HBRC Journal (2013) 9, 276–282

Housing and Building National Research Center

HBRC Journal

http://ees.elsevier.com/hbrcj

Removal of heavy metals from wastewater using agricultural and industrial wastes as adsorbents

Hala Ahmed Hegazi

Housing, Building and Research Center, Egypt

Received 19 November 2012; accepted 10 March 2013

KEYWORDS

Adsorption;
Adsorbents;
Agricultural wastes;
Industrial waste;
Heavy metals;
Wastewater

Abstract Adsorption processes are being widely used by various researchers for the removal of heavy metals from waste streams and activated carbon has been frequently used as an adsorbent. Despite its extensive use in water and wastewater treatment industries, activated carbon remains an expensive material. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest toward the production of low cost alternatives to commercially available activated carbon. Therefore, there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail. The objective of this research is to study the utilization possibilities of less expensive adsorbents for the elimination of heavy metals from wastewater. Agricultural and industrial waste by-products such as rice husk and fly ash have be used for the elimination of heavy metals from wastewater for the treatment of the EL-AHLIA Company wastewater for electroplating industries as an actual case study.

Results showed that low cost adsorbents can be fruitfully used for the removal of heavy metals with a concentration range of 20–60 mg/l also, using real wastewater showed that rice husk was effective in the simultaneous removal of Fe, Pb and Ni, where fly ash was effective in the removal of Cd and Cu.

Introduction

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless end products [1]. The presence of heavy metal ions is of major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, tanneries, chloralkali, radiator manufacturing, smelting, alloy industries and storage batteries industries [2].

Treatment processes for heavy metal removal from wastewater include precipitation, membrane filtration, ion exchange, adsorption, and co-precipitation/adsorption. Studies on the treatment of effluent bearing heavy metals have revealed

E-mail address: hegazi100@yahoo.com

Peer review under responsibility of Housing and Building National Research Center.

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http://dx.doi.org/10.1016/j.hbrcj.2013.08.004

Table 1 Low cost adsorbents data.

Low cost adsorbents	Main consistent	Primary source	Physical structure	Chemical characterization (%)		Primary use
Rice husk	Is collected from one of the rice processing factories	Rice	Granular structure insolubility in water, chemical stability, high mechanical strength and its local availability at almost no cost	Cellulose	32.2	Wastewater treatment
				Hemicellulose	21.3	
				Lignin	21.4	
				Extractives	1.82	
				Water	8.11	
Fly ash	A particulate material produced from the combustion of coal in power plants	Bituminous coal-burning power plant	Spherical shape and pozzolanic properties	SiO_2	57.82	Building materials, soil amendment and fillers
				Al_2O_3	22.10	
				Fe_2O_3	8.33	

adsorption to be a highly effective technique for the removal of heavy metals from waste stream and activated carbon has been widely used as an adsorbent [3]. Despite its extensive use in water and wastewater treatment industries, activated carbon remains an expensive material.

In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research Low cost agricultural waste by-products such as sugarcane bagasse [4–8], Rice husk [9–13], sawdust [14–16], coconut husk [17], oil palm shell [18], neem bark [19] etc., for the elimination of heavy metals from wastewater have been investigated by various researchers. Cost is an important parameter for comparing the sorbent materials. However, cost information is seldom reported, and the expense of individual sorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be termed as a low cost adsorbent if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. Of course improved sorption capacity may compensate the cost of additional processing [20]. Therefore there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail. The objective of this study is to contribute in the search for less expensive adsorbents and their utilization possibilities for various agricultural waste by-products, which are in many cases also pollution sources.

Relevant literature

Reviews of some agricultural and industrial adsorbents for the removal of heavy metals from wastewater are presented as follows.

Rice husk

Rice husk is an agricultural waste material generated in rice producing countries, especially in Egypt. The annual world rice production is approximately 500 million metric tons, of which 10–20% is rice husk. Dry rice husk contains 70–85% of organic matter (lignin, cellulose, sugars, etc.) and the remainder consists of silica, which is present in the cellular membrane [21]. In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants. Batch studies using tartaric acid modified rice husk as adsorbent have been carried out for the removal of lead and copper and have reported the effects of various parameters such as pH, initial concentration of adsorbate, particle size, temperature etc. It was reported that modified rice husk is a potentially useful material for the removal of Cu and Pb from aqueous solutions [22].

Fly ash

Fly Ash is a naturally-cementations coal combustion by-product. It is extracted by the precipitators in the smokestacks of coal-burning power plants to reduce pollution Since the fly ash disposal problem emerged with the advent of pollution control systems in the 1960's and 1970's, extensive research has been done to understand how it performs in its orthodox

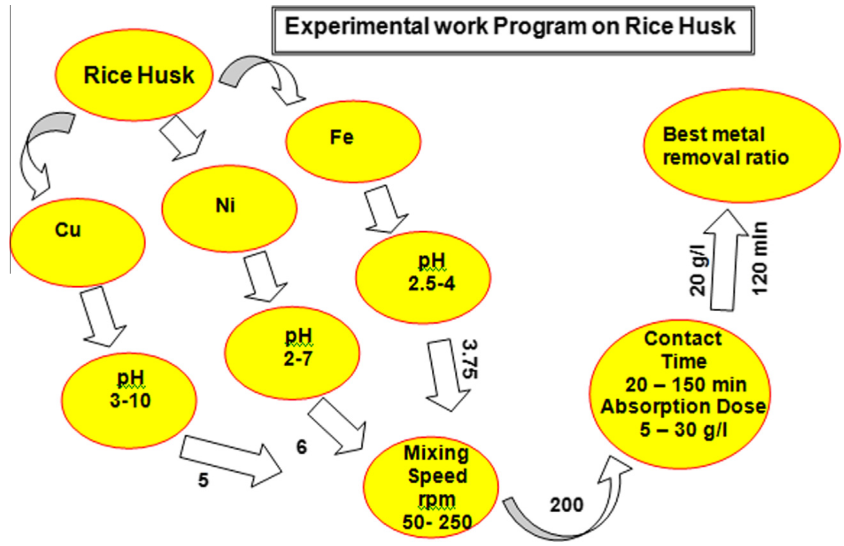

Fig. 1 Experimental work program for rice husk.

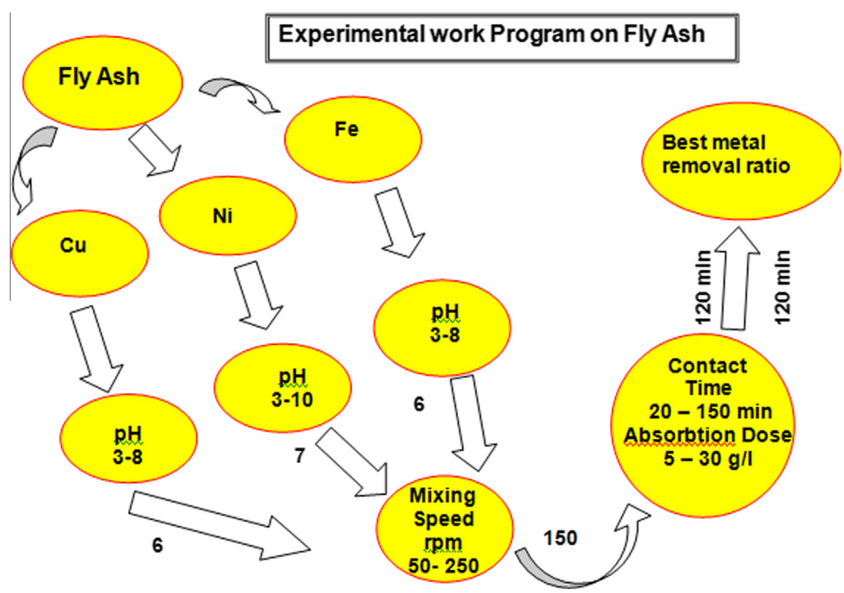

Fig. 2 Experimental work program for fly ash.

capacity – as a soil stabilizer and structural concrete admixture [23].

Experimental works

Materials

The adsorption of heavy metal ions by low cost adsorbents was evaluated under various conditions such as pH, heavy metal concentration, mixing speed and adsorbent dose through both kinetic and isotherm studies. The optimum removal condition was also identified for each metal ion. Table 1 indicates the main consistent, primary source, physical structure, chemical characterization and the primary use of low cost adsorbents such as rice husk and fly ash (see Figs. 1 and 2).

Batch study (synthetic wastewater)

Metal solutions of (Cu, Ni, Fe) were prepared by dissolving copper sulfate ($CuSO_4 \cdot 5H_2O$), nickel nitrate ($(NiNO_3)_2 \cdot 6H_2O$ and iron sulfate ($FeSO_4 \cdot 7H_2O$) separately in double distilled water in order to result in known concentrations of the metal ions required and to make synthetic wastewater.

All the experiments were carried out in duplicate and the relative standard deviation was less than 5%. In general the sorption consisted of 20 mg/l for the adsorbent dose in

Table 2 Experimental work program (synthetic water).

Low cost adsorption	Run	Metals	pH	Mixing speed (rpm)	Contact time (min)	Adsorbent dose (g/l)
Rice husk	1	Cu	3:10	200	20	10
	2		5	50:250	20	10
	3		5	200	20:150	5:30
	4		5	200	120	20
	5	Ni	2:7	200	20	10
	6		6	50:250	20	10
	7		6	200	20:150	5:30
	8		6	200	120	20
	9	Fe	2.5:4	200	20	10
	10		3.75	50:250	20	10
	11		3.75	200	20:150	5:30
	12		3.75	200	120	20
Fly ash	13	Cu	3:8	200	20	10
	14		6	50:250	20	10
	15		6	150	20:150	5:40
	16		6	150	120	20
	17	Ni	3:10	200	20	10
	18		7	50–250	20	10
	19		7	150	20:150	5:40
	20		7	150	120	20
	21	Fe	3:8	200	20	10
	22		6	50:250	20	10
	23		6	150	20:150	5:40
	24		6	150	120	20

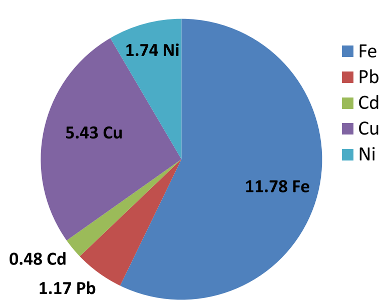

Fig. 3 Heavy metal concentration in El-AHLIA wastewater.

10 mg/l of concentration metal (Cu, Ni, Fe) at an agitation rate of 200 rpm with an adsorbent time of 20 min at room temperature (25 ± 3).To study the effect of pH on sorption, the pH of the metal ion solution was adjusted to values in the range of (2–10) by the addition of $CuSO_4 \cdot 5H_2O$, $(NiNO_3)2 \cdot 6\text{-}H_2O$, $FeSO_2 \cdot 7H_2O$ prior to the experiment. The Langmuir isotherms were obtained by equilibrating metal ion solutions of different adsorbent doses (5–30) mg/l with different times (20–150 min) at equilibrium pH and rpm with an initial metal concentration of 10 mg/l at room temperature.

The effect of agitation rate on metal ion uptake was carried out by varying the agitation rate from 50 to 200 rpm, and the

Table 3 Fe removal efficiency for different absorbent doses.

Heavy metal	Adsorbent dose	In- Fe mg/l	Rice husk		Fly ash	
			Outlet-Fe mg/l	Removal ratio %	Outlet-Fe mg/l	Removal ratio %
Fe	20	11.78	3.7	68.59	6.34	46.18
	30	11.78	2.1	82.17	4.9	58.4
	40	11.78	1.2	89.81	4.1	65.2
	50	11.78	0.09	99.236	2.97	74.788
	60	11.78	0.088	99.253	1.56	86.757

Table 4 Pb removal efficiency for different absorbent doses.

Heavy metal	Adsorbent dose	In- Pb mg/l	Rice husk		Fly ash	
			Outlet- Pb mg/l	Removal ratio %	Outlet- Pb mg/l	Removal ratio %
Pb	20	1.17	0.91	22.22	0.92	21.79
	30	1.17	0.66	43.59	0.7	40.17
	40	1.17	0.38	67.52	0.46	60.68
	50	1.17	0.28	76.068	0.33	71.795
	60	1.17	0.15	87.179	0.28	76.068

Table 5 Cd removal efficiency for different absorbent doses.

Heavy metal	Adsorbent dose	In- Cd mg/l	Rice husk		Fly ash	
			Outlet- Cd mg/l	Removal ratio %	Outlet- Cd mg/l	Removal ratio %
Cd	20	0.48	0.36	26.04	0.36	25.21
	30	0.48	0.31	35.42	0.30	37.50
	40	0.48	0.24	50.00	0.23	52.08
	50	0.48	0.190	60.417	0.180	62.500
	60	0.48	0.154	67.917	0.127	73.542

Table 6 Cu removal efficiency for different absorbent doses.

Heavy metal	Adsorbent dose	In- Cu mg/l	Rice husk		Fly ash	
			Outlet- Cu mg/l	Removal ratio %	Outlet- Cu mg/l	Removal ratio %
Cu	20	5.43	4.10	24.49	3.40	37.38
	30	5.43	2.84	47.70	1.81	66.67
	40	5.43	1.83	66.30	1.01	81.40
	50	5.43	1.210	77.716	0.089	98.361
	60	5.43	0.099	98.177	0.079	98.545

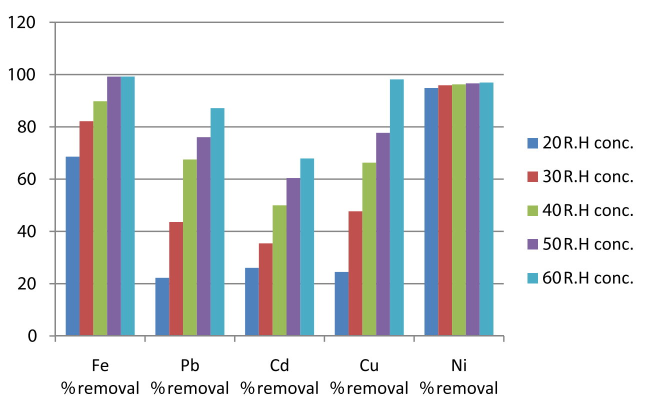

Fig. 4 Removal efficiency of various heavy metals using rice husk.

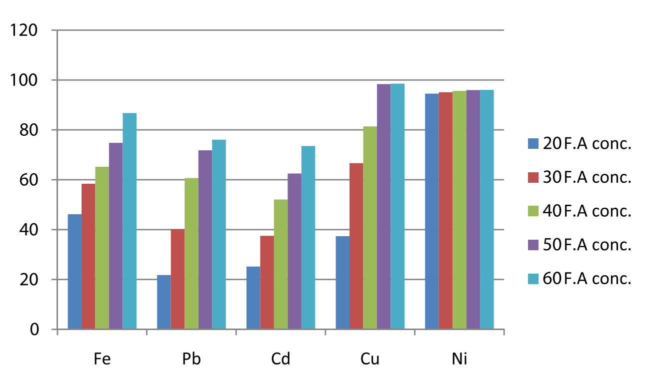

Fig. 5 Removal efficiency of various heavy metals using fly ash.

experiment on the effect of an adsorbent dose of 20 mg/l at equilibrium pH and rpm at an adsorbent time of 20 min with a concentration of 5–30 mg/l at room temperature.

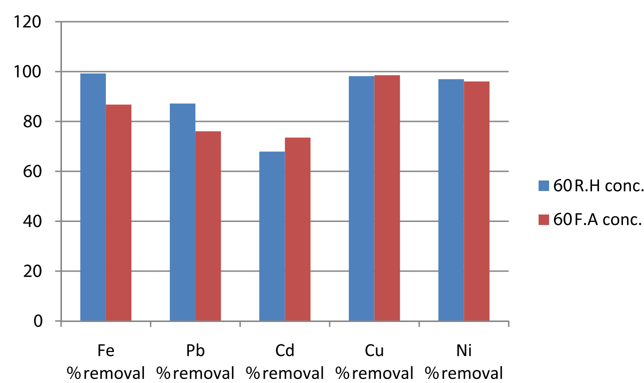

Fig. 6 Comparison between rice husk and fly ash removal efficiency at 60 mg/l absorbent concentration.

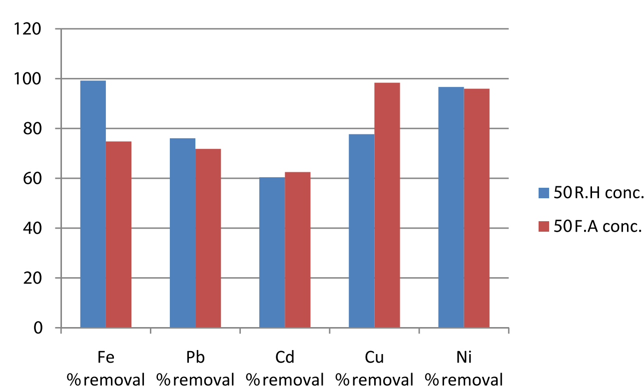

Fig. 7 Comparison between rice husk and fly ash removal efficiency at 50 mg/l absorbent concentration.

Adsorption batch experiments

Adsorption batch experiments were carried out by shaking a series of bottles containing various amounts of each of the

Table 7 Ni removal efficiency for different absorbent doses.

Heavy metal	Adsorbent dose	In- Ni mg/l	Rice husk		Fly ash	
			Outlet- Ni mg/l	Removal ratio %	Outlet- Ni mg/l	Removal ratio %
Ni	20	1.74	0.089	94.885	0.095	94.540
	30	1.74	0.071	95.920	0.085	95.115
	40	1.74	0.065	96.264	0.076	95.632
	50	1.74	0.058	96.667	0.070	95.977
	60	1.74	0.053	96.954	0.069	96.034

low cost adsorbents and heavy metal ions at different pH. The pH of the slurry was adjusted to a desired value in the range of 2–10 and was agitated in a shaking bath at (25 ± 3 °C) for 20 min until the pH was stabilized. Then, the nickel, iron and copper ions in the form of $CuSO_4{\cdot}5H_2O$, $(NiNO_3)_2{\cdot}6H_2O$, $FeSO_4{\cdot}7H_2O$ were added to the bottles to make initial concentrations of 5–30 mg/L and the bottles were further agitated for 2 or 2.5 h until equilibrium was obtained. The residual concentration of heavy metals was determined by an atomic absorption spectrometer. In addition to adsorption tests, a set of blank tests of low cost were conducted in order to evaluate the removal by metal hydroxide precipitation at various pH's.

Table 2 indicates the experimental work program i.e. mixing speed, contact time and adsorbent dose.

Case of study: treatment of wastewater in EL-AHLIA Company for electroplating industries

The wastewater produced from the EL-AHLIA Company is 750 m^3/day and discharged into the sewer system of the Ismailia canal in Abozabal. Wastewater from the electroplating department of 250 m^3/day represents the main source of pollution in this company. The unreacted rinse water contains high concentrations of Fe, Pb, Cd, Cu and Ni. Their typical concentrations were as high as 11.78, 1.17, 0.48, 5.43 and 1.74 mg/l respectively (see Fig. 3).

Results and discussion

Fe removal by different weights of absorbents

The effect of the amount of adsorbent on the removal of Fe ions by rice husk is depicted in Table 3 for varied adsorbent doses of 20, 30, 40, 50 and 60 mg/l. Fe removal using rice husk increased from 68.59% to 99.25% i.e. with the increase of the amount of absorbent concentration , while Fe removal using fly Ash varied from 46.18% to 86.757%.

Pb removal by different weights of absorbents

The effect of the amount of adsorbent on the removal of Pb ions by rice husk is depicted in Table 4 for varied adsorbent doses of 20, 30, 40, 50 and 60 mg/l. Pb removal with rice husk increased from 22.22% to 87.17% i.e. with the increase of the amount of absorbent concentration, while the Pb removal using fly Ash varied from 21.79% to 76.06%.

Cd removal by different weights of absorbents

The effect of the amount of adsorbent on the removal of Cd ions by rice husk is depicted in Table 5 for varied adsorbent doses of 20, 30, 40, 50 and 60 mg/l. Cd removal using rice husk increased from 26.04% to 67.917% i.e. with the increase of the amount of absorbent concentration, while the Cd removal using fly Ash varied from 25.21% to 73.54%.

Cu removal by different weights of absorbents

The effect of the amount of adsorbent on the removal of Cu ions by rice husk is depicted in Table 5 for varied adsorbent doses of 20, 30, 40, 50 and 60 mg/l. Cu removal using rice husk increased from 24.49% to 98.177% i.e. with the increase of the amount of absorbent concentration , while Cu removal using fly Ash varied from 37.38% to 98.545% (see Table 6).

Ni removal by different weights of absorbents

The effect of the amount of adsorbent on the removal of Ni ions by rice husk is depicted in Table 5 for varied adsorbent doses of 20, 30, 40, 50 and 60 mg/l. Ni removal using rice husk increased from 94.885% to 96.954% i.e. with the increase of the amount of absorbent concentration , while Ni removal using fly Ash varied from 94.540% to 96.034% (see Figs. 4–7, Table 7).

Conclusion

1. Results showed that low cost adsorbents can be fruitfully used for the removal of heavy metals with a concentration range of 20–60 mg/l.
2. The results of using real wastewater showed that rice husk was effective in the simultaneous removal of Fe, Pb and Ni, whereas fly ash was effective in the removal of Cd and Cu.
3. It was found that the percentage removal of heavy metals was dependent on the dose of low cost adsorbent and adsorbent concentration.
4. The contact time necessary for maximum adsorption was found to be two hours.
5. The optimum pH range for heavy metal adsorption was 6–7.0.

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