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REVIEW

Removal of hazardous heavy metals from aqueous environment by low-cost adsorption materials

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Abstract The rapid growth of the human population and industrialization in the world has indirectly increased environmental problems such as water, air and land pollution. Amongst all, heavy metals can be considered as the most problematic pollutants. Numerous efforts have been attempted to minimize the impact of heavy metals. This chapter discusses the recent developments and technical applicability of different treatment methods for heavy metal removal. The adsorption process using various low-cost materials as the potential alternative for heavy metal removal is being highlighted and summarized.

Keywords Heavy metals · Chemical precipitation · Ion exchange · Membrane filtration · Adsorption · Low-cost adsorbents

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Introduction

Heavy metals may be defined as the elements having atomic weights between 63.5 and 200.6 and have a minimum specific gravity of 5 (Srivastava and Majumder 2008). These metallic agents, once concentrated in the biosphere, generally persist and are not broken down. Therefore, water pollution by heavy metals poses one of the most serious environmental problems and of the most difficult to solve. Although some of the heavy metals such as iron, zinc, copper, iodine and molybdenum are recognized as essential for human health, some heavy metals are regarded as purely toxic metals. These include arsenic, nickel and lead, which are of widespread use and frequently found in industrial wastewater.

Arsenic (As) is a metalloid belonging to group 15 of the periodic table with atomic number of 33 and atomic weight of 74.92. The widespread usage of As can be found in wood preservation, making of special glass and semi-conductors and insecticides. However, due to its toxicity, the ingestion and inhalation of As and its compounds can cause various health problems. For instance, infertilities and miscarriages in women and dermatological effect which causes skin cancer are often associated with the prolonged and high exposure to As or its compounds (Hindmarsh and McCurdy 1986).

Nickel (Ni) is a silvery white, hard, malleable and ferromagnetic metallic element belonging to group 10 of the periodic table with atomic number of 28 and atomic weight of 58.69. Ni is corrosion resistant and used primarily for making of stainless steel and many other corrosion resistant alloys. The possible routes of Ni entry to human beings are through inhalation, ingestion and skin contact. Nevertheless, absorbed Ni is unable to be metabolized by human body. According to the Agency for Toxic Substances and

Disease Registry (ATSDR) of United States, the reference values for Ni in healthy adults are 0.2 μg/L in serum and 1–3 μg/L in urine (ATSDR 2005). For dermal contact of Ni, it causes dermatitis which is the most adverse health effect associated with Ni exposure.

Lead (Pb) is a soft, malleable, ductile and dense metal. Due to its corrosion resistant characteristics, Pb has been historically used in plumbing. The other major use of Pb is in lead-acid batteries manufacturing and formation of lead alloys. However, like As, lead is toxic in nature. The high exposure to Pb can increase the risk of kidney failure, disruption of central nervous system, brain damage and even death. This article is an abridged version of chapter 8 published in the book Environmental Chemistry for a Sustainable World (ECSW), volume 3, by Keng et al. (2013, ECSW book chapter).

Heavy metal removal: conventional and emerging methods

Extensive research and financial resources have been spent on the treatment of heavy metal pollution especially in industrial wastewater which is contaminated by heavy metals. These technologies include conventional physico-chemical methods and biological treatments, where the latter have gradually getting momentum because they are more eco-friendly and cost effective compare to the conventional techniques.

Chemical precipitation

Amongst all the physical–chemical methods, chemical precipitation is the most common and effective method used in the industry for treatment of wastewater containing heavy metals because it is relatively easy and inexpensive to operate (Kung and Jung 2001). This technique is employed in almost 75 % of electroplating facilities to treat wastewater (Karthikeyan et al. 1996). Generally, the metals are precipitated as insoluble hydroxides, carbonates or sulphides and separated from water by sedimentation and filtration (Table 1).

Although this technique is reported as the most widely used method for heavy metal removal in industry effluent, still it suffers from some limitations. For instance, hydroxide precipitation requires a large amount of chemicals to reduce metals to an acceptable level prior discharge especially if the effluents have high acidity where large amounts of lime are required for neutralization. In this case, excessive secondary sludge, such as gypsum ($CaSO_4 \cdot 2H_2O$), is produced that requires further treatment. These secondary precipitates not only increase the costs of sludge handling but also give long-term environmental impacts (Kurniawan et al. 2006). Secondly, some metal hydroxides are amphoteric, and the mixed metals create a problem using hydroxide precipitation since the ideal pH for one metal may change another metal back into solution. On top of these, some complexing agents present in the wastewater will inhibit the efficacy of metal hydroxide precipitation (Fu and Wang 2011).

Ion exchange

Ion exchange is the process through which an ion is removed out of an aqueous solution and is replaced by another ionic species. It has been continuously used in the treatment of heavy metals due to several advantages, such as high treatment capacity, high selectivity for certain heavy metal ions and most significantly, fast kinetics and most importantly it reduces the major problem faces in chemical precipitation—handling and disposal of large amount of sediments and sludge (Lacour et al. 2001; Abo-Farha et al. 2009; Al-Enezi et al. 2004). Strongly acidic resins with sulphonic acid groups ($-SO_3H$) and weakly acid resins with carboxylic acid groups ($-COOH$) are the most common cation exchangers. The degree of exchange that occurs depends on the size and ionic charge of the metal cations, initial metal concentration, nature (both physical and chemical) of the ion exchange substance, pH and temperature (Lee et al. 2006a; Al-Enezi et al. 2004). Since resins have different swelling characteristics, the total exchange capacity on a volumetric basis ranged from 1.0 to 4.0 meq/mL. Though the efficiency of ion exchange resins for heavy metal removal is evident, the cost incurred prohibits the treatment of highly concentrated wastewater. Thereby, it is typically used as a polishing step after precipitation.

Membrane filtration

The ultimate objective of most of the traditional methods in heavy metal treatments is not the recovery of the metal but rather its elimination. However, recovery of heavy metals shows greater benefits. It allows reuse of the metals and thus provides further economic and environmental benefits by reducing the disposal costs and raw material requirements. In this case, membrane processes exert as an alternative for heavy metal recovery. Other advantages of this technique including fewer chemicals are used in the process, simple operation, less space consuming and can be easily combined with other separation processes for better removal efficiency. The membrane processes used for wastewater treatment containing heavy metals including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and electrodialysis (ED) depending on the size of the particle that can be

Table 1 Removal of heavy metals using chemical precipitation

Cation (heavy metal)	Anion (precipitant)	Optimum pH	Contact time (h)	Initial metal concentration	Removal efficiency (%)	Reference
Cu^{2+}, Cr^{4+}	$Ca(OH)_2$, NaOH, Na_2CO_3	12.0, 8.7	2	48.51 mg/L, 30 mg/L	98.6, 99.97	Mirbagheri and Hosseini (2005)
Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}	$Ca(OH)_2$, NaOH	8.1–8.3	24	0.1–29.7 mg/L	50–100	Meunier et al. (2006)
Soil, fly ash and sewage leachates (Al^{3+}, Ba^{2+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cr^{3+}, Cu^{2+}, Fe, Mg^{2+}, Mn, Ni^{2+}, Pb^{2+}, Zn^{2+}, P, S)	NaOH, $Ca(OH)_2$, NaOH/Na_2S, NaOH/Na_2CO_3, NaOH/Na_2HPO_4	5.0 7.5 7.5 8.0	0.3	0.13–719 mg/L[a] 1.38–11,100 mg/L[b] 0.23–827 mg/L[c]	0.0–100[a] 23.9–100[b] 3.5–100[c]	Djedidi et al. (2009)
Ni^{2+}, Co^{2+}, Cu^{2+}	Na_2S	5.81–11.6	0.5–2	50–2051 mg/L	66.9–99.9	Lewis and van Hille (2006)
Zn^{2+}	Na_2S	6.5	NA	7,500 mg/L	99.9 (<0.01 mg/L)	Veeken et al. (2003)
Acid mine drainage (Fe^{2+}, Mn^{2+})	1,3-benzenediamido ethane-thiolate	4.5	20	194 mg/L 4.65 mg/L	99.9 (<0.009 ppm), 97.3	Matlock et al. (2002)

NA Not available

[a] Refers to the soil leachates

[b] Refers to the fly ash leachates

[c] Refers to the sewage sludge leachates

retained (Table 2). The membrane techniques that are often used for heavy metal removal are UF, NF, RO and ED. However, the performance of RO and its lifetime are highly sensitive to wastewater properties. The accumulation of particulate and colloidal matters at the feed side of the membrane surface caused membrane fouling and permeate flux decline (Lee et al. 2006b).

Adsorption

Adsorption is known as an efficient, convenient and economic method for wastewater treatment. The flexibility in design and operation, high removal efficiency and the possibility for most of the adsorbents to be regenerated and reuse by suitable desorption process have made adsorption process gaining its popularity (Krishnani et al. 2008; Elouear et al. 2008; Afkhami et al. 2010; Salehi et al. 2012). Activated carbon (AC) is being recognized as one of the most popular adsorbents used in the removal of heavy metal contaminants. AC has been used efficiently in both batch and column studies due to its large micropore and mesopore volumes. However, the drawback of AC is it remains as an expensive material because of depleting source of commercial coal-based AC. Higher cost is accounted for higher quality of activated carbon. Another limitation of AC adsorption in heavy metal removal is its high affinity towards organic molecules. As a result, these kinds of high molecular weight organic compounds will block the heavy metal ions from reaching the adsorbents bed. Due to these problems, many researchers have shown interest to search and explore on other potential adsorbents to replace AC.

Table 2 Pore size of the membrane processes

Membrane process	Pore size (nm)
Microfiltration	0.1–10 μm (>100)
Ultrafiltration	0.005–0.2 μm (5–200)
Nanofiltration	0.001–0.01 μm (<10)

Utilization of low-cost adsorbents in heavy metals removal

Techniques currently used for the removal of heavy metals from wastewaters are chemical precipitation, ion exchange, membrane filtration, electrolytic reduction, coagulation, solvent extraction and catalysis. However, owing to the drawbacks found in these techniques, there is thus a need to search for alternative process that could remove heavy metal that are commonly found in the industry effluent. In this regard, adsorption appeared to be an attractive alternative due to ease of operation. Besides, it can also be considered as an economical approach if it involves the

Table 3 Adsorption capacities of metals by fly ash

Metals	Adsorbent	Adsorption capacity[a]	Temperature (°C)	References
As(III)	Fly ash coal-char	3.7–89.2	25	Pattanayak et al. (2000)
	Fly ash brown coal-char	25.1–32.1	25	Polowczyk et al. (2011)
As(V)	Fly ash	7.7–27.8	20	Diamadopoulos et al. (1993)
	Fly ash coal-char	0.02–34.5	25	Pattanayak et al. (2000)
Cd(II)	Fly ash	0.67–0.83	20	Bayat (2002a)
	Bagasse fly ash	1.24–2.0	30–50	Gupta et al. (2003)
	Coal Fly ash	18.98	25	Papandreou et al. (2007)
	NaOH-activated fly ash	30.21	20–25	Visa et al. (2012)
Cr(III)	Fly ash	52.6–106.4	20–40	Cetin and Pehlivan (2007)
	Fly ash porous pellet	22.88	25	Papandreou et al. (2011)
Cr(VI)	Fly ash-chitosan composite	33.27	15	Wen et al. (2011)
	Fly ash	1.38	30–60	Banerjee et al. (2004)
	Fe-impregnated fly ash	1.82	30–60	Banerjee et al. (2004)
	Al-impregnated fly ash	1.67	30–60	Banerjee et al. (2004)
Cs(I)	Fly ash zeolite	443.9	25	Mimura et al. (2001)
Cu(II)	Fly ash	0.63–0.81	25	Lin and Chang (2001)
	Fly ash	0.76	32	Rao et al. (2003)
	Coal Fly ash pellets	20.92	25	Papandreou et al. (2007)
	Coal fly ash (CFA)	178.5–249.1	30–60	Hsu et al. (2008)
	CFA-600	126.4–214.1	30–60	Hsu et al. (2008)
	CFA–NAOH	76.7–137.1	30–60	Hsu et al. (2008)
Hg(II)	Fly ash	11.0	30–60	Banerjee et al. (2004)
	Fe-impregnated fly ash	12.5	30–60	Banerjee et al. (2004)
	Al-impregnated fly ash	13.4	30–60	Banerjee et al. (2004)
Ni(II)	Fly ash	9.0–14.0	30–60	Banerjee et al. (2003)
	Fe-impregnated fly ash	9.8–14.93	30–60	Banerjee et al. (2003)
	Al-impregnated fly ash	10–15.75	30–60	Banerjee et al. (2003)
	Bagasse fly ash	1.12–1.70	30–50	Gupta et al. (2003)
Pb(II)	Fly ash zeolite	70.6	20	Gan (2000)
	Bagasse fly ash	285–566	30–50	Goswami and Das (2000)
	Fly ash porous pellet	45.54	25	Papandreou et al. (2011)
	NaOH-activated fly ash	2000.0	20–25	Visa et al. (2012)
Zn(II)	Fly ash	6.5–13.3	30–60	Banerjee et al. (2003)
	Fe-impregnated fly ash	7.5–15.5	30–60	Banerjee et al. (2003)
	Al-impregnated fly ash	7.0–15.4	30–60	Banerjee et al. (2003)
	NaOH-activated fly ash	18.87	20–25	Visa et al. (2012)
	Fly ash	0.25–2.8	20	Bayat (2002a)
	Afsin-Elbistan fly ash	0.25–1.19	20	Bayat 2002b
	Seyitomer fly ash	0.07–1.30	20	Bayat 2002b
	Bagasse fly ash	2.34–2.54	30–50	Gupta and Ali (2000)
	Bagasse fly ash	13.21	30	Gupta et al. (2003)
	Fly ash	0.068–0.75	0–55	Weng and Huang (2004)
	Fly ash porous pellet	17.66	25	Papandreou et al. (2011)

These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[a] In the unit of (mg g^{-1}) unless specified

utilization of low-cost materials as the adsorbent. Generally, the low-cost adsorbent materials are referred to those available at free cost and exist abundantly in nature. They may also represent the unused resources after a manufacturing process with serious disposal problems. Apparently, utilization of naturally occurring material or locally available agricultural waste materials or industrial by-products as the adsorbents in removing heavy metals

Table 4 Adsorption capacities of metals by rice husk

Metals	Adsorbent	Adsorption capacity[a]	Temperature (°C)	References
As(III)	Copolymer of iron and aluminium impregnated with active silica derived from rice husk ash	146	–	Abo-El-Enein et al. (2009)
As(V)	Rice husk	615.11	–	Roy et al. (1993)
	Quaternized rice husk	18.98	–	Lee et al. (1999)
Au(I)	Rice husk	64.10	40	Nakbanpote et al. (2002)
	Rice husk	50.50	30	Nakbanpote et al. (2002)
	Rice husk	39.84	20	Nakbanpote et al. (2002)
Cd(II)	Partial alkali digested and autoclaved rice husk	16.7	–	Krishnani et al. (2008)
Cd(II)	Phosphate-treated rice husk	103.09	20	Ajmal et al. (2003)
	Rice husk	73.96	–	Ye et al. (2010)
	Rice husk	4	–	Tarley et al. (2004)
	NaOH-activated rice husk	125.94	–	Ye et al. (2010)
	NaOH-activated rice husk	7	–	Tarley et al. (2004)
	Rice husk ash	3.04	–	
	Polyacrylamide-grafted rice husk	0.889	–	Sharma et al. (2009)
	Partial alkali digested and autoclaved rice husk	9.57	–	Krishnani et al. (2008)
Cr(III)	Rice husk	1.90	–	Marshall et al. (1993)
Cr(VI)	Rice husk ash	26.31	–	
	Formaldehyde-treated rice husk	10.4	–	Bansal et al. (2009)
	Pre-boiled rice husk	8.5	–	Bansal et al. (2009)
Cu(II)	Rice husk	0.2	–	Srivastava et al. (2008)
	Rice husk	7.1	–	Nakbanpote et al. (2007)
	Rice husk ash	11.5191	–	Feroze et al. (2011)
	Raw rice hush	4.90	–	Luo et al. (2011)
	Expending rice husk	8.02	–	Luo et al. (2011)
	RH-cellulose	7.7	–	Nakbanpote et al. (2007)
	Rice husk heated to 300 °C (RHA300)	6.5	–	Nakbanpote et al. (2007)
	Rice husk heated to 500 °C (RHA500)	16.1	–	Nakbanpote et al. (2007)
	Microwave incinerated rice husk ash (800 °C)	3.497	–	Johan et al. (2011)
	Microwave incinerated rice husk ash (500 °C)	3.279	–	Johan et al. (2011)
	Partial alkali digested and autoclaved rice husk	10.9	–	Krishnani et al. (2008)
	Carbonized rice husk	42.1	15	Ye et al. (2012)
	Carbonized rice husk	45.5	25	Ye et al. (2012)
	Carbonized rice husk	55.2	35	Ye et al. (2012)
Fe(II)	Copolymer of iron and aluminium impregnated with active silica derived from rice husk ash	222	–	Abo-El-Enein et al. (2009)
Hg(II)	Rice husk ash	6.72	30	Feng et al. (2004)
	Rice husk ash	9.32	15	Feng et al. (2004)
	Polyaniline/rice husk ash nanocomposite	Not determined	–	Ghorbani et al. (2011)
	Partial alkali digested and autoclaved rice husk	36.1	–	Krishnani et al. (2008)

Table 4 continued

Metals	Adsorbent	Adsorption capacity[a]	Temperature (°C)	References
Mn	Copolymer of iron and aluminium impregnated with active silica derived from rice husk ash	158	–	Abo-El-Enein et al. (2009)
	Partial alkali digested and autoclaved rice husk	8.30	–	Krishnani et al. (2008)
Ni(II)	Microwave-irradiated rice husk (MIRH)	1.17	30	Pillai et al. (2009)
	Partial alkali digested and autoclaved rice husk	5.52	–	Krishnani et al. (2008)
Pb(II)	Rice husk ash	12.61	30	Feng et al. (2004)
	Rice husk ash	12.35	15	Feng et al. (2004)
	Partial alkali digested and autoclaved rice husk	58.1	–	Krishnani et al. (2008)
	Tartaric acid modified rice husk	21.55	–	Tarley et al. (2004)
Zn(II)	Rice husk ash	14.30	–	
	Rice husk ash	7.7221	–	Feroze et al. (2011)
	Rice husk ash	5.88	–	
	Partial alkali digested and autoclaved rice husk	8.14	–	Krishnani et al. (2008)
	Rice husk-polyaniline nanocomposite	24.3	–	Ghorbani et al. (2012)

These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[a] In the unit of (mg g^{-1}) unless specified

from wastewaters is not only cost effective in heavy metal removal, but it also contributes to a zero waste situation in the environment.

A numerous studies have been carried out to investigate as well as to further improve the usage of different low-cost adsorbent materials for adsorption of individual or multiple heavy metals in an aqueous solution. These low-cost adsorbents range from industrial by-products, agriculture waste to biosorbents, for example, wood bark, sawdust, mangoes teen peel, durian husk, oil palm empty fruit bunch, tea leaves, exhausted coffee, etc. In this section, some of the intensively studied low-cost adsorbents such as fly ash, rice husk, wheat straw, chitin and chitosan composites as well as algae and bacteria were discussed in terms of their efficiency for heavy metal removal. Recent reported adsorption capacities of the selected adsorbents are presented in Tables 3, 4, 5 and 6 to give some idea of adsorbent effectiveness. It is interesting to note that the reported values are strongly dependent on the experimental condition. Therefore, it is advisable for the reader to refer to the original work in order to have a better understanding on the specific conditions that have been imposed on the adsorption process.

Fly ash

Fly ash is an industrial by-product which is usually grey in colour, abrasive, mostly alkaline and refractory in nature. It contains mainly silica (SiO_2) of ~47 %, alumina (Al_2O_3) of ~25 %, iron oxide (Fe_2O_3) of ~16 % and calcium oxide (CaO) of ~5 % with varying amounts of carbon, calcium, magnesium and sulphur. The variations that are commonly found in fly ash, either in terms of their chemical composition or physical properties, are most likely due to different sources of coal as well as diversity in the design of coal-fired boilers. However, an empirical formula for fly ash based on the dominance of certain key elements has been proposed as below (Iyer and Scott 2001):

$$Si_{1.0}Al_{0.45}Ca_{0.51}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011}.$$

Fly ash has been used effectively as raw material in cement and brick production, soil amendment and as filler in road works. Besides, it can also be converted into zeolite, another versatile material which is widely used as catalyst and adsorbent due to its outstanding high surface area and porosity. However, all the fly ash produced from the power industry cannot be reused by these applications. Consequently, most of the fly ash generated is disposed of as landfill, a practice which is under examination for environmental concerns. Therefore, continuing research efforts have been made to explore other applications prior to discarding in order to lessen the environmental burden. Since fly ash is enriched with SiO_2 and contains a portion of unburned carbon, this material is potentially used as low-cost adsorbent to remove heavy metal from wastewaters. A lot of investigations have been reported on the usage of fly ash in adsorption of heavy metal from aqueous solution and overall, the results obtained are encouraging.

Table 3 summarized the adsorption capacities of different heavy metals by different fly ashes. In some of the works, the researchers found that the unburned carbon in fly ash is partly activated during the combustion process, resulting in a relatively high surface area and good porosity (Wang and Li 2007; Lu et al. 2008). These characteristics of unburned carbon are similar to that of activated carbon; hence, fly ash could be a potential adsorbent and substitute of commercial activated carbon. Recently, biomass fly ash has attracted attention to be used as adsorbent in wastewaters treatment (Pengthamkeerati et al. 2008). It could be a better adsorbent as compared to other fly ash due to its higher percentage of unburned carbon.

Table 5 Adsorption capacities of metals by wheat-based materials

Metals	Adsorbent	Adsorption capacity[a]	References
Cd(II)	Wheat straw	39.22	Farooq et al. (2011)
	Wheat straw	14.56	Dang et al. (2009)
	Wheat bran	21.0	Farajzadeh and Monji (2004)
	Wheat bran	101	Özer and Pirincci (2006)
Cr(III)	Wheat straw	21.0	Chojnacka (2006)
	Wheat bran	93.0	Farajzadeh and Monji (2004)
Cr(VI)	Wheat straw	47.16	Dhir and Kumar (2010)
	Wheat bran	35	Dupont and Guillon (2003)
	Wheat bran	310.58	Singh et al. (2009)
Cu(II)	Wheat straw	11.43	Dang et al. (2009)
	Wheat straw-citric acid treated	78.13	Gong et al. (2008)
	Wheat bran	12.7	Dupont et al. (2005)
	Wheat bran	6.85	Wang et al. (2009)
	Wheat bran	15.0	Farajzadeh and Monji (2004)
Hg(II)	Wheat bran	70.0	Farajzadeh and Monji (2004)
Ni(II)	Wheat straw	41.84	Dhir and Kumar (2010)
	Wheat bran	12.0	Farajzadeh and Monji (2004)
Pb(II)	Wheat bran	62.0	Farajzadeh and Monji (2004)
	Wheat bran	79.4	Özer and Pirincci (2006)
Zn(II)	Wheat bran	16.4	Dupont et al. (2005)
U(VI)	Wheat straw	19.2–34.6	Wang et al. (2011)

These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[a] In the unit of (mg g^{-1})

Rice husk

In rice milling industries, rice husk which is the hard outer shell of the rice grain is generated as the major by-product or waste, accounting for almost 20 % of the rice production. Throughout the world, the annual generation of rice husk was approximately 120 million tonnes in 2009, leading to serious environmental problems as the rice husk is usually disposed in the end of the production. It is considered as a lignocellulosic agricultural by-product that contains approximately 32 % cellulose, 21 % hemicelluloses, 21 % lignin, 20 % silica and 3 % crude proteins (Nadzi et al. 2007).

Obviously, the utilization of this abundant scaly residue will yield economic as well as environmental dividends. Therefore, exploration of possible usage of the rice husk is of great significance in many rice producing countries. The high content of cellulose, a polymer contains three reactive hydroxyl groups has made rice husk a potential adsorbent material. However, both lignin and silica that present in rice husk tend to reduce the binding between accessible functional group on the surface of rice husk and adsorbate ions/molecules. Therefore, considerable researches have been carried out to modify or treat the rice husk via different methods prior to the application in heavy metal removal. Adsorption capacities of metals by untreated and treated rice husk are presented in Table 4.

Wheat straw and wheat bran

Wheat (*Triticum aestivum*) is the major food crop of the world. Every year, over 200 million tons of wheat straw are produced, and every 100 million ton of wheat can create 25 million tons of bran. In addition to their use as feed and fuel, large amounts of redundant wheat straw and bran must be disposed of. Therefore, finding new applications for these abundantly available waste materials is a challenge to the wheat production countries. The wheat straw is a lignocellulosic agricultural waste consisting of about 34–40 % cellulose, 20–35 % hemicellulose, 8–15 % lignin and sugars as well as other compounds carrying different functional groups like carboxyl, hydroxyl, sulphydryl, amide and amine. As attempt to fully utilize these industry by-products, both wheat straw and wheat bran have been investigated for their adsorption behaviour towards metal ions (Table 5). The high adsorption capability of straw is closely related to high content of cellulose, presence of different functional groups and porosity of the material.

Table 6 Adsorption capacities of metals by chitosan and chitosan composites

Metal	Adsorbent	Adsorption capacity[a]	Temperature (°C)	References
Cd(II)	Chitosan/clay beads	72.31	25	Tirtom et al. (2012)
	Chitosan/cotton fibres (via Schiff base bond)	15.74	25	Zhang et al. (2008)
	Chitosan/glutaraldehyde	32.9	25	Vitali et al. (2008)
	Chitosan/perlite	178.6	25	Shameem et al. (2006)
	Chitosan/PVA	142.9	50	Kumar et al. (2009)
	Chitosan/xanthate	357.14	RT	Sankararamakrishnan et al. (2007)
Co(II)	Chitosan/clinoptilolite	467.90	25	Dinu and Dragan (2010)
Cr(III)	Chitosan/Reactive Blue 2	11.2	25	Vasconcelos et al. (2007)
Cr(VI)	Chitosan-coated acid-treated oil palm shell charcoal (CCAB)	60.25	–	Nomanbhay and Palanisamy (2005)
	Chitosan-coated oil palm shell charcoal (CCB)	52.68	–	Nomanbhay and Palanisamy (2005)
	Chitosan/ceramic alumina	153.8	25	Veera et al. (2003)
	Magnetic chitosan	69.40	–	Huang et al. (2009)
	Chitosan/montmorillonite	41.67	25	Fan et al. (2006)
	Chitosan/perlite	153.8	25	Shameem et al. 2003
Cu(II)	Chitosan/alginate	67.66	–	Wan Ngah and Fatinathan (2008)
	Chitosan/cellulose	26.50	25	Sun et al. (2009)
	Chitosan/clinoptilolite	574.49	–	Dragan et al. (2010)
	Chitosan/clinoptilolite	719.39	25	Dinu and Dragan (2010)

These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions

[a] In the unit of (mg g^{-1})

The reported metal adsorption capacities of wheat-based materials could depend on the structure of wheat bran used in different studies, along with other parameters.

Chitin, chitosan and chitosan composites

Chitin is a naturally and abundant occurring mucopolysaccharide from exoskeletons of insects, crustaceans shells, fungi cellular walls, annelids and molluscs. It is the second most abundant polymerin nature after cellulose. Chitin contains 2-acetamido-2-deoxy-β-D-glucose through a β (1 → 4) linkage. Through deacetylation process of chitin, a type of natural poly(aminosaccharide) so-called chitosan is produced. The chitosan consists mainly of poly (1 → 4)-2 amino-2-deoxy-D-glucose unit, and this derivative biopolymer has been known as a promising polymeric material of great scientific interest due to its special characteristics, for instance, hydrophilicity, biocompatibility, biodegradability, non-toxicity, good adsorption properties and wide range of applications. The chitosan has drawn particular attention for its feasible application in a variety of forms, from flake-types to gels, beads and fibres. Due to high content of amino and hydroxyl groups in chitosan, this by-product material has been found to be able on adsorbing several heavy metals, including copper, chromium, silver, platinum and lead physically or chemically. In fact, chitosan has binding capacities of more than 1 mmol/g for heavy metals which is far greater than that of activated carbon.

The extend of metal adsorption depends strongly on the chitosan source, deacetylation degree, nature of metal ion, variations in crystallinity, amino content and solution pH. A great number of chitosan derivatives have been obtained by introducing selected functional groups into the polymeric matrix of chitosan in order to enhance its interaction with variety of metallic ions, thus increase the adsorption capacity and selectivity for metal ions in solution. The reported chitosan derivatives are those containing nitrogen, phosphorus and sulphur as heteroatoms, and other derivatives such as chitosan crown ethers and chitosan ethylenediaminetetraacetic acid (EDTA)/diethylenetriaminepentaacetic acid (DTPA) complexes. Apart from that, chitosan composites have also been extensively investigated for heavy metal removal. Various types of substance have been used to form composite with chitosan, including activated clay, bentonite, montmorillonite, polyurethane, poly vinyl alcohol, poly vinyl chloride, kaolinite, oil palm ash and perlite. Table 6 shows the heavy metal removal capacities through adsorption process using these modified chitosan materials.

Conclusions

Removal of heavy metals from aqueous environment is indeed a challenging problem in the control of environmental pollution. A wide range of treatment technologies such as chemical precipitation, ion exchange, membrane filtration and adsorption can be employed to remove heavy metals, but these treatment methods still suffer from some inherent limitations. For instance, chemical precipitation, which has been traditionally and widely used to remove heavy metals from contaminated sources, is often associated with huge sludge production. Ion exchange process is generally applicable to treat or remove heavy metals at low concentration. As for membrane filtration, problems such as membrane fouling, high maintenance cost and low permeate flux are often unavoidable. Taking all these into considerations, the adsorption process thus appeared as one of the most promising methods. Various low-cost adsorbents have been investigated intensively in order to avoid the usage of costly activated carbon. It is evident that in most of the reported works, the study is still being centralized in the maximum adsorption capacities of the materials. While most of the low-cost adsorbents have shown its potential in heavy metal removal without any modifications, but it is interesting to note that their removal capabilities can generally be improved through certain chemical modifications. Also, more than one factors such as pH, contact time, initial influent concentration, temperature, adsorbent and dosage can significantly affect the adsorption process.

Future direction

Several low-cost adsorbents can be seen as attractive alternatives for the removal of heavy metals based on their outstanding removal ability. However, in most of the cases, attention seems to be focused on the maximum adsorption capacity of the low-cost adsorbents and the model pollutants are mainly synthetic types. In order to fully utilize the application of these materials in wastewater treatment, their removal efficiency should be further tested in effluents from industries. Besides, the characterization of the adsorbents as well as the study of the sorption mechanism is equally important. More effort is required to provide insight into the direction of modelling, the effects of adsorbent recycling and regeneration and the recovery of heavy metals from wastewater. The possibility of immobilized these adsorbents can also be viewed as a feasible approach as suspended system requires a filtration step which is not suited for practical applications. If modification is needed, it is desirable to have a material with a wide range of metal affinities as this will be particularly useful for industrial effluents which carry more than one type of metals. Further research involving the combination of methodologies/system should also be encouraged as this would minimize or overcome the problem associated with a single treatment process.

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