REVIEW

Regeneration of adsorbents and recovery of heavy metals: a review

S. Lata · P. K. Singh · S. R. Samadder

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Abstract In last a few decades, significant improvements were made in both efficiency and economy for removal of heavy metals and metalloid (arsenic) from water using adsorbents. But less attention was paid to recycling of used adsorbents and recovery of the heavy metals from the desorbing agents. For regeneration and reuse of adsorbents, various possible regenerating agents such as acids, alkalis and chelating agents (such as ethylene diamine tetraacetic acid) were used by many researchers with very limited success in some of the studies only up to a limited number of adsorption-desorption cycles. Only a few of the reported studies were focused on recovery of adsorbed (from saturated adsorbents) and desorbed metals (from regenerating agents). Though the management of the used adsorbent and recovery of heavy metals is one of the most important aspects, but only a limited number of research works considered the fate of spent adsorbents before disposal. This review summarizes the removal efficiency of various adsorbents, desorption efficiency of various regenerating agents and recovery of the heavy metals from both saturated adsorbents and desorbing solvents used for regeneration. The study will help the scientific community working on adsorption studies to take up research initiatives required to address the feasible recovery methods of heavy metals from the used adsorbents, to study the possible reuse of the desorbing agents and to choose a suitable desorbing/regenerating agent for a particular adsorbent.

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Introduction

Both surface water and groundwater were reported to be contaminated by various contaminants from natural and anthropogenic sources worldwide (Tzou et al. 2007). These contaminants may be organic or inorganic in nature, including heavy metals. Metals such as cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) are commonly associated with pollution and toxicity problems (O'Connell et al. 2008). Among metalloids such as boron, silicon, germanium, arsenic, antimony and tellurium, arsenic toxicity is of major concern. In drinking water, arsenic predominantly occurs in inorganic (arsenite, arsenate) and organic forms (methyl and dimethyl arsenic compounds) (Smedley and Kinniburg 2002). It was reported in a study of six administrative blocks of district Murshidabad of West Bengal (India) that about 1,248,580 people are exposed to arsenic concentrations above 0.05 mg/L (Samadder 2011). Mercury is another highly toxic heavy metal that should be removed. It is a neurotoxin that can cause damage to the central nervous system. High concentrations of mercury cause impairment of pulmonary and kidney function, chest pain and dyspnoea (Namasivayam and Kadirvelu 1999). Exposure to lead causes anemia, diseases of the liver and kidneys, brain damage and ultimately death (Jain et al. 1989). Though the presence of heavy metals is common in our environment and in the food chain that are necessary for survival of sustainable ecosystem, but excess amount of any of these heavy metals in the food chain may lead to acute or chronic poisoning. Heavy metal toxicity affects the nervous system, reduces energy level, alters blood composition and subsequently affects lungs, kidney, liver and other vital organs. Long-term exposure may lead to muscular and neurological degenerative disorder, including



alzheimer's disease, parkinson's disease, muscular dystrophy and multiple sclerosis. Repeated exposure to higher concentration of these heavy metals may even cause cancer (Baldwin and Marshal 1999). Heavy metals are nonbiodegradable, persistent and get accumulated in nature and thus are the sources of environmental pollution. Various anthropogenic sources such as industrial effluents, waste water disposal (Praveena et al. 2008), agricultural return flows (Conceição et al. 2013) and domestic sewage release heavy metals into the aquatic environment (Hejabi et al. 2010). Heavy metal(s) are widespread pollutants and pollute the environment such as air (Chiou et al. 2009), soil (Moaref et al. 2014) and water. The presence of these metals in the environment is now a grave matter of concern. To minimize the health risk and for the management of environmental degradation, strict quality standards were imposed for both drinking water and effluent discharge. Compliance with these strict standards is now a major challenge for the industries, drinking water providers and scientists alike for proper treatment of groundwater, surface water and industrial wastewater containing heavy metals (Tzou et al. 2007). There are several physical, chemical or biological techniques that are used for the treatment of groundwater, surface water and wastewater such as coagulation, filtration, flocculation, adsorption, reverse osmosis, activated sludge process, chemical precipitation, membrane separation process and bioremediation. Conventional methods for treating effluents, such as precipitation, redox, membrane technologies and electrolvsis, are costly and have problem of secondary waste generation (sludge) (Crini 2005). The safe disposal of sludge is another issue for the industries (Mamatha et al. 2013). Heavy metal(s) and metalloid (arsenic) removal techniques include coagulation and flocculation, precipitation, adsorption, ion exchange and membrane filtration. Alternative methods such as ozone oxidation, bioremediation and electrochemical treatments are also used in the removal of arsenic (Ahmed 2001, 2005; Mandal and Sujuki 2002; Choong et al. 2007). Among the various available techniques for water and wastewater treatment for heavy metal removal, adsorption is considered as the most attractive technique (Mohan and Pittman 2007). Adsorption technique has several advantages over other techniques, such as it is easy to implement in field condition, it has the potential regeneration capacity and the operation is sludge free, and has a high removal efficiency of metal ions (Ahmaruzzaman and Gupta 2011; Wu et al. 2013; Ranjan et al. 2009). Continuous improvements are being reported for the development of effective and suitable adsorbents for achieving higher removal efficiency (Gupta and Nayak 2012). Fu and Wang (2011) found different types of adsorbents such as (1) activated carbon, (2) carbon nanotubes, (3) low-cost adsorbents and (4) bio-adsorbents that



have been used for adsorption studies. They suggested that biosorption of heavy metals from aqueous solutions is relatively a new process that has been confirmed as a promising process in the removal of heavy metals. Davis et al. (2003) removed cadmium [Cd(II)], copper [Cu(II)], zinc [Zn(II)], lead [Pb(II)], chromium [Cr(III)] and mercury [Hg(II)] using the same adsorbent (brown algae). Similarly, Iqbal et al. (2002) performed both adsorption/ desorption study and removed heavy metals such as nickel [Ni(II)], Pb(II), Cd(II), Cu(II), Cr(III) and Zn(II) from contaminated water by using bio-adsorbent (petiolar felt sheath of palm-PFP). But in most of the studies, it was found that a single adsorbent was not effective for different types of water pollutants. Adsorption has other limitations also such as it could not achieve a good status at commercial levels due to lack of suitable adsorbents of high adsorption capacity and availability of commercial scale columns (Grassi et al. 2012). Moreover, less attention has been paid to the disposal or recycling of used adsorbents containing adsorbed heavy metals. Gupta et al. (2000) reviewed the efficiency of bio-adsorbents for removal of heavy metal(s) and suggested that biosorption depends on the efficiency of the regeneration of bio-adsorbents after metal desorption. The disposal of used adsorbents containing heavy metal(s) may be done after recovery of contaminants or directly without heavy metal recovery, but in both the cases there will be secondary pollution from the used adsorbents and the chemicals used to treat the adsorbents for metal recovery (Tzou et al. 2007). However, metal-loaded adsorbents have toxic effects on humans and environment. Therefore, the used adsorbents should be released into the environment only after recovery of the heavy metals completely. Considering the need of metal desorption and recovery, this paper summarizes the efficiency of various regenerating agents used by different authors, efficiency of the adsorbents for removal of heavy metals, and recovery of heavy metals.

Review of literature

The technologies that are available today for the removal of heavy metal(s) can be evaluated on the basis of three main criteria: (a) performance, (b) cost and (c) appropriateness. The appropriateness refers to the technologies that suits better the condition of the place where it has to be applied or installed (Murcott 1999). Apart from this, the technology should meet other technical criteria such as robustness and should not cause any adverse effect on the environment due to by-products of the technique, and the technique should have the capacity to provide water in adequate quantity in different seasons and in varying climatic conditions (Duarte et al. 2009). Vu et al. (2003) studied arsenic removal and mentioned that for the developing countries such as Vietnam and Bangladesh, it is not feasible to install large-scale treatment plant for arsenic removal from drinking water and maintain the acceptable limit of arsenic in drinking water (10-50 µg/l). So a lowcost, effective technology applicable at household or at community level is required. Various studies were reported for removal of heavy metals using various adsorbents to achieve a desirable target of removal efficiency. Adsorption on activated carbon has been found to be superior compared to other chemical and physical methods for both water and wastewater treatment in terms of its capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics and its simplicity in design (Tan et al. 2008; Bhatnagar et al. 2010). It has been observed that adsorption using different materials such as activated carbon (Huang and Fu 1984; Chuang et al. 2005), activated alumina (Lin and Wu 2001; Singh and Pant 2004), silica gel, basic yttrium carbonate (Wasay et al. 1996a, b), metalloaded coral limestone (Maeda et al. 1990), hematite (Giménez et al. 2007), feldspar (Singh et al. 2002) and hydrous zirconium oxide (Hang et al. 2012) have been used by several researchers. But most of them are not suitable for developing nations due to their high cost, low removal efficiency (Manju et al. 1998; Ranjan et al. 2009) and loss during regeneration (Sud et al. 2008). For this desorption is found to be better solution as it decreases the process cost and also the dependency of the process on a continuous supply of the biosorbent. A successful desorption process requires the proper selection of elutants, which strongly depends on the type of biosorbent and the mechanism of biosorption. Elutant must not damage the biomass and should be cost effective and eco-friendly (Das 2010).

For removal of arsenic from water, Manju et al. (1998) carried out batch studies using copper-impregnated activated coconut husk carbon. They observed maximum adsorption at pH 12.0. For regeneration of exhausted copper-impregnated activated coconut husk carbon, they used distilled water and 30 % H₂O₂ in 0.5 M HNO₃ solution separately. After regeneration, the spent adsorbent was treated with acetone and 0.1 M CuSO₄·5H₂O solution to restore original state and used for subsequent runs. Baipai and Chaudhari (1999) reported a column study and designed an arsenic removal unit using manganese dioxidecoated sand as adsorbent. They suggested the use of 0.2 N NaOH solutions as regenerating solution followed by backwashing with the treated water to regenerate the media. During regeneration, 85 % of the removed arsenic was recovered in the first cycle, and then, 94.6-98.3 % arsenic was recovered in the subsequent cycles in column study, but the recovery of arsenic was reduced to 82.3 % on field condition. The study was of limited scope as it did not address the effect of some important factors, such as water pH, concentration and type of competing anions, and cations that form soluble arsenic complexes. Using the same desorbent (NaOH), Xu et al. (2002) performed both column and batch studies for arsenic removal. They found NaOH effective to desorb the As(V) from aluminum-loaded Shirasu-zeolite adsorbent. In an another study for arsenic desorption, Thirunavukkarasu et al. (2003) used 4 1 of 0.3 M NaOH solution for regeneration of IOCS-2, followed by backwashing with deionized water. In acid digestion during treatment, regeneration and backwashing operation, 8 % of iron was lost from IOCS-2. This loss of iron might lead to decrease in adsorption efficiency. The recoveries of arsenite and arsenate were found to be 80-83 and 84-87 %, respectively, up to four cycles (Table 1). Kamala et al. (2005) also considered NaOH as desorbing agent and performed column study. They used immobilized biomass (Garcinia cambogia) as adsorbent, and they reused over five cycles of loading and elution, while desorption of arsenic from anion exchanger derived from coconut coir pith was carried out using 0.1 M HCl and 93-96 % regeneration efficiency was achieved (Anirudhan and Unnithan 2007; Table 1). But a small fraction of the adsorbate could not be recovered by regeneration due to very strong bond; as a result, adsorption capacity of the adsorbent reduced in subsequent cycles. 0.1 M NaOH was proved as a promising regenerating agent in a study by Zhu et al. (2009) as they found nearly 100 % desorption efficiency for arsenic from nano-zero-valent iron (Table 1). No reduction in adsorption efficiency was observed up to 8 cycles of adsorption-desorption studies. But, the recovery of arsenic from the alkaline solution (desorbing agent) was not addressed. Tian et al. (2011) used magnetic wheat straw with varying iron concentrations of 0.1 mol/L (MWS1), 0.2 mol/L (MWS2) and 0.5 mol/L (MWS5), respectively, for arsenic adsorption. The regeneration study of magnetic wheat straw was done using 0.1 mol/L NaOH aqueous solutions, and more than 80 % recycling efficiency was achieved up to 10 cycles (Table 1). In another study, Zhou and Haynes (2012) used three different desorption agents (NaNO₃, HNO₃ and NaOH) with different concentrations showed better desorption of arsenate [As(V)] and selenate [Se(VI)]. For regeneration, the metalloaded red mud (adsorbent) was shaken in 0.5 M NaOH for 1 h to remove the adsorbed metal. NaOH was more effective desorbent than HNO₃. In first desorption cycle, use of 0.1 N and 0.5 N NaOH was very effective for removing As(V) (78-85 %) but was less effective for As(III) (only 26-49 %).

Zhang et al. (2009) used 0.1 M NaOH for desorption of Se(IV) from titanium dioxide nanoparticles and found more than 95 % desorption efficiency. They found 95-105 % recovery for Se(IV) (Table 1). Using same desorbent with different concentration (0.5 N NaOH), Zhou



S. no.	Author(s)	Adsorbent (s) used	Metal (s) removed	Removal efficiency $(n = n0. \text{ of cycles})$	Desorbing/ regenerating agent (s) used	Desorption/ regenerating efficiency (n = n0. of	Recovery of metals $(n = n0. \text{ of cycles})$	Observation
(1)	(2)	(3)	(4)	(5)	(9)	cycles) (7)	(8)	(6)
<u>1</u> .	Benjamin et al. (1996)	Iron-oxide-coated sand	Pb(II) Cd(II) Cu(II)	307.6 mg/l n = 3 319.2 mg/l n = 3 395.8 mg/l n = 3	Water/acid recovery/base recovery	I	101 % 86 % 84 %	Most of the metals are recovered efficiently, but recovery of AsO ₃ is not efficient neither with acid nor with base
	Manju et al. (1998)	Copper- impregnated activated coconut husk carbon	As(III)	22.15 mg/g (88.6 %), 21.50 mg/g (86.0 %), 20.35 mg/g (81.6 %) n = 3	30 % H ₂ O ₂ in 0.5 M HNO ₃	20.84 (mg/g) 19.45 (mg/g) 16.97 (mg/g) n = 3	94.08 % 90.46 % 83.40 % n = 3	Used distilled water and $H_2O_2 + HNO_3$ for metal desorption and recovery but distilled water did not give satisfactory result; however, $H_2O_2 + HNO_3$ has given better results. Fate of spent adsorbent should be studied
3.	Bajpai and Chaudhuri (1999)	Manganese dioxide-coated sand	As(III) As(V)	1	0.2 N NaOH and Water	I	94.6-98.3% (n = 10)	Further study is required for the treatment of used adsorbent for safe disposal
4	Iqbal et al. (2002)	Petiolar felt sheath palm	Ni(II) Pb(II) Cd(II) Cu(II) Zn(II) Zn(II)	$96.7 \pm 1.4 \%$ $96.9 \pm 0.9 \%$ $76.3 \pm 1.4 \%$ $89.8 \pm 1.1 \%$ $77.5 \pm 2.3 \%$ $56.9 \pm 1.2 \%$ (n = 3)	Deionized water and 0.1 M HCI	99.9 \pm 0.1 % 99.6 \pm 0.2 % 96.9 \pm 0.6 % 97.0 \pm 0.9 % 99.9 \pm 0.1 % 60.6 \pm 1.4 % (n = 3)	I	Further study on larger scale for removal of mixture of heavy metals from the same adsorbent to be done
ý.	Jalali et al. (2002)	Algal biomass (<i>Sargassum</i> spp.)	Pb(II)	1	0.1 M HNO ₃ , 0.1 M CaCl ₂ and distilled water	1	95 %	98 % of lead-retaining capacity of adsorbent maintained after 10 adsorption–desorption cycles but actual adsorption capacity and fate of spent adsorbents are not clear. Metal recovery from the regenerating solution has not been studied
6.	Jeon et al. (2002)	Carboxylated alginic acid	Pb(II)	3.09 ± 0.06 mmol/ g dry mass	NTA (nitrilotriacetic acid.)	$80\pm1.3~\%$	I	NTA was found to be better eluent than EDTA

Table	Table 1 continued							
S. no.	Author(s)	Adsorbent (s) used	Metal (s) removed	Removal efficiency $(n = n0. \text{ of cycles})$	Desorbing/ regenerating agent (s) used	Desorption/ regenerating efficiency (n = no. of cvcles)	Recovery of metals $(n = n0. of cycles)$	Observation
(1)	(2)	(3)	(4)	(5)	(9)		(8)	(6)
7.	Liu et al. (2002)	Spherical cellulose adsorbent	Cu(II)	30.8 mg/g	HCI	1	100 % when 2.4 mol/L HCl solution is used	Used both HCl and NaOH. Cu(III) recovery is quite high using HCl. 2.6 % adsorption capacity decreased after 20 cycles and 7.2 % after 30 cycles. The concern is the disposal of spent adsorbent
×	Xu et al. (2002)	Aluminum-loaded Shirasu-zeolite (Al-SZP)	As (V)	99 % (0.13 mM; 20 ml, adsorbent dose 0.05 g)	0.04 M NaOH	% 16	I	In column study, 85 % adsorption capacity maintained after 2 adsorption/desorption cycles. Disposal option was not mentioned
<u>.</u>	Ajmal et al. (2003)	Phosphate-treated rice husk	Cd(II)	99 % (at pH 12)	0.1 M HCI	53.9 %	1	Recovery of Cd(II) from synthetic wastewater by column operation (83.9 %) was better than a batch process (53.9 %)
10.	Bai and Abraham (2003)	Immobilized fungal biomass (<i>Rhizopus</i> <i>nigricans</i>)	Cr(VI)	101.5 mg/g from 500 mg/l solution	0.01 N NaOH, NaHCO ₃ and Na ₂ CO ₃	78 % regeneration efficiency (after $n = 25$)	111-115 %	Used solution of NaOH, NaHCO ₃ and Na ₂ CO ₃ as desorbing agents. However, Na ₂ CO ₃ showed more regeneration efficiency of 91.91 \pm 3.9 %, in comparison with other eluent used
÷	Thirunavakk -arasu et al. (2003)	Iron-oxide-coated sand	As(III) As (V)	85.2 mg/l 50.1 mg/l 45.0 mg/l 45.0 mg/l <i>n</i> = 4 76.1 mg/l 76.1 mg/l 37.3 mg/l 34.7 mg/l <i>n</i> = 4	0.3 M NaOH	68 mg/l 40.4 mg/l 36.9 mg/l n = 4 64.2 mg/l 37.1 mg/l 32.1 mg/l 30.1 mg/l n = 4	 80 % 81 % 82 % 83 % n = 4 84 % 87 % 86 % n = 4 	Iron loss from the coated sand during acid digestion reduced the adsorption capacity. Recovery option for arsenic from NaOH solution must be considered

S. no. Author(s)	Author(s)	Adsorbent	Metal	Removal efficiency	Desorbing/ recenerating	Desorption/ recenerating	Recovery of metals	Observation
					agent (s) used	efficiency $(n = n0. \text{ of } cvcles)$		
(1)	(2)	(3)	(4)	(5)	(9)	(7)	(8)	(6)
12.	Jeon and Park (2005)	Aminated chitosan bead	Hg(II)	1	EDTA	% 56	1	Adsorption capacity of the recycled beads remained 90 % level up to fifth cycle but accurate adsorption capacity was not mentioned. EDTA was found to be most effective desorbent among HCl, HNO ₃ and EDTA. Metal recovery option is well defined in this study. But fate of used adsorbent must be studied further
13.	Gong et al. (2005)	Intact biomass (Spirulina maxima) Pretreated biomass (Spirulina maxima)	Pb(II)	84 % 92 %	HNO ₃ (pH-1.00)	92 % 93 %	I	EDTA also gave higher desorption (91 %) for both treated and untreated adsorbents
14.	Hu et al. (2005)	Maghemite (γ- Fe ₂ O ₃)	Cr(VI)	97.3 % (at initial conc. 50 mg/L)	0.01 M NaOH	87.7 % <i>n</i> = 6	1	Used basic solution of NaOH, Na ₂ CO ₃ and Na ₃ PO ₄ . But NaOH was found to be most effective. After desorption, disposal of metal-free adsorbent was not considered
15.	Kamala et al. (2005)	Immobilized biomass (<i>Garcinia</i> <i>cambogia</i>)	As(III)	95 % (at initial conc. 500 mg/L, adsorbent dose 5 g/L)	NaOH (0.1, 0.15, 0.2 M)	~ 100 %	1	Performed column study. NaOH eluted the bound arsenic without damaging the biomass. Though metal-free used biomass is biodegradable. But disposal should also be mentioned
16.	Saeed et al. (2005)	Papaya wood	Cu(II) Cd(II) Zn(II)	9.65 ± 0.04 9.33 ± 0.08 5.72 ± 0.08 (in mg/g)	0.1 N HCI	99.4 % 98.5 % 99.3 % <i>n</i> = 5	I	No loss in the efficiency of adsorbent after repeated biosorption-desorption for up to five cycles
17.	Cui et al. (2006)	Clinoptilolite	Acid rock drainage containing heavy metals such as Zn, Fe, Al, Cu, Mg and Mn	1	NaCl, distilled water	18 ppm (for Zn after 30 min.)	1	Order of adsorption of metal ions (found in ARD) was found to be Fe > Al > Cu > Zn > Mg > Mn. But efficiency was not mentioned clearly. Recovery of the desorbed metals from regenerating agent has not been addressed

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Table	Table 1 continued							
S. no.	Author(s)	Adsorbent (s) used	Metal (s) removed	Removal efficiency $(n = n0. \text{ of cycles})$	Desorbing/ regenerating agent (s) used	Desorption/ regenerating efficiency (n = no. of cvcles)	Recovery of metals $(n = n0. \text{ of cycles})$	Observation
(1)	(2)	(3)	(4)	(5)	(9)	(1)	(8)	(6)
18.	Engleman et al. (2006)	Charcoal	97 ⁶⁹	1	Hot 4 M nitric acid	1	98 % $(n = 3)$	Dry ashing with air in a quartz combustion tube at $400-450$ °C was used for recovery of technetium. 96 % (n = 5) metal recovery was achieved. Disposal of spent adsorbent has not been considered
.61	Nayak and Lahiri (2006)	Calcium alginate beads	97-200 Pb 197-200TI ¹⁹⁷ Hg	100 % ~ 65 % 100 %	0.1 M HCl and 0.1 M thiourea HCl, thiourea, sodium acetate, sodium oxalate and sodium nitrite Thiourea, sodium oxalate and oxalate and	8090 % 80-100 %	1	Calcium alginate beads are applicable to wide pH range. After desorption, beads can be reused and since it is biodegradable so safe to be disposed of
20.	Anirudhan and Unnithan (2007)	Coconut coir pith	As(V)	0.49 mg/g (99.5 %) 0.48 mg/g (96.0 %) 0.45 mg/g (90.0 %) 0.43 mg/g (86.8 %) (86.8 %)	0.1 M HCl	0.48 mg/g (96.0 %) 0.48 mg/g (95.7 %) 0.48 mg/g (95.3 %) 0.47 mg/g (93.8 %) 0.3.8 %)	1	Recovery option and ultimate fate disposal have not been considered
21.	Boricha et al. (2007)	Silica gel	Pd(II)	-	2 M HCI	- 2	% 66	99 % palladium was recovered as $PdCl_2$
22.	Deng et al. (2007)	Green algae (Cladophora fascicularis)	Pb(II)	198.5 mg/g at 298 K and pH 5.0	0.01 mo//L EDTA	1	82 %	0.01 mol/L Na ₂ EDTA was found an efficient desorbent (however, desorption efficiency was not motioned) for the recovery of Pb(II) from biomass

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Table	Table 1 continued							
S. no.	Author(s)	Adsorbent (s) used	Metal (s) removed	Removal efficiency $(n = n0. \text{ of cycles})$	Desorbing/ regenerating agent (s) used	Desorption/ regenerating efficiency (n = no. of cycles)	Recovery of metals $(n = n0. \text{ of cycles})$	Observation
(1)	(2)	(3)	(4)	(5)	(9)	(7)	(8)	(6)
23.	Deng et al. (2008)	Marine algal biomass (<i>Cladophora</i> <i>fascicularis</i>)	Cd(II)	1.00 mmol/g	EDTA	83 %	1	HNO ₃ , Ca(NO ₃) ₂ , H ₂ O and EDTA were used as eluents. However, EDTA was found to be most effective regenerating agent. But ultimate fate of biomass has not been addressed
24.	Gupta and Rastogi (2008)	Nonviable cyanobacterium (<i>Nostoc</i> muscorum) biomass	Cr(VI)	22.92 mg/g at 25 °C and pH 3.0.	0.1 M HNO ₃ and EDTA	% 06	80 %	Better desorption and recovery without damaging the adsorbent binding sites
25.	Kuang et al. (2008)	Silver-loaded activated carbon fiber Activated carbon fiber.	Hg(II)	192.3 mg/g 29.4 mg/g (at 70°)	Thermal desorption	94.73 % 69.93 %	I	Mercury recovery from regenerating solution has not been considered
26.	Okoniewska et al. (2008)	Impregnated activated carbon	Mn(II)	1	KMnO ₄ solution	89 % Mn ²⁺ (After 5 h.)	I	Column study done for 5 h, but most effective regeneration time was found to be 1 h. Safe disposal of adsorbent has not been considered
27.	Motsi et al. (2009), (2010)	Natural zeolite	Fe(II) Cu(II) Zn(II) Mn(II)	5.77 mg/g 6.51 mg/g 6.56 mg/g 2.8 mg/g $(n = 3)$	H ₂ SO ₄	I	56.37 % 84.51 % 79.05 % $(at 40 \ ^{\circ}C)$ (n = 3)	After 3 cycles, recovery of metal with H ₂ SO ₄ was found to be good. They recommended that other regenerating reagents be used, for example, NaCl, NaNO ₃ or EDTA. Ultimate fate of spent zeolite is a matter of concern
28.	Tseng et al. (2009)	Magnetic polymer adsorbent (M- PVAL, M-PVEP, M-PVAC-IDA)	Cu(II)	0.121 mmol/g (the monolayer adsorption capacity of M-PVAC-IDA, at pH 4.5)	EDTA	I	1	Using Crystal Field Theory, it was observed that affinity of EDTA to Cu(II) ion is stronger than that of M-PVAC-ID. So Cu can easily be separated from adsorbent. EDTA is effective up to 7 cycles of adsorption and desorption. But recovery of Cu(II) was not addressed; disposal of used adsorbent is of concern

Table	Table 1 continued							
S. no.	Author(s)	Adsorbent (s) used	Metal (s) removed	Removal efficiency $(n = n0. \text{ of cycles})$	Desorbing/ regenerating agent (s) used	Desorption/ regenerating efficiency (n = no. of cvcles)	Recovery of metals $(n = n0. \text{ of cycles})$	Observation
(1)	(2)	(3)	(4)	(5)	(9)	(1)	(8)	(6)
29.	Wambu et al. (2009)	Spent bleaching earth	Cu(II)	>70 % (in first 4 h) 90 % (at 42 h.)	0.5 M H ₂ SO ₄ and HCI	≥80 %	80 %	HCl, H ₂ SO ₄ , CaCl ₂ have been used for desorption study. Acids (HCl, H ₂ SO ₄) gave satisfactory desorption result. Cu should be recovered from both the used adsorbent and regenerating solution before ultimate disposal
30.	Zhu et al. (2009)	Nano-zero-valent iron	As(V) As(III)	94.3 % (As(III) and 65.3 % As(V) at pH 6.5 after 12 h.)	NaOH	~ 100 %	I	Nearly 100 % desorption efficiency was achieved that was quite promising, but recovery of metal from alkali solution was not addressed
31.	Zhang et al. (2009)	Nano-TiO ₂	Se(IV)	>96 % (at pH 2-6)	0.1 M NaOH	>95 %	95-105 %	Detailed desorption study was not mentioned, but they suggested recovery up to 105 % that may be due to addition of undisorbed metals in previous cycles
32.	Kordialik- Bogacka (2011)	Yeast biomass and waste yeast	Cd(II) Pb(II)	$88 \pm 3 \%$ $95 \pm 2 \%$	EDTA, HCl and H ₂ SO ₄ EDTA	85 % >85 %	85 %	85 % Cd from S. cerevisiae and > 85 % Pb from S. pastorianus were found to be desorbed. Desorbing agents are destructive to binding sites of biomass; hence, the study did not recommend these as effective adsorbents
33.	Katsou et al. (2011)	Clinoptilolite	Pb(II) Zinc(II)	23.03 mg/g 13.02 mg/g	3 M KCI 1 M KCI	>99.5 % >98.5 %	1 1	Metal recovery was partially successful, but further study is required for complete recovery
34.	Tian et al. (2011)	Magnetic wheat straw	As(V), As(III)	24.14 mg As/g Fe ₃ O ₄ (MWS5)	NaOH	80 %	I	MWS5 for As (V) can be used efficiently for at least 10 times. Recovery of arsenic from saturated adsorbent was not studied
35.	Zhou and Haynes (2011)	Inorganic solid waste materials (red mud)	Cd(II) Pb(II)	1	0.1 M HNO ₃	$\sim 80 \% n = 3$ $\sim 85 \% n = 3$	I	Regeneration of adsorbent for reuse was not completely successful and recovery of desorbed metals was not studied

Table	Table 1 continued							
S. no.	Author(s)	Adsorbent (s) used	Metal (s) removed	Removal efficiency $(n = n0. \text{ of cycles})$	Desorbing/ regenerating agent (s) used	Desorption/ regenerating efficiency (n = n0. of cvcles)	Recovery of metals $(n = no. of cycles)$	Observation
(1)	(2)	(3)	(4)	(5)	(9)	(7)	(8)	(9)
36.	Zelmanoy and Semiat (2011)	Fe(III) oxide/ hydroxide nanoparticle- based agglomerates suspension	Cr(V1)	31.5 mg/g (pH-4), 23.3 mg/g (pH-7)	NaOH and BaCl ₂	%	% 001-6.66	Firstly, barium chloride precipitate the chromium as barium chromate, and further by little amount of NaOH, 100 % recovery is possible. Both chromium crystals and regenerating agents were successfully recovered for reuse. Barium chromate as such also has industrial uses
37.	Gupta and Nayak (2012)	Orange peel powder with Fe ₃ O ₄ (MNP- OPP)	Cd(II)	76.00 mg/g 75.05 mg/g 74.10 mg/g 73.15 mg/g 72.40 mg/g <i>n</i> = 5	0.1 M HNO ₃	98.19 % 98.66 % 98.58 % 98.28 % 98.28 % n = 5	1	Recovery of cadmium from HNO ₃ solution and spent adsorbent was not considered before final disposal
38.	Hu and Shipley (2012)	Titanium dioxide nanoparticles	Pb(II) Cu(II) Zn(II)	I	0.01 M NaNO ₃ metal-free solution	 49 % 85 % 88 % (within 15 min. at pH 4) 	97 % of the initial metal concentration and 95 % of nano- TiO ₂ was recovered after each cycle of desorption	Mentioned the recovery and regeneration options in their further study
39.	Kyzas (2012)	Coffee waste	Cu(II) and Cr(VI)	70 mg/g	Alkalies	94 %	I	Fate of spent adsorbent and metal recovery must be considered
40.	Zhou and Haynes (2012)	Red mud	As(V) As(III) Se(V) Se(IV)	I	NaOH	78-85 % 26-49 % 90-92 % 43-58 %	1 1	Safe disposal of the adsorbent is matter of concern. Recovery option of metals must be considered
41.	Xu et al. (2012)	Clinoptilolite	Zn(II)	383–394 mg/kg	NaCl (5 g/kg)	125 mg/kg (of clinoptilolite)	1	Removal of Zn was found to be ~ 15 % higher after regenerating the clinoptilolite with NaCI. Further research work is required for cost effectiveness of removal process
42.	Hu and Shipley (2013)	TiO ₂ nanoparticles	Pb(II), Cu(II) and Zn(II)	94 % <i>n</i> = 4	EDTA	92 % <i>n</i> = 4	1	In this study, it has been already mentioned that release of spent adsorbent is an environmental risk. Recovery of adsorbed material was not considered

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and Haynes (2012) tried to desorb Se(VI) and Se(IV) and found desorption efficiency of 90–92 and 43–58 %, respectively.

For the desorption of Cu(II), Benjamin et al. (1996) used both acid and water for regenerating the adsorbent. The interesting result of their study regarding regeneration was that the regeneration efficiency was <90 % using water backwashing in first run, but the metal recovery efficiency during the subsequent run was greater than 100 % using backwashing by both water and acid recovery methods. It indicated that metals left on the IOCS during previous regeneration were released in subsequent cycles. Liu et al. (2002) optimized various factors affecting the adsorption and desorption efficiency of Cu(II). They used a new spherical cellulose adsorbent from aqueous solution and reported that adsorption of Cu(II) ions was dependent on the initial contact time, pH, Cu(II) concentration, and temperature. The Cu(II) ions adsorbed on the adsorbent were recovered with NaOH or HCl aqueous solution. The maximum percentage of recovery was 100 % when 2.4 mol/L of HCl solution was used (Table 1). In addition, only 7.2 % of the adsorption capacity was lost after 30 replications of the adsorption-desorption study. Tseng et al. (2009) used ethylene diamine tetraacetic acid (EDTA) to examine the desorption behavior of copper ions adsorbed on the magnetic polymer adsorbent (MPA) of polyvinyl acetate-iminodiacetic acid (M-PVAC-IDA). The Cu(II) adsorbed on M-PVAC-IDA was recovered by magnetic separation. To recover copper, the EDTA solution of pH 5.5 was used as regenerating solution and mixed with the A-M-PVAC-IDA in the completely stirred tank reactor (CSTR). Each time-saturated EDTA solution was replaced by the fresh EDTA solution, and the process was repeated until no presence of Cu(II) ion in the desorbing agent (EDTA) solution was detected. In order to continue the adsorption/desorption study, Wambu et al. (2009) conducted a study. For regeneration and possible applicability of spent bleaching earth (SBE), they performed batch study to assess the reversibility of Cu uptake by spent bleaching earth in H₂SO₄ and CaCl₂ disclosed that a recovery of 80 % of Cu was possible using acid. Desorption of Cu(II) was more effective when 0.25 M H₂SO₄ (or 0.5 M HCl) was used instead of 0.25 M CaCl₂. Recovery of Cu(II) ions from SBE was successful before the material could be disposed of into the environment. However, when 0.01 M NaNO3 was used as a desorbent, 98 % desorption occurred from nano-TiO₂ (anatase) but it was pH dependent (at pH 2) (Hu and Shipley 2012). In further study, Hu and Shipley (2013) used EDTA and common ion solutions such as NaNO₃, CaCl₂, MgSO₄, NaHCO₃, NaCl and NaHPO₄ to study the regeneration ability of nano-TiO₂ (anatase) for the recovery of Pb(II), Cu(II) and Zn(II). The common ions resulted negligible desorption while EDTA

gave 92 % desorption (Table 1). Both adsorption and desorption decreased with increased regeneration cycles and the decrease might be due to the stronger chelating property of EDTA that made it difficult to reverse adsorption after continuous cycles (Hu and Shipley 2012). A study was conducted by Kyzas (2012) to understand the applicability of commercial coffee wastes as adsorbent for removal of Cu(II) from aqueous solutions and the possible reuse of the coffee residuals in sequential adsorption–desorption cycles. Strong acidic conditions favored desorption of Cu(II) up to 94 % (Table 1). In contrast, at alkaline condition, the desorption rate was very low. After ten cycles of adsorption–desorption, the reduction in adsorption rate from first to tenth cycle was approximately 7 % for both coffee residues and ions.

Stirk and Staden (2002) found that acids (HCl, HNO₃ and H₂SO₄) and chloride salts (NaCl and CaCl₂) more effective for desorbing cadmium ions than the carbonate salts (NaHCO₃ and K₂CO₃) and chelator (Na₂EDTA). Both batch and column studies were performed by Ajmal et al. (2003) who used HCl for desorption of Cd(II) from phosphate-treated rice husk. They found less desorption (53.9 %) during batch study but later it increased (83.9 %) in column study. In an another adsorption/desorption study of Cd(II), Deng et al. (2008) used green marine algae biomass (Cladophora fascicularis) as an efficient adsorbent (for wastewater treatment), as it was of low cost and showed maximum adsorption capacity of 1 mmol/g. The effects of anions (chloride, nitrates, sulfate, acetate and EDTA) on the adsorption capacity of Cd(II) were studied and observed that with the change in concentration of EDTA from 1 to 10 mmol/L, the removal efficiency of Cd(II) reduced from 57 to 20 % and it was concluded that Cd(II) had strong bond with EDTA than the biomass, and, hence it could be used as an effective agent for recovering Cd(II). Out of the various desorbing agents [(H₂O₂, HNO₃, Ca (NO₃)₂, EDTA)] used for desorption of Cd(II), Deng et al. (2008) found EDTA as preferable desorbent (83 % desorption) (Table 1). Considering EDTA as an efficient desorbing agent for heavy metal removal from biomass a study of cadmium and lead recovery from yeast biomass (using Saccharomyces pastorianus, Sachharomyces cerevisiae and waste yeast), Kordialik-Bogacka (2011) found that the highest cadmium and lead uptake was obtained with Sachharomyces cerevisiae and all the biomasses had higher lead adsorption capacity than cadmium. They used different desorbing agents such as HCl, HNO₃, H₂SO₄, Na₂SO₄, Na₂CO₃, EDTA and NaOH and found EDTA and mineral acids effective (Table 1). They concluded that even having high desorption capacity these desorbents are inefficient as they damage the binding sites of adsorbent. However, in subsequent adsorption cycle with S. pastorianus to remove cadmium, dramatic decrease in adsorption



capacity was observed. HNO3 was selected as a regenerating agent by Zhou and Hynes (2011). They compared the heavy metal adsorption capacity of some inorganic waste materials such as air-cooled blast furnace (BF) slag, waterquenched BF slag, steel furnace slag, coal fly ash, coal bottom ash, red mud and water treatment sludge. After initial screening, three of the most promising materials (red mud, air-cooled BF slag and water treatment sludge) were chosen for the adsorption/desorption study of Cd and Pb. After eight adsorption-desorption cycles, it was concluded that acid (HNO₃) was not a suitable regenerating agent for slags and red mud due to which further research and development with water treatment sludge as a metal adsorbent was warranted. So the recovery of the metals (Cd and Pb) from acid solution was not solved. Further, Gupta and Nayak (2012) used 0.1 M HNO₃ and achieved desorption efficiency of about 98 % that was approximately same for all 5 cycles they studied (Table 1). But after five consecutive cycles, adsorption capacity decreased by 4.74 %. They developed an advanced class of adsorbent (magnetic nano-adsorbent) by surface modification of Fe₃O₄ nanoparticles (MNP) with orange peel powder (OPP) for the removal of cadmium. This modified adsorbent was the combination of nanotechnology and magnetic separation techniques. This is a noble adsorbent as it has a large surface to volume ratio, easy to synthesize, easy to recover, absence of secondary pollutants, cost effective and environment friendly. Desorption study was done using 0.1 M HNO₃ at a temperature of 45 °C using a rotary shaker (200 rpm) for 30 min.

Lead recovery of 101 % was obtained from iron-oxidecoated sand (Benjamin et al. 1996) (Table 1), while Jalali et al. (2002) studied the bio-adsorption of lead using nonliving biomass of eight different types of brown green and red marine algae. Of the eight algal species, three brown algae namely Sargassum hystrix, S. natans and Padina pavonia were found to be the most efficient in lead removal from aqueous solution. For the recovery of lead, metalladen biomass (S. hystrix) was separated by filtration and suspension in 15 ml of desorbing solution (0.1 M HNO₃). The recovered biomass was regenerated with 15 ml of 0.1 M CaCl₂ for 15 min and washed twice with distilled water. Ten cycles of adsorption-desorption experiments were performed; the regeneration process did not damage the biomass and achieved 95 % elution efficiency (Table 1). In a study of regeneration of lead (Pb)-loaded clinoptilolite, Katsou et al. (2011) used 3 M KCl as desorbing agent. With increase in regeneration cycle, regeneration efficiency decreased. But zeolite maintained part of the adsorption potential of lead. The desorption efficiency was found to be more than 99.5 % (Table 1). Zhou and Haynes (2011) also performed regeneration studies, but did not mention the recovery of Pb. KordialikBogacka (2011) used EDTA for desorption and found more than 85 % desorption rate, and recovery was about 85 % that was quite appreciable in comparison to other regenerating agents (Table 1). In their earlier study, Hu and Shipley (2012) found unsatisfactory desorption results, but in further study using EDTA as desorbent they found desorption efficiency of 92 % for Pb from TiO₂ (Hu and Shipley 2013) (Table 1).

Zinc desorption was found to be 18 ppm after 30 min in an adsorption/desorption study of heavy metals (zinc, iron, aluminum, copper) from acid mine drainage. In cyclic adsorption and desorption study, the adsorption by clinoptilolite remained satisfactory up to six cycles with EDTA and up to nine cycles with NaCl as regenerating chemicals, respectively. The order of adsorption of various metals on the clinoptilolite particles observed was Fe > Al > -Cu > Zn > Mg > Mn on the basis of normalized concentrations (Cui et al. 2006). While recovery of 60.11 % with NaCl and 79.05 % with H₂SO₄ was observed that was less than Mn (88.65 % with H₂SO₄) (Motsi et al. 2009; Table 1), Katsou et al. (2011) observed more than 98.5 % desorption efficiency for Zn from clinoptilolite using 1 M KCl as desorbent (Table 1). Xu et al. (2012) investigated removal of Zn, regeneration and reuse possibility of clinoptilolite (a low-cost and abundant adsorbent) using NaCl solutions with different concentrations, pH and with different adsorbent-regenerant ratio. Regeneration was carried out by suspension of 200 g of previously used clinoptilolite particles in aqueous NaCl solution in a column by an upward airflow. The effectiveness of regenerated clinoptilolite for Zn adsorption was tested using batch study with fresh acid rock drainage (ARD) and was observed that regenerated clinoptilolite achieved 440 mg/ kg of zinc uptake capacity. Tap water was used to prepare regeneration solution of NaCl instead of deionized water to reduce the cost. But further research work is required to explore Zn removal in repeated clinoptilolite regeneration cycles to ensure reducing zinc concentration in the product stream at a reasonable cost and continuous remediation. However, 88 % desorption was found within 15 min at pH 4 using NaNO₃ and 92 % with EDTA from TiO₂ nanoparticle (Hu Shipley 2012, 2013). The recovery of 97 % of Zn and 95 % of TiO₂ nanoparticle was also mentioned (Table 1).

Okoniewska et al. (2008) studied the regeneration of Mn from used impregnated activated carbons after adsorption. Due to the specificity of activated carbon impregnation, it was possible to use only chemical regeneration and KMnO₄ was used as a regeneration agent. Flooding-impregnated activated carbons by KMnO₄ solution for 1 h contact time with regenerating bed resulted in decrease of desorption efficiency (as both decrease and increase in the contact time with KMnO₄ solution further decreased

desorption efficiency). Mn recovery of 88.65 % was obtained with H_2SO_4 (Motsi et al. 2009), while NaCl did not give satisfactory result (Cui et al. 2006). The recovery of Fe using H_2SO_4 and NaCl as regenerating agent was found to be 56.37 and 12.72 %, respectively (Cui et al. 2006 and Motsi et al. 2009; Table 1).

For Chromium removal, immobilized powdered biomass (Rhizopus nigricans) was prepared by entrapping in polymeric matrices-sodium alginate, polyacrylamide, polyvinyl alcohol (PVA), polyisoprene and polysulfone by physical attachment to inert support materials, polyurethane foam cubes and coir fiber. Among these polymeric beads, polyisoprene and polysulfone were identified as the superior matrices for immobilization. The study reported that all the five types of immobilized beads and gels were resistant to acids. The biomass beads were regenerated and reused in multiple cycles that exhibited approximately 78 % regeneration efficiency after 25 cycles of adsorptiondesorption (Bai and Abraham 2003) (Table 1). But the disposal option for the saturated adsorbents and the recovery method of the metal from eluents were not addressed. Hu et al. (2005) found NaOH as the most effective desorbent in comparison with other desorbents such as Na₂CO₃ and Na₃PO₄. After six successive cycles, desorption efficiency was found to be 87.7 %. Gupta and Rastogi (2008) used deionized water, 0.1 M HCl, HNO₃ and H₂SO₄, 0.2 M CaCl₂ and MgCl₂, 0.5 M KOH and NaOH, 5 % HCHO, and 0.1 M EDTA for desorption of Cr(VI) from cyanobacterium (Nostoc muscorum) biomass (adsorbent). They observed that EDTA and HNO3 were most efficient among all the desorbents studied while desorption with deionized water was almost negligible. Zelmanov and Semiat (2011) also aimed at Cr(VI) removal using iron Fe(III) oxide/hydroxide nanoparticle-based agglomerates suspension as adsorbent. To reuse the adsorbent and to separate solid powder containing the chromate, a complete separation technique was used. When purification was complete, the loaded adsorbent was separated by filtration. Then, the filtered cake was treated with NaOH in the pH range of 9–10 to regenerate the adsorbent. The concentrated Cr(VI) solution was treated with BaCl₂ in order to remove the chromate ions. This technique allowed the recovery of the adsorbent efficiently and the production of concentrated Cr(VI) solution that might be treated further to obtain chromium crystals during recovery of the cleaning solution. In another study for desorption of chromium from coffee waste, about 94 % chromium (Table 1) was desorbed using alkalis (Kyzas. 2012).

In a study of mercury adsorption and desorption characteristics using novel aminated chitosan bead, desorption efficiency was found satisfactory (Jeon and Park 2005). The mercury-loaded beads were agitated with 100 ml of various desorbing agents including EDTA, HCl and HNO₃.

About 95 % desorption was achieved using EDTA, while using HCl and HNO₃ only 65 and 61 % desorption was achieved, respectively (Table 1). The study recommended EDTA as the best desorbing agent. The reusability of the beads was tested by repeating adsorption-desorption study up to 5 cycles. The adsorption capacity of the recycled beads was reported to be maintained at 90 % level up to fifth cycle. In their study, the EDTA metal complexes were successfully separated as solid EDTA and metal (mercury) chloride/sulfate by using hydrochloric acid or sulfuric acid after the elution. The successful separation of solid EDTA and metal chloride/sulfate can be a permanent solution for the disposal problem as the same can be reused. Nayak and lahiri (2006) used calcium alginate beads to adsorb radionuclide of mercury and thallium, because carboxyl groups in the alginate structure enhances the adsorption of many metal ion and biopolymers in the form of beads have advantages in terms of applicability to a wide variety of process configurations even with polluted streams and reusability for repeated runs following recovery. For desorption of metal radionuclide, they used 0.1 M HCl and 0.1 M thiourea, sodium acetate, sodium oxalate and sodium nitrite as desorbing agents. Kuang et al. (2008) reported good desorption of mercury from silver-loaded activated carbon fiber and activated carbon fiber. Activated carbon fiber was loaded with silver to improve its characteristic elemental adsorption and desorption properties. Thermal desorption characteristics of elemental mercury from the two adsorbents were investigated using thermogravimetric analysis. The mercury desorption from silverloaded activated carbon fiber was achieved up to 94.73 %, whereas the same from activated carbon fiber was only 69.93 % (Table 1).

Engelmann et al. (2006) found appreciable recovery of technetium (Tc) and suggested two methods for recovery of technetium adsorbed on charcoal. The first recovery method employed was liquid extraction method that involved extraction of ⁹⁹Tc from charcoal with a hot 4-M HNO₃ leaching, and the second method involved air ashing at elevated temperature of 400–450 °C to recover ⁹⁹Tc from the charcoal. The study found an average recovery of 98 and 96 % for first and second methods, respectively (Table 1). When the hot leaching method was repeated three times, recovery enhanced close to 100 %. The first method may be more suitable for air filter sampling operations, whereas the second method (relatively simple method) may be easily adapted to recover ⁹⁹Tc from vegetation and other types of organic samples.

Palladium (Pd) that was adsorbed on the silica gel as palladium phthalocyanine was first thermally calcined in air to partially burn the organic moiety of the complex. Then, 2 M HCl was added to calcine silica, so that palladium dissolution takes place as H₂PdCl₄. After that, the



palladium was recovered as $PdCl_2$ from the filtrate by adjusting pH at 6 by adding 0.1–0.5 M NaOH. A recovery of 99 % pure $PdCl_2$ with 99 % palladium was reported (Boricha et al. 2007; Table 1).

Critical discussion

In heavy metal removal processes, desorption/regeneration of adsorbents is one of the essential aspects as it controls the economy of water treatment technology (Ali 2012). For effective regeneration of adsorbents and metal recovery, acids (such as HCl, H₂SO₄, HNO₃, HCOOH and CH₃COOH), alkalis (such as NaOH, NaHCO₃, Na₂CO₃, KOH and K₂CO₃), salts (such as NaCl, KCl, (NH₄)₂SO₄, CaCl₂·2H₂O, NH₄NO₃, KNO₃ and C₆H₅Na₃O₇·2H₂O), deionized water, chelating agents and buffer solutions (such as bicarbonate, phosphate and tris) were used in various studies. Table 1 presents the performance of various desorbing agents that have been used for desorption of heavy metals, which will help to understand about the applicability of the desorbents.

Use of acids for regeneration and recovery of heavy metals

Desorption of metal ions in acidic media appeared to be rapid and higher than in basic and neutral media (Srivastava and Goyal 2010). Various acids such as HCl, H₂SO₄, HNO₃, HCOOH and CH₃COOH were used for desorption of heavy metals in various studies. Zhou and Haynes (2011) reported the possible mechanisms and conditions of desorption by acids. These are as follows: (1) Low pH favors desorption and/or dissolution of metal cations, (2) strong competition between H⁺ ions and metal cations for adsorption sites causes displacement of cations into the acid solution, (3) acidic condition favors dissolution of Fe and Al oxide/silicate adsorption surfaces and thus the release of adsorbed/surface-precipitated metals, and (4) acid reacts with residual alkalinity and lowers adsorption capacity. But they did not give detailed explanation about the desorption mechanism. Benjamin et al. (1996) used iron-oxide-coated sand (IOCS) for the removal of both soluble and insoluble fraction of metals using column packed with iron-oxide-coated sand and successfully recovered Cu, Cd, Pb, Ni, Zn and SeO₃, but were unable to recover AsO_3 using acids (Table 1). The regeneration study using both distilled water and 30 % H₂O₂ in 0.5 M HNO₃ solution was reported as quite successful for the removal of adsorbed arsenic from coconut husk carbon up to three cycles (Manju et al. 1998). For the recovery of Cu ions, HCl and NaOH were used and found HCl more effective (Liu et al. 2002). Iqbal et al. (2002) used



deionized water and 0.1 M HCl for desorption of heavy metals from PFP up to three cycles and found desorption efficiency more than 90 % for most of the heavy metals studied. HNO₃ was used as an eluent during the recovery of lead from algal biomass (Jalali et al. 2002). Liu et al. (2002) reported 100 % recovery of Cu^{2+} adsorbed on spherical cellulose using 2.4 mol/L of HCl (Table 1). Ajmal et al. (2003) found 53.9 % desorption using 0.1 M HCl as desorbent for Cd(II) that was not satisfactory, but further in column study the 83.9 % efficiency was found. Saeed et al. (2005) studied desorption up to five cycles using 0.1 N HCl and found 99.4, 98.5 and 99.3 % desorption of Cu(II), Cd(II) and Zn(II), respectively, from papaya wood. In a study of mercury adsorption using novel aminated chitosan beads and desorption characteristics revealed that the desorption efficiency was only about 65 and 61 % by the use of HCl and HNO₃, respectively, (Jeon and Park 2005). In contrast to this, Gong et al. (2005) used HNO₃ as desorbing agent and found desorption efficiency of 92, 93 % from intact or pretreated biomass of Spirulina maxima. Further using the same desorbent (HNO₃), Engelmann et al. (2006) carried out a study for the recovery of Tc and 98 % recovery rate was achieved. Nayak and Lahri (2006) found the desorption efficiency of approximately 90 % for Pb and Tl and 100 % for Hg, respectively, using various desorbing agents in combination with HCL (as mentioned in Table 1). As an efficient desorbing agent, HCl was also recommended by Boricha et al. (2007) and Anirudhan and Unnithan (2007). They found 99 and 93.8 % recovery of palladium and desorption of arsenic after four successive cycles, respectively. Deng et al. (2008) studied Cd(II) desorption using HNO₃ but desorption efficiency was not satisfactory. Wambu et al. (2009) successfully recovered 80 % Cu using acids (H₂SO₄ and HCl). Motsi et al. (2009, 2010) performed desorption study for Fe, Cu, Zn and Mn using H₂SO₄ and found good results for Cu and Mn. Gupta and Nayak (2012) developed magnetic nano-adsorbent by co-precipitating orange peel powder with Fe₃O₄ nanoparticles (MNP-OPP) for removal of Cd. For recovery of Cd from MNP-OPP, they used HNO₃ and successfully achieved 98 % desorption (up to five cycles), but Zhou and Haynes (2011) did not recommend acid as a suitable regenerating agent for slags and red mud.

Use of alkalis for regeneration and recovery of heavy metals

Like acids, various alkalis were also used for the desorption studies of adsorbed heavy metals. NaOH, NaHCO₃, Na₂CO₃, KOH and K₂CO₃ were the most commonly used alkalis for desorption and recovery of heavy metals. A good number of studies recommended alkalis as effective desorbing agents, but a few studies could not get satisfactory results using alkalis. Even in the same study, authors were unable to get consistent results for different metals (Benjamin et al. 1996). NaOH was found to be quite effective for recovery of metal up to 94.6-98.3 % in ten successive cycles (Bajpai and Chaudhari 1999). Bai and Abraham (2003) performed the desorption studies using 0.01 N solutions of acids (HCl, H₂SO₄, HNO₃, HCOOH and CH₃COOH), alkalis (NaOH, NaHCO₃ and Na₂CO₃), buffers and salts, but alkalis were recommended as the best desorbents for Cr(VI) removal from immobilized Rhizopus nigricans. Recovery of arsenic using NaOH was found to be effective up to 80-87 % from iron-oxide-coated sand (Thirunavukkarasu et al. 2003) and up to 100 % from biomass (Kamala et al. 2005). Hu et al. (2005) also found NaOH as the most effective desorbing agent (up to six cycles) as it removed 87.7 % of Cr(VI) from maghemite nanoparticle. In a further study by Zhang et al. (2009), NaOH again proved to be better desorbing agent as it helped in achieving desorption of >95 % and recovery of 95-105 % for Se(IV). Zhu et al. (2009) achieved almost 100 % desorption of adsorbed arsenic using alkaline solution (NaOH) from nano-zero-valent iron and recommended NaOH as a noble desorbing agent, but on the other hand when it was studied for recovery of Cd and Pb from yeast biomass, it was less effective in comparison with that of acids (Kordialik-Bogacka 2011; Table 1). NaOH was also found to be effective up to 80 % desorption from wheat straw (Tian et al. 2011). Zelmanov and Semiat (2011) recovered Cr from nanoparticles-based agglomerate suspension successfully using NaOH and BaCl₂, but Hu and Shipley (2013) reported insignificant regeneration ability of common ions (NaNO3, NaHCO3, NaCl and Na₂HPO₄) from nano-TiO₂ (anatase). Zhou and Haynes (2012) used NaOH and HNO₃ as desorbents and found NaOH as an effective desorbent for As(V) and Se(VI) up to 85 and 92 %, respectively, but NaOH was less effective for As(III) (only 26-49 %) and Se(IV) (43-58 %).

Use of other chemicals for regeneration and recovery of heavy metals

In order to avoid excessive amount of acid-base consumption of chemicals and salt production, Menoud et al. (1995) developed a new recovery method for metallic ions using recyclable chemicals. The idea is to solubilize the heavy metals with soluble strong complexing agents (e.g., EDTA) (Menoud et al. 2000). Jalali et al. (2002) used 0.1 M CaCl₂ for regeneration of biomass and found 95 % elution efficiency. Various salts such as NaCl, KCl, $(NH_4)_2SO_4,$ $CaCl_2.2H_2O$, NH_4NO_3 , KNO_3 and C₆H₅Na₃O₇·2H₂O were used for desorption of immobilized biomass of Rhizopus nigricans by Bai and Abraham (2003). EDTA was found to be one of the most effective desorbing agents in many studies. For example, Jeon and Park (2005) reported 95 % desorption capacity of EDTA for mercury loaded on aminated chitosan bead. Tzou et al. (2007) used hot water for the recovery of chromate from Li/Al Layered Double Hydroxides (LDH). Gupta and Rastogi (2008) also supported the EDTA as desorbing agent as it can be reused without losing its adsorption efficiency up to 5 cycles and without damaging the binding sites of adsorbent. Deng et al. (2007, 2008) also used EDTA for Pb(II) and Cd(II). They recovered 82 % Pb from green algae (Table 1). For Cd desorption, they studied the effects of five types of anions (chloride, nitrates, sulfate, acetate and EDTA) for removing adsorbed Cd(II) and reported 83 % desorption. CaCl₂ used as desorbent in earlier studies was not effective for recovery of Cu(II) (Wambu et al. 2009). Tseng et al. (2009) reported EDTA as an effective recovery agent for recovery of Cu(II) ion. Katsou et al. (2011) investigated the regeneration of clinoptilolite, contaminated with zinc and lead, using 1 M KCl and 3 M KCl, respectively. Kordialik-Bogacka (2011) tried to recover cadmium and lead from yeast biomass using EDTA, HCl and H₂SO₄ and found 85 % desorption efficiency with EDTA. While studying desorption efficiency using EDTA for Cu(II), Zn(II) and Pb(II) from TiO₂ nanoparticles, Hu and Shipley (2013) achieved 92 % desorption efficiency up to 4 cycles.

Comparing the various studies, it is found that heavy metal(s) from chemical adsorbents such as manganese dioxide-coated sand, iron-oxide-coated sand, nano-zerovalent iron, Fe(III) oxide/hydroxide nanoparticle-based agglomerate suspension, and magnetic wheat straw were desorbed in most of the cases using alkalis (generally NaOH). In case of desorption of heavy metal(s) from bioadsorbents such as copper-impregnated activated coconut husk carbon, spherical cellulose adsorbent, charcoal, coconut coir pith, impregnated activated carbon, inorganic solid waste materials, petiolar felt sheath palm, phosphatetreated rice husk, papaya wood and orange peel powder with Fe₃O₄ (MNP–OPP) mostly acids (such as HCl, H₂SO₄ and HNO₃) were used; while for adsorbents derived from biomass such as green algae (Cladophora fascicularis), Spirulina maxima biomass, nonviable cyanobacterium (Nostoc muscorum) biomass, yeast biomass and waste yeast, and marine algal biomass (Cladophora fascicularis), EDTA was used as desorbing agents successfully in most of the cases.

Instead of chemical adsorbents/chemically modified adsorbents, many researchers opted bio-adsorbents for removal of heavy metals and got promising results with minimum disposal problem as the bio-adsorbents can be degraded easily by microorganisms, but the concern is that is it scientific to directly dispose the spent adsorbent in



nature? How to recover the adsorbed metals from the adsorbent? What will happen to the recovered material after recovery?

The summary of the various adsorbents used for adsorption of heavy metals, metals removed, metal removal efficiency, desorbing or regenerating agents used for metal recovery, desorption efficiency, metal recovery, and the critical observations of each one of them is presented in Table 1 that will help in further studies on effective regeneration of adsorbents and recovery of heavy metals.

Conclusion

This paper presents an extensive review of the various desorbing agents used by different authors to regenerate the used adsorbents. An attempt was made to summarize the heavy metal removal efficiency of various adsorbents and performance of various desorbing agents for regeneration of the saturated adsorbents. This study concludes that alkalis are efficient desorbing agents for desorption of heavy metal(s) from chemical adsorbents or chemically modified adsorbents, acids are efficient for desorbing bio-adsorbents, and chelating agent EDTA is the most efficient desorbing agent for biomass desorption. The study found that many of the adsorbents can be reused effectively after regeneration. EDTA was reused in maximum cases without damaging the binding sites and without significant losses in its initial adsorption capacity. Further studies are required on successful separation, recovery of metal/adsorbent and reuse to solve the ultimate disposal problem. The study found that a single regenerating agent that was effective for one adsorbent, but was not necessarily effective for another adsorbent. Further studies are required to develop a noble eluent that can be applicable for many adsorbents, to study the ultimate fate of the metal-loaded spent adsorbents to reduce the secondary pollution, and to recover the metal ions that may be recycled as a raw material for manufacturing industries to reduce the waste to zero. Only a few studies are available on the mechanism of desorption. Therefore, further studies are required to understand the mechanism of desorption such as stripping, thermal desorption, change of chemical conditions, reduction in partial pressure and other forces acting at the time of desorption to help scientific community find the most efficient desorbing agent.

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