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Removal of Hexavalent Chromium-Contaminated Water and Wastewater: A Review

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Abstract Cr(VI) is a well-known highly toxic metal, considered a priority pollutant. Industrial sources of Cr(VI) include leather tanning, cooling tower blow-down, plating, electroplating, anodizing baths, rinse waters, etc. This article includes a survey of removal techniques for Cr(VI)-contaminated aqueous solutions. A particular focus is given to adsorption, membrane filtration, ion exchange, and electrochemical treatment methods. The primary objective of this article is to provide recent information about the most widely used techniques for Cr(VI) removal.

Keywords Cr(VI) · Chromium removal ·
Water pollution control

1 Introduction

Process waste streams from the mining operations, metal-plating facilities, power generation facilities, electronic device manufacturing units, and tanneries may contain heavy metals at concentrations exceeding the local discharge limits. These waste streams contain toxic heavy metals such as chromium,

cadmium, lead, mercury, nickel, and copper. They are not easily removed without specialized or advanced treatment.

Chromium is a common pollutant introduced into natural waters due to the discharge of a variety of industrial wastewaters. On the other hand, chromium-based catalysts are also usually employed in various chemical processes, including selective oxidation of hydrocarbons. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for total chromium is 0.05 mg l^{-1} .

Chromium is a chemical element in the periodic table that has the symbol Cr and atomic number 24. It is a steel-gray, lustrous, hard metal that takes a high polish and has a high melting point. Chromium is present in the environment in several different forms. The most common forms are chromium(0), chromium(III), and chromium(VI).

Chromium(III) occurs naturally in the environment and is an essential nutrient. Chromium(VI) and chromium(0) are generally produced by industrial processes.

The metal chromium, which is the chromium(0) form, is used for making steel. Chromium(VI) and chromium(III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving.

Cr(VI) is mobile in the environment and is highly toxic. Cr(VI) can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also

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a source of various cancer diseases (Barnowski et al. 1997; Gil et al. 2006). At short-term exposure levels above the maximum contaminant level, Cr(VI) causes skin and stomach irritation or ulceration. Long-term exposure at levels above maximum contaminant can cause dermatitis, damage to liver, kidney circulation, nerve tissue damage, and death in large doses (Katz and Slem 1994; Kotas and Stasicka 2000).

Cr(III), on the other hand, is less toxic than Cr(VI) and is nearly insoluble at neutral pH (Venitt and Levy 1974). Cr(III) is listed as an essential element, as micronutrient, to maintain good health and helps in maintaining the normal metabolism of glucose, cholesterol, and fat in human bodies (Kimbrough et al. 1999). It is poisonous only at high concentration.

Therefore, the removal or reduction of Cr(VI) to Cr(III) serve as a key process for removal of Cr(VI)-contaminated water and wastewater.

In view of the above, several methods such as adsorption, biosorption, reduction, and filtration reverse osmosis, ion-exchange, foam flotation, electrolysis, and surface adsorption have been reported for chromium removal. The primary objective of this work is to review and summarize the most widely used techniques for Cr(VI) removal and to provide recent information in this area.

2 Adsorption Techniques

Adsorption is the process where molecules are concentrated on the surface of the sorbent. The molecules go from the bulk phase to being adsorbed in the pores in a semiliquid state. The driving force for adsorption is the ratio of the concentration to the solubility of the compound. Adsorption is used widely to remove chromium metals from waters and industrial wastewaters. Suzuki (1990) described and investigated adsorption phenomenon with more details including adsorption equilibrium and kinetics and influences of parameters such as pH, temperature, surface area, etc.

Adsorption offers significant advantages like low cost, availability, profitability, easy of operation and efficiency, in comparison with conventional methods (such as membrane filtration or ion exchange) especially from economical and environmental points of view (Hashem et al. 2007; Ravikumar et al. 2005; Allen et al. 2005; Mittal et al. 2005).

A variety of natural and synthetic materials has been used as Cr(VI) sorbents, including activated carbons, biological materials, zeolites, chitosan, and industrial wastes.

2.1 Activated Carbon

The most studied adsorbent in adsorption of chromium is found to be the activated carbon derived from various sources (Mohan and Pittman 2006). Activated carbon adsorption seems to be an attractive choice for chromium removal both for its exceptionally high surface areas which range from 500 to 1,500 m² g⁻¹, well-developed internal microporosity structure as well as the presence of a wide spectrum of surface functional groups like carboxylic group (Chingombe et al. 2005). For these reasons, activated carbon adsorption has been widely used for the treatment of chromium containing wastewaters.

Based on its size and shape, activated carbon is classified into four types: powder-activated carbon (PAC), granular-activated carbon (GAC), activated carbon fibrous (ACF), and activated carbon clothe (ACC). Due to the different sources of raw materials, the extent of chemical activation, and the physico-chemical characteristics, each type of activated carbon has its specific application as well as inherent advantages and disadvantages in wastewater treatment (Babel and Kurniawan 2003).

Candela et al. (1995) used different types of PAC prepared from different raw materials to remove Cr(VI). It was found that the adsorption process depends on the pretreatment of activated carbon and that the highest removal performance was obtained with those prepared by physical activation. It was also reported that at pH of 1.0, the retention of Cr(VI) was affected by its reduction to Cr(III).

Sharma and Forster (1996) studied the removal of Cr(VI) from aqueous solution using GAC type Filtrasorb 400. It was reported that an adsorption capacity of 145 mg of Cr(VI)/g was achieved at a pH range of 2.5–3.0. This result is not in agreement with that obtained in the latter study (Han et al. 2000) conducting a similar comparative study using activated carbon LB 830 and Filtrasorb 400. It was reported that the maximum adsorption capacity of Filtrasorb 400 in the latter study is only 0.18 mg of Cr(VI)/g.

Hamadi et al. (2001) studied the removal of Cr(VI) from aqueous solution using GAC type Filtrasorb

400. It was found that reduction in particle size of adsorbents increases its surface area for metal adsorption, and it results in higher removal efficiency on Cr^{6+} . It was also indicated that the adsorption of Cr^{6+} was more favorable at higher temperature.

Park and Jung (2001) removed Cr(VI) by ACFs plated with copper metal. It was reported that the introduction of Cu^{2+} on ACFs lead to an increase in the adsorption capacity of Cr(VI) from an aqueous solution. It was pointed out that the adsorption of chromium ions was essentially dependent on surface properties, rather than by surface area and porosity of ACFs. Table 1 summarized some of the reported adsorption capacities for activated carbons with different size and shape.

Many investigations have been done to study the adsorption of Cr(VI) using activated carbon prepared from different raw material.

Natale et al. (2007) used activated carbon produced by Sutcliffe Carbon starting from a bituminous coal to uptake Cr(VI). It was found that the adsorption capacity for the activated carbon strongly depends on solution pH and salinity, with maximum values around 7 mg/g at neutral pH and low salinity levels.

Selomulya et al. (1999) used different types of activated carbons, produced from coconut shell, wood and dust coal to remove Cr(VI) from synthetic wastewater. The coconut shell and dust coal activated carbons have protonated hydroxyl groups on the surface (H-type carbons), while the surface of the wood-based activated carbon has ionized hydroxyl groups (L-type carbons). It was found that the optimum pH to remove total chromium was 2 for wood-based activated carbon, while for coconut shell and dust coal activated carbons, the optimum pH was around 3–4. The difference in the optimum pH for different activated carbons to remove Cr(VI) from water can be explained by the different surface

characteristics and capacity of the activated carbons to reduce Cr(VI) to Cr(III).

Koby (2004) used hazelnut shell-activated carbon for the adsorption of Cr(VI) from aqueous solution. It was reported that the adsorption of Cr(VI) was pH dependent. The adsorption capacity as calculated from the Langmuir isotherm was 170 mg/g at an initial pH of 1.0 for a Cr(VI) solution of 1,000 mg/l concentration. Thermodynamic parameters were evaluated, indicating that the adsorption was endothermic and involved monolayer adsorption of Cr(VI).

Mohanty et al. (2005) prepared several activated carbons from *Terminalia arjuna* nuts, an agricultural waste, by chemical activation with zinc chloride and then tested for aqueous Cr(VI) removal. The isotherm equilibrium data were well fitted by the Langmuir and Freundlich models. The maximum removal of chromium was obtained at pH 1.0.

Karthikeyan et al. (2005) used rubber wood sawdust-activated carbon for removal of Cr(VI) in a batch system. It was found that Cr(VI) removal is pH dependent and is maximum at pH 2.0. Table 2, summarizes activated carbons prepared from different raw material for Cr(VI) removal.

Many commercial activated carbons have been used for Cr(VI) adsorption. The mechanism for Cr(VI) removal in most of the studies is surface reduction of Cr(VI) to Cr(III) followed by adsorption of Cr(III).

Huang and Wu (1975) showed that Cr(VI) adsorption by activated carbon, filtrasorb 400 (Calgon), occurred by two major interfacial reactions: adsorption and reduction (Huang and Wu 1975). Cr(VI) adsorption reached a peak value at pH 5.0–6.0. Carbon particle size and the presence of cyanide do not change the magnitude of chromium removal.

Hu et al. (2003) used three commercial activated carbons FS-100, GA-3, and SHT to remove Cr(VI)

Table 1 Adsorption capacities (mg/g) for different activated carbons based on size and shape

Activated carbon	mg Cr^{6+} /g	Surface area	pH	Adsorption system	Wastewater	Reference
PAC	390.00	1264	2.0	Batch	Synthetic	Candela et al. 1995
	145.00	–	2.5–3.0	Batch	Synthetic	Sharma and Forster 1996
GAC-Filtrasorb 400	0.18	–	–	Batch	Synthetic	Han et al. 2000
	53.19	832	2.0	Batch	Synthetic	Hamadi et al. 2001
GAC-LB 830	0.13	–	–	Batch	Synthetic	Han et al. 2000
ACF	40.00	–	–	Batch	Synthetic	Park and Jung 2001

Table 2 Adsorption capacities (mg/g) for activated carbons prepared from different sources

Raw material	mg Cr ⁶⁺ /g	pH	Initial conc. (mg/l)	Adsorption system	Wastewater	Surface area	Reference
Bituminous coal	7.0	5.0–8.0	25	Batch	Synthetic	950	Natale et al. 2007
Coconut shell	6.0	3.0–4.0	120	Batch	Synthetic	1,280	Selomulya et al. 1999
Wood	5.1	2.0	120	Batch	Synthetic	1,700	Selomulya et al. 1999
Dust coal	4.4	3.0–4.0	120	Batch	Synthetic	1,120	Selomulya et al. 1999
Hazelnut shell	170.0	1.0	1,000	Batch	Synthetic	441	Koby 2004
Coconut shell	20.0	2.5	50	Batch	Synthetic	–	Alaerts et al. 1989
Hazelnut shell	17.7	2.0	30	Batch	Synthetic	–	Cimino et al. 2000
Terminalia arjuna nuts	28.4	1.0	10	Batch	Synthetic	1,260	Mohanty et al. 2005
Rubber wood sawdust	44.1	2.0	–	Batch	Synthetic	1,673	Karthikeyan et al. 2005

from aqueous solution (Hu et al. 2003). Physiochemical factors such as equilibrium time, temperature, and solution pH that affect the magnitude of Cr(VI) adsorption were studied. It was found that both micropores and mesopores have important contribution on the adsorption. However, desorption is more dependent on the mesoporosity of activated carbons. Therefore, regeneration is easier for the carbon with high mesoporosity.

Hamadi et al. (2001) used commercial activated carbon F-400 for batch removal of Cr(VI) from wastewater under different experimental conditions (Hamadi et al. 2001). It was reported that the adsorption capacity as calculated from the Langmuir isotherm was 48.5 mg/g at an initial pH of 2.0 for a Cr(VI) solution of 60 mg/l concentration.

Mohan et al. (2005) used commercially available activated carbon fabric cloth for the removal of Cr(VI) from tannery wastewater (Mohan et al. 2005). The results indicated that the Langmuir adsorption isotherm model fitted the data better than the Freundlich adsorption isotherm model. It was found that the activated carbon fabric cloth performed better than the other tested adsorbents with adsorption capacity of 22.29 mg/g at an initial pH of 2.0. Table 3 summarizes different commercial activated carbons used for Cr(VI) removal.

2.2 Biosorbents

Biosorption of chromium from aqueous solutions is relatively a new process that has proven very promising in the removal of contaminants from aqueous effluents. Adsorbent materials derived from low-cost

agricultural wastes can be used for the effective removal and recovery of chromium ions from wastewater streams (Volesky and Holan 1995; Lee and Volesky 1997; Kratochvil et al. 1998; Kratochvil and Volesky 1998; Basso et al. 2002; Pagnanelli et al. 2003; Volesky 2003; Park et al. 2006).

The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical and/or biological sludge regeneration of biosorbent, no additional nutrient requirement, and the possibility of metal recovery (Ahalya et al. 2003).

At low concentrations of heavy metals, the conventional techniques such as chemical precipitation, membrane filtration, electrolysis, ion exchange, carbon adsorption are not cost-effective and suitable (Demirbas 2008). Low-cost biosorbents are much suitable for high concentrations of metals (Chaiyasith et al. 2006).

Various biosorbents have been widely used for the treatment of chromium containing wastewaters. Table 4 gives the agricultural by-products or wastes used in Cr(VI) uptake.

Metal biosorption is a rather complex process affected by several factors. Mechanisms involved in the biosorption process include chemisorption, complexation, adsorption–complexation on surface and pores, ion exchange, microprecipitation, heavy metal hydroxide condensation onto the biosurface, and surface adsorption (Gardea-Torresdey et al. 2004; Volesky 2001; Brown et al. 2000).

Table 3 Adsorption capacities (mg/g) for commercial activated carbons

Activated Carbon	mg Cr ⁶⁺ /g	pH	Initial conc. (mg/l)	Adsorption system	Wastewater	Reference
Activated carbon, FS-100	69.30	3.0	—	Batch	Synthetic	Hu et al. 2003
Activated carbon, GA-3	101.40	3.0	—	Batch	Synthetic	Hu et al. 2003
Activated carbon, SHT	69.10	3.0	—	Batch	Synthetic	Hu et al. 2003
Activated carbon, F-400	48.50	2.0	60	Batch	Synthetic	Hamadi et al. 2001
Activated carbon fabric cloth	22.29	2.0	50	Batch	Synthetic	Mohan et al. 2005

2.3 Modified Sorbents

Most of the adsorbents are not nearly effective at removing heavy metals like Cr(VI). Therefore, the adsorption capacities and the feasible removal rates must be substantially boosted by modification of the sorbent with suitable technique. For this reason, modification and impregnation techniques were used to increase surface adsorption and, so, removal capacity and to add selectivity to sorbents.

2.3.1 Modified Activated Carbon

Various factors influence the adsorption capacity of activated carbon prior to their modification, so that it can be tailored to their specific physical and chemical attributes to enhance their affinities toward metal present in aqueous solutions. These factors include

specific surface area, pore-size distribution, pore volume, and presence of surface functional groups. Generally, the adsorption capacity increases with specific surface area due to the availability of adsorption sites, while pore size, and micropore distribution are closely related to the composition of the activated carbon, the type of raw material used, the degree of activation during production stage, and the frequency of regeneration (Ruthven 1984).

The techniques of modification of activated carbon can be categorized into three broad groups, namely, modification of chemical, physical, and biological characteristics. Among these methods, modification of chemical characteristics was used more frequently to increase removal capacity of activated carbon. In order to facilitate a more focused discussion, only studies on modification of chemical characteristics of activated carbons were reviewed. Table 5 lists and compares the

Table 4 Agricultural byproducts adsorbents used in Cr(VI) uptake

Biosorbent	Cr(VI) removal (%)	pH	Adsorption system	Wastewater	Reference
Hazlenut shell	99.4	1.0	Batch	Synthetic	Cimino et al. 2000
	98.9	2.0			
	97.8	3.0			
Wool	69.3	2.0	Batch	Synthetic	Dakiky et al. 2002
	5.8	5.0			
Olive cake	47.1	2.0	Batch	Synthetic	Dakiky et al. 2002
	8.4	5.0			
Sawdust	53.5	2.0	Batch	Synthetic	Dakiky et al. 2002
	13.8	5.0			
Pine needles	42.9	2.0	Batch	Synthetic	Dakiky et al. 2002
	13.0	5.0			
Almond shell	23.5	2.0	Batch	Synthetic	Dakiky et al. 2002
	2.3	5.0			
Coal	23.6	2.0	Batch	Synthetic	Dakiky et al. 2002
	2.4	5.0			
Cactus	19.8	2.0	Batch	Synthetic	Dakiky et al. 2002
	8.2	5.0			
Walnut shell	85.3	3.5	Batch	Synthetic	Pehlivan and Altun 2008
Hazelnut shell	88.4	3.5	Batch	Synthetic	Pehlivan and Altun 2008

Table 5 Technical advantages and disadvantages of existing modification techniques (Yin et al. 2007)

Modification	Treatment	Advantages	Disadvantages
Chemical characteristics	Acidic	Increases acidic functional groups on AC surface Enhances chelation ability with metal species	May decrease BET surface area and pore volume
	Basic	Enhances uptake of organics	May, in some cases, decrease the uptake of metal ions
	Impregnation of foreign material	Enhances in-built catalytic oxidation capability	May decrease BET surface area and pore volume
Physical characteristics	Heat	Increases BET surface area and pore volume	Decreases oxygen surface functional groups
Biological characteristics	Bioadsorption	Prolongs AC bed life by rapid oxidation of organics by bacteria before the material can occupy adsorption sites	Thick biofilm encapsulating AC may impede diffusion of adsorbate species

advantages and disadvantages of existing modification techniques with regard to technical aspects (Yin et al. 2007).

It is an established fact that the activated carbon surface can display acidic, basic, and/or neutral characteristics depending on the presence of surface functional groups (Kinoshita 1988).

It has been widely recognized that heavy metal removal by activated carbon adsorption is due predominantly to the surface complex formation between the metals and the surface functional groups. So, modification of chemical characteristics of activated carbons is modifying the inherent surface functional groups. Major types of surface functional group on activated carbon are surface oxygen complexes such as carbonyl groups.

The available methods to modify the surface functional groups are acidic and basic treatment and impregnation of foreign materials (Yin et al. 2007). Table 6 summarizes some recent studies on the modification of carbon surfaces for creation of specific surface functional groups to enhance removal of Cr(VI).

2.3.2 Modified Biosorbents

Besides the advantages of using biosorbents like plant wastes for wastewater treatment, the application of untreated biosorbents can also bring several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD),

as well as total organic carbon (TOC) due to release of soluble organic compounds contained in the plant materials (Gaballah et al. 1997; Nakajima and Sakaguchi 1990). The increase of the COD, BOD, and TOC can cause depletion of oxygen content in water and can threaten the aquatic life. Therefore, plant wastes need to be modified or treated before being applied for the removal of heavy metals.

Modification of plant wastes can extract soluble organic compounds and enhance chelating efficiency (Gaballah et al. 1997). Modification methods for the purpose of increasing efficiency of metal adsorption include basic treatment (using sodium hydroxide, calcium hydroxide, sodium carbonate), acidic treatment (using hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycolic acid), using organic compound solutions (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide), dye (Reactive Orange 13), etc.

The types of chemicals used for modifying plant wastes for Cr(VI) adsorption and their maximum adsorption capacities are shown in Table 7.

2.4 Industrial Waste Sorbents

Industrial wastes can be used as low-cost adsorbents with capability to adsorb heavy metals. Iron(III) hydroxide is a waste from fertilizer industries and one of the principle sorbents of the oxyanionic pollutants such as phosphates, arsenates, and chromates in aqueous systems. It has been extensively investigated

Table 6 Recent studies on modification of activated carbons to enhance removal of Cr(VI)

Activated carbon	Created surface functional group	Technique used	Surface area	mg Cr ⁶⁺ /g	Adsorption system	Wastewater	Reference
GAC-E	Weakly acidic and non-acidic (quinones-postulated)	Oxidization using nitric acid	–	10.0	Batch	Synthetic	Aggarwal et al. 1999
		Oxidization using ammonium persulphate	–	20.0			
		Oxidization using oxygen	–	28.0			
ACF-307	Weakly acidic and non-acidic (quinones-postulated)	Oxidization using nitric acid	–	14.0	Batch	Synthetic	Aggarwal et al. 1999
		Oxidization using ammonium persulphate	–	19.0			
Commercial	Weakly acidic (carboxylic, lactic and phenolic)	Oxidization using HNO ₃	–	13.3	Batch	Synthetic	Zhao et al. 2005
		Oxidization using H ₂ O ₂	–	13.0			
		Oxidization using Fe(NO ₃) ₃	–	15.1			
Commercial	Weakly acidic	Oxidization using HNO ₃	853	13.7	Batch	Synthetic	Liu et al. 2007
		Oxidization using HNO ₃ , treated with a mixture of NaOH and NaCl	851	13.9			
Commercial	Weakly acidic	Oxidized with H ₂ SO ₄	–	8.9	Batch	Synthetic	Babel and Kurniawan 2004
		Oxidized with HNO ₃	–	10.4			
Oil palm shell	NH ₃ ⁺ group	Oxidized with H ₂ SO ₄ and coated with chitosan	–	154	Batch	Synthetic	Nomanbhay 2005

for removing Cr(VI) from wastewater (Namasivayam and Ranganathan 1993). It was reported that the maximum adsorption capacity of iron(III) hydroxide was found to be 0.47 mg of Cr⁶⁺/g at pH of 5.6.

In another study, Aoki and Munemori (1982) investigated the adsorption of Cr(VI) on iron(III)

hydroxide. It was found that Cr(VI) is effectively adsorbed at a pH of 8.5. This difference with the previous study can be explained due to the fact that adsorption of Cr⁶⁺ in the latter study is suppressed by the presence of both SO₄^{2–} and SCN[–] anions, which compete for adsorption sites.

Table 7 Summary of modified plant wastes that are used as adsorbents for the removal of Cr(VI)

Adsorbent	Modifying agent	mg Cr ⁶⁺ /g	pH	Adsorption system	Wastewater	Reference
Sawdust	H ₂ CO	3.60	–	–	–	Baral et al. 2006
Sawdust	HCl	1.74	3.0	Batch	Synthetic	Argun et al. 2007
Groundnut husk	H ₂ SO ₄ , Ag impregnation	11.40	3.0	Batch	Synthetic	Dubey and Gopal 2007
Terminalia arjuna nuts	ZnCl ₂	28.43	1.0	Batch	Synthetic	Mohanty et al 2005
Coirpith	ZnCl ₂	–	5.6	Batch	Synthetic	Namasivayam and Ranganathan 1993

Waste slurry is also one of the industrial by-products generated in fertilizer plant due to liquid fuel combustion. Efforts made to convert the waste slurry into a cheap carbonaceous adsorbent and utilization of the product for the removal of metal ions and phenols has already been reported (Srivastava et al. 1987; Srivastava et al. 1989). Srivastava et al. (1989) studied the removal of Cr(VI) using carbonaceous material developed from the waste slurry (Srivastava et al. 1989). It was reported that this product shows excellent adsorption capacity for Cr(VI).

Another industrial waste adsorbent showing capability to adsorb heavy metals is blast-furnace slag, an industrial by-product generated in steel plants. Srivastava et al. (1997) used blast-furnace waste for the removal of Cr(VI) (Srivastava et al. 1987). It was found that the maximum metal uptake observed under identical conditions is 7.5 mg/g of Cr⁶⁺.

Gupta et al. (1999) used Bagasse fly ash generated in the sugar industry as a low-cost adsorbent for the removal of Cr(VI) from synthetic and actual wastewater (Gupta et al. 1999). It was found that the sorption capacity decreases with an increase in pH. It was also reported that the adsorption of Cr⁶⁺ on bagasse fly ash followed both Freundlich and Langmuir isotherm and that the sorption capacity of bagasse fly ash was found to be 260 mg of Cr⁶⁺/g.

Another industrial waste adsorbent showing capability to adsorb chromium is red mud, a by-product of the aluminum industry. Red mud is composed mainly of the particles of silica, aluminum, iron, and titanium oxide. Pradhan et al. investigated the adsorption of Cr (VI) using activated red mud (Pradhan et al. 1999). It was found that an adsorption capacity of 1.6 mg of Cr⁶⁺/g red mud was achieved at a pH of 5.2.

Table 8 summarized the Cr(VI) adsorption capacities of different industrial waste adsorbent.

2.5 Chitosan

Another material shown to adsorb metals is chitin. Chitin is second only to cellulose in terms of abundance in nature and is found in the exoskeletons of crabs and other arthropods and in the cell walls of some fungi (Berkeley 1979). Chitin is also a waste product of the crab meat canning industry. Chitosan can be produced chemically from chitin and is found naturally in some fungal cell walls.

The growing need for new sources of low-cost adsorbent, the increased problems of waste disposal, the increasing cost of synthetic resins undoubtedly make chitosan one of the most attractive materials for wastewater treatment.

Not only is chitosan inexpensive and abundant, it is highly adsorbent for heavy metals. It was reported that chitosan chelates five to six times greater amounts of metals than chitin due to the free amino groups exposed during deacetylation (Yang and Zall 1984). It is widely known that the excellent adsorption behaviors of chitosan for heavy metal removal is attributed to high hydrophilicity of chitosan due to a large number of hydroxyl groups, a large number of primary amino groups with high activity and flexible structure of polymer chain of chitosan making a suitable configuration for adsorption of metal ions.

Udaybhaskar et al. (1990) investigated the interaction between chitosan and Cr(VI). It was found that an adsorption capacity of 273 mg of Cr⁶⁺/g chitosan was achieved at a pH of 4.0.

Schmuhl et al. (2001) studied the cross-linking effects of chitosan. Cross-linking is the process of chemically joining two or more molecules by a covalent bond.

Cross-linking reagents contain reactive ends to specific functional groups (primary amines, sulfhydryls, etc.) on molecules. Chitosan are commonly cross-linked

Table 8 Adsorption capacities for different industrial waste adsorbent

Adsorbent	mg Cr ⁶⁺ /g	pH	Adsorption system	Wastewater	Reference
Iron(III) hydroxide	0.5	5.6	Batch	Synthetic	Namasivayam and Ranganathan 1993
Waste slurry	640.0	—	Batch	Synthetic	Srivastava et al. 1989
Blast-furnace slag	7.5	—	Batch	Synthetic	Srivastava et al. 1997
Bagasse fly ash	260.0	1.0	Batch	Synthetic	Gupta et al. 1999
Red mud	1.6	—	Batch	Synthetic	Pradhan et al. 1999

with chemical agents such as diisocyanate, epoxy compounds, carbodiimides, glutaraldehyde, and other reagents. It was found that non-cross-linked chitosan has a potential to adsorb 30 mg more of Cr^{6+} /g than that of chitosan. This is consistent with the fact that cross-linking reduces the adsorption capacities of chitosan, but this loss of capacity may be necessary to ensure the stability of chitosan.

Lee et al. (2005) prepared chitosan-based polymeric surfactants (CBPSs) and applied for the removal of Cr(VI) commonly found in wastewater; a batch test was conducted to evaluate the adsorption capacity. The removal efficiency of Cr(VI) by the CBPS depended on several factors, including the solution pH, CBPS dose, and ionic strength. The results show that the CBPSs exhibited a greater adsorption capacity for Cr(VI) than have other modified chitosans reported in the literature. The maximum adsorption capacity of Cr(VI) was 180 mg/g of CBPS at a final pH of 5.3.

Sankararamakrishnan et al. (2006) used chitosan cross-linked with glutaraldehyde, xanthate group, and chemically modified chitosan beads (CMCB) and flakes (CMCF) for the recovery of toxic chromium(VI). It was found that the sorption depends on both pH and concentration and pH 3 was the optimum value. Also, the maximum capacities for CMCF and CMCB were 625 and 256.4 mg/g, respectively.

Spinelli et al. (2004), synthesized quaternary chitosan salt (QCS) and applied it to adsorb Cr(VI). It was reported that the adsorption capacity for Cr(VI) at pH 9.0 was 30.2 mg/g (0.58 mmol/g), while at pH 4.5 the capacity was 68.3 mg/g (1.31 mmol/g). Cr(VI) ions can be eluted from cross-linked QCS by treatment with a 1-mol/l solution of NaCl/NaOH showing an efficiency of more than 95%.

Table 9 summarizes the Cr(VI) adsorption capacities of different chitosan sorbent.

3 Membrane Filtration Techniques

Membrane filtration has received a significant attention for the wastewater treatment. Membrane is capable of removing heavy metals such as Cr(VI). Various types of membrane filtration such as inorganic, polymeric, and liquid membrane can be employed for Cr(VI) removal and are presented as follows. The characteristics of some membranes and their treatment performance for hexavalent chromium are listed in Table 10.

3.1 Inorganic Membrane

Inorganic membranes are one of the most important porous materials because of their high chemical and great thermal stability. Most of the ceramic and other inorganic membranes today are in the tubular configuration.

Some studies have been done to remove Cr(VI) using inorganic membrane. Pugazhenthil et al. (2005) prepared supported non-interpenetrating modified ultrafiltration carbon membrane by gas phase nitration using NO_x and amination using hydrazine hydrate. The membrane was used for the separation of Cr(VI) from the aqueous solution. It was found that the effective pore radius of the unmodified, nitrated, and aminated carbon membranes are found to be 2.0, 2.8, and 3.3 nm, respectively. The water flux of the modified membrane, however, has been found to increase by two times compared to that for the unmodified membrane. Separation experiments on the chromic acid solution have been carried out using unmodified (giving 96% rejection), nitrated (giving 84% rejection), and aminated (giving 88% rejection) carbon membrane.

Dzyazko et al. (2007) used ceramic membranes containing ion-exchange component, such as hydrated

Table 9 Adsorption capacities for different types of chitosan

Adsorbent	mg Cr^{6+} /g	pH	Adsorption system	Wastewater	Reference
Chitosan	273	4	—	—	Udaybhaskar et al. 1990
Non-crosslinked chitosan	80	5	Batch	Synthetic	Schmuhl et al. 2001
Crosslinked chitosan	50	5	Batch	Synthetic	Schmuhl et al. 2001
Chitosan-based polymeric surfactants	180	5.3	Batch	Synthetic	Lee et al. 2005
Chemically modified chitosan beads	625	3	Batch	Synthetic	Sankararamakrishnan et al. 2006
Chemically modified chitosan flakes	256	3	Batch	Synthetic	Sankararamakrishnan et al. 2006
Quaternary chitosan salt	68	4.5	Batch	Synthetic	Spinelli et al. 2004

Table 10 Uptake of Cr(VI) using various membranes

Type of membrane	Initial Cr(VI) concentration (mg/L)	Removal system	Wastewater	Rejection rates (%)	References
Carbon membrane	1,000	Batch	Synthetic	96	Pugazhenthii et al. 2005
Nitrated carbon membrane	1,000	Batch	Synthetic	84	Pugazhenthii et al. 2005
Aminated carbon membrane	1,000	Batch	Synthetic	88	Pugazhenthii et al. 2005
Polymer-enhanced ultrafiltration	10	Continuous	Synthetic	30	Aroua et al. 2007
Composite polyamide membranes (NFI)	1,000	Continuous	Synthetic	99	Muthukrishnan and Guha 2008
Composite polyamide membranes (NFII)	1,000	Continuous	Synthetic	94	Muthukrishnan and Guha 2008
Polyacrylonitrile fibre	0.2	Continuous	Synthetic	90	Bohdziewicz 2000
Polyamide thin-film membrane	–	Continuous	Synthetic	77	Hafiane 2000

zirconium dioxide (HZD) for Cr(VI) removal from dilute solutions.

3.2 Polymeric Membrane

Polymeric membrane separation systems have nowadays become an important wastewater treatment technology, which facilitate the removal and recovery of pollutants as well as solvent, i.e., water.

Aroua et al. (2007) removed Cr(VI) from aqueous dilute solutions using polymer-enhanced ultrafiltration (PEUF) process. Three water soluble polymers, namely, chitosan, polyethyleneimine (PEI), and pectin were used. The ultrafiltration studies were carried out using a laboratory scale ultrafiltration system equipped with polysulfone hollow fiber membrane. The effects of pH and polymer composition on rejection coefficient and permeate flux at constant pressure were investigated. It was reported that the solution pH was found to be the major factor which controls the rejection of chromium species.

Muthukrishnan and Guha (2008) studied removal of Cr(VI) with different nanofiltration composite polyamide membranes for varying concentration and pH of the membrane feed solution. Two membranes were used for this investigation: one, a high rejection membrane (NFI) and the other, a low rejection membrane (NFII). The percent rejection of chromium was found to increase with the increase of feed solution pH. It has been observed that the effect of feed concentration on the percent rejection was quite low, but the nature of effect varies with the pH of the solution with a transition happening at above pH 7.0.

In another investigation, nonmatted polyacrylonitrile fiber (PAN) membrane was used for chromium ion (VI) removal from underground water by means of complexed hexadecylpyridine chloride (Bohdziewicz 2000). It was found that membranes of a 17.5% polymer content retain 98% of the chromium complex (VI), while the remaining ions present in water pass to the permeate. The results obtained confirmed that the complexation–ultrafiltration system presents an effective method for chromium ion (VI) removal.

Hafiarle et al., used an aromatic polyamide thin-film membrane, denoted as TFCS to remove Cr(VI) from water. It was found that the rejection rate depended on the ionic strength and pH. The increase in ionic strength decreased the retention, and better retention was obtained at a basic pH.

3.3 Liquid Membrane

High selectivity is one of the advantages of liquid membranes. There are two basic types of liquid membranes, emulsion liquid membrane (ELM), and immobilized liquid membrane (ILM), also called a supported liquid membrane (SLM).

The emulsion liquid membrane uses surface forces to maintain a very thin yet stable immiscible membrane between the two miscible phases (Li and Calo 1992). Immobilized liquid membrane consists of a polymer support impregnated with a viscous solution of carrier. Many different types of polymer supports are available to prepare ILM including cellulose acetate reverse osmosis membrane, microporous polypropylene ultrafiltration membrane, polyvinylchloride filter, and hollow fiber membrane (Araki and Tsukube 1990).

Liquid membranes have been proved to be an effective and inexpensive method with potential application for the removal of heavy metals. In this process, both extraction and stripping steps were combined in one stage, which led to simultaneous purification and concentration of the solute.

Chiha et al. (2006) used emulsion liquid membrane for the batch extraction of chromium (VI) from sulfuric acid aqueous solutions. Yilmaz et al. (2008) transported the Cr(VI) ions through a liquid membrane containing *p*-tert-butylcalixarene dioxaoctylamide derivative as a carrier from the aqueous solution. Djane et al. (1999) employed supported liquid membrane (SLM) method for the speciation of Cr(VI). Chaudry et al. (1997) employed supported liquid membrane technique for removal of Cr(VI) from tannery waste.

4 Ion Exchange Techniques

Among the physicochemical methods developed for chromium removal from wastewater, ion exchange is becoming a popular method that has received much attention in recent years.

In many studies, various kinds of ion exchange resin were used to study the uptake of hexavalent chromium, and some of the studies are listed in Table 11. Synthetic Dowex 2-X4 ion exchange resin was employed to investigate the uptake of Cr(VI) from real plating wastewater (Sapari et al. 1996). A strongly basic anion resin in hydroxide form was used

in the columns as anionic exchangers. A 100% removal of Cr(VI) was achieved in the studies.

Another synthetic ion exchange resin, Ambersep 132 was also explored to recover chromic acid from synthetic plating solution in a four-step ion exchange process (Lin and Kiang 2003). Ion exchange resin was used in the first step to capture chromic acid which was converted to sodium chromate by sodium hydroxide solution in the second step. Sodium chromate was converted back to chromic acid using strong base cationic (H-type) ion exchange resin in the third step, and in the fourth step, the exhausted ion exchange resin was regenerated by hydrochloric acid solutions. The four-step process was proved to be efficient and was capable of providing continuous chromic acid recovery operation.

Kabay et al. (2003) prepared a solvent-impregnated resin (SIR) with aliquat 336 and used for the batch removal of Cr(VI). Batch sorption studies indicated that solvent impregnated resins containing Aliquat 336 can be effectively used for the removal of Cr(VI) from aqueous solutions. It was reported that the sorption capacity of the SIR increases with increasing impregnation ratio.

5 Electrochemical Treatment Techniques

Electrochemical treatment techniques are becoming an alternative wastewater treatment method because many industrial processes produce toxic wastewaters, which are not easily biodegradable and

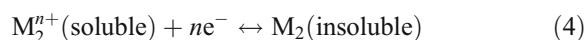
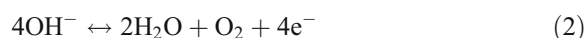
Table 11 Cr(VI) uptake using ion exchange resins

Ion-exchanger	Nature of resin	Dose (g/l)	Initial Conc. (mg/L)	pH	System	Wastewater	Capacity (mg/g)	Removal efficiency	References
Dowex 2-X4	Strongly basic resin with trimethylbenzyl-ammonium as the active group	—	9.8	—	Continuous	Real	—	100.0	Sapari et al. 1996
Ambersep 132	Strongly basic resin (H type)	0.4	750.0	—	Batch	Synthetic	92.1	—	Lin and Kiang 2003
		10.0	750.0	—	Continuous	Synthetic	100.0	—	
Solvent impregnated resin with aliquat 336	An acidic resin based on hydrophilic polymer	1.0	0.1	5.0	Batch	Synthetic	38.0	99.5	Kabay et al. 2003

require costly physical or physicochemical pretreatments. The two effective electrochemical techniques for chromium removal are described in the following sections. Some researches in the electrochemical treatment techniques to remove heavy metals are listed in Table 12.

5.1 Membrane Electrolysis

Membrane electrolysis is one of the techniques used for the removal of hexavalent chromium from wastewater. Membrane electrolysis is a chemical process driven by an electrolytic potential. There are two types of cathodes used: a conventional metal cathode (electrowinning) and a high surface area cathode (Janssen and Koene 2002). The oxidation and reduction reactions in the anode and cathode are as follows:



M and n represent the metal and the coefficient of the reaction component, respectively. The n coefficient depends on the state oxidation of the metal ions.

Rana et al. (2004) investigated the electrochemical removal of Cr(VI) ions from industrial wastewater using carbon aerogel electrodes. It was reported that the metal ion removal was significantly increased at reduced pH and high charge conditions. It was found that the metal concentration in the wastewater can be reduced by 98.5% under high charge (0.8 Ah) and acidic conditions (pH 2).

Martinez et al. (2004) studied Cr(VI) removal from synthetic plating wastewater using electrochemical reduction technique with ring iron rotary electrodes. It was found that the higher current density, the less treatment time and less energy spent on agitation. After the electrochemical treatment, the Cr(VI) concentration in the rinsing wastewater was less than 0.5 mg/l.

5.2 Electrochemical Precipitation

To maximize the removal of heavy metal from contaminated wastewater, electrical potential has been utilized to modify the conventional chemical precipitation (Kurniawan et al. 2006).

Some studies using electrochemical precipitation (ECP) was carried out for the removal of Cr(VI) from real electroplating wastewater. Kongsricharoern and Polprasert (1995) investigated the Cr(VI) removal from an electroplating wastewater using the ECP process. The ECP unit consisted of an electrolytic cell made of two steel plates representing anode and cathode. Cr^{6+} was in the range of 215–3,860 mg/l, and the pH was 1.5. The parameters varied during the ECP experiments were: electrical potential, hydraulic retention time, Cr^{6+} concentration, conductivity, and initial pH. It was found that the optimum ECP conditions are: electrical potential, 75 V; current, 4.8 A; hydraulic

Table 12 Electrochemical treatment technologies used for the removal of chromium

Anode	Cathode	Electrical current (A/m ²)	Power Consumption (kW h/m ³)	Initial metal concentration (mg/l)	pH	Removal efficiency (%)	Ref.
Carbon aerogel	Carbon aerogel	0.8	–	8	2.0	98.5	Rana et al. 2004
Iron rotary	Iron rotary	113.0	7.9 × 10 ³	130	8.5	99.6	Martinez et al. 2004
Fe ₂ O ₃	–	1.7	12	–	10–11	77.0–100.0	Kongsricharoern and Polprasert 1995
Fe ₂ O ₃	–	6.7	20	2,100	10–11	85.1	Kongsricharoern and Polprasert 1996

retention time, 50 min; initial pH, above 3.2. Under these conditions, the Cr^{6+} concentrations remaining in the effluent were less than 0.2 mg/l.

The result is comparable to that of Kongsricharoern and Polprasert (1996), which also employed bipolar ECP for Cr(VI) removal using the same type of wastewater. Bipolar ECP was also technically applicable for 85% of Cr removal with an initial Cr concentration of 2,100 mg/l.

6 Cr(VI) Industrial Emission Sources

Chromium removal from industrial wastewaters is a process of great significance on account of the widespread use of this hazardous metal in many industrial and manufacturing processes and of its serious environmental impact.

The major industrial source of Cr(VI) emissions included chemical manufacturing industry, e.g., dyes for paints, rubber, and plastic products, metal finishing industry, e.g., chrome plating, manufacturers of pharmaceuticals, wood, stone, clay, and glass products, electrical and aircraft manufacturers, steam and air conditioning supply services, cement-producing plants as cement contains chromium. The Cr(VI) concentration in wastewater produced by industries are estimated to be between 0.1 and 200 mg/l. The concentrations of Cr(VI) in the wastewater of some industries are listed in Table 13.

7 Full-scale Cr(VI) Removal Technologies

This section provides an example of full-scale Cr(VI) removal system. The Lawrence Livermore National Laboratory (LLNL) (Fig. 1) which is operated for the Department of Energy by the University of California designed and constructed an ion-exchange unit to treat hexavalent chromium in the ground water. The unit was designed to treat influent ground water with concentrations of Cr(VI) at an average of 0.034 mg/l.

In this treatment unit, the ground water is filtered to remove particulate and sediment to a nominal 5 μm , then passed through two tank-type air strippers in series, where the volatile organic compounds (VOCs) are removed and collected onto vaporphase granular activated carbon. The ground water then travels through two columns, connected in series, which are

Table 13 Industrial wastewater containing Cr(VI)

Industry	Cr(VI) concentration (mg/L)	Ref.
Hardware factory	60.0	Xu et al. 2005
Chrome tanning plant	3.7	Gupta et al. 1999
Electroplating plant	1.0	Jancuk and Fisher 1995
Electropolishing plant	42.8	Davis et al. 1995
Tannery plant	3,950.0	Esmaeili et al. 2005
Tannery plant	100.0	Song et al. 2000
Tannery plant	1,770.0z	Tobin and Roux 1998
Electroplating plant	20.7	Kiptoo et al. 2004
Electroplating plant	75.4	Tukaram Bai et al. 2005
Tannery plant	8.3	Onyancha et al. 2008

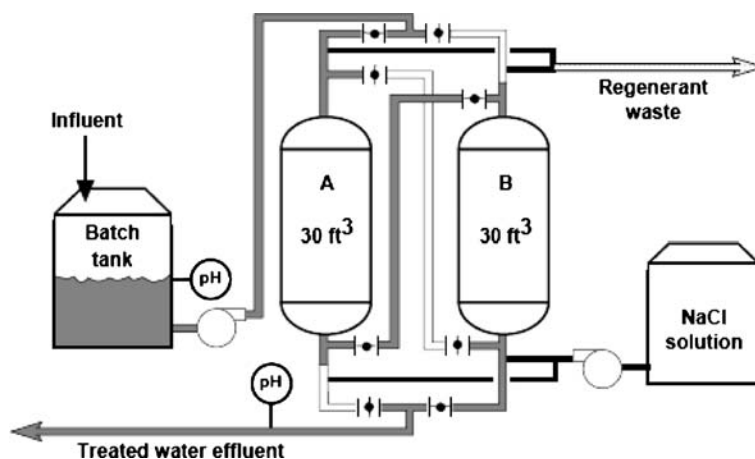
filled with ion exchange resin. After passing through both ion exchange columns, the treated ground water is discharged to a surface arroyo.

The two ion exchange columns each contain 30 ft³ of resin. They are part of a larger system called the hexavalent chromium removal unit (HCRU). The HCRU has an internal programmable logic controller (PLC). Both normal water processing and the regeneration sequence are automatically sequenced by the PLC. Process hardware consists of a batch tank, pump, sand filter, ion exchange columns, and valving and piping for treated water. The HCRU also contains a salt tank, pump, and separate piping for regenerating the resin. Regeneration is counterflow to the process flow direction. During normal processing, the effluent ground water is sampled in between the columns for Cr(VI). When the level between the two columns exceeds 11 ppb, the upstream column is regenerated and returned to service as the downstream column. In this way, the freshly regenerated resin serves as the backup column.

The resin used was Purolite® A-600, a strongly basic Type I quaternary ammonium anion exchange resin with a styrene-divinylbenzene copolymer gel matrix. It has a nominal capacity of 1.5 eq/l of resin bed. The ion exchange system removes Cr(VI) to below its limit of detection (0.002 mg/l).

This ion exchange unit for the removal of Cr(VI) costed 150,000 USD including the initial resin. The estimated yearly cost to operate the unit is: salt,

Fig. 1 Schematic representation of the process flow and regeneration of the Lawrence Livermore National Laboratory's hexavalent chromium removal unit



1,000 USD; resin replacement, 6,000 USD; filter, valve, pump maintenance, 2,000 USD, and waste disposal, 1,900 USD.

8 Conclusion

The Cr(VI), appear to be one of the major heavy metal pollutants globally in this century. Cr(VI), derived from industrial wastewater, is highly toxic and present a serious threat to human health and environment.

This review shows that the various techniques for Cr(VI) removal has been studied widely and has attracted the attention of more scientists.

Comparisons of different techniques are very difficult because of inconsistencies in the data presentation. Cr(VI) removal was evaluated at different conditions, such as pH, initial chromium concentration, temperature, ratios. Various chromium-contaminated water such as ground water, drinking water, tannery wastewater, electroplating wastewater, and synthetic industrial wastewater were used. This makes comparisons more complicated and difficult to pursue. So, the comparison is just done for the advantage and disadvantage of the discussed removal methods (Table 14).

Adsorption is relatively new practice for the removal of chromium. It has been a useful tool for controlling the extent of metal pollution. Different types of activated carbons and their performance in Cr(VI) removal were discussed. Activated carbons are expensive and can remove a few milligrams of metal ions per gram of activated carbon, and there

are still some problems encountered in the regeneration process.

Biosorption is a relatively new process that has proven very promising in the removal of chromium ions from aqueous effluents.

As mentioned previously, chitosan is a good adsorbent for Cr(VI) because of high its hydrophilicity, large number of primary amino groups and flexible structure of polymer chain.

Improvement of removal efficiencies and adsorption capacities of activated carbon and some biosorbent using chemical modifications were discussed. Chemical modification in general improved the adsorption capacity of adsorbents probably due to a higher number of active binding sites after modification, better ion-exchange properties, and formation of new functional groups that favors chromium uptake. Although chemically modified adsorbents can enhance the adsorption of Cr(VI), the cost of chemicals used and methods of modification also have to be taken into consideration in order to produce “low-cost” adsorbents.

Membrane filtration is another removal technique which is discussed in this study. Membranes can treat inorganic effluent with a high Cr(VI) concentration. Depending on membrane characteristics, membrane filtration system can remove chromium at a wide range of operational conditions. However, the operational cost is the major problem.

In addition to membrane filtration, ion exchange is also one of the most frequently applied treatment techniques for chromium uptake. Despite the advantages, ion exchange also has some limitations in treating wastewater laden with heavy metals such as

Table 14 Advantages and disadvantages of various Cr(VI) removal techniques

Tech.	Method	Advantages	Disadvantages
Adsorption	Activated carbon	The most effective adsorbent; very high surface areas	Expensive; the higher the quality, the greater the cost
		Porous sorbent; high capacity and high rate of adsorption	Performance is dependent on the type of carbon used
		Fast kinetics; a high quality-treated effluent is obtained	Requires complexing agents to improve its removal performance; nonselective; ineffective for disperse
	Chitosan	High reactivation costs; reactivation results in a loss of the carbon	
		Low cost natural polymer; environment friendly	Nonporous sorbent; the sorption capacity depends on the origin of the polysaccharide and the degree of <i>N</i> -acetylation
Filtration	Biosorbents	Extremely cost-effective; outstanding metal-binding capacities; high efficiency and selectivity in detoxifying both very dilute or concentrated solutions; excellent diffusion properties; high quality-treated effluent is obtained	Variability in the bead characteristics; pH-dependence
		Easy regeneration if required	Requires chemical modification to improve its performance
		Low cost; cost effective at low concentration	Sensitivity to operating conditions like pH and ionic strength
	Inorganic membrane	Less biological sludge production and optimal use of chemicals; regeneration of biosorbent; no additional nutrient requirement; possibility of metal recovery	Sensitivity to the presence of organic or inorganic ligands
		High chemical stability; high thermal stability	Requirement of large amount of biosorbent
Ion exchange	Polymeric membrane	Replacement after 5 to 10 sorption–desorption cycles	High cost; low surface
		Less space requirement	Membrane fouling
	Liquid membrane	Less space requirement	Low chemical and thermal stability; membrane fouling
		High selectivity; high diffusion rate	Instability of SLM due to loss of the membrane liquid into the aqueous phases
Electrochemical treatment	Membrane electrolysis	Emulsion swelling in ELM	
		No sludge generation; less time consuming	Not all ion exchange resin is suitable for metal removal
		Low energy demand	High capital cost; requires tight operation and maintenance
Electrochemical treatment	Electrochemical precipitation	Feed concentration must be monitored closely	
		Energy efficient; low maintenance	Solution concentration must be monitored
		No additional chemical reagents required	Solution heating encouraged to maximize efficiency
Electrochemical treatment	Electrochemical precipitation	High selectivity; low cost	Production of dendrite, loose or spongy deposit
			Production of sludge

Cr(VI). Prior to ion exchange, appropriate pretreatment systems for secondary effluent such as the removal of suspended solids from wastewater are required. In addition, suitable ion exchanger resins are not available for all heavy metals, the capital and operational cost is high.

Another technique that was discussed for removal of Cr(VI) was electrochemical treatment with the advantage of low-cost and high selectivity.

Among the several techniques discussed in this study to employ for Cr(VI) removal, selection of a suitable technique depends on initial Cr(VI) concentration, plant flexibility and reliability, environmental impacts and economic consideration and operational cost.

Most of the studies that are reviewed in this work are limited only to an initial evaluation of removal capacity, and there is a need to continue future studies at the pilot-plant scale. Despite the large number of papers published on the removal of chromium (VI), a few reports exist of full comparative studies of various techniques. As already noted, comparisons of various techniques are not easy because of inconsistencies in the data presentation. It is, therefore, the opinion of the authors that much study is necessary to better understand chromium removal phenomenon and to demonstrate possible useful technology at a variety of scales for applications at various locations and scales worldwide.

References

- Aggarwal, D., Goyal, M., & Bansal, R. C. (1999). Adsorption of chromium by activated carbon from aqueous solution. *Carbon*, 37(12), 1989–1997. doi:10.1016/S0008-6223(99)00072-X.
- Ahalya, N., Ramachandra, T. V., & Kanamadi, R. D. (2003). Biosorption of heavy metals. *Research Journal of Chemistry and Environment*, 7(4), 71–79.
- Alaerts, G. J., Jitjaturant, V., & Kelderman, P. (1989). Use of coconut shell-based activated carbon for chromium (VI) removal. *Water Science and Technology*, 21(12), 1701–1704.
- Allen, S. J., Gan, Q., Matthews, R., & Johnson, P. A. (2005). Kinetic modeling of the adsorption of basic dyes by kudzu. *Journal of Colloid and Interface Science*, 286(1), 101–109. doi:10.1016/j.jcis.2004.12.043.
- Aoki, T., & Munemori, M. (1982). Recovery of Cr (VI) from wastewater with Iron (III) Hydroxide: I. Adsorption mechanism of Cr (VI) on Iron (III) hydroxide. *Water Research*, 16, 793–796. doi:10.1016/0043-1354(82)90006-9.
- Araki, T., & Tsukube, H. (1990). Liquid Membranes: Chemical Applications CRC Press, pp. 35–36.
- Argun, M. E., Dursun, S., Ozdemir, C., & Karatas, M. (2007). Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *Journal of Hazardous Materials*, 141(1), 77–85. doi:10.1016/j.jhazmat.2006.06.095.
- Aroua, M. K., Zuki, F. M., & Sulaiman, N. M. (2007). Removal of chromium ions from aqueous solutions by polymer-enhanced ultrafiltration. *Journal of Hazardous Materials*, 147(3), 752–758. doi:10.1016/j.jhazmat.2007.01.120.
- Babel, S., & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials*, 97(1–3), 219–243. doi:10.1016/S0304-3894(02)00263–7.
- Babel, S., & Kurniawan, T. A. (2004). Cr(VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere*, 54(7), 951–967. doi:10.1016/j.chemosphere.2003.10.001.
- Baral, S. S., Das, S. N., & Rath, P. (2006). Cr(VI) removal from aqueous solution by adsorption on treated sawdust. *Biochemical Engineering Journal*, 31(3), 216–222. doi:10.1016/j.bej.2006.08.003.
- Barnowski, C., Jakubowski, N., Stuewer, D., & Broekaert, J. A. C. (1997). Speciation of chromium by direct coupling of ion exchange chromatography with ICP-MS. *At. Spectrom*, 1155(12), 1155–1161. doi:10.1039/a702120h.
- Basso, M. C., Cerrella, E. G., & Cukierman, A. L. (2002). Lignocellulosic materials as potential biosorbents of trace toxic metals from wastewater. *Industrial & Engineering Chemistry Research*, 41(15), 3580–3585. doi:10.1021/ie020023h.
- Berkeley, R. C. W. (1979). Chitin, Chitosan and Their Degradative Enzymes. In R. C. W. Berkeley, C. W. Gooday, & D. C. Elwood (Eds.), *Microbial polysaccharides* (pp. 205–236). New York: Academic Press.
- Bohdziewicz, J. (2000). Removal of chromium ions (VI) from underground water in the hybrid complexation-ultrafiltration process. *Desalination*, 129(3), 227–235. doi:10.1016/S0011-9164(00)00063-1.
- Brown, P. A., Gill, S. A., & Allen, S. J. (2000). Metal removal from wastewater using peat. *Water Research*, 34(16), 3907–3916. doi:10.1016/S0043-1354(00)00152-4.
- Candela, M. P., Martinez, J. M., & Macia, R. T. (1995). Chromium (VI) removal with activated carbons. *Water Research*, 29(9), 2174–2180. doi:10.1016/0043-1354(95)00035-J.
- Chaiyasith, S., Chaiyasith, P., & Septhu, C. (2006). Removal of cadmium and nickel from aqueous solution by adsorption onto treated fly ash from Thailand. *Thammasat International Journal of Science and Technology*, 11(2), 13–20.
- Chaudry, M. A., Ahmad, S., & Malik, M. T. (1997). Supported liquid membrane (SLM) technique applicability for the speciation of chromium from tannery wastes. *Waste Management (New York, N.Y.)*, 17(4), 211–218. doi:10.1016/S0956-053X(97)10007-1.
- Chiha, M., Samar, M. H., & Hamdaoui, O. (2006). Extraction of chromium (VI) from sulphuric acid aqueous solutions by a liquid surfactant membrane (LSM). *Desalination*, 194(1–3), 69–80. doi:10.1016/j.desal.2005.10.025.

- Chingombe, P., Saha, B., & Wakeman, R. J. (2005). Surface modification and characterisation of a coal-based activated carbon. *Carbon*, 43(15), 3132–3143. doi:10.1016/j.carbon.2005.06.021.
- Cimino, G., Passerini, A., & Toscano, G. (2000). Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. *Water Research*, 34(11), 2955–2962. doi:10.1016/S0043-1354(00)00048-8.
- Dakiky, M., Khamis, M., Manassra, A., & Mer'eb, M. (2002). Selective adsorption of Cr(VI) in industrial wastewater using low-cost abundantly available adsorbents. *Advances in Environmental Research*, 6(4), 533–540. doi:10.1016/S1093-0191(01)00079-X.
- Davis, A. P., Bernstein, C., & Gietka, P. M. (1995). Waste minimization in electropolishing: Process control. In Arup K. Sengupta (Ed.), *Proceedings of the Twenty-Seventh Mid-Atlantic Industrial Waste Conference: Hazardous and industrial wastes* (pp. 62–71). Lancaster: Technomic Publishing.
- Demirbas, A. (2008). Heavy metal adsorption onto agro based waste materials: A review. *Journal of Hazardous Materials*, 157(2–3), 220–229. doi:10.1016/j.jhazmat.2008.01.024.
- Djane, N. K., Ndung'u, K., Johnsson, C., Sartz, H., Tornstrom, T., & Mathiasson, L. (1999). Chromium speciation in natural waters using serially connected supported liquid membranes. *Talanta*, 48(5), 1121–1132. doi:10.1016/S0039-9140(98)00334-8.
- Dubey, S. P., & Gopal, K. (2007). Adsorption of chromium(VI) on low cost adsorbents derived from agricultural waste material: a comparative study. *Journal of Hazardous Materials*, 145(3), 465–470.
- Dzyazko, Y. S., Mahmud, A., Lapique, F., & Belyakov, V. N. (2007). Cr(VI) transport through ceramic ion-exchange membranes for treatment of industrial wastewaters. *Journal of Applied Electrochemistry*, 37(2), 209–217.
- Esmaili, A., Mesdaghi nia, A., & Vazirinejad, R. (2005). Chromium (III) removal and recovery from tannery wastewater by precipitation process. *American Journal of Applied Sciences*, 2(10), 1471–1473.
- Gaballah, I., Goy, D., Allain, E., Kilbertus, G., & Thauront, J. (1997). Recovery of copper through decontamination of synthetic solutions using modified barks. *Met. Metall. Trans B*, 28(1), 13–23.
- Gardea-Torresdey, J. L., de la Rosa, G., & Peralta-Videa, J. R. (2004). Use of phytofiltration technologies in the removal of heavy metals: A review. *Pure and Applied Chemistry*, 76(4), 801–813.
- Gil, R. A., Cerutti, S., G'asquez, J. A., Olsina, R. A., & Martinez, L. D. (2006). Preconcentration and speciation of chromium in drinking water samples by coupling of on-line sorption on activated carbon to ETAAS determination. *Talanta*, 1065(68), 1065–1070.
- Gupta, V. K., Morhan, D., Sharma, S., & Park, K. T. (1999). Removal of chromium(VI) from electroplating industry wastewater using bagasse fly ash—a sugar industry waste material. *Environmentalist*, 19(2), 129–136.
- Hafiane, A., Lemordant, D., & Dhahbi, M. (2000). Removal of Cr(VI) by nanofiltration. *Desalination*, 130(3), 305–312.
- Hamadi, N. K., Chen, X. D., Farid, M. M., & Lu, M. G. Q. (2001). Adsorption kinetics for the removal of chromium (VI) from aqueous solution by adsorbents derived from used tyres and sawdust. *Chemical Engineering Journal*, 84(2), 95–105.
- Han, I., Schlautman, M. A., & Batchelor, B. (2000). Removal of Cr(VI) from Groundwater by Granular Activated Carbon. *Water Environment Research*, 72(1), 29–39.
- Hashem, A., Akasha, R. A., Ghith, A., & Hussein, D. A. (2007). Adsorbent based on agricultural wastes for heavy metal and dye removal. A review. *Energy Edu. Sci. Technol*, 19, 69–86.
- Hu, Z., Lei, L., Li, Y., & Ni, Y. (2003). Chromium adsorption on high-performance activated carbons from aqueous solution. *Sep. Purif. Technol*, 31(1), 13–18.
- Huang, C. P., & Wu, M. H. (1975). Chromium removal by carbon adsorption. *J. Water Pollut. Control Federation*, 47(10), 2437–2446.
- Jancuk, W. A., & Fisher, J. R. (1995). Research laboratory wastewater treatment process. In Arup. K. Sengupta (Ed.), *Proceedings of the Twenty-Seventh Mid-Atlantic Industrial Waste Conference: Hazardous and industrial wastes* (pp. 405–413). Lancaster: Technomic Publishing.
- Janssen, L. J. J., & Koene, L. (2002). The role of electrochemistry and electrochemical technology in environmental protection. *Chemical Engineering Journal*, 85(2–3), 137–146.
- Kabay, N., Arda, M., Saha, B., & Streat, M. (2003). Removal of Cr(VI) by solvent impregnated resins (SIR) containing aliquat 336. *Reactive & Functional Polymers*, 54(1–3), 103–115.
- Karthikeyan, T., Rajgopal, S., & Miranda, L. R. (2005). Chromium(VI) adsorption from aqueous solution by *Hevea brasiliensis* sawdust activated carbon. *Journal of Hazardous Materials*, 124(1–3), 192–199.
- Katz, F., & Slem, H. (1994). *The biological and environmental chemistry of chromium* (pp. 51–58). New York: VCH.
- Kimbrough, D. E., Cohen, Y., Winer, A. M., Creelman, L., & Mabuni, C. A. (1999). Critical Assessment of Chromium in the Environment Critical Reviews in Environmental Science and Technology. *Critical Reviews in Environmental Science and Technology*, 29(1), 1–46.
- Kinoshita, K. (1988). *Carbon electrochemical and physico-chemical properties*. New York: Wiley.
- Kiptoo, J. K., Ngila, J. C., & Sawula, G. M. (2004). Speciation studies of nickel and chromium in wastewater from an electroplating plant. *Talanta*, 64(1), 54–59.
- Koby, M. (2004). Adsorption, Kinetic and Equilibrium Studies of Cr(VI) by Hazelnut Shell Activated Carbon. *Adsorption Science & Technology*, 22(1), 51–64.
- Kongsricharoern, N., & Polprasert, C. (1995). Electrochemical precipitation of chromium (Cr⁶⁺) from an electroplating wastewater. *Water Science and Technology*, 31(9), 109–117.
- Kongsricharoern, N., & Polprasert, C. (1996). Chromium removal by a bipolar electrochemical precipitation process. *Water Science and Technology*, 34(9), 109–116.
- Kotas, J., & Stasicka, Z. (2000). Chromium occurrence in the environment and methods of its speciation. *Environmental Pollution*, 107(3), 263–283.
- Kratochvil, D., Pimentel, P., & Volesky, B. (1998). Removal of trivalent and Cr(VI) by seaweed biosorbent. *Environmental Science & Technology*, 32(18), 2693–2698.
- Kratochvil, D., & Volesky, B. (1998). Advances in the biosorption of heavy metals. *J. Trends Biotechnol*, 16(7), 291–300.

- Kurniawan, T. A., Chan, G. Y. S., Lo, W. H., & Babel, S. (2006). Physico-chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal*, 118(1–2), 83–98.
- Lee, H. S., & Volesky, B. (1997). Interaction of light metals and protons with seaweed biosorbent. *Water Research*, 31(12), 3082–3088.
- Lee, M. Y., Hong, K. J., Shin-Ya, Y., & Kajiuchi, T. (2005). Adsorption of Cr(VI) by chitosan-based polymeric surfactants. *Journal of Applied Polymer Science*, 96(1), 44–50.
- Li, N. N., Calo, J. M. (1992). Separation and purification technology. CRC Press, pp. 198–199.
- Lin, S. H., & Kiang, C. D. (2003). Chromic acid recovery from waste acid solution by an ion exchange process: equilibrium and column ion exchange modeling. *Chemical Engineering Journal*, 92(1–3), 193–199.
- Liu, S. X., Chen, X., Chen, X. Y., Liu, Z. F., & Wang, H. L. (2007). Activated carbon with excellent chromium(VI) adsorption performance prepared by acid-base surface modification. *Journal of Hazardous Materials*, 141(1), 315–319.
- Martinez, S. A., Rodriguez, M. G., Aguilar, R., Soto, G. (2004). Removal of chromium hexavalent from rinsing chromating waters electrochemicals reduction in a laboratory pilot plant. *Water Science and Technology*, 49(1), 115–122.
- Mittal, A., Krishnan, L., & Gupta, V. K. (2005). Removal and recovery of malachite green from wastewater using an agricultural waste material. *Sep. Purif. Technol.*, 43(2), 125–133.
- Mohan, D., & Pittman, C. U. Jr. (2006). Activated carbons and low cost adsorbents for remediation of tri- and Cr (VI) from water. *Journal of Hazardous Materials*, 137(2), 762–811.
- Mohan, D., Singh, K. P., & Singh, V. K. (2005). Removal of Cr (VI) from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. *Industrial & Engineering Chemistry Research*, 44(4), 1027–1042.
- Mohanty, K., Jha, M., Meikap, B. C., & Biswas, M. N. (2005). Removal of chromium(VI) from dilute aqueous solutions by activated carbon developed from Terminalia arjuna nuts activated with zinc chloride. *Chemical Engineering Science*, 60(11), 3049–3059.
- Muthukrishnan, M., & Guha, B. K. (2008). Effect of pH on rejection of Cr(VI) by Nanofiltration. *Desalination*, 219(1–3), 171–178.
- Nakajima, A., & Sakaguchi, T. (1990). Recovery and removal of uranium by using plant wastes. *Biomass*, 21, 55–63.
- Namasivayam, C., & Ranganathan, K. (1993). Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater. *Environmental Pollution*, 82(3), 255–261.
- Natale, F. D., Lancia, A., Molino, A., Musmarra, D. (2007). Removal of chromium ions from aqueous solutions by adsorption on activated carbon and char. *Journal of Hazardous Materials*, 145(3), 381–390.
- Nomanbhay, S. M. (2005). Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology*, 8(1), 43–53.
- Onyancha, D., Mavura, W., Ngila, J. C., Ongoma, P., & Chacha, J. (2008). Studies of chromium removal from tannery wastewaters by algae biosorbents, *Spirogyra condensata* and *Rhizoclonium hieroglyphicum*. *Journal of Hazardous Materials*, 158(2–3), 605–614.
- Pagnanelli, F., Mainelli, S., Veglio, F., & Toro, L. (2003). Heavy metal removal by olive pomace: biosorbent characterization and equilibrium modeling. *Chemical Engineering Science*, 58(20), 4709–4717.
- Park, S. J., & Jung, W. Y. (2001). Removal of chromium by activated carbon fibers plated with copper metal. *Carbon Science*, 2(1), 15–21.
- Park, D., Yun, Y. S., Jo, J. H., & Park, J. M. (2006). Biosorption process for treatment of electroplating wastewater containing Cr(VI): Laboratory-scale feasibility test. *Industrial & Engineering Chemistry Research*, 45(14), 5059–5065.
- Pehlivan, E., & Altun, T. (2008). Biosorption of chromium(VI) ion from aqueous solutions using walnut, hazelnut and almond shell. *Journal of Hazardous Materials*, 155(1–2), 378–384.
- Pradhan, J., Das, S. N., & Thakur, R. S. (1999). Adsorption of Cr (VI) from aqueous solution by using activated RedMud. *Journal of Colloid and Interface Science*, 217(1), 137–141.
- Pugazhenth, G., Sachan, S., Kishore, N., & Kumar, A. (2005). Separation of chromium (VI) using modified ultrafiltration charged carbon membrane and its mathematical modeling. *Journal of Membrane Science*, 254(1–2), 229–239.
- Rana, P., Mohan, N., & Rajagopal, C. (2004). Electrochemical removal of chromium from wastewater by using carbon aerogel electrodes. *Water Research*, 38(12), 2811–2820.
- Ravikumar, K., Deebika, B., & Balu, K. (2005). Decolourization of aqueous dye solutions by a novel adsorbent: Application of statistical designs and surface plots for the optimization and regression analysis. *Journal of Hazardous Materials*, 122(1–2), 75–83.
- Ruthven, D. M. (1984). *Principles of adsorption and adsorption process*. New York: Wiley.
- Sankaramakrishnan, N., Dixit, A., Iyengar, L., & Sanghi, R. (2006). Removal of Cr(VI) using a novel cross linked xanthated chitosan. *Bioresource Technology*, 97(18), 2377–2382.
- Sapari, N., Idris, A., & Hisham, N. (1996). Total removal of heavy metal from mixed plating rinse wastewater. *Desalination*, 106(1–3), 419–422.
- Schmuhl, R., Krieg, H. M., & Keizer, K. (2001). Adsorption of Cu(II) and Cr(VI) ions by chitosan: Kinetics and equilibrium studies. *Water. S.A.*, 27(1), 1–7.
- Selomulya, C., Meeyoo, V., & Amal, R. (1999). Mechanisms of Cr(VI) removal from water by various types of activated carbons. *Journal of Chemical Technology and Biotechnology*, 74(2), 111–122.
- Sharma, D. C., & Forster, C. F. (1996). Removal of hexavalent chromium from aqueous solutions by granular activated carbon. *Water S.A.*, 22(2), 153–160.
- Song, Z., Williams, C. J., & Edyvean, R. G. J. (2000). Sedimentation of tannery wastewater. *Water Research*, 34(7), 2171–2176.
- Spinelli, V. A., Laranjeira, M. C. M., Fa'vere, V. T. (2004). Preparation and characterization of quaternary chitosan

- salt: adsorption equilibrium of chromium(VI) ion. *Reactive & Functional Polymers*, 61(3), 347–352.
- Srivastava, S. K., Gupta, V. K., & Mohan, D. (1997). Removal of lead and chromium by activated slag—A blast-furnace waste. *Journal of Environmental Engineering*, 123(5), 461–468.
- Srivastava, S. K., Pant, N., & Pal, N. (1987). Studies on the efficiency of a local fertilizer waste as a low cost adsorbent. *Wat. Res.*, 21(11), 1389–1394.
- Srivastava, S. K., Tyagi, R., & Pant, N. (1989). Adsorption of heavy metal ions on carbonaceous material developed from the waste slurry generated in local fertilizer plants. *Water Research*, 23(9), 1161–1165.
- Suzuki (1990). Adsorption Engineering, Elsevier, Amsterdam, (37–39).
- Tobin, J. M., & Roux, J. C. (1998). Mucor biosorbent for chromium removal from tanning effluent. *Wat. Res.*, 32(5), 1407–1416.
- Tukaram Bai, M., Venkata Ratnam, M., Subba Rao, D., Venkateswarlu, P. (2005). Removal of chromium from wastewater by adsorption with used coffee powder, In: Vibhuti N Misra, Vibhuti
- Udaybhaskar, P., Iyengar, L., & Rao, A. V. S. P. (1990). Cr(VI) interaction with chitosan. *Journal of Applied Polymer Science*, 39(3), 739–747.
- Venitt, S., & Levy, L. S. (1974). Mutagenicity of chromates in bacteria and its relevance to chromate carcinogenesis. *Nature*, 250(5466), 493–495.
- Vigneswaran, S., Ngo, H. H., Chaudhary, D. S., & Hung, Y. T. (2004). Physico-chemical treatment processes for water reuse. In L. K. Wang, Y. T. Hung, & N. K. Shamas (Eds.), *Physicochemical treatment processes*, vol. 3 (pp. 635–676). New Jersey: Humana Press.
- Volesky, B. (2001). Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy*, 59(2–3), 203–216.
- Volesky, B. (2003). Sorption and Biosorption, Montreal-St. Lambert, Quebec, Canada. *BV Sorbex Inc.*, 11, 258–263.
- Volesky, B., & Holan, Z. R. (1995). Biosorption of heavy metals. *Biotechnology Progress*, 11(3), 235–250.
- World Health Organization (WHO) (2004). Guidelines for drinking-water quality (third ed.). Recommendations. WHO, Geneva, 1, 334–335.
- Xu, Y., Xiao, H., & Sun, S. (2005). Study on anaerobic treatment of wastewater containing hexavalent chromium. *Journal of Zhejiang University Science*, 6(6), 574–579.
- Yang, T. C., & Zall, R. R. (1984). Absorption of metals by natural polymers generated from seafood processing wastes. *Industrial & Engineering Chemistry Product Research and Development*, 23(1), 168–172.
- Yilmaz, A., Kaya, A., Alpoguz, H. K., Ersoz, M., & Yilmaz, M. (2008). Kinetic analysis of chromium(VI) ions transport through a bulk liquid membrane containing *p*-tert-butylcalix[4]arene dioxaoctylamide derivative. *Separation and Purification Technology*, 59(1), 1–8.
- Yin, C. Y., Aroua, M. K., & Wan Daud, W. M. A. (2007). Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. *Separation and Purification Technology*, 52(3), 403–415.
- Zhao, N., Na, W., Li, J., Qiao, Z., Jing, C., & Fei, H. (2005). Surface properties of chemically modified activated carbons for adsorption rate of Cr(VI). *Chemical Engineering Journal*, 115(1–2), 133–138.