	Damage to the nervous system, protoplasm poisoning, spontaneous abortion, minor physiological changes, tremors, gingivitis, acrodynia characterised by pink hands and feet	0.01
Zinc	Damage to nervous membrane	15.0
Chromium	Damage to the nervous system, fatigue, irritability	0.05
Copper	Anemia, liver and kidney damage, stomach and intestinal irritation	0.10



where coal-COOH and coal-OH represent the carboxylic and phenolic functional groups within the coal that are responsible for metal exchange, and Me⁺ is a metal ion.

Thus, this property has been successfully utilized in removing a range of metals from aqueous waste streams since the 1930s [74].

Cullen et al. [27] investigated the extraction of several metal ions such as Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Ag²⁺ and Co²⁺ from ammoniacal solution using lignite and brown coal. The amount of metals adsorbed was determined by analyzing the solutions before and after coming into contact with coal. It was found that metal extractions increased with an increase in contact time, liquid to solid ratio, and with metal concentration at short contact times, but extractions decreased with increases in coal particle size, ammonium ion concentration, and with metal concentration at long contact times. In similar studies of this nature, Altekar et al. [75] and Saha et al. [76] used lignite to remove nickel and cobalt from synthetic solutions of ammoniacal nickel carbonate and ammoniacal cobalt carbonate, respectively. The results showed that the adsorption of nickel was much more rapid than the adsorption of cobalt. As will be discussed later, the affinity for adsorption of nickel and cobalt on coal seems to follow the Irving-Williams order [77]. The difference in the adsorption kinetics of cobalt and nickel may be helpful in developing selective adsorption techniques for separating the two metals.

Other studies have reported the use of lignite to extract cobalt of valence three (Co³⁺) from ammoniacal solutions. For example, Slavens et al. [78] studied the recovery of Co³⁺ from ammoniacal ammonium sulfate leach liquor. The Co³⁺ was extracted as a cobaltic ammine complex rather than as Co³⁺ ions. Both steam stripping and a pH controlled wash removed some of the ammines, but presented cost, crystallization, and/or dilution problems. The study found that the non-selective extractive nature of lignite resulted in the simultaneous extraction of ammonium ions and other divalent metal cations. Sulfuric acid effectively eluted the cobalt from lignite, but any ammonium ions and ammines present were also removed. Also noted with the use of lignite for Co³⁺ extraction followed by acid elution was the reduction to Co²⁺ during the extraction-elution process. Bradbury and Um [79] in their patent described the extraction of Co³⁺ from ammoniacal ammonium carbonate solution at pH of 9.2. The results in the patent showed that the amount of cobalt which was adsorbed on the lignite pretreated with an acid solution was much higher than the amount of cobalt adsorbed on lignite pretreated with water or used in a dry state without any pretreatment.

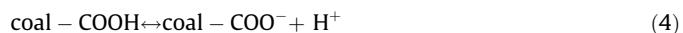
In a study by Mohan and Chander [80], lignite was used to remove and recover metal ions from acid mine drainage (AMD) in single and multiple column setups. The single and multiple

columns in downward flow modes were used to simulate industrial conditions for acid mine wastewater treatment. The study was aimed at treating AMD which was contaminated by iron (Fe²⁺ and Fe³⁺), Mn²⁺, and Ca²⁺ and not Al³⁺. The results showed that the lignite usage rate was higher in a single column (0.981 g/L) compared to multiple columns (0.085 g/L); three columns in this study. In this study lignite usage was defined as follows:

$$\text{Lignite usage rate(g/L)} = \frac{\text{Weight of lignite in column(g)}}{\text{Volume at breakthrough(L)}} \quad (3)$$

Furthermore, a study by Lafferty et al. [70] showed that using multi-stage treatments of heavy metal solutions with lignite could reduce the pollutants to acceptable discharge limits at a lower cost than using conventional heavy metal treatment processes. Mohan and Chander [80] used a batch mode to examine the effect of pH. The sorption of Fe²⁺, Mn²⁺ and Fe³⁺ on lignite was found to increase with an increase in pH of the test solution. However, it must be noted that for sorption studies, the pH of solution must be less than the pH for precipitating respective metal ions [80]. In their study, Mohan and Chander [80] observed that the sorption of Fe²⁺ was very low at pH_{in} ≤ 2, but it increased from 6% to 84% at pH of 4.0. The insignificant removal of metal ions at low pH is attributed to the competition between the protons and the metal ions for the same binding sites [81]. Furthermore, the increase in the positive surface charges at low pH results in a higher electrostatic repulsion between the surface and metal ions [82,83]. However, at pH_{in} > 4.0, the removal of Fe²⁺ was considered to have taken place by sorption as well as precipitation, i.e., the OH⁻ ions from the solution formed some complexes with Fe²⁺ as described by the reaction in Eq. (6). Similarly, the removal of Mn²⁺ was also negligible at pH_{in} ≤ 2, but increased with an increase in pH_{in} though precipitation occurred at pH_{in} ≥ 8. These results show that solution pH is a significant factor that determines the degree of metal adsorption. Furthermore, the study by Lafferty et al. [70] found equilibrium solution pH to be a major parameter governing the extent of metal adsorption. Coals that generated higher solution pHs were found to exhibit the largest metal adsorption.

In general, the dependence of cation exchange capacity of the low coal on solution pH can be explained by the following reactions illustrated in Eq. (4) through to (6) [84–87]:



For pH lower than pK_a of the carboxylic acid functional groups on coal surface, there is high concentration of H⁺ ions, therefore,

Eq. (4) lies to the left. In other words, the ion exchange sites are mainly protonated and are less available for ion exchange. As the solution pH approaches or exceeds the pK_a (e.g., between approximately pH 2.0 and 5.0), the carboxylic acid sites are appreciably deprotonated (i.e., Eq. (4) lies to the right); resulting in the formation of carboxylate salts with cations present in solution, and Eq. (5) proceeds further to the right, thus metal ion removal is increased by increased pH. Within this pH range, the ion exchange process is the major mechanism for the removal of metal ions from solution. For very high pH (i.e., above 5.0), the amount of hydroxide ions increases and the formation of metal hydroxides becomes more prevalent (Eq. (6)) [85]. Therefore, at high pHs both ion exchange and metal hydroxide precipitation become significant in metal removal processes [86]. Furthermore, adjusting the pH of the solution to higher values could increase the exchange capacity of the coal as the phenolic functional groups would become deprotonated near a pH of 9 [87].

A study by Arpa et al. [84] reported the removal of Hg^{2+} , Cd^{2+} and Pb^{2+} ions from wastewater of a mining industrial plant using low rank Turkish coal. The equilibrium pH of the coal/solution mixture was found to be the principal factor controlling the extent of removal of Hg^{2+} , Cd^{2+} and Pb^{2+} ions from the aqueous solutions. The order of affinity on a mole basis for both the single and ternary systems was as follows: $Pb^{2+} > Hg^{2+} > Cd^{2+}$; with the actual cation exchange capacities obtained as 0.041 mmol for Pb^{2+} , 0.039 mmol for Hg^{2+} and 0.008 mmol for Cd^{2+} per gram of coal. Low rank Turkish coals were also investigated by Karabulut et al. [86] for the extraction of Cu^{2+} and Zn^{2+} ions from wastewater. The results obtained were similar to the findings by Arpa et al. [84]. Furthermore, the adsorption phenomena appeared to follow a typical Langmuir isotherm. The Fourier transform infrared (FTIR) studies of the raw and exchanged coals revealed that a significant amount of the metal removal observed was due to the formation of exchanged metal carboxylates on the coal surface [70] as shown in Eq. (5).

In their study, Mohan and Chander [88] showed that the sorption capacity of lignite was more superior than most of the other adsorbents tested for AMD treatment as shown in Table 4. Their study clearly demonstrated the advantage of lignite as an adsorbent for the removal and recovery of metals from AMD. In their study, the Langmuir and Freundlich models were applied to describe the equilibrium isotherms for metal ions uptake and the analysis of the regression coefficients showed that Langmuir and Freundlich models concurred very well with experimental data. However, the Langmuir model was found to be slightly better for

Mn^{2+} , while the Freundlich model was better fitted for Fe^{2+} sorption. Lafferty and Hobday [71] conducted a study that compared the cation exchange capacities of three Victorian brown coals obtained from different sources. All coals showed increased cation exchange capacities as solution pH was increased, but one of the coals (named YNE) exhibited a cation exchange capacity double that of the other coals for all cations except sodium. The higher exchange capacity for YNE coal compared with the other coals was attributed to a greater concentration of sodium carboxylate sites present in the coal. Actually, sodium carboxylates are known to exchange for a divalent cation more readily than protonated groups [70] which accounts for the high level of metal adsorption measured for YNE coal. A study by Lafferty and Hobday [74] showed that the selectivity trend for the metal ions studied from the first transition metal series follows the Irving-Williams order ($Mn < Co < Ni < Cu < Zn$) irrespective of the source of coal. This shows that metal removal from solution by low rank coals is consistent with metal complexation involving oxygen containing functional groups such as carboxylic acid sites. In other words, the observed trend for the coals irrespective of the source is consistent with ion exchange and subsequent metal complex formation being the major cation removal process, and that this process is associated with oxygen containing ligand groups [74,77]. Ideally, for metal-ligand complex formation, the stability order: $Mn < Fe < Co < Ni < Cu > Zn$ has been found to hold for all oxygen and/or nitrogen donor ligands and divalent metals from the first transition metal series [77]. On the other hand, other materials such as calcium-loaded coal and char deviated from the Irving-Williams order, presumably because processes other than ion exchange were also occurring, i.e., hydroxide precipitation for calcium-loaded coal and surface adsorption for the char [74].

Several studies have been carried out to remove chromium, in its various oxidation states, from waste solutions using low rank coal [8,73,89–93]. It must be noted, however, that the environmental and biological effects of chromium are dependent upon its oxidation state [90]. On one hand, Cr^{3+} is essentially non-toxic and, in fact, Cr^{3+} complexes (picolinate) are applied to human food supplements, and these are also bioavailable to plants [90]. On the other hand, Cr^{6+} is poisonous to most living organisms and has found application in wood preservation [90,94]. Nevertheless, both states of chromium are non-biodegradable and thus must be removed from wastewater. Depending on the type of ion and surface functionalities, the uptake can involve ion sorption, ion exchange, chelation, and redox mechanisms with the surface functionalities being considered as partners in the electron transfer processes [90]. Gode and Pehlivan [73] used two Turkish brown coals to investigate the equilibrium and kinetic properties of Cr^{3+} ion adsorption. The Cr^{3+} ion adsorption on both brown coals was described by the Langmuir isotherm model. Though the adsorption efficiencies of the two coals differed, in general, the adsorption of Cr^{3+} ions was dependent on the initial concentrations of adsorbate, sorbent amount, pH, and time of contact. Anwar et al. [8] studied the adsorption of Cr^{3+} ions using two Pakistani coals in a batch mode. From the Langmuir isotherm, the value of the maximum amount of Cr^{3+} ions adsorbed per unit mass of coal (Q_{max}) for Lakhra coal was higher than that of Thar coal indicating that Lakhra coal had more active sites as compared to Thar coal. However, the bonds formed between Thar coal and Cr^{3+} ions were relatively stronger than the bond between Cr^{3+} ions and Lakhra coal as evidenced from the desorption studies. Lakatos et al. [90] conducted a comprehensive study in which a wide range of coals were used to determine the characteristics of Cr^{6+} removal with the view of using coals for the reduction and removal of Cr^{6+} from waste streams and leachates. Air oxidized samples were also prepared from bituminous coals to increase their Cr^{6+} removal capacities. The study showed that redox mechanisms play an

Table 4
Adsorption capacities of Fe^{2+} , Fe^{3+} and Mn^{2+} on lignite versus other adsorbents [88].

Adsorbent	Fe^{2+} (mg/L)	Fe^{3+} (mg/g)	Mn^{3+} (mg/g)
Lignite	34.22	11.90	28.52
Sphagnum peat (SFO6)	32.25	–	–
Merck carbon (No. 2514)	–	0.92	–
Maize cob	–	2.50	2.28
Palm fruit bunch	–	1.98	2.21
Wollastonite	0.43	–	–
Collophane	–	49.80	–
China clay	0.27	–	1.04
Nigerian coal	8.83	–	–
Biomass	19.20	–	–
Rice husk	0.15	–	–
Carbon SA	25.60	52.62	4.16
Carbon SN	22.27	–	5.00
Carbon WV-B	21.28	31.62	7.28
Carbon B4	25.61	4.13	0.50
Carbon B3	28.78	2.74	2.31
Carbon F-400	14.59	–	9.72
Carbon UU	46.36	4.76	16.42

important role in Cr⁶⁺ uptake, with sorption of the resulting Cr³⁺ ions being aided by the functionalities arising from oxidation of the coal surfaces. In acidic media, much of the resulting Cr³⁺ was exchanged back into solution by hydrogen ions, but some of the sorbed chromium was found to be irreversibly bound to the coal implying that chemisorption took place during the adsorption.

Khur et al. [87] evaluated the ability of a Western Kentucky low rank coal as a remediating agent for removing radionuclides and heavy metals from aqueous solutions in a batch mode. Their study used cobalt as a model metal for investigating the chemistry of the system. The kinetic and thermodynamic properties and effect of pH and charge density on the ion exchange process were investigated. For the majority of metals investigated, the maximum metal adsorption was achieved at pHs above 3.5. The initial rate of metal adsorption was found to follow first-order kinetics, and the variation of the reaction rate with temperature was used to determine the energy of activation for the reaction as $17.1 \pm 1.1 \text{ kJ/mol}$. This value shows that the process is not merely physical adsorption of the metal to the surface of the coal particles, but also involves a chemical reaction [87,95]. The metal adsorption process was well described by the Langmuir adsorption isotherm with a Gibbs free energy of $-8.85 \pm 0.24 \text{ kJ/mol}$, indicating a chemical process that is thermodynamically favourable [87,96]. Additional studies with environmentally significant metals and radionuclides demonstrated that cations with higher charge density were preferentially adsorbed. In other words, the cation exchange capacity increased as the charge density of the cation increased for all metals investigated. The only exception was thorium. The reduced cation exchange capacity for thorium could be due to the fact that thorium is known to form polyatomic ions in solution [87,97], which could reduce its charge density and, therefore, decrease its cation exchange capacity.

Marsalek [98] used altered (oxidative and thermally) and non-altered bituminous coal as immobilization agents for removing Pb²⁺ ions (as model metal) from aqueous solutions in batch and packed column modes. In addition, 'humic acid' and commercial activated carbon were also studied for comparison purposes. A sample of 'humic acid' was obtained from oxidative altered coal by leaching it with aqueous NaOH ($\approx 10\%$) and subsequent precipitation of alkali-soluble portion by HCl ($\approx 1 \text{ M}$). The pH of the solutions was found to be a relevant factor that affected the amount of ions adsorbed; an increase in the adsorption capacities was generally observed with a rise in the pH. The study also showed that higher adsorption obtained for smaller particles of coal was due to larger surface area per unit mass of coal. However, higher amount of immobilized cations for the 'humic acid' sample suggested that the specific surface area is not so important a factor while the content of acidic groups appears to be significant. In column studies, an increase in the initial concentration of the adsorbate resulted in an early breakthrough and exhaustion of the bed indicating that the fluid to adsorbent mass transfer rate of the solute increases with an increase in adsorbate concentration [99,100].

Butler et al. [101] presented a study in which brown coal was used to remove dissolved organic carbon (DOC) and selected inorganic cation species (K⁺, Na⁺, Ca²⁺, Cu²⁺, Mg²⁺, Zn²⁺, Al³⁺, and Fe²⁺) from mechanical thermal expression (MTE) product waters in packed bed columns. The MTE is a non-evaporative coal dewatering technology [102] which involves the application of heat and mechanical pressure to coal [103]. Initially, the coal bed was conditioned with water adjusted to a pH as close as possible to that of MTE water tested. This was to mitigate the concomitant leaching of water-soluble components inherent in the coal. The passing of pH-adjusted water solutions through the bed of brown coal resulted in an increase in the pH of the effluent waters. This was due to the washing of acidic components and the establishment of a new equilibrium between the adsorbent coals and the waters

with a higher pH. However, passing the MTE waters through the pre-rinsed adsorbent coal bed resulted in a drop in the effluent pH and then a slow increase towards the pH of the influent MTE waters. This was typical of ion exchange processes where the displacement of protons into the water phase can result in a decrease in the pH. Significant amounts of DOC were adsorbed from MTE water in excess of the amounts removed from the coal during washing with pH-adjusted water prior to the fixed-bed adsorbent runs. The amount of DOC adsorbed increased with an increase in the concentration of DOC in the MTE product waters. Monovalent cations, K⁺ and Na⁺, showed similar adsorption behaviour, and the ability of the coal to remove the two ions was exhausted quickly. The adsorption of divalent cations did not (generally) reach saturation within the volumes tested. Mg²⁺ was an exception, possibly due to the higher concentration of Mg²⁺ resulting in a rapid exhaustion of the available exchange sites. However, Zn²⁺ adsorption was significantly lower due to its low concentration in the MTE product waters. For both the monovalent and divalent cations, there was a direct relationship between the extent of cation exchange and the concentration of each type of cation in the influent MTE water. In other words, as the concentration of the cations in the MTE product water increased, the amount of cations exchanged onto the coal also increased. In a small number of cases, there was a release of Ca²⁺ and Mg²⁺ from the coal adsorbent. This seems to have been the result of the low concentrations of Ca²⁺ and Mg²⁺ in the MTE product water relative to the coal, resulting in a net desorption. Thus, these results suggest that the adsorption/desorption phenomena is equilibrium driven. It was expected that the trivalent cation (Al³⁺) would be preferentially exchanged onto acidic functional groups over monovalent and possibly divalent cations. However, Al³⁺ was found to desorb (or released) from the coal after passing about 100 mL of MTE water, possibly because the relatively large hydration sphere of Al³⁺ compared with the other ions in solution affected its ability to exchange at sites which can accommodate smaller ionic species.

An earlier study by Butler et al. [85] investigated the ability of brown coals to adsorb organic and inorganic impurities from MTE product water in a batch mode. The results showed that at equilibrium, up to approximately 70% of the DOC and in some cases 99% of the divalent inorganic species were removed from MTE product waters. However, depending upon the composition of the adsorbent coals and the MTE waters tested, the extent of removal of organic and inorganic components from the waters varied. Furthermore, the coal had less affinity to adsorb monovalent K⁺ and Na⁺ cations. This is in contrast to the study in packed bed columns by Butler et al. [101] where a direct increase in the extent of cation exchange was observed as the concentration of monovalent cations increased in the MTE influent waters.

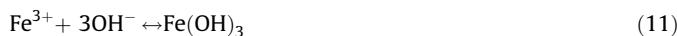
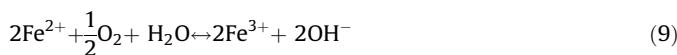
In an attempt to elucidate the mechanism of the binding of metal elements on coals, Eskenazy [104] used peat and coal macerals to adsorb titanium. This study showed that titanium was attached to peat and coals primarily by an ion-exchange mechanism.

5.1.2. Demineralized coals

Coals are often demineralized before use [105,106]. The demineralization procedure usually employed involves washing coal with hydrochloric acid followed by treatment with hydrofluoric acid [105–107]. The effect of demineralization on the characteristics of coals (coal structure, properties and reactivity) has been examined by several researchers [105,106,108–116], though with conflicting results [105]. However, this kind of work is beyond the scope of this paper. In general, demineralization is expected to cause structural and reactivity changes [105,116] due to acid-induced chemistry, such as ester hydrolysis and Friedel-

Crafts reactions [105]. For example, new carboxylic groups are formed replacing carboxylate anions—an ion exchange phenomenon [105].

Eligwe and Okolue [117] investigated the kinetics and mechanism of Fe^{2+} adsorption on a Nigerian brown coal. The coal was demineralized and subsequently converted into its acid form by washing with 2 M HCl for 1 hour at room temperature. The results showed that the initial rate of Fe^{2+} adsorption on demineralized brown coal was first-order with respect to its concentration in solution. The adsorption process exhibited Langmuir behaviour and that the adsorption process was essentially irreversible (i.e., the adsorption process was chemical in nature). Just like other metal ions discussed so far (e.g., Lafferty et al., [70]), the dependence of Fe^{2+} adsorption on pH was expected for carboxylic and phenolic exchange groups on the acid-washed coal, and can be explained by the following equations [117]:



Eq. (7) represents deprotonation of the acid-washed coal, and Eq. (8) shows attachment of the metal cation (e.g., Fe^{2+}) to the deprotonated coal surface. As already discussed, at low pH values Eq. (7) dominates as a result of the adsorption surface being surrounded by H^+ ions which compete for binding sites on the coal surface [81]. Furthermore, the presence of H^+ ions result in the reduction of Fe^{2+} ions interaction with the binding sites because of higher repulsive force that arises [82,83]. Eq. (9) represents aqueous oxidation of Fe^{2+} to Fe^{3+} , and Eqs. (10) and (11) the precipitation of metal hydroxides. Thus at high pHs, hydroxide precipitation (Eqs. (10) and (11)) and surface adsorption (Eq. (8)) may contribute significantly to the overall metal ion uptake [74].

Ajaero et al. [118] tested the adsorption potential of demineralized Nigerian brown coal for the removal of Cu^{2+} ions from aqueous solution. The adsorption capacity of demineralized Nigerian brown coal was found to increase with increasing solution concentration, contact time and pH of the system. In addition, the adsorption process was found to be spontaneous and exothermic in nature. A study by Radović et al. [107] examined the loading of calcium onto demineralized lignite coal. Ion exchange with calcium acetate resulted in a loading of about 2.9 wt% calcium (dry).

5.1.3. Sulphonated coals

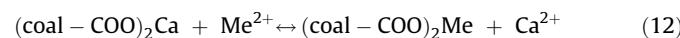
It must be noted that though the adsorption capacity of low rank coals is somewhat low, it can be enhanced by suitable transformations which can increase the content of functional groups [72]. In a number of studies, the number of functional groups in low rank coals was increased by means of reactions such as demineralization, oxidation, nitration, humic acid fraction isolation, and sulphonation [72,119,120]. Following these studies, it was concluded that the best ion-exchange properties are obtained by sulphonation reactions [72]. The sulphonated lignites have high exchange capacities (carboxylic-sulphonic groups) and, in

addition, the sulphonic groups introduced give a strongly acidic nature to the lignites, so that they can be used in ion exchange reactions over a wide pH range [72]. Oleum is the widely used sulphonation media. However, though oleum can produce lignites with higher cation exchange capacities, these highly sulphonated coals are easily and readily leached so they cannot be useful in practical applications [71]. Ibarra et al. [72] studied the sulphonation of lignite using oleum. The sulphonated lignite was tested for stability (leaching and swelling) in solution. It was found that, though the exchange capacity was increased (up to 3.7 meq/g), the sulphonated lignite produced was readily leached such that it cannot be practically used in ion-exchange processes. Ibarra and Moliner [120] investigated the removal of copper by concentrated sulphuric acid sulphonated lignites under equilibrium and dynamic conditions. Adsorption isotherms were fitted to the Langmuir equation from which saturation capacity and distribution coefficients for the sulphonated lignite were calculated. Breakthrough curves were determined and the overall mass transfer coefficients and exchange zone height were calculated from them.

Pandey and Chaudhuri [121] studied the adsorption of inorganic mercury from water using bituminous coal (as-received and chemically pretreated) and activated carbon. It was found that the adsorption of mercury onto some of the as-received coal samples was comparable to that of activated carbon. Chemical pretreatment of coal (e.g. nitric acid oxidation, sulphonation, and sulphurization) further improved the sorption capacity. Through the nitric acid oxidation, carboxyl and phenolic functional groups lost during the coalification process were reintroduced giving the pretreated coal an increased ion-exchange capacity [122]. Sulphonation of coal increased the ion-exchange capacity by imparting sulfonate groups [123]. Sulphurisation of coal possibly formed some chelating groups on the coal surface (e.g. xanthates, dithiocarboxylates or dithiocarbamates) as indicated in the case of activated carbon [124]. These functional groups improved the binding of mercury. Whilst using the chemically pretreated coals, an important consideration to note would be the pH and chloride content of the system. Waters with high pH and/or high chloride content may reduce the efficiency of coals because of the presence of anionic mercury species under such conditions. Column studies indicated the feasibility of using coal for removing mercury from water supplies or industrial wastewater.

5.1.4. Calcium-loaded coals

Equation (1) shows the reaction that leads to the acidification of the sorption solution. Thus, the increase in H^+ concentration in the solution due to Equation (1) decreases $-\text{COOH}$ ionisation and, consequently, the ion exchange capacity of coal. However, if the ion exchanger is in a suitable salt form, the ion-exchange reaction does not increase H^+ concentration and thus the ion-exchange capacity is not decreased. Actually, the adsorption properties of natural coal can be markedly improved by the chemically fixed calcium [66,125–127]. For example, if a mixture of coal and lime ($\text{Ca}(\text{OH})_2$) is contacted with water, $\text{Ca}(\text{OH})_2$ dissolves, and the active groups in coal are gradually converted into the Ca^{2+} form. The Ca^{2+} form of coal would then retain the metals according to Equation (12):



Coal modified this way retains most heavy metals selectively and almost removes them from water [66]. Jochová et al. [66] used calcium-loaded lignite to remove heavy metals from wastewater by ion exchange. The calcium-loaded lignite was found to be very efficient especially in the case where pollutants in water were present in low concentrations and common methods are either economically unfavourable or technically complicated. The

selectivity of calcium-loaded lignite was found to decrease in the sequence: $\text{Pb}^{2+} > \text{Cr}^{3+} > \text{Fe}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} \geq \text{Cd}^{2+} \geq \text{Co}^{2+} \geq \text{Ni}^{2+}$.

Horáček et al. [127] studied two types of brown coal, oxyhumolite and peat with respect to their ability to remove heavy metals from waste waters. The results showed that the calcium-loaded form of these materials can be effectively used for metal extraction by ion exchange with calcium. Furthermore, the proposed method could be recommended for concentrations of metals less than 10 mM. However, the method was found to be limited by the pH values above which individual metals hydrolyse. Earlier study by Horáček et al. [126] also investigated the use of calcium-loaded Czech low rank coal in removing heavy metals from waste solution. The results showed that calcium-loaded coal can be effectively used for extraction of heavy metals from aqueous solutions. The study also found the main advantages of the method, compared to other methods, are its simplicity and low costs.

Cullen and Sivior [125] contacted low rank coals, peat or wood sawdust and a solution of calcium hydroxide to produce calcium loaded adsorbents which was used to extract many metals from solution by ion exchange of the calcium. The results showed that the method was capable of extracting copper, nickel, chromium, cadmium, lead, zinc, mercury, cobalt, silver, iron, manganese, vanadium, germanium, gallium, aluminum, antimony, and uranium. For most of the metals more than 99% was removed from 1 g/L solutions. The adsorbed metals could be stripped to form solutions of useful concentrations and the adsorbents re-used, or alternatively, metals were recovered by combustion of the loaded adsorbent and subsequent treatment of the metal residues. Thus, the method was found to be an environmentally preferred effluent treatment procedure because it enabled collection and recycling of heavy metal pollutants. The calcium-loaded coal method was found to be favourable to treat waste solutions from a wide range of industrial operations, particularly those of AMD, metallurgical processing, and electroplating. Patents by Cullen et al. [128] also explored the use of calcium-loaded coals to extract metals from metal contaminated solutions.

5.1.5. Chitosan-doped coals

As already discussed in Section 3, the sorption properties of low rank coal are given mainly by oxygen functional groups (carboxyl and phenolic) of humic substances immobilized in situ in the organo-mineral coal matrix [129–131]. Partial solubility (leaching) of humic substances from coal and lower mechanical stability of coal particles in neutral and alkaline solutions limit coal sorption capabilities, particularly, when utilized for dynamic column operations [130,132]. Thus, it is imperative to provide the humic substances functionalities with an additional physical support while preserving their accessibility [130]. For example, in order to reduce coal sorption deficiency due to leaching of soluble metal-humic complexes, Havelcova et al. [132] investigated the possibility of stabilizing coal in neutral and basic media by combining it with chitosan. Chitosan (2-amino-2-deoxy-(1→4)- β -D-glucopyranose) is derived from chitin, a major component of shells of crustacean organisms (crabs, shrimps), insects, and some fungi mycelia, the second most abundant biopolymer next to cellulose [130]. A combined sorbent was prepared by impregnating lignite with chitosan. Sorption performance of the combined sorbent and the untreated lignite were tested for Co^{2+} , Cu^{2+} , and Cd^{2+} with respect to pH and metal concentration in batch mode. The study showed that the leaching of humic substances was strongly suppressed by chitosan covering. However, the impregnation of coal with chitosan had significant effect on its acidobasic and sorption properties. This may be attributed to reduction in (or interference of) the available functional groups of humic substances for metal ion binding due to their interaction with

chitosan. For example, the sorption of Co^{2+} and Cd^{2+} was either less pronounced or negligible (or even reversed). Nevertheless, sorption of Cu^{2+} was significantly higher on the combined sorbent than on the original lignite in the entire pH range (2–10).

The results of Mizera et al. [133] differed from a study by Havelcová et al. [132] in many aspects. Although chitosan provided only surface coating of the coal sorbents, its presence had affected the sorption performance of lignite and naturally oxidized lignite (oxihumolite, leonardite) significantly. At identical pH values, the sorption efficiencies of the chitosan coated coals were higher than those of the raw coals for Co^{2+} and Cd^{2+} , and the difference increased with pH. However, the effect was reversed for Cu^{2+} adsorption. Furthermore, the study by Mizera et al. [133] found that chitosan impregnation caused an increase in specific surface, total volume of mesopores and macropores, their surface, average pore size, and porosity, and decrease in micropore volume and surface. In contrast, the results by Havelcova et al. [132] were generally reversed in chitosan-doped lignite. The above parameters slightly decreased except for micropore volume and surface, which increased in the lignite upon impregnation with chitosan. Furthermore, contrary to a study by Mizera et al. [133], the chitosan impregnation caused a decrease in the proton exchange capacity in the lignite system in a study by Havelcova et al. [132]. The differences between the two studies were not clearly explained though they were carried out by one research group.

Mizera et al. [130] also investigated the effect of chitosan on the sorption performance of low rank coal (lignite, oxidized lignite and oxihumolite). Cesium (Ce^+), Co^{2+} and europium (Eu^{3+}) were chosen as representative metals because of their diverse properties (cation charge, strength of binding with humic substances). For example, they do not hydrolyze significantly in acidic or neutral media, their radioisotopes produced in nuclear and radiation technology represent potential risk for the environment (^{137}Cs , ^{60}Co , Eu as a homolog of trivalent actinides), and their radioisotopes are readily prepared by irradiation in a nuclear reactor. An improved sorption efficiency of the coal (oxihumolite) at neutral pH was obtained in mixture with chitosan for sorption of Eu^{3+} and Co^{2+} . Chitosan prevented deterioration of the sorption ability of coal at higher pHs probably by forming insoluble complexes resulting from soluble humic substances leached from coal. Therefore, results obtained in the study supported the idea that chitosan coating stabilizes coal in basic solution and inhibits leaching of humic substances and their complexes with the metals from coal into solution. Besides fixing metal humates within the sorbents, chitosan may also positively affect the sorption efficiency by its buffering action against the hydroxide addition [133]. On the other hand, when the interaction of chitosan with the binding sites on coal surface prevails over scavenging of dissolved metal species, the presence of chitosan can reduce the sorption ability, as observed for the oxidized lignite.

5.1.6. Activated carbon from coals

Most commercial activated carbon is derived from coal, and has been extensively studied by several researchers for comparison with other adsorbents from other sources. Therefore, the use of activated carbon derived from coal will not be discussed further, but is available elsewhere in this review. However, this section endeavours only to compare the characteristic differences between coal based activated carbon and some of those derived from other sources.

The search for low cost activated carbons has led to extensive amount of research focused on studying different forms of activated carbon precursors. Any cheap material with high carbon content and a relatively low ash can be sought after, and used as a raw material for the production of activated carbon [134]. Currently, activated carbon precursors can be derived from conventional (agricultural and wood industry) and non-

conventional (municipal and industrial) wastes. However, extensive amount of research has been focused on studying different agricultural waste because of its availability and low cost. Moreover, activated carbons obtained from agricultural waste perform better than non-conventional waste. Some of the common agricultural waste include products such as rice husk [135], sugarcane bagasse [136], olive stones, wall nut shells [137], and wood saw dust [138] to mention a few.

Studies have shown that physical and chemical properties such as surface area, porosity, surface functional groups, pore structure, composition, elemental analyses, and ash content of activated carbon depend largely on the type of precursor. For example, it has been reported that materials with high lignin content develop activated carbon with macroporous structure, while materials with high cellulose content produce an activated carbon comprised of microporous structure [139]. Activated carbons with acidic surface chemical properties favour basic gas adsorption, while activated carbon with basic surface chemical properties favours acidic gas adsorption [140]. Therefore, the adsorption capacity of activated carbon will depend largely on the type of raw material the activated carbons are derived from. Activated carbon characteristics of different raw materials produced from various raw materials are presented in Table 5. Furthermore, an article by Ioannidou and Zabaniotou [141] gives a comprehensive overview of the properties of activated carbons derived from different agricultural products. The study presents the different activation conditions (chemical and physical activation) used to produce activated carbons, and the characteristics of activated carbons from agricultural waste.

5.1.7. Coal fly ash

In recent past, coal fly ash has been investigated for its direct use as an adsorbent for the removal of a variety of metal ions from wastewaters. The studies have been prompted by the fact that most fly ash is alkaline, and its surface is negatively charged at high pH; hence, it can be expected to remove metal ions from solutions by precipitation or electrostatic adsorption [54]. Besides, it contains a reasonable amount of unburnt carbon, which has a high adsorption capacity [54,142]. As early as 1982, fly ash was considered as a potential adsorbent for removing Cr⁶⁺ from industrial wastewaters [54,143]. Readers are referred to Ahmaruzzaman [144] for detailed information on research that directly used coal fly ash for the removal of heavy metals. In summary, Ahmaruzzaman [144] showed that coal fly ash has great potential for use in the removal of heavy metals from wastewater. However, this potential is limited by the variability in chemical composition of coal fly ash and the large volumes that might be required for it to be effective.

5.1.8. Coal fly ash-derived zeolite

Extensive research has been carried out on the potential application of the coal fly ash-derived zeolite in the field of water purification. In particular, the removal of heavy metals and ammonium ions from solutions has been tested extensively [61,145–154]. The high Al³⁺/Si⁴⁺ ratio in coal fly ash-derived

zeolites accounts for the high cation exchange capacity in some of them. In fact, some studies have shown that the zeolitic material obtained may reach cation exchange capacity of up to 5 meq/g [58].

Research has shown that the composition of the wastewater solution affects the uptake of pollutants by zeolites. In other words, there is competition between cations to occupy exchangeable sites in zeolites. In a study by Moreno et al. [61], the affinity of different metal ions studied for coal fly ash-derived zeolite was found to be in the following order: Fe³⁺ > Al³⁺ ≥ Cu²⁺ ≥ Pb²⁺ ≥ Cd²⁺ = Tl⁺ > Zn²⁺ > Mn²⁺ > Ca²⁺ = Sr²⁺ > Mg²⁺. In addition to the ion exchange process, precipitation of metal-bearing solid phases may have enhanced metal ion removal because of drastic pH rise induced upon addition of zeolite. However, ion exchange was considered as a dominant mechanism.

An important limitation to the application of the zeolitic material for the cation uptake from wastewaters is the possible occurrence of potentially hazardous leachable elements (such as Mo, As, Cr, V) in the residual fly ash particles when direct conversion products are used [58]. However, this limitation is minimized if the leachable elements are in low concentrations, and the limitation is completely eliminated if pure zeolitic material synthesized from Si fly ash extracts is used.

Another use of the zeolitic material synthesized from coal fly ash is in the immobilization of heavy metals in contaminated soils. When phyto-remediation strategies are adopted for the final recovery of polluted soils, the immobilization of metals is necessary to avoid leaching of the metals and the consequent ground water pollution. A study by Moreno et al. [154] showed that the application of zeolitic material to polluted soils considerably decreased the leaching of elements such as Cd, Co, Cu, Ni, and Zn. Although the reduction of the leachable proportion was mainly due to the ion exchange mechanism, the precipitation of insoluble phases (as a consequence of the pH rise from 3.3 to 7.6 due to the zeolite addition) may have also contributed to the immobilization of the pollutants. Similar studies have also been performed by Lin et al. [151] to immobilize Cd in contaminated soils. A drastic reduction of the leachable Cd contents (from 88% to 1% wt) was obtained by adding zeolitic products synthesized from fly ash to polluted soils with a dose of 16% wt/wt.

5.2. Metalloids

Metalloid group of metals include germanium (Ge), silicon (Si) and arsenic (As). These are elements that exhibit properties of metals and non-metals. The special interest in these metals arise from the fact that if they are to be removed from aqueous solutions using adsorbents, then the adsorbents must be modified to cater for this dual property. Typically, adsorbents are either characterized as metal or non-metal adsorbents. Among the most commonly encountered metalloids are Ge and As, of which As has attracted a lot of attention due to its toxic and carcinogenic properties. Typically, As exists in As(III) and As(V) forms, for which the ionic structures are AsO₃³⁻ and AsO₄³⁻, respectively. Coal-based mesoporous activated carbon has been used effectively to remove As(III) and As(V) from aqueous solution [155]. The adsorption of As(III) and As(V) was reported to be sensitive to the co-existence of other ions such as phosphate, silicate, carbonate and sulfate. These ions suppress the adsorption of As and the order in which they do so is: phosphate > silicate > carbonate > sulfate [155]. It has been explained by Gong et al. [155] that the high performance of coal-based activated carbon is due to the high average pore size and total pore volume. Furthermore, coal contains ash which offers active sites for positive charges on the carbon surface [155] that can enhance adsorption.

As for the Ge, some of the most common applications for Ge include infrared vision system and chemotherapeutic treatment

Table 5
Characteristics of activated carbons from agricultural residues and coal [33,141].

Raw material	S _{BET} (m ² /g)	V _o (cm ³ /g)
Apricot stones	1190	0.50
Cherry stones	875	0.28
Grape seeds	497	0.12
Nut shells	743	0.21
Corn cob	960	0.486
Macadamia nutshell	1718	0.723
Coal	1163	1.310

[156]. Marco-Lozar et al. [156] studied the effect of the adsorption properties and surface chemistry of activated carbons on the adsorption of Ge (IV) from dilute aqueous solutions (50 ppm) using coal and two lignocellulosic chars. The results of the study showed that the performance of the adsorbents including the coal-based one can be improved by the use of ligands such as catechol that form a chelate complex with Ge.

5.3. Organic pollutants

A wide range of organic compounds are currently being used, and many of these become potential water pollutants when they are released into water bodies [157]. Water pollution due to organic contaminants is a serious issue because of acute toxicities and carcinogenic nature of the pollutants [158,159]. Various types of recalcitrant organic pollutants include dyes, pesticides and herbicides, phenolic compounds, pharmaceuticals, antibiotics and hormones, plasticizers, perfluorinated chemicals, surfactants and derivatives, chelating agents, and microcystin toxins [160]. Among the different types of organic pollutants, phenolic compounds will be taken as model organic pollutants, in this review. Due to their widespread applications, phenolic compounds are common contaminants in aqueous streams and are considered as priority pollutants since they are harmful to plants, animals, and human even at low concentrations [9,161]. In fact, many phenols and their derivatives have been classified as hazardous pollutants because of their potential toxicity to human health [162].

The following subsections discuss literature published on the removal or degradation of organic pollutants from water and wastewater using coal-based adsorbents.

5.3.1. Phenolic compounds

Hobday et al. [33] studied the suitability of using a variety of Victorian brown coal-based adsorbents (raw coal, grus, briquette char, power station char and an activated carbon) for the removal of nitrophenol from aqueous solution. The influence of adsorbent dosage levels, particle size, and the presence of buffer solution components, other electrolytes, and pH on the kinetics of adsorption of nitrophenol were investigated. The activated carbon was found to be the most efficient adsorbent examined in terms of adsorbate per unit mass of adsorbent under the experimental conditions used. The influence of particle size variation on the rate of adsorption for raw coal was found to be minimal. In contrast, particle size significantly influenced the kinetics of adsorption with, for example, briquette char, where discrete particle size ranges were maintained due to greater adsorbent hardness. It must be noted that, though particle size may influence the kinetics of adsorption, it is thought to have little influence on adsorption capacity. This is due to the fact that the kinetics of adsorption is determined mostly by the rate of adsorbate access to transitional pores. Whereas, the adsorption capacity is determined mainly by surface area, which is itself largely determined by micropores; the micropore surface area is not significantly affected by particle size [163]. The pH of the solution is an important parameter and, therefore, plays a preponderant role in the adsorption processes [164]. Changes in pH may influence adsorption by changing the electrical charge on the adsorbate and coal material. For example, in aqueous solution, nitrophenol is a weak acid ($pK_a = 7.15$) [165], hence at pH lower than 7, nitrophenol is almost exclusively in the neutral molecular form, whereas at neutral pH, nitrophenol has significant levels of both neutral and anionic phenolate forms [33]. For some adsorbents, pH changes in the acidic region appeared to have little influence on adsorption rates of nitrophenol, but for chars, reduced pH conditions appeared to reduce adsorption rates. In the alkaline pH range, some of the adsorbents were leached, with the extent of leaching reducing as the carbon content of the

adsorbent increased. This is one aspect that could limit the usefulness of coal as an adsorbent. However, coal leaching may be mitigated by providing the coal surface functionalities with an additional physical support such as coating with chitosan as already discussed [130,132,133].

Humenick et al. [166] evaluated coal ash and activated coal-char produced from an underground gasification facility for the in-situ treatment of contaminated groundwater. Adsorption isotherm studies performed indicated that both sorbents irreversibly adsorbed phenol, *o*, *m*, and *p*-cresol from the aqueous phase. Uptake was modelled to the Freundlich and Langmuir isotherms, and adsorption capacities were found to be comparable to that of activated carbon.

Ishaq et al. [9] studied the adsorption of environmentally objectionable phenol using Pakistani coal treated with NaOH and HCl leachants in packed bed columns. Coal was treated with NaOH and HCl so as to make the carbon in coal perfectly nonpolar. The eluates from the column were studied using UV-vis spectrophotometer. Complete adsorption of phenol from the aqueous solution onto virgin coal samples was evident from the shape of the adsorption curves, which was flatter at 270 nm. However, new absorption bands could also be seen in the region 200–250 nm. This was attributed to the fact that phenol, being organic in nature, might have caused extraction of other chemicals from coal as reported elsewhere [167,168]. The shape and intensity of UV-vis spectra showed that the adsorption of phenol was poor on NaOH-treated coal. Several peaks were observed in the region 250–300, which showed that phenol was not effectively adsorbed. In addition, the existence of bands in the region 200–250 nm showed the presence of other organics in the eluates. The UV-vis spectra obtained for eluates from the HCl-treated coal showed that phenol was significantly adsorbed. The curves were flatter in the region 200–400 nm. In summary, the study showed that phenol was effectively adsorbed on HCl-treated coal compared to NaOH-treated samples. The study also showed that adsorption capacity of all the coal samples decreased when phenol concentration was increased beyond a certain limit.

The adsorption of phenolic compounds on coal-reject derived adsorbents was investigated by Haghseresh and Lu [169]. Coal-rejects were chemically treated in HNO_3 , H_2SO_4 , and NaOH at 25 °C and 75 °C, and then subjected to heat treatment at 600 °C. Pore structure characterization and the phenol adsorption capacities of the resulting carbonaceous adsorbents showed that HNO_3 pretreatment significantly enhanced the surface properties; consequently, the adsorption capacities of the adsorbents. The results also showed that by increasing the HNO_3 concentration during pretreatment, the adsorption capacities of the resulting carbonaceous adsorbents increased, implying that the micropore volume became more accessible to the organic adsorbate molecules. Applications of theoretical equations to fit the experimental data demonstrated that the extent of the adsorption was dependent on the size of the phenolic compounds, whereas the strength or the energy of the adsorption was dependent on the adsorbate-adsorbent interaction, characterized by K_L , n , and β , respectively, in the Langmuir, Freundlich, and the Redlich-Peterson equations. It was shown that when a phenolic compound has a stronger electron-withdrawing substituent on the aromatic ring, the adsorbate-adsorbent interactions are stronger. In the case of the two-parameter equations (Langmuir and Freundlich), the Freundlich equation was found to give the best fit.

Ahmaruzzaman and Sharma [170] had used coal, residual coal, and the residual coal treated with H_3PO_4 as a medium for removal of phenolic compounds from wastewater in batch and column operations. The effects of system variables such as pH, contact time, and temperature were investigated. The results showed that the adsorption capacity for all the phenolic compounds on

different adsorbents in column operations was higher than that in batch operations. The uptake of phenols was found to decrease with an increase in temperature which showed the exothermic nature of adsorption. The adsorption capacities of adsorbents studied for different phenols were found to be in the following order: phenol < *p*-chlorophenol < *p*-nitrophenol; and all the phenols followed first order kinetics. The pH was found to significantly affect adsorption capacity of the different adsorbents. First and foremost, it must be noted that the adsorption of weak electrolyte such as phenolic compounds, on the surface of a porous amphoteric solid, such as coal or activated carbon, from aqueous solutions, is affected mainly by two important factors which depend on pH of the aqueous solution [170]. One of them is the degree of dissociation of the electrolyte and the other is the dominant charge on the surface of the solid. The first factor can be qualitatively predicted by the pKa (activity constant) of the weak electrolyte, because at a solution pH lower than the pKa it will remain undissociated [170,171]. The study showed that at acid pH, the amount of phenols adsorbed, remained constant or increased slightly with the pH, and at a certain value of pH, there was a decrease in the value of the amount of phenols adsorbed, which continued with an increase in pH. The results indicate that the phenolic compounds are preferentially adsorbed on the surfaces of coal and activated carbons in their molecular form, because at acidic pH values they are not dissociated. The phenolic compounds started to dissociate at a pH close to their pKa values, which varied between 9.96 (phenol) and 7.13 (*p*-nitrophenol). However, the amount of phenolic compound adsorbed depended also on the surface charge of the coal and activated carbon. The coal and activated carbons used continued to acquire negative charge progressively from the external to the internal surface of the pores as the solution pH increased. This variation in the surface charge density of the coal and activated carbons affects adsorption capacity, essentially when the phenolic compounds are dissociated, because now the phenolate anions are repelled by the negative charge on the surface of the carbons. The suitability of the Freundlich, Langmuir, and Redlich–Peterson adsorption models to the equilibrium data was also investigated for each phenol–adsorbent system. The results showed that the equilibrium data for all the phenol–sorbent systems best fitted the Redlich–Peterson model.

Tarasevich [172] reported that natural long-flame coal from the Donbas field of Ukraine, Georgia and Russia could adsorb a wide range of organic compounds from wastewater because of a well-developed micro and meso-porous structure. The microporosity and mesoporosity structure and thus a large specific surface area, along with its low cost, suggests the Donbas field coal is a promising material for the adsorption of organic pollutants from natural and wastewaters.

A comparative study of the sorption of phenol and *p*-chlorophenol from water was performed by Streat et al. [173] using novel samples prepared by carbonisation and subsequent activation of straw and used rubber tyres as well as conventional activated carbons based on coal, coconut shell and wood. The results showed higher adsorption capacities for *p*-chlorophenol than for phenol on all granular activated carbons—wood, shell, rubber, and coal-based adsorbents—which agrees with a study by Ahmaruzzaman and Sharma [170]. However, this is in contrast to a study by Haghseresht and Lu [169] which observed the following order: phenol > *p*-chlorophenol > *p*-nitrophenol. Nevertheless, it is accepted that the solute uptake by activated carbon increases with a decrease in its solubility and increase in its molar mass [173,174]. For example, Caturla et al. [174] in investigating adsorption characteristics of a number of phenolic compounds, found that the amount of the solute adsorbed per gram of the adsorbent follows the order: phenol > *p*-chlorophenol > 2,4-dichlorophenol, as

expected from the respective molecular volumes of the adsorbates. However, when the adsorption capacities of various phenolic compounds in the literature are compared, conflicting observations are found as observed above. The conflicting observations or discrepancies arise from the variation in the pore size distributions of activated carbons as well as the differences in their surface chemistry properties [169]. Another significant factor in aqueous-phase adsorption is the adsorbate–adsorbent interactions. Phenolic compounds having electron-withdrawing groups are expected to be adsorbed more strongly. This is because such groups would deactivate the aromatic ring, thereby assisting the formation of a more stable electron donor-acceptor bond [175].

Moreno-Castillia et al. [175] studied the adsorption of phenol, *p*-cresol, *m*-chlorophenol, *m*-aminophenol, and *p*-nitrophenol from aqueous solutions on activated carbons obtained from an original and a demineralized bituminous coal at 25 °C. The adsorption capacities of the activated carbon for the phenols studied depended on the degree of activation of the activated carbon, the solubility of the phenolic compound in water, and the hydrophobicity of the substituents of the phenols. Thus, the adsorption capacity of the activated carbons rose with increased surface area and porosity of the carbon, with decreased water solubility of the phenolic compound, and with increased hydrophobicity of the substituents of the phenols. The relative affinity of the phenolic compounds toward the surface of the activated carbon was found to be related to the electron donor-acceptor complexes formed between the basic sites on the carbon surface (basic surface oxygen complexes and/or π electron-rich regions at the basal planes) and the aromatic ring of the phenols. Thus, the relative affinity increased with the basicity of the carbon surface and with the electron-withdrawing property of the substituent of the phenol. For a given activated carbon and for the different phenolic compounds studied, the adsorption capacities were found to be in the following order: *m*-aminophenol < *p*-cresol < phenol < *p*-nitrophenol < *m*-chlorophenol. This order, found with all carbons, seems to be related to the electron-withdrawing or electron-donating properties of the substituents of the phenol compound. Thus, the electron-donating property of the substituents decreases in the above order, which goes from a very powerful electron-donating group on the benzenic ring, such as the $-\text{NH}_2$ group, to electron withdrawing groups such as $-\text{NO}_2$ or $-\text{Cl}$ [176]. The study also showed that the adsorption capacity of the activated carbon depended on the solution pH. At acid pH, the amount of phenols adsorbed remained practically constant or increased slightly with increasing pH. When the pH increased further, there was a decrease in the amount of phenolic compounds adsorbed. The pH at which this decrease took place depended on the difference between the external and internal surface charge density as measured by electrophoretic and titration measurements, respectively.

Studies on the adsorption of phenol from aqueous solution by using pretreated noncoking low-grade bituminous coal were reported by Das and Sharma [177]. The coal was HNO_3 oxidized for different periods, and the adsorption of phenol on oxidized coal was estimated and compared to that on activated carbon. A comparison of the phenol adsorption by solvent-extracted residual coal (using quinoline or ethylenediamine) to the adsorption by the oxidized or the untreated coal was also made. Coal was only found to show better adsorption after oxidation for more than 12 h. The highest adsorption of phenol was given by the activated carbon. However, the solvent-extracted residual coal showed almost 43% adsorption of phenol, which was close to that observed for activated carbon. Solvent extraction of coal results in the removal of organic matter from the coal and reduces the particle size of coal with a consequent increase in surface area of the coal [178]. In fact, removal of volatile matter from coal due to solvent extraction is a

step toward carbonization (devolatilization) of coal [179]. Furthermore, solvent extraction of coal creates more pores and active sites [177,178,180]. When the residual coals were oxidized and then used for adsorption of phenol, the percentage of phenol adsorbed reduced significantly. The possible reason could be that the oxidation of the residual coal by nitric acid caused condensation reactions, resulting in the blocking of the pores and active adsorption sites on coal surfaces.

Ahsan et al. [181] studied the interactions of citric acid treated and untreated low coals with phenol from aqueous solution by flow microcalorimetry, and by adsorption isotherms. Both techniques showed that citric acid washing improved the adsorption of phenol. Essentially, an increase in the sorption capacity at all regions for the citric acid washed low coals suggested that the acid washing procedure opened up the pore structure and created some extra surface for the adsorption of phenol. However, no improvement in adsorption as a result of such treatment was found for high-rank coals [177].

Aksu and Yener [182] investigated the potential for coal fly ash to be used in place of activated carbon for the adsorption of phenol. They reported an adsorption capacity of 27.9 mg/g for the coal fly ash compared to 108.0 mg/g for activated carbon. Coal fly ash has also been used for the removal of 2-chlorophenol and 2,4-dichlorophenol with adsorption capacities of 1 mg/g and 1.7 mg/g, respectively [183]. This did not compare well with the results reported in a further study by Aksu and Yener [184], in which they found the adsorption capacity of coal fly ash to be 98.7 mg/g and 118.6 mg/g for 2-chlorophenol and 2,4-dichlorophenol, respectively, although this appears to be due to difference in experimental conditions. The 2,4-dichlorophenol and pentachlorophenol have also been removed from waste water in a fixed bed column operating continuously; removal efficiencies of over 99% were achieved for an initial concentration of 10 mg/L of chlorophenols [185].

Coal fly ash has also been found to be effective for the removal of two types of polychlorinated biphenyls: 2,3,4-trichlorobiphenyl and 2, 20,3,30,4,5,6-heptachlorobiphenyl [186]. The general conclusion from studies such as these is that, although coal fly ash is an inferior adsorbent relative to activated carbon, its low cost could make it an economically viable alternative for the removal of organics from waste water.

5.3.2. Dyes

Qada et al. [187] investigated the adsorption capacity of basic dyes on different types of activated carbons produced from bituminous coal. The three activated carbons were named as, (1) PAC1 (produced from Venezuelan bituminous coal in a laboratory scale process using physical activation), (2) PAC2 (produced by the steam activation of New Zealand bituminous coal on a pilot scale using rotary kiln), and (3) F400 (commercial bituminous coal-based activated carbon). Equilibrium behaviour of the activated carbons was investigated by performing batch adsorption experiments using bottle-point method. Three basic dyes, considered as the most problematic classes of dyes and which pose significant problems for removal by conventional technologies, were chosen as the model adsorbates, i.e., methylene blue (MB), basic red (BR), and basic yellow (BY). Generally, basic dyes are cationic, with cationic properties originating from the positive charge that is generally delocalized throughout the chromophoric system, although it is probably more localized on the nitrogen atoms [187] and are so called basic dyes because of their affinity to basic textile materials with net negative charge [188]. Langmuir, Freundlich and Redlich-Peterson isotherm models were used to simulate the equilibrium data at different experimental parameters (pH and adsorbent particle size). The results showed that PAC2 had the highest adsorptive capacity towards MB dye (588 mg/

g) followed by F400 (476 mg/g) and PAC1 (380 mg/g). BR and BY showed higher adsorptive affinity towards PAC2 and F400 than MB. The study found that net surface charge and physical properties of adsorbents play a significant role in explaining the differences in adsorptive capacities of the activated carbons used in this investigation. In fact, adsorbent surface chemistry, surface area and pore structure proved to be important factors in governing the adsorption process. Under comparable conditions, adsorption capacity of basic dyes, MB, BR and BY onto PAC1, PAC2 and F400 increased in the order: MB < BR < BY. Solution pH also played a major role in the adsorption process. The optimum pH for the removal of MB and BR from aqueous solution under the experimental conditions employed was pH 11. Earlier studies by Qada et al. [189] also obtained similar pH trends for MB. The effect of pH can be described on the basis of the influence of pH on the point of zero charge (pH_{PZC}). Activated carbon adsorbents acted as positively charged surfaces in the solution when the pH was lower than pH_{PZC} , and as negatively charged surfaces when the pH was greater than pH_{PZC} . Experimental data also indicated that adsorbent particle size had an influence on the adsorption capacities of activated carbons. As the particle size decreased, the adsorption capacity of activated carbons increased. The increase in capacity with decreasing particle size indicated that the dyes did not completely penetrate the particle or that the dyes preferentially adsorbed near the outer surface of the particle. This could also be attributed to an increase in surface area that is associated with a reduction in particle size at fixed mass. Of the three equilibrium isotherm models applied, the Redlich-Peterson isotherm was found to best describe the experimental data over the whole concentration range as indicated from the high values of the correlation coefficients ($R^2 > 0.99$). All the adsorption systems studied showed favourable adsorption of the basic dyes as indicated by the low values of Langmuir separation factor, R_L ($0 < R_L < 1$).

Yuliani et al. [190] reported the adsorption of anionic (alizarin red) and cationic (safranin) dyes from aqueous solutions onto raw and treated Victorian brown coal. The performance of Victorian brown coal was also compared with coal-based activated carbon. Treated brown coal was obtained by water and acid washing. Raw brown coal showed a high capacity in adsorbing the cationic dye (>100 mg/g). However, when anionic dye was used, the adsorption capacity of raw brown coal decreased significantly. On the contrary, activated carbon performed well in adsorbing both dyes. While the adsorption capacity of activated carbon for anionic dye was higher than that for cationic dye, the adsorption capacity of the raw brown coal for anionic dye was only 15% of that for cationic dye. The surface area of raw brown coal measured by CO_2 adsorption was $202 \text{ m}^2/\text{g}$, only a quarter of that of activated carbon. However, despite the lower surface area compared to activated carbon, brown coal had a considerable adsorption capacity for the cationic dye. This suggests the role of functional groups (carboxyl and phenolic) on the raw brown coal's surface in adsorbing cationic dye molecules. Washing of the raw brown coal improved its adsorption capacity for cationic dye, and the adsorption capacity of the raw brown coal increased according to the following trend: raw lignite < water washed lignite < acid washed lignite. During water washing, water soluble inorganics that are dissolved in the pores of the raw brown coal (e.g., NaCl and KCl) were expected to be removed. Little or no removal of exchangeable cations such as calcium and magnesium was expected [191]. However, during acid washing, the exchangeable cations originally bound to the organic matrix, and some acid soluble minerals could also be efficiently removed. The ash contents of raw, water washed and acid washed coal were determined as 2.28%, 1.07% and 0.93%, respectively. The acid washed coal exhibited the lowest ash content, signifying the highest removal of inorganics. The removal of these inorganic

constituents resulted in the increased availability of exchangeable sites. It is the exchangeable sites where the cationic dye molecules can most effectively interact and adsorb onto the coal, as shown in Equation (13). As for the anionic dye this mechanism of exchange is not available, thus its adsorption was relatively poor.



The adsorption data fitted the Langmuir model better than the Freundlich model which supports the involvement of cation exchange mechanism that is best described as a monolayer adsorption process.

Depci et al. [192] studied the removal of crystal violet dye from aqueous solution using activated carbon derived from Gölbaşı (Turkish) lignite coal. The experimental results showed that the activated carbon obtained from Gölbaşı lignite coal is an effective sorbent for removing crystal violet dye from aqueous solutions. In fact, it was found that the adsorption capacity of crystal violet dye on activated carbon derived from Gölbaşı lignite had a considerably high value compared to many other activated carbons and/or adsorbents as shown in Table 6.

Iordanidis and Georgakopoulos [193] investigated whether lignite could accelerate the reduction of azo dyes (e.g., Acid Orange 7) by sulphides. Azo group of dyes (monoazo, diazo, triazo and polyazo) are considered to be the largest chemical groups of dyes in existence (around 26,000 dyes) [194]. The decolourisation experiment showed that lignite did not accelerate the chemical reduction of azo dyes by sulphides. Thus, further studies that could use other forms of lignite (e.g., demineralized and oxidized) and take the effect of different parameters (pH, temperature, particle size, etc) into consideration were suggested.

Mohan et al. [194] reported the removal of direct trisazo dye colour by various abundantly available coal-based sorbents (charfines, lignite coal, bituminous coal) and compared the results with activated carbon (F400). The results showed that the adsorption of direct azo dye onto coal-based adsorbents obeyed the first-order irreversible rate equation whereas adsorption onto activated carbon was well fitted with the first-order reversible rate equation. The colour removal capacities of the studied adsorbents were found to be in the following order: activated carbon > charfines > lignite coal > bituminous coal. The differences in adsorption capacity of coal-based adsorbents may be attributed to the grade of the coal samples (i.e., progression of the coalification process that the coal may have undergone) which is related to their inherent ion-exchange capacity [194,195]. The inherent ion-exchange capacity decreases with the progression in the coalification process from lignite to bituminous coal [121,122]. With the coalification process, the loss of water which gradually converts the peripheral carbon structure originally existing as carboxyl and hydroxyl groups into methyl groups, results in a marked decrease in the hydroxyl and carboxyl content of coal

[194,195]. In other words, through the coalification process, polar functional groups especially hydroxyl ($-OH$) groups are eliminated along with water [196]. Besides the hydroxyl groups, carboxyl ($COOH$), methoxyl (OCH_3), and carbonyl ($>CO$) groups as well as ring oxygen are also decomposed and so the carbon content increases. As discussed previously, the presence of hydroxyl and carboxyl groups impacts positively on the ion-exchange properties of coal-based adsorbents; thus if these functional groups are limited and/or reduced, coal-based adsorbents will have low adsorption capacity. Furthermore, the increasing sorption capacity (e.g., in lignite coal compared to bituminous coal) also corroborates well with decreasing carbon content and increasing ash content of the coal-based adsorbents [194,195].

An earlier study by Mohan et al. [195] compared the removal of monoazo acid dye (e.g., Acid Red 88) by coal based sorbents (lignite coal, charfines and bituminous coal and F400 activated carbon) to chemical coagulation employing aluminum sulfate, ferric chloride, manganese sulfate, manganese chloride and barium chloride. The study suggested that the treatment of coloured dye effluents by chemical coagulation and the removal by adsorption onto coal and activated carbon result in good colour removal, and that these methods may prove helpful in meeting environmental regulations.

McKay et al. [197] compared low-cost materials (teakwood bark, ricehusk, coal, bentonite clay, hair and cotton waste) for the adsorption of dyestuffs (Sandolan Rhodine, Sarranine, Congo Red, Foron Brill Red, Sandolan Blue, Methylene Blue, Solar Blue, Foron Blue) from aqueous solutions. The equilibrium isotherm for each dye-adsorbent system was determined and adsorption capacities from 0 to 200 mg dye/g of adsorbent were obtained. The study found that different low-cost materials responded in various ways in their uptake of different dyestuffs. None of the adsorbents adsorbed Sandolan Blue or Sandolan Rhodine, whereas bentonite was the best adsorbent followed by tree bark, cotton waste and rice husk.

The adsorption of cationic Astrozon Red dye on the activated lignite coal from aqueous solutions was studied by Mahramanlioğlu et al. [198]. The adsorption kinetic data was found to follow the Lagergren equation, and also the equilibrium data conformed to the Langmuir isotherm. The adsorption of Astrozon Red was found to increase with an increase in pH values of the solution. The adsorption also depended on the solution temperature and adsorbent concentration. The negative value of Gibbs free energy (ΔG°) confirmed the feasibility of the adsorption process and spontaneous nature of adsorption. However, the adsorption capacity decreased with an increase in temperature. The negative value of ΔH° indicated that the adsorption process was exothermic in nature.

A study by Ishaq et al. [199] investigated the physico-chemical characteristics and maleic acid adsorption capacity of Lakhra (Pakistani) coal. The coal was treated with various extractants and/or leachants such as HCl, H_2O_2 and $KMnO_4$, for the generation of porosity as well as active sites for the removal of maleic acid from aqueous solution. The treatment was found to be effective in removing ash as well as total sulphur and chlorine from coal samples, which not only resulted in emptying the coal pores, but also created active sites on the coal. Both the emptiness of coal pores and generation of active sites made the coal a good adsorbent for the removal of maleic acid from aqueous solutions. The adsorption study showed that the $KMnO_4$ treated coal sample adsorbed higher quantity of maleic acid (49 mg/g) compared to H_2O_2 and HCl treated coal sample. The adsorption of maleic acid reached equilibrium after 1 h in the case of $KMnO_4$ treated coal while its adsorption on H_2O_2 and HCl treated coal samples increased gradually and then stabilized after 2 and 3 hrs, respectively.

Table 6

Adsorption capacities of various adsorbents for the adsorption of crystal violet dye [192].

Adsorbents	Q_0 (mg/g)
Phosphoric acid activated carbon	60.42
Sulphuric acid activated carbon	85.84
Activated carbon derived from waste apricot	57.80
Jute fiber carbon	27.99
Kaolin	47.27
Semi-IPN hydrogels	35.09
Sepiolite	77.00
Activated carbon derived from waste biomass of wood apple rind	16.50
Magnetic nanocomposite	81.70
Ginger waste	19.80
Activated carbon derived from Gölbaşı lignite	60.80–65.80

5.3.3. Natural organic matter

Natural organic matter (NOM) is a complex matrix of organic materials and a key component in aquatic environments [200]. It is formed by the breakdown of animal and plant matter in the environment and from chemicals that are biologically or chemically synthesized from these degradation compounds [201]. Organic matter in natural waters can be divided into dissolved and particulate organic carbon [202]. Research of NOM in water has been concerned mostly with the dissolved fraction. The dissolved organic fraction can be further divided into six categories—hydrophobic: acids, bases and neutrals, and hydrophilic: acids, bases and neutrals [203]. The NOM causes problems in the production of drinking water. It has an adverse effect on the aesthetic water quality and may also result in the bio fouling of water pipelines thus resulting in negative health consequences [203].

Research studies have shown that NOM can be bound onto porous solid material and, therefore, solid porous material such as activated carbon can be used as an approach for the treatment of drinking water systems. Actually, NOM is known to be readily adsorbed onto activated carbon through hydrogen bonding and electrostatic forces [204]. As already discussed in various sections of this paper, the pore size and distribution of adsorbent has been found to be an important factor that affects adsorption capacity of several pollutants and further play an important role in influencing competitive adsorption in multisolute systems. Mass transfer within the carbon is slow for sorption in aqueous systems, thus, a higher proportion of larger pores is desired for distribution of solute to the sorbent surfaces.

Principally, the raw material used and activation process influences the pore structure of the carbon and, therefore, its efficiency in adsorbing different contaminants. Coal and wood based carbons are predominantly microporous and mesoporous, but with some macroporous character. Since these carbons have both a fine and wide pore diameter, they are generally well-suited for the removal of a wider variety of organic chemical contaminants from water. In addition, they are ideal for application in the water industry where target micro pollutants have a large range of molecule sizes [205]. Removal of mineral matter from the precursor carbon has also been shown to improve the pore structure of the activated carbon [206]. However, the optimum pore size distribution for a given NOM will depend on its molecular size distribution, a property that is system specific.

It has been shown that electrostatic interactions tend to play a significant role on the adsorption of NOM onto activated carbon [207]. As a result of the amphoteric nature of the activated carbon, its pore surface can be negatively or positively charged or neutral depending on the pH of the water under treatment as well as the carbon activation process [208]. In most aqueous solution, acidic activated carbon carries a negative surface charge at neutral pH while basic carbon carries a positive charge. As a result of the presence of carboxylic acids and phenolic groups in the NOM structure, NOM carries a negative charge at pHs encountered in most drinking water treatment processes [208,209]. As a result, NOM with the highest carboxylic acidity and hence the highest charge density are generally difficult to remove by conventional treatment [210]. However, chemical and surface modification of activated carbon can affect its adsorption capability for NOM.

The role of chemical modification of thermally activated coal based carbon on its capacity for NOM adsorption was investigated by Karanfil et al. [211]. The carbon was first washed in acid to remove ash and alkaline impurities. Subsequently, it was heat treated to remove oxygen containing functionalities, and was further oxidized to increase surface acidity. A portion of the oxidized carbon was heat treated to remove acidic and other carbon dioxide evolving groups. The results of the study showed

that the oxidation of the coal based carbon led to a decrease in NOM adsorption. Since the oxidation increased the acidity of the carbon surface, electrostatic interactions between the negatively charged carbon surface and the negatively charged NOM could have played a role in the reduction of NOM adsorption. The subsequent heat treatment was shown to restore some of the adsorption capacity of the activated carbon. The work done by Karanfil et al. [211] suggests that not only does the mineral content of the coal significantly affect the pore structure of the subsequent carbon, but it can also significantly affect the chemical factors that are important in sorption.

Research has also shown that when the removal of inorganic and organic pollutants as well as taste and odour causing substances are the main task, competitive sorption with NOM may play a big role in the effectiveness of the whole process. Research results have shown that the adsorption capacity of activated carbon for micro pollutants is lowered in the presence of NOM [212,213]. The magnitude of the decrease in adsorption capacity is dependent on the size of the competing NOM and the initial concentration of the micro pollutant relative to that of the competing NOM. The NOM constituents with molecular sizes similar to that of the targeted micro pollutant cause the largest decrease in adsorption capacity because the NOM constituents compete directly with the micro pollutant for the adsorption site. The NOM constituents of larger molecular size have been noted to have very little effect on the adsorption capacity of small organic micro pollutants. However, preloading the activated carbon with larger NOM constituents can lead to a decrease in the rate of micro pollutant adsorption [209,214,215].

5.3.4. Refractory organic materials

As already stated, most commercial activated carbon is derived from coal. Activated carbon, and in particular granular activated carbon (GAC), is used in drinking water treatment to remove compounds that are not usually present in water at high concentrations [201]. However, over time, the adsorption sites on activated carbon become saturated with, for example, organic compounds, thus losing its initial effectiveness [216]. In addition, microorganisms are immobilized on the surface of the activated carbon [201,216,217]. Microbial colonization of activated carbon is considered to result from, (1) adsorptive properties of carbon, which enrich nutrients and oxygen concentrations, (2) the porous surface of the carbon particles, which provide a protective environment from fluid shear forces, (3) the presence of a variety of functional groups on the carbon surface, which enhance microbial attachment, and (4) neutralization of stressor compounds [201]. Activated carbon covered with microorganisms is called biological activated carbon (BAC) [218].

It has been demonstrated by several researchers that, under the proper conditions of design and operation, biological activity in activated carbon systems can improve the removal of certain chemical components and prolong the required periods between carbon regeneration and replacement [217]. Ideally, the micro-organisms immobilized on the surface of activated carbon, can remove pollutants (e.g., organics) via the process of biaodsorption, biodegradation or bioregeneration [218]. Furthermore, the biofilm formed on the activated carbon can change the surface charge density of the activated carbon, mainly by increasing its negative value, which could enhance its adsorption capacity for some positively charged pollutants, such as most of the heavy metals [201,219]. However, microbial degradation of certain organic pollutants (e.g., chlorinated nitroaromatic compounds) is difficult because such organics are more resistant to microbial attack due to the electron-withdrawing properties of the chloro- and nitro-groups on the aromatic ring [220,221]. Therefore, in order to improve the removal efficiency of such refractory organics,

ozonation is commonly used in preoxidation before the BAC process [222]. Actually, ozonation is proven to be one of the most promising oxidative techniques for the abatement of refractory and/or toxic organic pollutants in water and wastewater [221]. The process which combines ozonation and BAC treatment is termed ozone-BAC (O_3 -BAC).

Ozone partially oxidizes and breaks down biologically refractory organic matter into smaller size molecules, thus increasing the concentration of biodegradable organics in water [223]. Ideally, in aqueous solution, ozone reacts with organic compounds through two pathways: direct reaction of ozone molecule, and radical type reaction that involves hydroxyl radical ($\cdot OH$) from the decomposition of ozone [221,224]. The $\cdot OH$ ($E^\circ = +2.80\text{ V}$) radical is non-selective and reacts very fast with most of the species, while direct reaction involving ozone molecule ($E^\circ = +2.07\text{ V}$) is very selective and unable to effectively degrade some refractory pollutants [221,225]. In principle, when O_3 -BAC process is used, organic is, firstly, oxidized by ozone into small degradable molecules, then the small degradable molecules are adsorbed onto the activated carbon and degraded by microorganisms [222]. At the same time, the oxygen produced from the decomposition of ozone increases the level of dissolved oxygen in water, which in turn, provides the necessary conditions for biodegradation [222].

5.3.5. Other organic compounds

Lian et al. [226] compared the adsorption of hydrophobic organic compounds (HOCs) such as trichloroethylene (TCE), 1,3-dichlorobenzene (DCB), 1,3-dinitrobenzene (DNB) and γ -hexachlorocyclohexane (HCH) on commercial coal-based activated carbon with three polymer-based activated carbons and multi-walled carbon nanotubes (MWCNTs). Compared with coal-based activated carbon and MWCNTs, activated carbons derived from polyvinyl chloride (PVC) and polyethyleneterephthalate (PET) exhibited fast adsorption kinetics and high adsorption capacity, particularly towards the bulky HOCs. This was attributed to their high surface area (up to $2700\text{ m}^2/\text{g}$), mesoporous structure, and narrow pore size distribution. For bulky chemicals, coal-based activated carbon and MWCNTs may not have been effective adsorbents due to the molecular sieving effect and slow adsorption kinetics resulting from the highly heterogeneous pore structure. Adsorption of small-sized TCE was stronger on the tire-rubber-based activated carbon and coal-based activated carbon due to the pore-filling effect. In general, MWCNT exhibited the lowest adsorption capacity towards HOCs because of its low surface area and aggregating characteristics in aqueous solution. The significant discrepancy in pore structure and surface chemistry of the three activated carbons based on waste polymers indicated that the parent polymers may play a crucial role in the properties of the obtained activated carbons. Therefore, raw polymers should be selected carefully to improve the HOCs adsorption efficiency of the waste polymer-derived activated carbons.

Torunño et al. [227] studied the use of an immature coal (leonardite) as an adsorbent for removing polycyclic aromatic hydrocarbons (PAHs) from water. In a series of batch experiments, the effects of some of the important factors such as pH, contact time, and PAHs concentration on the adsorption capacity of leonardite were studied. The results showed no significant differences in the removal percentages for the various pH values studied, except for fluorene which was higher at lower pH values. Its removal rate rose to 86% at pH 2 from 69% at pH 6. This observed phenomenon was due to a decrease in the polarity of leonardite as pH decreased, thus allowing it to adsorb most soluble PAHs on the matrix. The contact time was found to be an important factor in the adsorption of PAHs by leonardite. Though the equilibrium time was reached after 24 h, the adsorption was controlled by two transport processes – a fast one (up to 2 h) and a slow one (> 2 h). In other

words, during the first 2 h, the adsorption rate increased rapidly. Thereafter, however, there was a minor decrease. Equilibrium data was fitted to Freundlich models in order to determine the organic carbon-water partition coefficient (K_{OC}). The low log K_{OC} values found for the adsorption of PAHs by leonardite suggested that the interaction between the PAHs and the adsorbent could be assumed to be promoted by aromaticity of PAHs. This shows that physical adsorption caused by the aromatic nature of PAHs was the main mechanism that governed the removal process. The results also showed that the adsorption onto leonardite increased as octanol-water partition coefficient (K_{ow}) increased and as the solubility of PAHs decreased.

Extraction of organic pollutants from super heavy oil wastewater using lignite activated coke was investigated by Tong et al. [228]. Various factors studied include the exposure time, temperature, and concentrations of the organic pollutants in the wastewater. The equilibrium adsorption data was analyzed by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The best fit was obtained by the Freundlich isotherm and a chemical mechanism was suggested based on the Dubinin-Radushkevich model. The kinetics analysis showed that adsorption of organic compounds was multilayered on the lignite activated coke surface and followed the pseudo-second-order model. The mass transfer model showed that external and intraparticle diffusion influenced the adsorption process. Thermodynamics studies revealed that adsorption of organic materials from the super heavy oil wastewater was spontaneous at high temperature, but not so at lower temperatures. The positive value of enthalpy (ΔH°) confirmed the endothermic nature of adsorption, while positive entropy change (ΔS°) indicated the increased randomness at the solid-liquid interface during adsorption. The surface of the lignite activated coke before adsorption was porous, rough, and uneven, but after adsorption, the porosity decreased and the lignite activated coke surface became flat and smooth.

A study by Simonovic et al. [229] examined the applicability of hard coal as a low-cost adsorbent for adsorbing mineral oil from industrial wastewater. In a series of batch and continuous flow experiments, the effects of important process factors such as pH, contact time and pollutant concentration on the adsorption capacity of hard coal were examined. The results showed that initial pH had no significant effect on the adsorption process of mineral oil. For example, differences in oil removal between pH values of 3.0 and 10.5 were under 15%. This was due to the chemical stability of mineral oil; mineral oil is chemically very inert as it is composed mainly of alkanes. In fact, research has shown that heavier oils with longer chains are less affected by pH. Furthermore, these compounds do not have ionizable or hydrophilic groups that can be influenced by the pH value [227]. Because the sorption of oils onto hard coal is a hydrophobic interaction, the adsorption of compounds with higher molecular mass is affected, to a lesser degree, by the pH values studied, as it was expected. It seemed, therefore, that adhesion or the interfacial tension between mineral oil and hard coal surface was the predominant process. In other words, physical adsorption caused by properties of mineral oil and hard coal was the predominant mechanism in the removal process. Equilibrium data was fitted to Freundlich model in order to determine the water-hard coal partitioning coefficient. The isotherm was found to be almost linear ($n = 1$). In fact, according to literature data, the sorption of mineral oil to hard coal is often characterized by linear isotherms in which the ratio of sorbed and aqueous oil concentration is independent of concentration [230]. Nevertheless, non-linear sorption isotherms are also common [231] implying that in addition to the physico-chemical properties and concentration of the pollutants, the properties of the adsorbents and environmental conditions play an important role in the adsorption process [232]. In spite of the low adsorption

capacity of hard coal compared to other adsorbents such as activated carbon, its removal percentages at the concentrations evaluated, and those found in the environment, suggested that hard coal could be useful for abating mineral oil pollution [229].

6. Summary and future perspectives

With the fast development of various industries, huge quantities of wastewater are produced from industrial processes and are discharged into soil and water systems [59]. As a result, soil and water systems usually contain many pollutants such as cationic and anionic ions, oil and organics, which have poisonous and toxic effects on ecosystems, human being, animals and plants [59]. As a result of toxic effects of many pollutants, their removal and/or recovery from aqueous effluents using various methods has received considerable attention. However, cost effective technologies for the treatment of pollutant-contaminated waste streams are needed. This review has covered the use of coal-based adsorbents for removing pollutants from water and wastewater. Despite the large number of papers published on coal-based adsorbents for organic and inorganic pollutants, no single report exists that gives a full comparative analysis. Therefore, this review also serves as a collection of research studies that are hinged on coal-based adsorbents and critically analyses and/or compares them. However, it must be noted that it is very difficult to directly compare adsorption capacities of various adsorbents due to inconsistency in the literature data [55,233]. For example, sorption capacities were evaluated at different pHs (and not necessarily at the optimum pH values), temperatures, pollutant concentration ranges, and adsorbent doses. The adsorbents were used for treating ground water, drinking water, synthetic industrial wastewater, and actual wastewater; therefore, the types and concentrations of interfering ions are different and in most cases rarely reported. Some adsorption capacities were reported using batch experiments and others using continuous column modes. Certainly, these cannot be readily compared with each other. In batch sorption experiments, the sorption capacities were mainly computed by the Langmuir isotherm or the Freundlich isotherm or experimentally. This makes comparisons more complicated to follow. In other words, rigorous direct comparisons of the tested coal-based adsorbents were very difficult. However, with the limitations stated above, this review was still able to show that coal-based adsorbents are extensively used for removing pollutants from water and wastewater. In other words, today, coal-based adsorbents still attract considerable interest in their usage. It is also evident from this review that although the pollutant exchange capacities of various types of coal-based adsorbents are in some cases lower in comparison to other adsorbents, the substantially lower cost of coal showed great potential for the utilization of coal as a means to removing a range of pollutants from water and wastewater effluents. However, due to the scarcity of consistent cost information, cost comparisons are difficult to make [55], and consequently, in this review, such comparisons were not done for the coal-based adsorbents. Nevertheless, it is also noted that the properties of the coal-based adsorbents are dependent upon the production and/or conversion methods and the nature of the coal itself. For example, a study by Mohan and Chander [88] showed that sorption capacity of lignite was more superior than most of the other adsorbents tested for AMD treatment (see Table 4); and that studies of Victorian brown coals obtained from different sources exhibited different cation exchange capacities [71].

In recent past, extensive research efforts have been devoted to the surface modification of coal, aimed at increasing the surface area or introducing surface functional groups. Such approaches include demineralization, heat treatment, oxidation, nitration, sulphonation, etc [66,72,105,106,119,120,130,132]. In general, the

review showed that adsorption of pollutants was usually dependent on surface area of adsorbents. The higher the surface area the greater was the adsorption. However, this was often not true for the adsorption of metal ions or inorganics; in some instances, processes such as ion exchange and precipitation also contributed or even dominated. The uptake of pollutants was also found to be strongly influenced by the surface charge on the sorbent and solution pH, typical of processes dominated by ion-exchange processes. There is a neutral pH below or beyond which the coal-based adsorbents will be either positively or negatively charged. Furthermore, a number of water contaminants such as phenols are weak acids, which may dissociate into protons and anions, for example,



where HA = neutral species; H⁺, A⁻ = ionic species.

For such ionisable species, aqueous phase pH plays an important role on their sorption, because hydrophobicity and solubility of the solute are strongly affected [234]. In general, ionised species are much more soluble and thus less hydrophobic than their neutral counterparts. Thus, it follows that sorption of the ionised and non-ionised species will differ and that the neutral species are expected to sorb much stronger.

Even though tremendous amount of work has been accomplished in the development and use of coal-based adsorbents, a lot of work still needs to be done to ascertain the sustainable and effective usage of coal-based adsorbents. In fact, most of the recent achievements are still based on laboratory scale tests. However, using the lessons from laboratory scale tests, low cost, but high efficacy coal-based adsorbents for commercial application should be developed in future. Research work is also necessary to better understand coal-based adsorbents with their underlying adsorption processes and to demonstrate the technology. Therefore, in conclusion, the use of coal in water and wastewater treatment, now and in future, depends upon the continuation of research into the development of cost-effective coal-based adsorbents. Simply stated, further research work on developing cost-effective coal-based adsorbents is highly recommended.

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References

- [1] C.J. Cleveland, C. Morris, *Handbook of Energy: Chronologies, Top Ten Lists, and Word Clouds*, Elsevier Science, Oxford, 2014.
- [2] F. Mushtaq, R. Mat, F.N. Ani, A review on microwave assisted pyrolysis of coal and biomass for fuel production, *Renew. Sustainable Energy Rev.* 39 (2014) 555–574.
- [3] C. Bain, *The Economist Guide to Commodities: Producers, Players and Prices, Markets, Consumers and Trends*, Profile Books Limited, London, 2013.
- [4] J.M.K. O'Keefe, A. Bechtel, K. Christianis, S. Dai, W.A. DiMichele, C.F. Eble, J.S. Esterle, M. Mastalerz, A.L. Raymond, B.V. Valentim, N.J.C.R. Wagner Ward, J.C. Hower, On the fundamental difference between coal rank and coal type, *Int. J. Coal Geol.* 118 (2013) 58–87.
- [5] L. Daniels, Available at, *Coal Energy*, (2014) . (accessed: September 2014) <http://prezi.com/mrfyzy2ysjm/coal-energy/>.
- [6] J.S. Laskowski, *Coal Flotation and Fine Coal Utilization*, Elsevier Science, Amsterdam, 2001.
- [7] D.G. Levine, R.H. Schlosberg, B.G. Silbernagel, Understanding the chemistry and physics of coal structure (a review), *Proc. Natl. Acad. Sci. U. S. A.* 79 (1982) 3365–3370.

- [8] J. Anwar, U. Shafique, M. Salman, W. Zaman, S. Anwar, J.M. Anzano, Removal of chromium (III) by using coal as adsorbent, *J. Hazard. Mater.* 171 (2009) 797–801.
- [9] M. Ishaq, I. Ahmad, M. Shakirullah, H. Rehman, M.A. Khan, I. Ahmad, I. Rehman, Adsorption study of phenol on Lakhra coal, *Toxicol. Environ. Chem.* 89 (1) (2007) 1–6.
- [10] M. Polat, H. Polat, S. Chander, Physical and chemical interactions in coal flotation, *Int. J. Miner. Process.* 72 (2003) 199–213.
- [11] R.M. Flores, Coal and Coalbed Gas: Fuelling the Future, Elsevier Science, Waltham/San Diego, 2013.
- [12] R. Falcon, Available at, Coal, Coke and Carbon in the Metallurgical Industry, (2013) . (accessed: September 2014) <http://www.fossilfuel.co.za/conferences/2013/CoalCokeCarbon/Day-One/01-Rosemary-Falcon.pdf>.
- [13] R. Falcon, Coal petrography, in: D. Osborne (Ed.), *The Coal Handbook: Towards Cleaner Production*, 1st edition, Woodhead, Cambridge, 2013.
- [14] I. Demir, A.A. Lizzio, E.L. Fuller, R.D. Harvey, Evaluation of the Surface Properties of Illinois Basin Coals, (1993) .(accessed: September 2014) https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/38_4_CHICAGO_08-93_1178.pdf.
- [15] J.W. Larsen, P. Hall, P.C. Wernett, Pore structure of the argonne premium coals, *Energy Fuels* 9 (1995) 324–330.
- [16] G. Abotsi, Interfacial properties of coal: a guide to catalyst loading and dispersion for coal conversion, *Energeia* 7 (5) (1996) 1–6.
- [17] R.C. Neavel, E.J. Hippo, S.E. Smith, R.N. Miller, Coal characterization research: sample selection, preparation, and analyses, *ACS Div. Fuel Chem.* 25 (3) (1980) 246–257.
- [18] L. Blom, L. Edelhausen, D.W. van Krevelen, Chemical structure and properties of coal: XVIII oxygen groups in coal and related products, *Fuel* 36 (2) (1957) 135–153.
- [19] H. Marsh, Adsorption methods to study microporosity in coals and carbons—a critique, *Carbon* 25 (1987) 49–58.
- [20] G.M.K. Abotsi, K.B. Bota, G. Saha, Interfacial phenomena in coal impregnation with catalysts, *Energy Fuels* 6 (1992) 779–782.
- [21] R.L. Bond, Capillary structure of coal, *Nature* 178 (1956) 104–105.
- [22] K.M. Smith, G.D. Fowler, S. Pullket, N.J.D. Graham, Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications, *Water Res.* 43 (2009) 2569–2594.
- [23] D.R. Spears, W. Sady, L.D. Kispert, An Investigation of the Chemistry of the Pore Structure of Coal in the Presence of a Swelling Solvent Using a Novel EPR Technique, (1991) . (accessed: February 2015) https://web.anl.gov/PCS/acs-fuel/preprint%20archive/Files/36_3_NEW%20YORK_08-91_1277.pdf.
- [24] D.R. Spears, W. Sady, L.D. Kispert, Low temperature swelling of Argonne premium coal samples: micropore wall chemistry during swelling, *Fuel* 72 (8) (1993) 1225–1233.
- [25] Y.B. Melnichenko, L. He, R. Sakurovs, A.L. Khodenko, T. Blach, M. Mastalerz, A.P. Radilński, G. Cheng, F.R. Mildner, Accessibility of pores in coal to methane and carbon dioxide, *Fuel* 91 (2012) 200–208.
- [26] H. Gan, S.P. Nandi, P.L. Walker, Nature of the porosity in American coals, *Fuel* 51 (4) (1972) 272–277.
- [27] G.V. Cullen, N.G. Sivivour, G.M. Pearson, Extracting metals from ammoniacal solution with low rank coals. American Society for Metals and the Metallurgical Society of AIME, *Metall. Trans.* 9B (1978) 409–413.
- [28] J.S. Bae, D.W. Lee, S.J. Park, Y.J. Lee, J.C. Hong, C. Han, Y.C. Choi, Synthesis gas and char production from Mongolian coals in the continuous devolatilization process, *Korean J. Chem. Eng.* 30 (2) (2013) 321–326.
- [29] B.A. Akash, W.S. O'Brien, The production of activated carbon from a bituminous coal, *Int. J. Energy Res.* 20 (1996) 913–922.
- [30] T. Wigmans, Industrial aspects of production and use of activated carbons, *Carbon* 27 (1989) 13–22.
- [31] R.E. Mitchell, P.A. Campbell, L. Ma, Characterization of Coal and Biomass Conversion Behaviors in Advanced Energy Systems. GCEP Technical Report 2006, (2006) . (accessed: September 2014) https://gcep.stanford.edu/pdfs/QeJ5maLQQrugISYM3ATDA/2.6.4_mitchell_06.pdf.
- [32] N. Nsakala, R.H. Esseenhigh, P.L. Walker, Characteristics of chars produced from lignites by pyrolysis at 808 °C following rapid heating, *Fuel* 57 (1978) 605–611.
- [33] M.D. Hobday, P.H.Y. Li, D.M. Crewdson, S.K. Bhargava, The use of low rank coal-based adsorbents for the removal of nitrophenol from aqueous solution, *Fuel* 73 (12) (1994) 1848–1854.
- [34] D. Mohan, K.P. Singh, Granular activated carbon, in: J. Lehr, J. Keeley, J. Lehr (Eds.), *Water Encyclopedia: Domestic, Municipal, and Industrial Water Supply and Waste Disposal*, John Wiley & Sons, Inc., New York, 2005, pp. 92–107.
- [35] A. Ahmadpour, D.D. Do, Characterization of modified activated carbons: equilibria and dynamics studies, *Carbon* 33 (10) (1995) 1393–1398.
- [36] H. Teng, H.C. Lin, Activated carbon production from low ash subbituminous coal with CO₂ activation, *AIChE J.* 44 (5) (1998) 1170–1177.
- [37] M.J. Muñoz-Guillena, M.J. Illán-Gómez, J.M. Martín-Martínez, A. Linares-Solano, C. Salinas-Martínez de Lecea, Activated carbons from Spanish coals: I. Two-stage CO₂ activation, *Energy Fuels* 6 (1) (1992) 9–15.
- [38] M. Greenbank, S. Spotts, Six criteria for coal-based carbons, *Water Technol.* 16 (1993) 56.
- [39] D.O. Cooney, Activated Charcoal: Antidotal and Other Medical Uses, Dekker, New York, 1980.
- [40] M.M. Yeganeh, T. Kaghazchi, M. Soleimani, Effect of raw materials on properties of activated carbons, *Chem. Eng. Technol.* 29 (10) (2006) 1247–1251.
- [41] R.C. Bansal, J.B. Donnet, F. Stoeckli, *Active Carbon*, Marcel Dekker, Inc., New York, 1988.
- [42] D. Cuhadaroglu, O.A. Uygun, Production and characterization of activated carbon from a bituminous coal by chemical activation, *African J. Biotechnol.* 7 (20) (2008) 3703–3710.
- [43] Z. Hu, M.P. Srinivasan, Preparation of high-surface-area activated carbons from coconut shell, *Microporous Mesoporous Mater.* 27 (1999) 11–18.
- [44] P. Nowicki, R. Pietrzak, H. Wachowska, Siberian anthracite as a precursor material for microporous activated carbons, *Fuel* 87 (2008) 2037–2040.
- [45] B. Sivakumar, C. Kannan, S. Karthikeyan, Preparation and characterization of activated carbon prepared from balsamodendron caudatum wood waste through various activation processes, *Rasayan J. Chem.* 5 (3) (2012) 321–327.
- [46] Qi Ying, F.A.H. Andrew, L.C. Alan, G. Gil, Characterisation of lignite as an industrial adsorbent, *Fuel* 90 (2011) 1567–1574.
- [47] J.W. Zondlo, M.R. Velez, Development of surface area and pore structure for activation of anthracite coal, *Fuel Process. Technol.* 88 (2007) 369–374.
- [48] A. Ahmadpour, D.D. Do, The preparation of active carbons from coal by chemical and physical activation, *Carbon* 34 (4) (1996) 471–479.
- [49] R. Kandiyoti, J.I. Lazaridis, B. Dyrvold, C. Ravindra, Pyrolysis of a ZnCl₂-impregnated coal in an inert atmosphere, *Fuel* 63 (11) (1984) 1583–1587.
- [50] L.C. Ram, R.E. Masto, Fly ash for soil amelioration: a review on the influence of ash blending with inorganic and organic amendments, *Earth Sci. Rev.* 128 (2014) 52–74.
- [51] J. Skousen, J.E. Yang, J. Lee, P. Ziemkiewicz, Review of fly ash as a soil amendment, *Geosyst. Eng.* 16 (2013) 249–256.
- [52] S.M. Shaheen, P.S. Hooda, C.D. Tsadilas, Opportunities and challenges in the use of coal fly ash for soil improvements—a review, *J. Environ. Manag.* 145 (2014) 249–267.
- [53] R.S. Blissett, N.A. Rowson, A review of the multi-component utilisation of coal fly ash, *Fuel* 97 (2012) 1–23.
- [54] Z.T. Yao, X.S. Ji, P.K. Sarker, J.H. Tang, L.Q. Ge, M.S. Xia, Y.Q. Xi, A comprehensive review on the applications of coal fly ash, *Earth Sci. Rev.* 141 (2015) 105–121.
- [55] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, *Water Res.* 33 (11) (1999) 2469–2479.
- [56] V.C. Pandey, N. Singh, Impact of fly ash incorporation in soil systems, *Agric. Ecosyst. Environ.* 136 (1–2) (2010) 16–27.
- [57] H. Höller, U. Wirsching, Zeolite formation from fly ash, *Fortsch. Miner.* 63 (1985) 21–43.
- [58] X. Querol, N. Moreno, J.C. Umaña, A. Alastuey, E. Hernández, A. López-Soler, F. Plana, Synthesis of zeolites from coal fly ash: an overview, *Int. J. Coal Geol.* 50 (2002) 413–423.
- [59] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment, *Chem. Eng. J.* 156 (2010) 11–24.
- [60] D.W. Breck, *Zeolite Molecular Sieves, Structure, Chemistry and Use*, John Wiley & Sons, New York, 1974.
- [61] N. Moreno, X. Querol, C. Ayora, Utilization of zeolites synthesized from coal fly ash for the purification of acid mine waters, *Environ. Sci. Technol.* 35 (2001) 3526–3534.
- [62] A. Ayati, A. Ahmadpour, F.F. Bamoharram, B. Tanhaei, M. Mänttäri, M. Sil-lanpää, A review on catalytic applications of Au/TiO₂ nanoparticles in the removal of water pollutant, *Chemosphere* 107 (2014) 163–174.
- [63] P. Govind, S. Madhuri, Heavy metals causing toxicity in animals and fishes, *Res. J. Anim. Vet. Fishery Sci.* 2 (2) (2014) 17–23.
- [64] G.S. Simate, S. Ndlovu, Acid mine drainage: challenges and opportunities, *J. Environ. Chem. Eng.* 2 (3) (2014) 1785–1803.
- [65] O.B. Akpor, M. Muchie, Remediation of heavy metals in drinking water and wastewater treatment systems: processes and applications, *Int. J. Phys. Sci.* 5 (12) (2010) 1807–1817.
- [66] M. Jochová, M. Punčochář, J. Horáček, K. Štamberg, D. Vopálka, Removal of heavy metals from water by lignite-based sorbents, *Fuel* 83 (2004) 1197–1203.
- [67] M. Monachese, J.P. Burton, G. Reid, Bioremediation and tolerance of humans to heavy metals through microbial processes: a potential role for probiotics? *Appl. Environ. Microbiol.* 78 (18) (2012) 6397–6404.
- [68] R. Singh, N. Gautam, A. Mishra, R. Gupta, Heavy metals and living systems: an overview, *Indian J. Pharmacol.* 43 (3) (2011) 246–253.
- [69] F. Solomon, Impacts of Metals on Aquatic Ecosystems and Human Health, (2008) . (accessed: January 2014) <http://www.infomine.com/library/publications/docs/Mining.com/APr2008c.pdf>.
- [70] C.J. Lafferty, J.D. Robertson, J.C. Hower, T.V. Verheyen, Ion Exchange Properties of Selected North American Low Rank Coals, (1993) . (accessed: October 2014) https://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/38_2_DEN-VER_03-93_0468.pdf.
- [71] C.J. Lafferty, M.D. Hobday, The use of low rank brown coal as an ion exchange material 1. Basic parameters and the ion exchange mechanism, *Fuel* 69 (1) (1990) 78–83.
- [72] J.V. Ibarra, M. Rebollar, J.M. Gavilán, Preparation of cation exchange materials by oleum sulphonation of an Utrillas Spanish lignite, *Fuel* 63 (1984) 1743–1747.
- [73] F. Gode, E. Pehlivan, Adsorption of Cr(III) ions by Turkish brown coals, *Fuel Process. Technol.* 86 (2005) 875–884.

- [74] C.J. Lafferty, M.D. Hobday, The use of low rank brown coal as an ion exchange material 2. Ionic selectivity and factors affecting utilisation, *Fuel* 69 (1) (1990) 84–87.
- [75] V.A. Altekar, M.J. Shahani, A.K. Saha, Adsorption of nickel by lignite, *Fuel* 53 (1974) 29–31.
- [76] A.K. Saha, M.J. Shahani, V.A. Altekar, Adsorption of cobalt by lignite, *Hydrometallurgy* 2 (3) (1977) 285–292.
- [77] H. Irving, R.J.P. Williams, The stability of transition-metal complexes, *J. Chem. Soc.* (1953) 3192–3210.
- [78] G.J. Slavens, D.E. Traut, L.R. Penner, Jack L. Henry, Lignite Recovery of Cobalt³⁺ from an Ammoniacal Ammonium Sulfate Solution. USA Bureau of Mines Report of Investigations No. 8870, (1984). (accessed: October 2014) file:///C:/Users/a0009328/Downloads/cdc_10579_DS1%20(1).pdf.
- [79] Bradbury J.A., Um R.T., 1981. Recovery of cobalt values, U.S. Patent 4,261,737, April 14, 1981 (assigned to UOP Inc., Des Plaines, IL). Available at <http://www.google.com/patents/US4261737> (accessed: October 2014).
- [80] D. Mohan, S. Chander, Removal and recovery of metal ions from acid mine drainage using lignite—A low cost sorbent, *J. Hazard. Mater.* B137 (2006) 1545–1553.
- [81] S. Schiewer, B. Volesky, Modeling of the proton-metal ion exchange in biosorption, *Environ. Sci. Technol.* 29 (12) (1995) 3049–3058.
- [82] Z. Reddad, C. Gerente, Y. Andres, P. Le Cloirec, Adsorption of several metal ions onto a low-cost biosorbent: kinetic and equilibrium studies, *Environ. Sci. Technol.* 36 (9) (2002) 2067–2073.
- [83] X.S. Wang, J. Wang, C. Sun, Removal of copper(II) ions from aqueous solutions using natural kaolinite, *Adsorpt. Sci. Technol.* 24 (6) (2006) 517–530.
- [84] Ç. Arpa, E. Başyilmaz, S. Bektaş, Ö. Genç, Y. Yürüm, Cation exchange properties of low rank Turkish coals: removal of Hg, Cd and Pb from waste water, *Fuel Process. Technol.* 68 (2000) 111–120.
- [85] C.J. Butler, A.M. Green, A.L. Chaffee, Remediation of mechanical thermal expression product waters using raw Latrobe Valley brown coals as adsorbents, *Fuel* 86 (2007) 1130–1138.
- [86] S. Karabulut, A. Karabakan, A. Denizli, Y. Yürüm, Batch removal of copper(II) and zinc(II) from aqueous solutions with low-rank Turkish coals, *Sep. Purif. Technol.* 18 (2000) 177–184.
- [87] J.H. Kuhr, J.D. Robertson, C.J. Lafferty, A.S. Wong, N.D. Stalnaker, Ion exchange properties of a Western Kentucky low-rank coal, *Energy Fuels* 11 (2) (1997) 323–326.
- [88] D. Mohan, S. Chander, Single, binary, and multicomponent sorption of iron and manganese on lignite, *J. Colloid Interface Sci.* 299 (1) (2006) 76–87.
- [89] N.V. Kannan, A study on removal of chromium(VI) by adsorption on lignite coal, *Indian J. Environ. Prot.* 11 (4) (1991) 241–245.
- [90] J. Lakatos, D. Brown, C.E. Snape, Coal as sorbents for removal and reduction of hexavalent chromium from aqueous waste streams, *Fuel* 81 (2002) 691–698.
- [91] J. Mei, Adsorption and desorption of chromium(III and VI) in waste water with weathered coal, *Cailiao Baohu* 32 (8) (1999) 34–35.
- [92] N. Nagesh, A. Krishnaiah, A study on removal of Chromium by adsorption on bituminous coal from synthetic effluents, *Indian J. Environ. Health* 31 (4) (1989) 304–308.
- [93] N.S. Rawat, C.D. Singh, Removal of chromium(VI) on bituminous coal, *Asian Environ.* 14 (3) (1992) 30–41.
- [94] L. Helsen, E. van den Bulck, Metal behaviour during the low temperature pyrolysis of chromated copper arsenate-treated wood waste, *Environ. Sci. Technol.* 34 (2000) 2931–2938.
- [95] D.M. Ruthven, *Principles of Adsorption and Adsorption Processes*, Wiley, New York, 1984.
- [96] J. Oćcik, *Adsorption*, Wiley, New York, 1982.
- [97] E.K. Hyde, *The Radiochemistry of Thorium*, National Academy of Sciences-National Research Council, Washington, 1960.
- [98] R. Marsalek, The adsorption of lead using altered coals, 2nd International Conference on Chemical Engineering and Application, IPCBEE, Volume23, IACSIT Press, Singapore, 2011.
- [99] S. Singh, M.K.N. Yenkie, Adsorption of o-cresol its aqueous solution on granular activated carbon columns, *Asian J. Chem.* 13 (4) (2000) 1349–1362.
- [100] D.P. Tiwari, D.K. Singh, D.N. Saksena, Hg(II) adsorption from aqueous solutions using rice-husk ash, *J. Environ. Eng.* 121 (6) (1995) 479–481.
- [101] C.J. Butler, A.M. Green, A.L. Chaffee, MTE water remediation using Loy Yang brown coal as a filter bed adsorbent, *Fuel* 87 (2008) 894–904.
- [102] K. Strauss, 1996. Method and device for reducing the moisture content of water-containing brown coal. Patent number—EP 0 784 660 B1 WO 96/10064, Germany.
- [103] D.J. Allardice, A.L. Chaffee, W.R. Jackson, M. Marshall, Water in brown coal and dewatering, in: C.Z. Li (Ed.), *Advances in the Science of Victorian Brown Coal*, Elsevier, Oxford, 2004, pp. 85–125.
- [104] G. Eskenazy, Adsorption of titanium on peat and coals, *Fuel* 51 (1972) 221–223.
- [105] J.W. Larsen, C.S. Pan, S. Shawver, Effect of demineralization on the macromolecular structure of coals, *Energy Fuels* 3 (1989) 557–561.
- [106] M. Krzesińska, Effect of the HCl-demineralization process on the elastic properties of coals, *Energy Fuels* 11 (1997) 686–690.
- [107] L.R. Radović, P.L. Walker, R.G. Jenkins, Effect of lignite pyrolysis conditions on calcium oxide dispersion and subsequent char reactivity, *Fuel* 62 (1983) 209.
- [108] S. Choudhury, Studies on demineralization of coal: fractional factorial design, *Int. J. Innovative Technol. Res.* 1 (1) (2013) 2320–5547.
- [109] S. Kizgut, K. Baris, S. Yilmaz, Effect of chemical demineralization on thermal behaviour of bituminous coals, *J. Therm. Anal. Calorim.* 86 (2) (2006) 483–488.
- [110] V. Gómez-Serrano, M.C. Fernández-González, M.L. Rojas-Cervantes, M.F. Alexandre-Franco, A. Macías-García, Carbonization and demineralization of coals: a study by means of FT-IR spectroscopy, *Bull. Mater. Sci.* 26 (7) (2003) 721–732.
- [111] M. Kumar, R.C. Gupta, Demineralization study of Indian Assam coking coal by sodium hydroxide leaching, *Energy Sources* 19 (1997) 723–730.
- [112] M. Kumar, R.H. Shankar, Removal of ash from Indian Assam coking coal using sodium hydroxide and acid solutions, *Energy Sources* 22 (2000) 187–196.
- [113] P. Samaras, E. Diamadopoulos, G.P. Sakellaropoulos, The effect of demineralization on lignite activation, *Carbon* 29 (8) (1991) 1181–1190.
- [114] P. Samaras, E. Diamadopoulos, G.P. Sakellaropoulos, The effect of mineral matter and pyrolysis conditions on the gasification of Greek lignite by carbon dioxide, *Fuel* 75 (9) (1996) 1108–1114.
- [115] R.T. Wang, S.K. Das, B.M.C. Tsai, Coal demineralization using sodium hydroxide and acid solutions, *Fuel* 64 (1985) 735–742.
- [116] J. Liu, X. Jiang, X. Han, J. Shen, H. Zhang, Chemical properties of superfine pulverized coals Part 2. Demineralization effects on free radical characteristics, *Fuel* 115 (2014) 685–696.
- [117] C.A. Eligwe, N.B. Okolie, Adsorption of iron by a Nigerian brown coal, *Fuel* 73 (4) (1994) 569–572.
- [118] C. Ajaeoro, B.N. Okolie, R.N. Oze, Adsorption of copper(II) by a nigerian brown coal, *J. Emerg. Trends Eng. Appl. Sci.* 1 (1) (2010) 1–4.
- [119] J.V. Ibarra, R. Juan, R. Moliner, Intercambiadores catiónicos a partir de lignitos, *Afinidad* 40 (1983) 229–232.
- [120] J.V. Ibarra, R. Moliner, Copper removal from effluents using a sulphonated lignite: bath and fixed-bed studies, *Fuel* 63 (1984) 373–377.
- [121] M.P. Pandey, M. Chaudhuri, Removal of inorganic mercury from water by bituminous coal, *Water Res.* 16 (1982) 1113–1118.
- [122] S.E. Manahan, *Cleaning Coal with Coal: Coal Humic Acids Removal of Acid, Iron, Heavy Metals and Organic Pollutants Associated with the Use of Coal as a Fuel*, Missouri Water Resources Center, University of Missouri, Columbia, 1975.
- [123] D.L. Michelsen, J.A. Gideon, G.P. Griffith, J.E. Pace, H.L. Kutat, Removal of soluble mercury from water by complexing techniques, *Water Resources Center Bulletin* 74, Virginia Polytechnic Institute, Blacksburg, VA, 1975.
- [124] M.I. Humenick, J.L. Schnoor, Improving mercury(II) removal by activated carbon, *J. Environ. Eng. Div.* 100 (6) (1974) 1249–1262.
- [125] G.V. Cullen, N.G. Siviu, G.M. Pearson, Removing metals from waste solutions with low rank coals, *Water Res.* 16 (1982) 1357–1366.
- [126] J. Horáček, M. Punčochář, J. Drahoš, Utilization of calcium-loaded low-rank brown coal for removing heavy metals from waste solutions, *Water Qual. Res. J. Can.* 27 (1992) 693–699.
- [127] J. Horáček, L. Soukupová, M. Punčochář, J. Slezák, J. Drahoš, K. Yoshida, A. Tsutsumi, Purification of waste waters containing low concentrations of heavy metals, *J. Hazard. Mater.* 37 (1994) 69–76.
- [128] Cullen, G. V., Siviu, N. G., Pearson, G. M., MacDonald, D., 1973, 1976. Extraction of metals from solution with metal loaded brown coal. Australian Patent 491,555; Canadian Patent 981,593.
- [129] M. Kurková, Z. Klíka, C. Klíková, J. Havel, Humic acids from oxidized coals I. Elemental composition, titration curves, heavy metals in HA samples, nuclear magnetic resonance spectra of HAs and infrared spectroscopy, *Chemosphere* 54 (2004) 1237–1245.
- [130] J. Mizera, G. Mizerová, V. Machovíč, L. Borecká, Sorption of cesium, cobalt and europium on low-rank coal and chitosan, *Water Res.* 41 (2007) 620–626.
- [131] J. Novák, J. Kozler, P. Janoš, J. Cežíková, V. Tokarová, L. Madronová, Humic acids from coals of the Nort-bohemian coal field I. Preparation and characterisation, *React. Funct. Polym.* 47 (2001) 101–109.
- [132] M. Havelcová, J. Mizera, V. Machovíč, L. Borecká, O. Přibyl, I. Krausová, Sorption of heavy metals on lignite impregnated with chitosan, *Acta Geodynamica et Geomaterialia* 10 (1) (2013) 105–110.
- [133] J. Mizera, M. Havelcová, V. Machovíč, L. Borecká, I. Krausová, Sorbents of heavy metals based on combination of low rank coals and chitosan, 10th International Multidisciplinary Scientific GeoConference SGEM 2010—Conference Proceedings Volume II, STEF92 Technology Ltd., Sofia, June 20–26, 2010, pp. 781–786.
- [134] W.T. Tsai, C.Y. Chang, S.L. Lee, Preparation and characterization of activated carbon from corn cob, *Carbon* 35 (1997) 1198–1200.
- [135] M.M. Mohamed, Acid dye removal: comparison of surfactants modified mesoporous FSM with activated carbon derived from rice husk, *J. Colloid Interface Sci.* 272 (2004) 28–34.
- [136] K.A. Krishnan, K.G. Sreejalekshmi, R.S. Baiju, Nickel(II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith, *Bioresour. Technol.* 102 (2011) 10239–10247.
- [137] M.L. Martinez, M.M. Torres, C.A. Guzmán, D.M. Maestri, Preparation and characteristics of activated carbon from olive stones and walnut shells, *Ind. Crops Prod.* 23 (2006) 23–28.
- [138] C. Srinivasakannan, M.Z.A. Bakar, Production of activated carbon from rubber wood sawdust, *Biomass Bioenergy* 27 (2004) 89–96.
- [139] D. Savova, E. Apak, E. Ekinci, F. Yardim, N. Petrova, T. Budinova, Biomass conversion to carbon adsorbents and gas, *Biomass Energy* 21 (2001) 133–142.
- [140] T. Yang, A.C. Lua, Characteristics of activated carbons prepared from pistachio-nut shells by physical activation, *J. Colloidal Interface Sci.* 267 (2003) 408–417.

- [141] O. Ioannidou, A. Zabaniotou, Agricultural residues as precursors for activated carbon production: a review, *Renew. Sustainable Energy Rev.* 11 (2007) 1966–2005.
- [142] W. Astuti, E.T. Wahyuni, A. Prasetya, I.M. Bendiyasa, The character of dual site adsorbent on coal fly ash toward Pb (II) adsorption, *IOSR J. Eng.* 3 (11) (2013) 31–35.
- [143] M. Grover, M.S. Narayanaswamy, Removal of hexavalent chromium by adsorption on fly ash, *J. Inst. Eng. (India)* 63 (1) (1982) 36–39.
- [144] M. Ahmaruzzaman, Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals, *Adv. Colloid Interface Sci.* 166 (2011) 36–59.
- [145] X. Querol, A. Alastuey, A. Lo'pez-Soler, F. Plana, J.M. Andre's, R. Juan, P. Ferrer, C.R. Ruiz, A fast method for recycling fly ash: microwave-assisted zeolite synthesis, *Environ. Sci. Technol.* 31 (9) (1997) 2527–2533.
- [146] X. Querol, J.C. Umana, F. Plana, A. Alastuey, A. Lo'pez-Soler, A. Medinaceli, A. Valero, M.J. Domingo, E. Garcia-Rojo, Synthesis of Na zeolites from fly ash in a pilot plant scale. Examples of potential environmental applications, *Fuel* 80 (2001) 857–865.
- [147] X. Querol, N. Moreno, J.C. Umana, R. Juan, S. Hernández, C. Fernández, C. Ayora, M. Janssen, J. García, A. Linares, D. Cazorla, 2001. Application of zeolitic material synthesized from fly ash to the decontamination of waste water and flue gas PROGRES Workshop on Novel Products from combustion residues, Morella, Spain, 163–172.
- [148] V. Berkgaat, A. Singer, Cation exchange properties of hydrothermally treated coal fly ash, *Environ. Sci. Technol.* 7 (1995) 1748–1753.
- [149] V. Berkgaat, A. Singer, High capacity cation exchanger by hydrothermal zeolitization of coal fly ash, *Appl. Clay Sci.* 10 (1996) 369–378.
- [150] C.F. Lin, H.C. His, Resource recovery of waste fly ash: synthesis of zeolite-like materials, *Environ. Sci. Technol.* 29 (4) (1995) 1109–1117.
- [151] C.F. Lin, S.S. Lo, H.-Y. Lin, Y.J. Lee, Stabilization of cadmium contaminated soils using synthesized zeolite, *J. Hazard. Mater.* 60 (3) (1998) 217–226.
- [152] M. Park, J. Choi, Synthesis of phillipsite from fly ash, *Clay Sci.* 9 (4) (1995) 219–229.
- [153] A. Singer, V. Berkgaat, Cation exchange properties of hydrothermally treated coal fly ash, *Environ. Sci. Technol.* 29 (9) (1995) 1748–1753.
- [154] N. Moreno, X. Querol, A. Alastuey, A. García, A. Lo'pez, C. Ayora, Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash, 2000 Fly Ash Utilization Symposium, Lexington, KY, USA, 2001.
- [155] X.J. Gong, W.G. Li, D.Y. Zhang, W.B. Fan, X.R. Zhang, Adsorption of arsenic from micro-polluted water by an innovative coal-based mesoporous activated carbon in the presence of co-existing ions, *Int. Biodeterior. Biodegrad.* 102 (2015) 256–264.
- [156] J.P. Marco-Lozar, A. Linares-Solano, D. Cazorla-Amorós, Effect of the porous texture and surface chemistry of activated carbons on the adsorption of a germanium complex from dilute aqueous solutions, *Carbon* 49 (10) (2011) 3325–3331.
- [157] M. Luan, G. Jing, Y. Piao, D. Liu, L. Jin, Treatment of refractory organic pollutants in industrial wastewater by wet air oxidation, *Arabian J. Chem.* (2012). <http://dx.doi.org/10.1016/j.arabjc.2012.12.003>.
- [158] M. Yang, A current global view of environmental and occupational cancers, *J. Environ. Sci. Health* 29 (2011) 223–249.
- [159] I. Ali, M. Asim, T.A. Khan, Low cost adsorbents for the removal of organic pollutants from wastewater, *J. Environ. Manag.* 113 (2012) 170–183.
- [160] W. Wu, Z.H. Huang, T.T. Lim, Recent development of mixed metal oxide anodes for electrochemicaloxidation of organic pollutants in water, *Appl. Catal. A* 480 (2014) 58–78.
- [161] S. Larous, A.H. Menia, The use of sawdust as by product adsorbent of organic pollutant from wastewater: adsorption of phenol, *Energy Procedia* 18 (2012) 905–914.
- [162] M.T. Uddin, M.S. Islam, M.Z. Abedin, Adsorption of phenol from aqueous solution by water hyacinth ash, *ARPJ. Eng. Appl. Sci.* 2 (2) (2007) 11–17.
- [163] P.N. Cheremisinoff, A.C. Morresi, Carbon adsorption applications, in: P.N. Cheremisinoff, F. Ellerbusch (Eds.), *Carbon Adsorption Handbook*, Ann Arbor Science, Michigan, 1978.
- [164] G.S. Simate, S.E. Ilyuke, S. Ndlovu, M. Heydenrych, The heterogeneous coagulation and flocculation of brewery wastewater using carbon nanotubes, *Water Res.* 46 (4) (2012) 1185–1197.
- [165] A.E. Martell, R.M. Smith, *Critical Stability Constants*, Plenum Press, New York, 1977.
- [166] M.J. Humenick, J.R. Morgan, B.T. Nolan, Adsorption of UCG organics by coal, char, activated char and ash, *In Situ* 11 (4) (1987) 329–347.
- [167] T.M. Aida, T. Sato, G. Sekiguchi, T. Adschiri, K. Arai, Extraction of Taiheiyo coal with supercritical water-phenol mixtures, *Fuel* 81 (2002) 1453–1461.
- [168] N.N. Dutta, S. Borthakur, G.S. Patil, Phase transfer catalyzed extraction of phenolic substances from aqueous alkaline stream, *Sep. Sci. Technol.* 27 (2001) 1435–1448.
- [169] F. Haghseresht, G.Q. Lu, Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents, *Energy Fuels* 12 (1998) 1100–1107.
- [170] M. Ahmaruzzaman, D.K. Sharma, Adsorption of phenols from wastewater, *J. Colloid Interface Sci.* 287 (2005) 14–24.
- [171] J.C. Liu, C.P. Huang, Adsorption of some substituted phenols onto hydrous ZnS (s), *J. Colloid Interface Sci.* 153 (1) (1992) 167–176.
- [172] Y.I. Tarasevich, Porous structure and adsorption properties of natural porous coal, *Coll. Surf. A* 176 (2-3) (2001) 267–272.
- [173] M. Streat, J.W. Patrick, M.J.C. Perez, Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbon, *Water Res.* 29 (2) (1995) 467–472.
- [174] F. Caturla, J.M. Martin-Martinez, M. Molina-Sabio, F. Rodrigues-Reinoso, R. Torregrosa, Adsorption of substituted phenols on activated carbon, *J. Colloid Interface Sci.* 124 (2) (1987) 528–534.
- [175] C. Moreno-Castilla, J. Rivera-Utrilla, M.V. López-Ramón, F. Carrasco-Marín, Adsorption of some substituted phenols on activated carbons from a bituminous coal, *Carbon* 33 (6) (1995) 845–851.
- [176] R.T. Morrison, R.N. Boyd, *Organic Chemistry*, Allyn and Bacon Inc., Boston, 1983.
- [177] A. Das, D.K. Sharma, Adsorption of phenol from aqueous solutions by oxidized and solvent-extracted residual coal, *Energy Sources* 20 (1998) 821–830.
- [178] C.C. Giri, Studies on development of a process for solvent deashing of coal to obtain environmentally clean fuels and characterization of products, PhD Thesis, IIT Delhi, India, 1995.
- [179] D.K. Sharma, S. Mishra, Studies of successive extraction of coals in coal derived solvents under ambient conditions to recover volatile matter (volatile components) from coal and to get partially devolatilized residual coal and solvent refined coal as clean and detoxified fuels, *Fuel Sci. Technol. Int.* 13 (6) (1995) 761–774.
- [180] D.K. Sharma, N.K. Sandle, S.K. Singh, M. Venugopal, Solvolytic extractive disintegration and gasification of coal, *J. Mines Met. Fuels* 34 (1991) 60–64.
- [181] T. Ahsan, J.H. Wu, E.M. Amett, Effects of citric acid washing of the thermodynamic interaction of some coals with acids, *Fuel* 73 (3) (1994) 417–422.
- [182] Z. Aksu, J. Yener, The usage of dried activated sludge and fly ash wastes in phenol biosorption/adsorption: comparison with granular activated carbon, *J. Environ. Sci. Health* 34 (9) (1999) 1777–1796.
- [183] P.C. Kao, J.H. Tzeng, T. Huang, Removal of chlorophenols from aqueous solution by fly ash, *J. Hazard. Mater.* 76 (2-3) (2000) 237–249.
- [184] Z. Aksu, J. Yener, A comparative adsorption/biosorption study of mono-chlorinated phenols onto various sorbents, *Waste Manag.* 21 (8) (2001) 695–702.
- [185] B.N. Estevinho, I. Martins, N. Ratola, A. Alves, L. Santos, Removal of 2,4-dichlorophenol and pentachlorophenol from waters by sorption using coal fly ash from a portuguese thermal power plant, *J. Hazard. Mater.* 143 (1–2) (2007) 535–540.
- [186] H. Nollet, M. Roels, P. Lutgen, P. Van der Meeren, W. Verstraete, Removal of PCBs from wastewater using fly ash, *Chemosphere* 53 (6) (2003) 655–665.
- [187] E.N.E. Qada, S.J. Allen, G.M. Walker, Adsorption of basic dyes from aqueous solution onto activated carbons, *Chem. Eng. J.* 135 (2008) 174–184.
- [188] R. Juang, S. Swee, Effect of dye nature on its adsorption from aqueous solution onto activated carbon, *Sep. Sci. Technol.* 31 (15) (1996) 2143–2158.
- [189] E.N.E. Qada, S.J. Allen, G.M. Walker, Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: a study of equilibrium adsorption isotherm, *Chem. Eng. J.* 124 (2006) 103–110.
- [190] G. Yuliani, A.L. Chaffee, G. Garnier, Adsorption of Anionic and Cationic Dyes on Raw and Treated Victorian Brown Coal, (2011). (accessed: November 2014) <http://www.conference.net.au/chemeca2011/papers/449.pdf>.
- [191] Y. Qi, Characterisation of organic and inorganic components in process water from a novel lignite dewatering process, PhD Thesis, Monash University, 2004.
- [192] T. Depci, A.R. Kul, Y. Onal, E. Disli, S. Alkan, Z.F. Turmenoglu, Adsorption of crystal violet from aqueous solution on activated carbon derived from Gölbasi lignite, *Physicochem. Problems Miner. Process.* 48 (1) (2012) 253–270.
- [193] A. Iordanidis, A. Georgakopoulos, Adsorption of Dye Pollutants by Greek: A Preliminary Experimental Study, (2002). (accessed: November 2014) <http://users.auth.gr/ageorgak/EDUCATION/Dimosiefsis/6371-377.pdf>.
- [194] S.V. Mohan, N.C. Rao, J. Karthikeyan, Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study, *J. Hazard. Mater.* B 90 (2002) 189–204.
- [195] S.V. Mohan, P. Sailaja, M. Srimurali, J. Karthikeyan, Color removal of monoazo acid dye from aqueous solution by adsorption and chemical coagulation, *Environ. Eng. Policy* 1 (1999) 149–154.
- [196] J. Yu, A. Tahmasebi, Y. Han, F. Yin, X. Li, A review on water in low rank coals: the existence, interaction with coal structure and effects on coal utilization, *Fuel Process. Technol.* 106 (2013) 9–20.
- [197] G. McKay, G. Ramprasad, P.P. Mowli, Equilibrium studies for the adsorption of dyestuffs from aqueous solutions by low-coast materials, *Water Air Soil Pollut.* 29 (1986) 273–283.
- [198] M. Mahramanlıoğlu, I. Kızılıkılıç, A. Çınarlı, Ö. Özgen, Removal of Astrozon Red from aqueous solutions by adsorbents produced from lignite coal, *J. Eng. Sci.* 8 (1) (2001) 53–60.
- [199] M. Ishaq, K. Saeed, I. Ahmad, M. Shakirullah, M.I. Khan, Physicochemical characteristics and maleic acid adsorption capacity of Lakhra (Pakistani) coal, *J. Chem. Soc. Pak.* 33 (3) (2011) 360–363.
- [200] H. Särkkä, M. Vepsäläinen, M. Sillanpää, Natural organic matter (NOM) removal by electrochemical methods—a review, *J. Electroanal. Chem.* 755 (2015) 100–108.
- [201] J.R. Utrilla, I.B. Toledo, M.A.F. Garcia, C.M. Castilla, Activated carbon surface modifications by adsorption of bacteria and their effect on aqueous lead adsorption, *J. Chem. Technol. Biotechnol.* 76 (2001) 1209–1215.
- [202] L.G. Danielsson, On the use of filters for distinguishing between dissolved and particulate fractions in natural waters, *Water Res.* 16 (1982) 179–182.

- [203] J.A. Leenher, Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters, *Environ. Sci. Technol.* 15 (1981) 578–587.
- [204] J. Fettig, Removal of humic substances by adsorption/ion exchange, *Water Sci. Technol.* 40 (1999) 73–182.
- [205] P. Thiel, P. Cullum, Evaluating the Performance of Different Powdered Activated Carbons for Taste and Odour Reduction, (2007). (accessed: February 2016) http://www.wioa.org.au/conference_papers/07_qld/documents/peta-thiel.pdf.
- [206] E.S. Olson, D.J. Stepan, Activated Carbon from Lignite for Water Treatment, (2000) . (accessed: February 2016) <http://www.osti.gov/scitech/servlets/purl/824974>.
- [207] M. Bjelopavlic, G. Newcombe, R. Hayes, Adsorption of NOM onto activated carbon: effect of surface charge, ionic strength, and pore volume distribution, *J. Colloid Interface Sci.* 210 (2) (1999) 271–280.
- [208] D.R.U. Knappe, L. Li, P.A. Quinlivan, T.B. Wagner, Effects of Activated Carbon Characteristics on Organic Contaminant Removal, American Water Works Association, Research Foundation, Denver, 2003.
- [209] P.A. Quinlivan, L. Li, D.R.U. Knappe, Effects of activated carbon characteristics on the simultaneous adsorption of aqueous organic micropollutants and natural organic matter, *Water Res.* 39 (2005) 1663–1673.
- [210] M.R. Collins, G.L. Amy, C. Steelink, Molecular weight distribution, carboxylic acidity and humic substances content of aquatic organic matter: implications for removal during water treatment, *Environ. Sci. Technol.* 20 (1986) 1028–1032.
- [211] T. Karanfil, M. Kitis, J.E. Kilduff, A. Wigton, Role of granular activated carbon surface chemistry on the adsorption of organic compounds. 2. Natural organic matter, *Environ. Sci. Technol.* 33 (1999) 3225–3233.
- [212] D.R.U. Knappe, Y. Matsui, V.L. Snoeyink, P. Roche, M.J. Prados, M.M. Bourbigot, Predicting the capacity of powdered activated carbon for trace organic compounds in natural waters, *Environ. Sci. Technol.* 32 (1998) 1694–1698.
- [213] I.N. Najm, V.L. Snoeyink, Y. Richard, Effect of initial concentration of a SOC in natural water on its adsorption by activated carbon, *J. Am. Water Works Assoc.* 83 (8) (1991) 57–63.
- [214] Q. Li, V.L. Snoeyink, B.J. Mariñas, C. Campos, Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds, *Water Res.* 37 (2003) 773–784.
- [215] G. Newcombe, M. Drikas, R. Hayes, Influence of characterized natural organic matter on activated carbon adsorption II. Effect on pore volume distribution and adsorption of 2-methylisoborneol, *Water Res.* 31 (1997) 1065–1073.
- [216] M. Rattier, J. Reungoat, W. Gernjak, J. Keller, Organic Micropollutant Removal by Biological Activated Carbon Filtration: A Review, (2012) . (accessed: February 2016) <http://www.urbanwateralliance.org.au/publications/UWSRA-tr53.pdf>.
- [217] Y.G. Park, The effect of porosity of sieving particles on the removal efficiency of organic substances via biofilter in the fixed bed, *Biotechnol. Bioproc. E* 7 (2002) 31–37.
- [218] D.Y. Zhang, W.G. Li, H.N. Gong, L. Zhang, X.J. Gong, B.Y. Liu, Evaluation of long term stability of seeded bacteria in a bio-enhanced activated carbon filter used for treating drinking water, *Int. Biodeterior. Biodegrad.* 85 (2013) 701–708.
- [219] L.R. Radovic, M.C. Castilla, R.J. Utrilla, Carbon materials as adsorbents in aqueous solutions, in: L.R. Radovic (Ed.), *Chemistry and Physics of Carbon*, Marcel Dekker, New York, 2000.
- [220] J.F. Siuda, J.F. DeBernardis, Naturally occurring halogenated organic compounds, *Lloydia* 36 (2) (1973) 107–143.
- [221] B.Z. Li, X.Y. Xu, L. Zhu, Catalytic ozonation-biological coupled processes for the treatment of industrial wastewater containing refractory chlorinated nitroaromatic compounds, *J. Zhejiang Univ. Sci. B* 11 (3) (2010) 177–189.
- [222] P. Jin, X. Jin, X. Wang, Y. Feng, X.C. Wang, Available at, Biological Activated Carbon Treatment Process for Advanced Water and Wastewater Treatment, (2013) . (accessed: February 2016) <http://cdn.intechopen.com/pdfs-wm/44410.pdf>.
- [223] J. Lohwacharin, Y. Yang, N. Watanabe, A. Pettrak, H. Sakai, M. Murakami, K. Oguma, S. Takizawa, 2011. Characterization of DOM removal by full-scale biological activated carbon (BAC) filters having different ages.
- [224] J. Hoigné, H. Bader, The role of hydroxyl radical reaction in ozonation process in aqueous solution, *Water Res.* 10 (5) (1976) 377–386.
- [225] R.G. Rice, Application of ozone for industrial wastewater treatment—a review, *Ozone Sci. Eng.* 18 (6) (1997) 477–515.
- [226] F. Lian, C. Chang, Y. Du, L. Zhu, B. Xing, C. Liu, Adsorptive removal of hydrophobic organic compounds by carbonaceous adsorbents: a comparative study of waste-polymer-based, coal-based activated carbon, and carbon nanotubes, *J. Environ. Sci.* 24 (9) (2012) 1549–1558.
- [227] Z.C.Z. Torunño, C.L. Luque, F.X.C. de las Heras, M.S. Sardans, Removal of PAHs from water using an immature coal (leonardite), *Chemosphere* 67 (2007) 505–512.
- [228] K. Tong, Y. Zhang, D. Fu, X. Meng, Q. An, P.K. Chu, Removal of organic pollutants from super heavy oil wastewater by lignite activated coke, *Coll. Surf. A* 447 (2014) 120–130.
- [229] B.R. Simonovic, D. Arandelovic, M. Jovanovic, B. Kovacevic, L. Pezo, A. Jovanovic, Removal of mineral oil and wastewater pollutants using hard coal, *Chem. Ind. Chem. Eng.* Q. 15 (2) (2009) 57–62.
- [230] R.P. Schwarzenbach, P.M. Gschwend, D.M. Imboden, *Environmental Organic Chemistry*, John Wiley and Sons Inc., 1993.
- [231] H. Gaboriau, A. Saada, Influence of heavy organic pollutants of anthropic origin on PAH retention by kaolinite, *Chemosphere* 44 (2001) 1633–1639.
- [232] S. Hwang, T.J. Cutright, Preliminary evaluation of PAH sorptive changes in soil by Soxhlet extraction, *Environ. Int.* 30 (2) (2004) 151–158.
- [233] D. Mohan, C.U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, *J. Hazard. Mater. B* 137 (2006) 762–811.
- [234] F. Amiri, Influence of pH and NOM on sorption of phenols onto aquifer material, MSc Dissertation, University of Dresden, Germany, 2005.



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Phosphorus removal by electric arc furnace steel slag and serpentinite

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ABSTRACT

Electric arc furnace (EAF) steel slag and serpentinite were tested in columns either alone or mixed with limestone to determine their capacity to remove phosphorus (P) from a solution containing initially 20 mg P/L (for 114 days) than 400 mg P/L (for 21 days). EAF steel slag was nearly 100% efficient due to specific P adsorption onto metal hydroxides and precipitation of hydroxyapatite. Serpentinite also showed a good performance that decreased with time, adsorption appearing to be the dominant mechanism for P removal. Mixing limestone with these two materials did not improve their performance and in the case of serpentinite, it actually even decreased it. In 114 days of experimentation, serpentinite alone and the mixture of serpentinite and limestone removed 1.0 mg P/g while in 180 days of experimentation, EAF steel slag and the mixture of slag and limestone removed an average of 2.2 mg P/g, without attaining their maximum P removal potential. The void hydraulic retention time (HRTv) was a key factor for growing hydroxyapatite crystals and had a significant effect on P removal efficiency by EAF steel slag. A temporary increase in HRTv caused by clogging resulted in an increase in EAF steel slag efficiency (from 80% to almost 100%) towards the end of investigation. Results from this study indicate that the use of EAF steel slag in constructed wetlands or filter beds is a promising solution for P removal via adsorption and precipitation mechanisms.

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1. Introduction

With increasing pressure and changes in water discharge legislation since the 1970's, phosphorus (P) has become a pollutant of a concern, due to the eutrophication and deterioration of watercourses if discharged to water bodies in excessive amounts (Sedlak, 1991). Constructed wetland systems (CWS) have been tested and emerged as a promising solution for treating various types of wastewater effluents around the world (Moshiri, 1993; Kadlec and Knight, 1996, Vymazal et al., 1998, Kadlec et al., 2000). When designing a

CWS for P removal, the selection of the material for a wetland substrate plays a crucial role (Mann, 1997; Johansson, 1999; Drizo et al. 1999; Drizo et al., 2002). Because it was established that the principal P removal/retention mechanisms by CWS are adsorption and precipitation within the substrate, various iron (Fe), calcium (Ca) or aluminum (Al) rich materials were tested for their ability to enhance these processes (Mann, 1997; Drizo et al., 1999; Brooks et al., 2000; Arias et al., 2001; Drizo et al., 2002). There are two major factors that make P removal particularly difficult: the first one relates to the principal phosphorus removal mechanism, adsorption/precipitation,

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being a finite process, which requires the P saturated substrate to be either washed or replaced (Faulkner and Richardson, 1989; Mann, 1997; Drizo et al., 2002; Shilton et al., 2005b). The second factor is the type, quantity and diversity of the effluents that need to be treated. For example, rural, municipal and agricultural effluents (e.g. dairy, manure runoff, slaughterhouses, and pig farms) are typically characterized by high to very high concentrations of P (15–2000 mg P/L). However, the biological and chemical composition of these effluents and their quantities vary to a great extent depending, in particular, on the size of the community or industry (in a case of rural or municipal effluent treatment), or farm size and activity (e.g. animal species, farm practices and daily nutrients turnover) (Geary and Moore, 1999; Longhurst et al., 2000). Fish farm effluents, however, represent an opposite problem. These effluents are characterized by much lower P concentrations (0.3 mg P/L) than most other types of effluent. However, due to high water requirements (e.g. 10 000 m³/day, for a farm producing 100 tonnes of trout/year) fish farms still produce excess organic and P loads that impose serious threat to surrounding water courses (Comeau et al., 2001).

It has been established that selection of the most suitable material for P removal is site specific and is dependent upon various factors such as physico-chemical characteristics, P retention capacity, recycling potential, the cost and local availability of the material (Richardson and Craft, 1993; Mann, 1997; Johansson, 1999; Arias et al., 2001; Drizo et al., 1999, 2002). When tested in batch and column laboratory experiments at both low and high P concentrations, blast furnace (BF) and basic oxygen (BOF) steel slags, waste products from iron production in various parts of the world demonstrated high P removal efficiencies (Yamada et al., 1986; Mann, 1997; Baker et al., 1998; Johansson, 1999). Forget. (2001) tested 57 different materials in batch tests, and showed that another type of steel slag material, an electric arc furnace (EAF) steel slag and serpentinite showed highest potential of achieving efficient P removal. Following the results obtained by Forget (2001), Soulard (2001) evaluated P removal efficiencies by three different types of slag (blast furnace, basic oxygen and EAF slag) materials obtained from three different slag producers (Dofasco located in Ontario, QIT Fer et Titane and Ispat Sidbec located in Quebec, Canada) in a series of batch tests. The results from these experiments further confirmed that an EAF steel slag produced by Ispat Sidbec had superior P removal efficiency when compared to the other investigated materials. The study of P removal by serpentinite was previously reported only in one study, conducted in batch scale experiments in the presence of various electrolytes (Bonifacio et al., 2001).

Although batch tests provide good indication of the materials' capacity to retain P, when making a selection of potential substrates to be used in designing constructed wetlands and/or filters for P removal it is necessary to conduct longer-term column or pilot-scale experiments (Drizo et al., 2002; Shilton et al., 2005a). In this paper, serpentinite and EAF steel slag material P removal efficiencies were explored in longer-term column experiments. In addition, mixtures of EAF steel slag and serpentinite materials with limestone were also tested to verify whether the

addition of limestone would contribute to P precipitation and enhance P removal. The amount of P retained by each of the materials, as well as the factors affecting P removal performance, were determined. Chemical analyses of each material were carried out to determine the dominant constituents responsible for P removal. Finally, P deposition on the EAF steel slag surfaces was characterised using X-ray diffraction (XRD) analyses.

2. Materials and methods

2.1. Materials

The materials tested in columns were selected as a function of their P removal coefficient (R_d), which is determined in batch experiments following a simple and comparative procedure suggested by the standard method ASTM D4646-87 (1993), their physical properties and their cost (Forget, 2001). The tested materials were serpentinite (0.6–3.2 mm) and EAF steel slag (2.5–10 mm). Serpentinite was supplied by Bell mine, Thetford Mines (Quebec). It is a magnesium-rich (Mg) silicate mineral associated with ultra basic igneous rocks (Deer et al., 1985). The principal minerals of the serpentinite group all have approximate composition of $H_4Mg_3Si_2O_9$, but they occur in the three principal polymorphic forms: chrysotile, antigorite and lizardite $Mg_6[(OH)_8Si_4O_{10}]$ (Deer et al., 1985). The later one, $Mg_6[(OH)_8Si_4O_{10}]$ was the predominant form in serpentinite material used in this study (Forget, 2001). EAF slag material was obtained from Ispat Sidbec (now Mittal), Tracy, a steel production company which generates approximately 250 000 tonnes of slag annually (Piché, 2005). As EAF steel slag contains a large proportion of amorphous material that is not detectable by XRD (Bernier, 2001) chemical analyses were employed to determine major constituents of this material. The chemical analyses were carried out with atomic absorption spectrometry (AA-5000 Perkin Elmer) following a standard digestion method (2 mL HCl+9 mL HNO₃+1 mL 30% hydrogen peroxide, 0.5 g of material) and treatment with hydrofluoric acid (HF) to dissolve silicates (NWRI, 2003).

Serpentinite and EAF slag materials were tested alone or mixed with limestone (2.5–10 mm) rich in calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) to test whether the addition of this material would contribute to P precipitation. Both of these minerals have been reported to have high potential to remove P from wastewaters (Freeman and Rowell, 1981; Brix et al., 2001; Roques, et al., 1991). Granitic gravel (0.08–10 mm) was chosen as a control since its constituents quartz (SiO_2) and feldspars ($(Na,K)Si_3AlO_8$) are practically chemically inert to P sorption.

2.2. Methods

The experimental set-up was comprised of 10 columns with five materials or mixtures tested in duplicate: Sp1 and Sp2 (100 wt% serpentinite); SpL1 and SpL2 (47 wt% serpentinite and 53 wt% limestone); Sl1 and Sl2 (100 wt% EAF steel slag); SlL1 and SlL2 (79 wt% EAF steel slag and 21 wt% limestone); G1 and G2 (100 wt% gravel). Given that P removal is essentially a

surface reaction, the weight percentage of the mixed materials was calculated to obtain about 50% specific surface for each material. Specific surfaces of the materials were 0.7 and $0.6 \text{ m}^2/\text{kg}$ for serpentinite and EAF steel slag, respectively, and were determined using the method developed by Chapuis and Légaré (1992), which is based on the grain size distribution.

Each column consisted of a base, a clear plastic cylinder, a covering plate and one valve connected at each inlet and outlet ends. The inside diameter of each column was between 15.2 cm and the height of material placed in each column was between 43.4 and 48.4 cm. Perforated plastic plates and geotextiles were used to distribute the solution evenly through the base of each column and to avoid fines washing. The tested materials were added and lightly compacted in successive layers of 5 cm to obtain a homogenous sample with a porosity of $37 \pm 3\%$ for columns filled with serpentinite or serpentinite and limestone, and of $44 \pm 2\%$ for columns filled with steel slag or steel slag and limestone. The dry mass in each column was $14.8 \pm 0.6 \text{ kg}$ for the columns filled with serpentinite, serpentinite mixed with limestone and gravel, while for the columns filled with steel slag and steel slag mixed with limestone, the dry mass was $18.3 \pm 0.5 \text{ kg}$. Water saturation of the materials was obtained by vacuuming and filling with water using a bottom to top flow to minimize air bubbles entrapment (Chapuis et al., 1989).

Each column was gravity fed from the top with a reservoir filled with a P solution (20 mg P/L with KH_2PO_4 , $\text{pH} \approx 6.0$) at a flowrate of $2.1\text{--}2.8 \text{ mL/min}$ depending on the pore volume of each column, resulting in an initial void hydraulic retention time (HRT_v) of about 24 h. This P concentration was chosen because it represented not only the supernatant of the sludge from fish farm effluent after passing through a microscreen (which is a recommended practice for fish farms in Quebec as a primary solids separation stage), but also the average rural effluent concentration (Sedlak, 1991). The P removal potential was then studied by applying a higher P concentration (400 mg P/L) for each material or mixture of materials using one column of each studied material for a period of 56 days.

The samples were kept under saturated conditions by positioning the outlet at the height of each column and the effluent was collected in closed buckets to minimise evapo-

ration (Fig. 1). The EAF steel slag columns (Sl1 and Sl2), EAF steel slag and limestone columns (SlL1 and SlL2), and gravel columns (G1 and G2) were fed during a period of 124 days. The serpentinite (Sp1 and Sp2) and serpentinite mixed with limestone columns (SpL1 and SpL2) were fed for a shorter period of time (58 days). P removal efficiency data were plotted as a function of pore volumes to reduce the effect of flow variations on the curve slopes which would occur when the data is plotted as a function of time.

Effluent volume applied to all columns was recorded once a day by weighing and the flow rates were accordingly adjusted to their setpoints. The effluent of each column and the feeding solution were sampled twice a week and analyzed for orthophosphates, using a vanadomolybdophosphoric acid colorimetric method (APHA et al., 1998). At the end of the first phase of the experiment ($[\text{P}]_{\text{in}} = 20 \text{ mg P/L}$), one duplicate column of each mixture (Sp2, SpL2, Sl2, SlL2 and G2) was dismantled and solid samples were collected from every 5 cm of the column height. The EAF steel slag particles in the upper parts of columns Sl2 and SlL2 were covered with a white precipitate, which was analysed by XRD (Goldstein, 1981).

3. Results and discussion

3.1. Chemical analyses

EAF steel slag was rich in Fe and calcium oxides, representing 35% and 30%, respectively (Table 1). Both Fe and Ca are known to play an important role in P retention by soils and sediments (Stumm and Morgan, 1981; Richardson, 1985). Phosphate ions react with iron oxides by ligand exchange forming inner-sphere complexes (Parfitt, 1978; Barrow, 1978). The presence of Ca facilitates P retention via precipitation, and formation of Ca-P deposition on the solids surfaces (Lindsay, 1979). Depending on the pH and the solution composition of Ca and P (H_2PO_4^- or HPO_4^{2-}), several Ca-P may form: amorphous calcium phosphates (ACPs), octacalcium phosphate (OCP), dicalcium phosphate (DCP), dicalcium phosphate dihydrate (DCPD), tricalcium phosphate (TCP) and hydroxyapatite (HAP) (Lindsay, 1979; Lazic, 1995; House, 1999; Valsami-Jones, 2001). The pH values of the effluents were fairly high (between 10.6 and 11.4 for slag, and 9.4 and 10.2 for serpentinite) which was in the range of values that support formation of hydroxyapatite (HAP) (House, 1999; Johansson and Gustafsson, 2000).

Magnesium oxides (MgO) constituted 36% of serpentinite (Table 1). Phosphate can react with Mg^{2+} by ligand exchange with water molecules and/or hydroxyl ions (Lindsay, 1979; Stumm and Morgan, 1981). Mg-rich materials (granular magnesia clinker and half-burned $\text{CaMg}(\text{CO}_3)_2$) were previously shown to have a good potential for P removal from wastewater (Kaneko and Nakajima, 1988; Suzuki and Fuji, 1988). Roques et al. (1991) reported that with an increase in pH, significant quantities of Mg^{2+} were dissolved in solution. They postulated that superficial hydrolysis of MgO and partial solubilisation of the formed hydroxide result in the exchange of OH^- and Mg^{2+} ions, which, under elevated pH, lead to the P fixation at the liquid-solid interface.

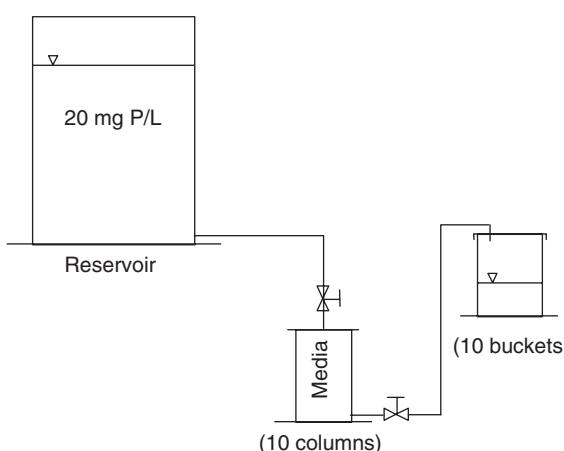


Fig. 1 – Experimental set-up for the column study.

Table 1 – Chemical composition of the tested materials (%)

Oxides	Steel slag	Serpentinite	Limestone	Gravel
SiO ₂	13.7	41.2	6.83	64.8
Al ₂ O ₃	4.67	1.80	1.53	15.2
Fe ₂ O ₃	34.7	7.15	0.82	5.92
MgO	13.1	36.0	18.0	0.88
CaO	30.4	0.50	29.0	3.99
Na ₂ O	< 0.01	0.33	< 0.10	3.43
K ₂ O	< 0.01	0.34	0.90	4.06
TiO ₂	0.68	0.03	0.07	1.03
MnO	1.30	0.10	0.07	0.10
P ₂ O ₅	0.32	< 0.01	0.03	0.31
Cr ₂ O ₃	0.32	0.36	< 0.01	< 0.01
Li ^a	0.00	11.9	42.1	0.60
Total	99.2	99.7	99.4	100.3

^a LI: loss on ignition (550 °C).

Ca and Mg were the main constituents of limestone on an oxide basis (29 and 18%, respectively) and they contributed to P removal via both adsorption and precipitation mechanisms. Mg has been shown to have a strong effect on the morphology, crystal perfection, nucleation and growth kinetics of ACPs (Abbona and Baronnet, 1996). Serpentinite was also high in Si (Table 1), however, it was previously reported that Si has little efficiency for P retention (Baker et al., 1998; Johansson and Gustafsson, 2000).

3.2. P removal efficiency

The P removal efficiency by serpentinite (Sp1 and Sp2) and the mixture of serpentinite and limestone (SpL1 and SpL2) as a function of number of pore volumes is presented in Fig. 2(A). Two data sets were plotted for each material (Sp1 and Sp2, SpL1 and SpL2, Sl1 and Sl2, SlL1 and SlL2, and G1 and G2) for the comparison of P removal efficiencies (Fig. 2(A)).

The columns filled with serpentinite (Sp1 and Sp2) were very efficient for the first 37 pore volumes (40 days), achieving a P removal efficiency of more than 95% (Fig. 2A). During this time 3.0 g P was added to the columns (0.21 g P/kg). Over the following 30 pore volumes, the amount of added P increased 6.6-fold (19.7 g P or 1.37 g P/kg serpentinite) resulting in almost linear decrease in P removal efficiency, falling to 40% at the end of the experiment (after 70 pore volumes). At this point, a total of 24.0 g P (1.67 g P/kg) had been added to the column filled with serpentinite, of which 13.2 g P (0.92 g P/kg) was retained (Figs. 2 and 3).

Organic matter was not present in the P feeding solution in this experiment and the efficiency and life span of serpentinite material could decrease significantly if applied at field-scale treating an actual effluent (Drizo et al., 1999). From a practical application point of view this kind of information supports the need for coupling batch experiments with longer term column studies when selecting materials for P removal from wastewaters. The discrepancy that can occur between the materials P retention capacity estimated from the laboratory experiments and their field-scale efficiency per-

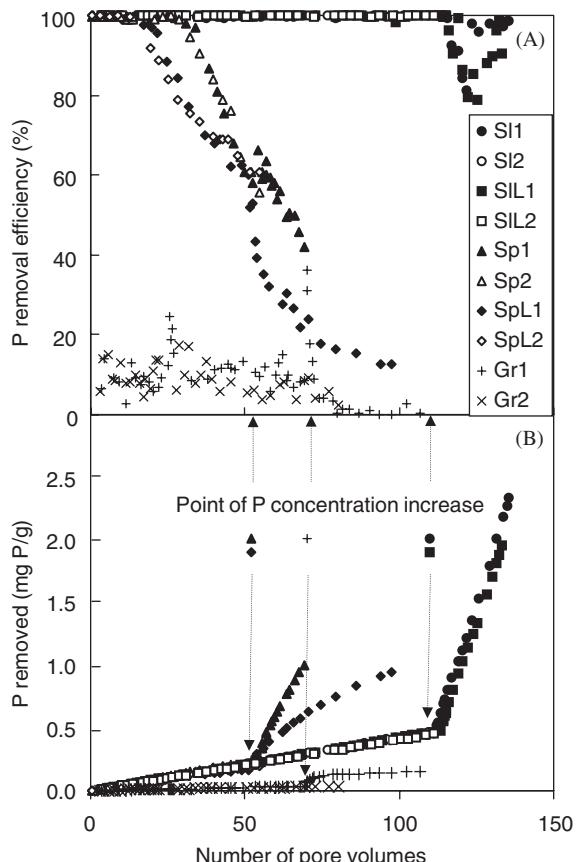


Fig. 2 – P removal efficiency (A) and P removed (B) as a function of pore volumes. The arrows identify the points of influent P concentration increase from 20 to 400 mg P/L for one of the two columns of each media tested. Media tested: Gr: gravel; Sl: slag; SlL: slag and limestone; Sp: serpentinite; SpL: serpentinite and limestone; 1 and 2 refer to each media duplicates.

formances was demonstrated in a study carried out by Arias et al. (2003). The field-scale CaCO₃ filter described in their study had a tenfold lower P removal efficiency than previously estimated in their laboratory batch investigations (Brix et al., 2001).

The P removal rate did not seem much influenced by the HRTv increase caused by clogging after the increase in the feeding solution P concentration (at 53 pore volumes). The columns filled with the mixture of serpentinite and limestone (SpL1 and SpL2) were equally efficient for the first 22 pore volumes (30 days), and then gradually decreased to only 15% (Fig. 2(A)). Ca-rich materials are subject to the dissolved carbonate equilibrium leading to dissolution or precipitation of the solid phase. (Stumm and Morgan, 1981). Ca-P precipitation is dependent upon the formation of stable nuclei after which crystal growth can take place, and degree of supersaturation (Feeenstra and Bruyn, 1979; Stumm and Morgan, 1996). Supersaturation could be developed either by increasing Ca, PO₄³⁻ and OH ionic concentration in solution.

Addition of limestone to serpentinite in our experiments increased the content of Ca when compared to the Mg content (Table 1). The presence of liberated Mg²⁺ ions in

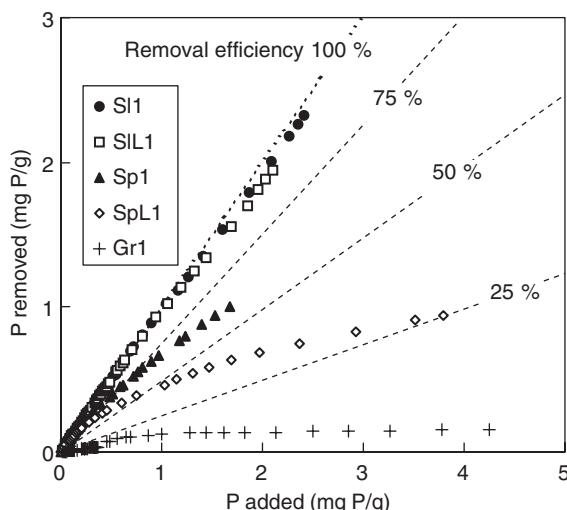


Fig. 3 – P removed as a function of P added. Media tested: see caption of Fig 2.

solution could have prolonged the induction period of calcium phosphate formation. Because Mg^{2+} ions have higher hydration energy when compared with Ca^{2+} , they could have hindered crystal formation (Kuo and Mikkelsen, 1979). Abbona and Baronnet (1996) showed that the presence of Mg in Ca phosphate solution retards P retention through incorporation in the ACP clusters and HAP pre-nuclei, as well as through adsorption onto ACP surfaces and HAP crystallites. Ca precipitation in the columns filled with the mix of serpentinite and limestone could have also been retarded by a decrease in pH values which fell from 9.6 to 7.7, at the end of the experimental period. The precipitation of Ca requires high total Ca^{2+} concentration and high pH, while on the other hand, dissolution of $Mg(OH)_2$ requires pH values lower than 8.6 (Ádám et al., 2005). Bonifacio et al. (2001) suggested that P retention by serpentinite material is likely to depend on the charge of the mineral surface at the equilibrium pH (Barrow, 1984, 2002).

EAF steel slag alone or mixed with limestone was nearly 100% efficient for the first 116 pore volumes (Fig. 2(A)). The 20-fold increase in the feeding solution P concentration at 111 pore volumes (from 20 to 400 mg P/L), resulted in a decrease in efficiency to 80% over the following 2 weeks (11 pore volumes). After this point, columns SI1 and SIl1 started to clog, probably due to the formation of precipitates in the valves, which diminished the flow rate and increased the hydraulic retention time (HRTv) (Fig. 2(A)). The 2.5-fold increase in HRTv led to an increase in the P removal efficiency, reaching the initial efficiency of near 100% (Fig. 2(A)). These results confirm the effect of HRTv on P removal efficiency observed by other researchers (Brookes et al., 2000; Shilton et al., 2005a). During the whole experimental period, a total of 47.4 g P (2.51 g P/kg) and 39.3 g P (2.2 g P/kg) was added to EAF slag (SI1) and EAF slag and limestone columns (SIL1), respectively (Fig. 3).

The P removal efficiency of gravel was stable at around 10% at the lower P concentration ($P = 20 \text{ mg P/L}$) and then decreased to nearly zero, except for two instances when the removal efficiency increased punctually. The first increase

could be explained by an increase in the HRTv and the second one by the increase in the feeding P concentration (Fig. 2(A)).

3.3. P removal capacity, P mass removal and P removal mechanisms

The P removal capacity of a material is an important parameter for practical applications as it enables designers to estimate the longevity of a full-scale system (Drizo et al., 1999; 2002; Johansson, 1999; Shilton et al., 2005b). Determination of the maximum P removal capacities by materials tested in column studies are still lacking, however, the most common reason being the time required to conduct such experiments (Brix et al., 2001; Drizo et al., 2002; Shilton et al., 2005a).

The P removal capacity of the materials investigated in this study as a function of pore volumes is presented in Fig. 2(B). Apart from gravel, which was used as a control, none of the materials reached P saturation at the end of the experiment. As in other studies, the experiment was terminated due to time constraints, and only the two serpentinite containing materials seemed to approach a maximum P removal at that time (Fig. 2(B)). For the whole period of investigation, serpentinite and serpentinite mixed with limestone removed 1.0 mg P/g, while EAF steel slag and EAF steel slag mixed with limestone removed 2.3 and 2.0 mg P/g, respectively (Fig. 2(B)).

Comparing values of P removed should be done cautiously given that both the number of pore volumes passed through each column, and the mass of P added to the materials, were different at the end of the experiment, due to the differences in HRTv (Fig. 2(B)). The effects of HRTv and the mass of P added on P removal efficiency can be demonstrated by comparing the results from the current study with those from a previous study carried out by Drizo et al. (2002). While in these experiments, the total mass of P added was 2.4 mg P/g of EAF steel slag, resulting in nearly 100% efficiency, Drizo et al. (2002) added 75.2 mg P/g slag with a much shorter HRTv (8 h) and showed that the same material was able to retain only 1.4 mg P/g before reaching saturation. More recently, Weber and Drizo (2005) investigated P removal from dairy farm effluent in field scale EAF slag filters. In this study, an HRTv of 12 h was employed during the first 120 days of investigation, achieving high P removal efficiency (average 90%) from influent P concentrations that averaged 50 mg/L. When filter efficiency started to decrease (falling to 60% on day 125) they increased HRTv to 24 h, which resulted in an increase of the efficiency to 80–85%, for the following 180 days.

Presenting P removal efficiency in the form of mass of P removed (mg P/g of material) as a function of the mass of P added to the system (mg P/g of material) provides a useful way of comparing the performance of different materials, as it allows to determine the mass of P that each material can retain (Fig. 3). It also enables determination of P removal efficiency as a function of the amount of P added. For example, the EAF steel slag (SI1) and the mixture of EAF steel slag and limestone (SIL1) were very efficient and their curves always remained close to the 100% efficiency curve (Fig. 3). Serpentinite (Sp1) and the mixture of serpentinite and

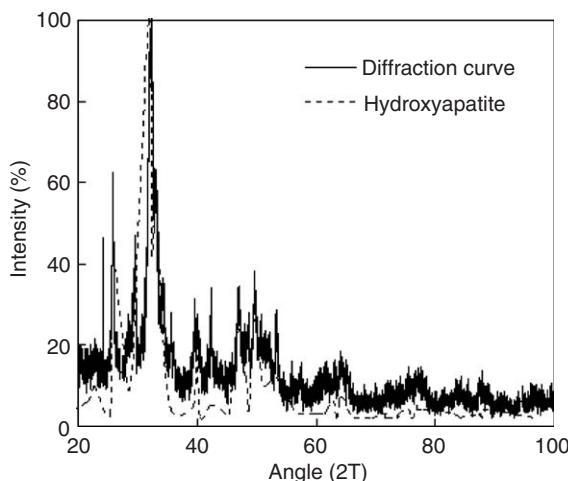


Fig. 4 – Mineralogical analysis of precipitates deposited on the EAF steel slag surfaces.

limestone (SpL1) were less efficient, resulting in cumulative P removal being around 60% and 25%, respectively.

The fact that no macroscopic precipitation could be visually observed in the columns filled with serpentinite containing materials suggested that adsorption through ligand exchange was the main mechanism responsible for P removal by these materials under the conditions studied. Other elements present in the serpentinite could also affect P retention. Deer et al. (1985) showed some evidence that the replacement of Si with Al, and of Mg by Al, ferrous iron and ferric iron may take place in serpentinite materials.

Important mechanisms involved in P removal by EAF steel slag are specific adsorption on metal hydroxides and precipitation (Forget, 2001; Drizo et al., 2002). A previous study using a short HRTv of 8.3 h (3-times shorter than in this study) showed that that Ca-P precipitation was affected and that 1.4 mg P/g removed P was essentially attributed to adsorption processes (Drizo et al., 2002). In this study, we showed that EAF steel slag was able to remove 2.4 mg P/g, the material still being far from saturation, with 80% efficiency. These results indicate that precipitation was the major P removal mechanism accounting for additional 42% increase in P removal capacity by this material, when compared to the previous study. XRD analyses confirmed that the precipitation of P by Ca as a white precipitate of hydroxyapatite was a prevailing mechanism responsible for the P removal, for a given HRTv (Fig. 4).

3.4. Effect of limestone addition

Adding limestone to the EAF steel slag did not significantly improve P removal efficiency, probably because steel slag is already rich in Ca due to lime addition during the steel-making process. In the case of serpentinite, adding limestone even led to a decrease in its P removal efficiency. The difference between columns filled with serpentinite (Sp1) and serpentinite and limestone (SpL1) could be related to the proportion of serpentinite added to each column. For a 1.7 mg P/g added, the P removed by columns Sp1 and SpL1 were 1.0

and 0.6 mg P/g, respectively (Fig. 3). These P removal ratios are closely related to the specific surface ratio of serpentinite comprised in each column, which was 100% of the specific surface in column Sp1 and 50% of the specific surface in column SpL1 (100:50). Therefore, the limestone contribution to P removal appeared to be minimal, and could even lead to a decrease in P removal efficiency. The interaction between CaCO_3 and phosphate has been previously described as monolayer adsorption that occurs only on a small percentage of the CaCO_3 surface, followed by nucleation and precipitation of calcium phosphate under supersaturated conditions (Freeman and Rowell, 1981; Baker et al., 1998). In a study carried out by Baker et al. (1998), addition of limestone to reactive mixtures of other materials did not contribute to the P attenuation. Similarly, Johansson (1999) demonstrated that while adding amorphous slag to sand did not improve the P removal efficiency by this material in a long-term column study (55 weeks), adding crystalline slag to sand even had negative effects, gradually decreasing the P removal efficiency after only 6 weeks of experimentation. Therefore, our results are consistent with other observations reported in the literature that suggest that addition of the limestone does not appear to contribute to the increased P removal performance by materials.

4. Conclusions

EAF steel slag showed a very high efficiency (nearly 100%) in P removal from an effluent (20 then 400 mg P/L) over a period of 180 days, accumulating 2.2 mg P/g of slag, presumably through the processes of specific adsorption onto metal hydroxides and precipitation as hydroxyapatite. The maximum amount of P that could be removed by EAF steel slag was not determined but exceeded 2.2 mg P/g of slag. Serpentinite material, which was tested for P removal performance for the first time in a long-term column study, was also very efficient for the first 35 days and then started to show a decrease in performance, indicating that adsorption onto serpentinite minerals appeared to be the predominant mechanism responsible for P removal by this material. Overall, serpentinite removed approximately 1.0 mg P/g of material, less than half the amount removed by EAF steel slag. However, it is still in the range of higher P removal efficiency when compared to other materials reported in the literature. Given the availability of this material in Quebec and other parts of the world, it merits further investigations. Mixing limestone with EAF steel slag and serpentinite did not seem to improve the P removal efficiency of slag and even decreased the P removal performance of serpentinite.

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REFERENCES

- Abbona, F., Baronnet, A., 1996. A XRD and TEM study on the transformation of amorphous calcium phosphate in the presence of magnesium. *J. Crystal Growth* 165, 98–105.
- Ádám, K., Krogstad, T., Suliman, F.R.D., Jenssen, P.D., 2005. Phosphorus sorption by filtralite P-small scale box experiment. *J. Environ. Health* 40 (6–7), 1239–1250.
- APHA, AWWA, WEF, 1998. In: Eaton, A.D., Clesceri, L.S., Greenberg, A.E. (Eds.), *Standard Methods for the Examination of Water and Waste Water*, 19th ed. American Public Health Association, Washington DC.
- ASTM D4646-87, 1993. Standard test method for 24-h batch type measurement of contaminant sorption by soils and sediments. *Am. Soci. Test. Mater.* 44–47.
- Arias, C.A., Del Bubba, M., Brix, H., 2001. Phosphorus removal by sands for use as media in subsurface flow constructed reed beds. *Water Res.* 35, 1159–1168.
- Arias, C.A., Brix, H., Johansen, N.H., 2003. Phosphorus removal from municipal wastewater in an experimental two-stage vertical flow constructed wetland system equipped with a calcite filter. *Water Sci. Tech* 48 (5), 51–58.
- Baker, M.J., Blowes, D.W., Ptacek, C.J., 1998. Laboratory development of permeable reactive mixtures for the removal of phosphorus from onsite wastewater disposal systems. *Environ. Sci. Technol.* 32, 2308–2316.
- Barrow, N.J., 1984. Modelling the effect of pH on phosphate sorption by soils. *J. Soil Sci.* 34, 751–758.
- Barrow, N.J., 2002. Influence of pH on a secondary effect of phosphate reaction: the decrease in sorption of newly added phosphate. *Aus. J. Soil Res.* 40, 775–779.
- Bernier, L.R., 2001. *Analyses minéralogiques sur cinq échantillons, Projet phosphate*. Géoberex Recherche. Internal Report, Ecole Polytechnique, Montreal.
- Bonifacio, E., Celi, L., Barberis, E., 2001. Effect of phosphate on the dissolution of serpentinite. *Soil Sci* 166 (10), 708–716.
- Brix, H., Arias, C.A., del Bubba, M., 2001. Media selection for sustainable phosphorus removal in subsurface flow constructed wetlands. *Water Sci. Tech* 44 (11–12), 47–54.
- Brooks, A.S., Rozenwald, M.N., Geohring, L.D., Lion, L.W., Steenhuis, T.S., 2000. Phosphorus removal by wollastonite: A constructed wetland substrate. *Ecol. Eng.* 15, 121–132.
- Chapuis, R.P., Baass, K., Davenne, L., 1989. Granular soils in rigid-wall permeameters: Method for determining the degree of saturation. *Can. Geotech. J.* 26, 71–79.
- Chapuis, R.P., Légaré, P.P., 1992. A simple method for determining the surface area of fine aggregates and filters in bituminous mixtures. In: Meininger, R.C. (Ed.), *Effects of Aggregates and Mineral Filters on Asphalt Mixture Performance*, ASTM STP 1147. American Society for Testing and Materials, Philadelphia, pp. 177–186.
- Comeau, Y., Brisson, J., Réville, J.P., Forget, C., Drizo, A., 2001. Phosphorus removal from trout farm effluents by constructed wetlands. *Wat. Sci. Tech.* 44 (11–12), 55–60.
- Deer, W.A., Howie, R.A., Zussman, J., 1985. An introduction to the rock forming minerals, 15th ed. Longman Group Ltd, England.
- Drizo, A., Frost, C.A., Grace, J., Smith, K.A., 1999. Physico-chemical screening of phosphate-removing substrates for use in constructed wetland systems. *Wat. Res.* 33, 3595–3602.
- Drizo, A., Forget, C., Chapuis, R.P., Comeau, Y., 2002. Phosphorus removal by EAF steel slag—A parameter for the estimation of the longevity of constructed wetland systems. *Environ. Sci. Technol.* 36, 4642–4648.
- Faulkner, S.P., Richardson, C.J., 1989. Physical and chemical characteristics of freshwater wetland soils. In: Hammer, D.A. (Ed.), *Constructed Wetlands for Waste Water Treatment*. Municipal, Industrial and Agricultural. Lewis Publishers Inc., Chelsea, MI.
- Feeenstra, T.P., Bruyn, P.L., 1979. Formation of Calcium Phosphates in Moderately Supersaturated Solutions. *J. Crystal Growth*, 83 (4), 475–479.
- Forget, C., 2001. *Élimination du phosphore dissous des effluents piscicoles à l'aide de matériaux granulaires réactifs*. M.Sc. Thesis, Ecole Polytechnique of Montreal, Canada.
- Freeman, J.S., Rowell, D.L., 1981. The adsorption and precipitation of phosphate onto calcite. *J. Soil Sci.* 32, 75–84.
- Geary, P.M., Moore, J.A., 1999. Suitability of a treatment wetland for dairy wastewaters. *Wat. Sci. Tech.* 40 (3), 179–186.
- Goldstein, J.I., 1981. *Scanning electron microscopy and X-ray microanalysis: A text for biologists, materials scientists and geologists*. Plenum Press, NY.
- House, W.A., 1999. The physico-chemical conditions for the precipitation of phosphate with calcium. *Environ. Technol.* 20, 727–733.
- Johansson, L., 1999. Blast furnace slag as phosphorus sorbents—Column studies. *Sci. Total Environ.* 229, 89–97.
- Johansson, L., Gustafsson, J.P., 2000. Phosphate removal using blast furnace slags and opoka-mechanisms. *Wat. Res.* 34 (1), 259–265.
- Kadlec, R.H., Knight, R.L., 1996. *Treatment Wetlands*. Lewis Publishers, Boca Raton, FL.
- Kadlec, R.H., Knight, R., Vymazal, J., Brix, H., Cooper, P., Haberl, R., 2000. *Constructed Wetlands for Pollution Control*. Published by International Water Association, London, UK.
- Kaneko, S., Nakajima, K., 1988. Phosphorus removal by cristallization using a granular activated magnesia clinker. *J. Wat. Pollut. Control Fed.* 60, 1239–1244.
- Kuo, S., Mikkelsen, D.S., 1979. Effect of magnesium on phosphate adsorption by calcium carbonate. *Soil Sci* 127, 65–69.
- Lazic, S., 1995. Microcrystalline hydroxyapatite formation from alkaline solutions. *J. Crystal Growth* 147, 147–154.
- Lindsay, W.L., 1979. *Chemical Equilibria in Soils*. Wiley, New York.
- Longhurst, R.D., Roberts, A.H.C., O'Connor, M.B., 2000. Farm dairy effluent: A review of published data on chemical and physical characteristics in New Zealand. *N. Zeal. J. Agric. Res.* 43, 7–14.
- Mann, R.A., 1997. Phosphorus adsorption and desorption characteristics of constructed wetland gravels and steelworks by-products. *Austr. J. Soil Res.* 35, 375–384.
- Moshiri, G.A., 1993. (Ed.), *Constructed Wetlands for Water Quality Improvement*. Lewis Publishers, Boca Raton, FL.
- NWRI, 2003. Trace Element Method Descriptions. National Laboratory for Environmental Testing (NLET), National Water Research Institute, Environment Canada, Burlington, Ontario (<http://www.nwri.ca/publications/publist-e.html>).
- Piché, M., 2005. Heckett MultiServ Company, Personal communication.
- Parfitt, R.L., 1978. Anion adsorption by soils and soil materials. *Advances in Agronomy* 30, 1–49.
- Richardson, C.J., Craft, C.B., 1993. Effective phosphorus retention in wetlands: fact or fiction? In: Moshiri, G. (Ed.), *Construction Wetlands for Water Quality Improvement*. Lewis Publishers, Boca Raton, FL, pp. 271–282.
- Roques, H., Nugroho-Jeudy, L., Lebugle, A., 1991. Phosphorus removal from wastewater by half-burned dolomite. *Water Res.* 25, 959–965.
- Sedlak, R., 1991. (ed.), *Phosphorus and Nitrogen Removal from Municipal Wastewater: Principles and Practice*, 2nd ed, Lewis Publishers, NY.

- Shilton, A., Pratt, S., Drizo, A., Mahmood, B., Banker, S., Billings, L., Glenny, S., Luo, D., 2005a. 'Active' filters for upgrading phosphorus removal from pond systems. *Water Sci. Tech.* 51 (12), 111–116.
- Shilton, A.N., Elmetri, I., Drizo, A., Pratt, S., Haverkamp, R.G., Bilby, S.C., 2005b. Phosphorus Removal by an 'Active' Slag Filter—a Decade of Full Scale Experience. *Wat. Res.* 40 (1), 113–118.
- Soulard, C., 2001. Critères de sélection des scories d'aciéries pour la déphosphatation des eaux par lits filtrants. Internal Report, Ecole Polytechnique of Montreal, Montreal, Canada.
- Stumm, W., Morgan, J.J., 1981. Aquatic Chemistry—An Introduction Emphasizing Chemical Equilibria in Natural Waters, 2nd ed. Wiley, NY.
- Stumm, W., Morgan, J.J., 1996. Aquatic Chemistry, Chemical Equilibria and Rates in Natural Waters, third ed. Wiley, New York, 1022p.
- Suzuki, M., Fujii, T., 1988. Simultaneous removal of phosphate and ammonium ions from wastewater by composite adsorbent. In: *Proceedings of Water Pollution Control in Asia*, Bangkok, pp. 239–245.
- Valsami-Jones, E., 2001. Calcium phosphate precipitation. In: *Presented at the second International Conference on Phosphorus Recovery for Recycling from Sewage and Animal Wastes*, Amsterdam, The Netherlands, 12–14 March.
- Vymazal, J., Brix, H., Cooper, P.F., Green, M.B., Haberl, R., 1998. Constructed Wetlands for Wastewater Treatment in Europe. Backhuys Publishers, Leiden, The Netherlands.
- Weber, D., Drizo, A., 2005. Alternative technology for phosphorus removal from agricultural effluents. In: *Presented at the ASA-CSSA-SSSA International Annual Meeting*, Salt Lake City, UT, 6–10 November 2005.
- Yamada, H., Kayama, M., Saito, K., Hara, M., 1986. A fundamental research on phosphate removal by using slag. *Water Res.* 20, 547–557.