

Adsorption–desorption of heavy metal ions

S. P. Mishra*

Department of Chemistry, Institute of Technical Education and Research, Siksha 'O' Anusandhan University, Bhubaneswar 751 030, India

Adsorption and desorption studies on different types of adsorbents, including natural materials such as teak tree bark powder, rice husk, natural bentonite, different algae like *Ecklonia maxima*, *Escherichia coli*, *Ascophyllum nodosum*, *Rhizopus nigricans*, *Cladophora fascicularis*, goethite and soils of three nuclear power plant and artificial materials such as Fe oxide-coated sand, goethite pretreated with phosphate, dithizone-modified sodium trititanate whisker, modified nanometre sized TiO₂, Chromosorb 102 resins and poly(m-phenylenediamine) are summarized. The kinetics, thermodynamics, sorption/desorption mechanism of different metal ions on different adsorbents under different experimental conditions are discussed. It is found that desorbing agent is greatly dependent on the adsorbate used. All the metal ions are desorbed using acids like HCl, HNO₃ and H₂SO₄ in most of the cases, except Cr(VI). EDTA can be used to remove Pb²⁺ and Zn²⁺ in addition to acids. Since Cr(VI) is present in anionic form; it can be eliminated from the loaded adsorbents using bases like NaOH, Na₂CO₃ or NaHCO₃.

Keywords: Adsorption, desorption, heavy metals, eluant.

THE heavy metals present in the aquatic environment are considered to be the major inorganic contaminant due to their mobility in the aqueous ecosystem, toxicity to higher life forms and non-biodegradable nature. The heavy metals hazardous to human health include Pb, Hg, Cd, As, Cu, Zn and Cr. As and Cd cause cancer, Hg can cause mutations and genetic damage, while Cu, Pb and Hg can cause brain and bone damage. The problem of heavy metal pollution in water and aquatic organisms, including fish needs continuous monitoring and surveillance as these elements do not degrade and tend to bio-magnify in man through food chain. Hence, there is a need to remove heavy metals from the aquatic ecosystem. Several methods have been devised for the treatment and removal of heavy metals. The commonly adopted procedure for removing the heavy metal ions from aqueous streams includes chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction¹. These so-called conventional methods are not so effective when the metal concentration in the effluent is low. These methods are also non-selective. Adsorption

process may be an alternative technology for the removal of heavy metals, which are present in very low concentration in the aquatic environment. In the adsorption process, both biosorbents and chemical sorbents can be used for metal removal and recovery. Biosorbents include Earth's forests and plants, ocean and freshwater plankton, algae, fish and all living creatures. Similarly, in chemisorption process, several adsorbents like zeolite, activated carbon, fly ash, clay and red mud can be used.

The process of biosorption can only be economical if a suitable eluant is used for the recovery of metals from the loaded adsorbent. In a complete metal removal and recovery process, the adsorbents are to be used in a continuous sorption–desorption cycle. For this purpose, the adsorbents should fulfill the following criteria²: (i) They should be cheap and reusable. (ii) Both uptake and release of metal ions should be efficient and rapid. (iii) Desorption of metal ions from the sorbents should be metal-selective and economically feasible.

Although U uptake capacity of *Penicillium* and *Actinomyces* is the same, *Penicillium* sp. is considered as a better biosorbent as metals can be eluted from it more efficiently³. Therefore, selection of specific eluants is more important. Sodium carbonate⁴, potassium cyanide⁵, EDTA⁶, nitric acid⁷, sulphuric acid and hydrochloric acid⁸ are some of the common eluants used for the recovery of metal ions from the loaded adsorbents. The main objective of the present article is to review adsorption–desorption characteristics of different heavy metals from their respective adsorbents.

Competitive adsorption–desorption

Competitive adsorption of heavy metal ions Cu(II), Cd(II) and Pb(II) from aqueous media onto northern Anatolian smectites was investigated by Arpa *et al.*⁷. The maximum adsorption of individual metal ions onto smectites was found to be 41.46 mg of Cd(II), 36.11 mg of Pb(II) and 18.7 mg of Cu(II) per g of smectite. But from their mixture, the amounts of Cd(II), Pb(II) and Cu(II) adsorbed are reduced to 11.86, 11.23 and 16.76 mg per g of smectite respectively, under the same condition. Desorption studies of these metal ions carried out using 0.5 M HNO₃ from the adsorbents loaded with the individual metal solutions and their ternary solution. The desorption rate is very high, i.e. more than 95% in all the cases⁷. Kaolinite is used for the removal of Cd, Cu, Pb and Zn in single- and multi-component systems. The

*e-mail: spm_iter@rediffmail.com

initial metal loadings were 66.67 and 333.33 μM in single-element system and 16.67 and 83.33 μM in multi-element systems. The metal-adsorbed kaolinite is aged in moist condition under nitrogen environment. This dried, metal-adsorbed, aged kaolinite powder is used for desorption of heavy metals with 0.01 M NaNO_3 (pH 6.0). Desorption of heavy metals from kaolinite decreases with ageing and increase in temperature in both single- and multi-component systems. These phenomena can be explained through processes like change in the type of surface complexes, diffusion into micro pores or intraparticle spaces. The order of heavy metal desorption is in the sequence $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb}$ in both single- and multi-component systems⁹. Fischer *et al.*¹⁰ studied the adsorption of heavy metals like Cd, Cu, Ni, Pb and Zn onto typical soil components like bentonite and peat. The metal-loaded sorbents were taken for desorption studies. Glycine at pH 7.0 and 4.5 was taken as desorbing agent. The desorption of heavy metals from bentonite ranges from 95% to 9.5% and decreases in the order $\text{Cu} > \text{Ni} > \text{Zn} > \text{Cd} > \text{Pb}$ at pH 7.0. The desorption rate is significantly lower at pH 4.5 and in suspension of peat. At lower pH, with the increase in proton concentration the solubility of metal cations is reduced. The amphoteric character and isoelectric point of glycine also play a major role in the reduced desorption rate at pH 4.5. Similarly, a specific complexation by organic matter is the major factor for higher metal fixation on peat particles compared to clay minerals which bind metal cations by electrostatic attraction only¹⁰. Jute fibre is used as adsorbent after chemically modifying it by two different techniques viz. loading of a dye with specific structure, e.g. C.I. Reactive Orange 13, and oxidizing with hydrogen peroxide. The dye-loaded jute fibres show metal ion uptake values of 8.4, 5.26 and 5.95 mg/g for Cu(II), Ni(II) and Zn(II) respectively, while the corresponding values for oxidized jute fibres are 7.73, 5.57 and 8.02 mg/g as against 4.23, 3.37 and 3.55 mg/g for unmodified jute fibres. The efficiency of desorption, regenerative and reuse capacity of these adsorbents is assessed for three successive adsorption–desorption cycles. The adsorption capacity is retained only when caustic soda regeneration is carried out as an intermediate step after desorption. Possible mechanism has been given by Shukla and Pai¹¹. Cheap cellulose containing natural materials like groundnut shell and sawdust is assessed for Cu(II), Ni(II) and Zn(II) adsorption from their aqueous solutions. These materials show good adsorption capacities and the application of a specific dye, C.I. reactive orange 13 onto the material further enhances the adsorption capacity. The maximum metal ion uptake values for Cu(II), Ni(II) and Zn(II) are 7.6, 7.49 and 9.57 mg/g respectively, for the dye-loaded groundnut shells, whereas maximum load for the unloaded groundnut shells is 4.46, 3.83 and 7.62 mg/g respectively. Similarly, the dye-loaded sawdust gives adsorption values of 8.07 mg/g for Cu(II), 9.87 mg/g for

Ni(II) and 17.09 mg/g for Zn(II), whereas it is 4.94, 8.05 and 10.96 mg/g for unloaded sawdust as the adsorbents for Cu, Ni and Zn respectively. The metal uptake capacity for dye-loaded adsorbents is quite high at lower pH in comparison to that for unloaded adsorbents. The regeneration and reusability of the adsorbents are also assessed for three successive adsorption–desorption cycles and is found to retain the absorptive capacity¹². Multi-walled carbon nanotubes (MWCNTs) are modified with 8-hydroxy quinoline and used for the removal of Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solution. After systematic study of different adsorption parameters, the results show that most of the metals are removed from aqueous solution using 250 mg MWCNTs at pH 7.0 and 298 K in 0.01 M KNO_3 after 10 min of adsorption. These results also show that the percentage of adsorption of different metal ions is in the order $\text{Cu(II)} > \text{Pb(II)} = \text{Zn(II)} > \text{Cd(II)}$. Most of the metal ions are desorbed at $\text{pH} < 2.0$ and the sorbent could be reused up to three cycles of adsorption/desorption without losing efficiency. Both modified and unmodified MWCNTs are treated with real samples containing heavy metals. Modification of MWCNTs with 8-hydroxy quinoline shows greater efficiency¹³.

Cu(II)

A novel adsorbent (AMPS-silica) is synthesized by binding AMPS (2-acrylamido-2-methyl propane sulphonic acid) onto silica surface, which functions with gamma methacryloxypropyltrimethoxysilane reagent. The adsorbent is examined for Cu ion removal in a series of batch adsorption experiments. The maximum Cu^{2+} adsorption capacity is 19.9 mg/g. The involved mechanism may be adsorption through metal-binding with organic functional groups such as carboxyl, amino and sulphonic groups. Cu^{2+} loaded on AMPS-silica can be desorbed in HNO_3 solution and the adsorption-properties remain stable after three adsorption–desorption cycles¹⁴. Diethylene triamine (DETA) is successfully grafted through a relatively simple solution reaction onto polyglycidyl methacrylate (PGMA) microgranules to obtain an adsorbent (PGMA–DETA) with a very high content of amine groups. The PGMA–DETA adsorbent is examined for copper ion removal in a series of batch adsorption experiments. It shows very good adsorption towards Cu(II) and the adsorption is most effective at $\text{pH} > 3$ in the pH range 1–5 examined. X-ray photoelectron spectroscopy (XPS) reveals that there are different types of amine sites on the surface of the PGMA–DETA adsorbent, resulting in better adsorption performance at a higher solution pH values. The adsorption capacity reaches 1.5 mmol/g at pH 5. The adsorption process is fast with adsorption equilibrium time less than 1–4 h and closely follows pseudo second-order kinetic model. Desorption of Cu ions from the

PGMA–DETA adsorbent is most effectively achieved by 0.1 M dilute nitric acid solution, with 80% of the desorption being completed within the first 1 min. Consecutive adsorption–desorption experiments show that the PGMA–DETA adsorbent can be reused almost without any loss in the adsorption capacity¹⁵. A novel silica-supported 2-aminomethyl pyridine adsorbent is synthesized using a post-grafting route. This synthetic route involves the reaction of 2-aminomethyl pyridine (AMP) with gamma-chloropropyltrimethoxysilane (CPTS) prior to immobilization on the silica support. The synthesized silica-supported AMP adsorbent under both amine and acid-catalysed conditions is abbreviated as Si-AMP-M-H and characterized. The adsorption capacity of Si-AMP-M-H for Cu^{2+} is comparable to commercial silica-supported AMP adsorbent. Si-AMP-M-H shows a favourable selectivity for Cu^{2+} in simulated cobalt electrolyte solution in the presence of Ni. Adsorbed Si-AMP-M-H can be readily regenerated by acid ammonia treatment¹⁶. An investigation is conducted on the adsorption–desorption of Cu(II) from aqueous solution with a new spherical cellulose adsorbent containing the carboxyl anionic group. The adsorption of Cu(II) ions on the adsorbent is found to be dependent on time and pH, concentration and temperature. The adsorption process follows both Freundlich and Langmuir isotherms and is found to be endothermic ($\Delta H = 23.99$ kJ/mol). The Cu(II) ions adsorbed on the adsorbent can be recovered with aqueous NaOH or HCl solution. The maximum recovery percentage is about 100 when 2–4 mol/l HCl solution is used. In addition, only 7.2% of the adsorption capacity is lost after 30 replications of adsorption and desorption¹⁷. Lai *et al.*¹⁸ studied the use of iron oxide-coated sand in water treatment. BET and SEM/EDAX techniques are employed to study the properties of adsorption and desorption reactions of Cu^{2+} ions on the iron-coated sand surface in water. The results indicate that the iron-coated sand has more micropores and higher specific surface area because of the attachment of iron oxide. Cu(II) ions could penetrate into the micro pores and meso pores of iron oxide on sand surface and the regeneration of iron coated sand could be achieved by soaking with pH 3.0 acid solution. The result of EDAX analyses shows that Cu ion adsorption is chemisorption in nature. This is an innovative technology for coating iron oxide on sand surface for the treatment of heavy metals in water¹⁸.

Cd(II)

Wang and Xing¹⁹ studied Cd sorption and desorption by goethite pretreated with phosphate. It was found that phosphate not only enhances Cd adsorption, but also accelerates the adsorption process. The equilibrium of Cd adsorption by the pretreated goethite is achieved within 24 h at 20°C, while such equilibrium is not observed after

4 weeks in the absence of phosphate. Desorption of Cd is more from phosphate-treated goethite. In this study, 5M HCl is used as eluant because such a strong acid effectively releases Cd from the goethite surface and prevents readsorption. The authors explained that phosphate blocks the pores on goethite surface, which leads to the fast adsorption kinetics and high extraction percentage. These results provide strong support for the diffusion of Cd into goethite particles¹⁹. The dithizone-modified sodium trititanate whisker as a solid sorbent is prepared using impregnation method. During modification, dithizone is dissolved in ammonia solution and evenly loaded onto the surface of sodium trititanate. At higher pH, the surface of sodium trititanate whisker is covered with OH^- ions. In dithizone-modified form of whisker, surface cladding is formed by a combination of NH of dithizone surface and OH^- of whisker and stabilization of the prepared sorbent was found to be better. Sodium trititanate whisker has special laminated structure. In the entire laminar space, there are several Na^+ ions which are readily exchangeable with the heavy metal ions. The adsorption properties of the sorbents to Cd(II) in static system, the main factors affecting adsorption and desorption, adsorption capacity and influence of co-existing ions on the determination of Cd(II) are investigated by flame atomic absorption spectrometry (FAAS). The results show that Cd(II) could be adsorbed by 0.2 g of modified sodium trititanate whisker at pH 6.2, and eluted by 10 ml 0.5 mol/l HNO_3 . Compared with non-modified sodium trititanate whisker, the sorbent possesses excellent absorptivity and better selection. The process can be applied to the determination of Cd(II) in environmental water samples²⁰. Cadmium adsorption onto and desorption from sodium alginate and sodium alginate with polyvinyl alcohol (PVA) are studied. The first 20 min of adsorption is governed by intra-particle diffusion method. At equilibrium, the adsorption is more effective onto 2% alginate and is lower for the alginate sorbent containing PVA. The maximum adsorption capacities in Langmuir isotherm for both the 2% and 1.5% alginate with 0.5% PVA are similar and are 176 and 178 mg/g dry weight respectively. However, the adsorption capacity decreases to 48 mg/g dry weight for 2% alginate with 5% PVA. Cd desorption is more effective for nitric acid than for sulphuric acid and hydrochloric acid. The optimum pH for desorption is 2.2. More Cd is desorbed from 2% alginate with 5% PVA than from 2% alginate or 1.5% alginate with 0.5% PVA (ref. 21). Cyclical Cd adsorption and desorption by activated sludge immobilized on alginate carriers were studied by Kuczajowska-Zadrozna *et al.*²². Their study concerns Cd desorption in subsequent cycles of adsorption/desorption by chemical sorbents such as 2% sodium alginate, sodium alginate with the addition of PVA in the following proportions: 1.5% alginate and 0.5% PVA, 2% alginate and 2% PVA, 2% alginate and 5% PVA, and two kinds of activated sludge immobilized on alginate

sorbents. Here also it is proved that higher the amount of PVA in alginate, lower is the reaction rate. Mineral acids such as HCl and H₂SO₄ are used as desorption agents. It is observed that all the sorbents tested remove Cd with high and almost constant efficiency from the solution containing 50 mg Cd/dm³, whereas desorption effectiveness depends on the kind of sorbents and desorbing agents²². Dried and ground material of the brown alga *Ecklonia maxima* and waste product from the manufacture of Kelpak, seaweed concentrate used in agriculture, have previously been shown to be effective biosorbents of heavy metals. The recovery of bound Cd and subsequent reuse of the biosorbents are studied. Acids (HCl, HNO₃ and H₂SO₄) and the chloride salts (NaCl and CaCl₂) are more effective in desorbing Cd ions than the carbonate salts (NaHCO₃ and K₂CO₃) and the chelator Na₂EDTA. The optimum concentration of the acids for desorption is 0.01 M ± 0.1 M. Depending on the acid and concentration used for desorption, optimum time for desorption ranges from 30 min to 2 h. The sorbent derived from ground *E. maxima* could be used for more than four adsorption–desorption cycles, whereas the sorbent derived from Kelpak waste could only be used effectively for up to three adsorption–desorption cycles²³.

Ni(II)

Six low-cost adsorbents are used for Ni adsorption from aqueous solution. Those are almond tree (*Terminalia cattapa*) bark powder (ATBP), teak tree (*Tectona grandis*) bark powder (TTBP), mangrove plant (*Sonneratia apetala*) leaf powder (MPLP), jackfruit plant (*Artocarpus heterophyllus*) leaf powder (JPLP), cinnamon plant (*Cinnamomum zeylanicum*) leaf powder (CPLP) and chiku (*Manikara zopata*) leaf powder (CLP). After thorough washing and drying, these materials are used for adsorption studies. Different adsorption parameters are studied like pH, temperature, contact time, initial metal ion concentration and adsorbent dose. Thermodynamic analysis shows that the adsorption is favourable, spontaneous and endothermic in nature. The monolayer (maximum) adsorption capacity (q_m) is found to be between 4.975 and 10.10 mg/g for these adsorbents. TTBP is found to have excellent adsorption capacity towards Ni(II) than the other natural materials under study. Desorption studies are carried out by taking metal ion-loaded adsorbents from 10 mg l⁻¹ initial metal ion concentration. Distilled water at pH 1, 2, 4 and 6 using dilute solution of HCl is taken as desorbing media. At pH 1, 2, 4 and 6 maximum desorption occurs for CPLP (80.95%), JPLP (84%), CPLP (35.71%) and MPLP (26.36%) respectively²⁴. The biosorption of Ni by immobilized *Escherichia coli* on biobeads and biofilm has been studied by Saravanan *et al.*²⁵. Different parameters such as effect of pH, effect of contact time, initial metal ion concentration and adsorbent dosage are studied. Batch kinetic studies is carried out

to determine biosorption and desorption efficiency of the biosorbent. Due to high Ni sorption capacity on immobilized *E. coli* on biofilm, it is concluded as the best biosorbent for Ni uptake in the effluent. Maximum sorption capacity for biofilm and biobeads is found to be 0.5024 and 0.8972 mg/g respectively. In order to determine the reusability of the biobeads and biofilm, consecutive desorption cycles are repeated three times using the same biosorbent. Here H₂O having pH 6.0 is taken as eluant. For desorption study, the Ni-loaded adsorbents (both biobeads and biofilm) are added to the required amount of eluant on a shaker at 180 rpm for 6 h. The adsorption capacities do not noticeably change during the repeated adsorption–desorption operations. The results from the desorption studies show that biobeads and biofilm could be repeatedly used in heavy metal adsorption studies without detectable losses in their initial adsorption capacities. Further analyses are being made to prove the utility of these adsorbents for treatment of domestic and industrial effluents in continuous system²⁵. Economically, cheaper cellulose containing natural material and agricultural waste rice husk is tested to remove Ni from the aqueous solution. Optimum pH for Ni removal is found to be 6.0. For dilute solution at 20 g l⁻¹ adsorbent dose, 51.8% Ni can be removed by rice husk. The rice husk can be regenerated using 0.15 M HCl and desorption percentage is 78.93. Desorption studies indicate good possibility of reusing the adsorbent and it is an economical method for the removal of Ni from aqueous solution²⁶. Comparative studies on the removal of Ni(II) from aqueous solution using C-derived from palmyra palm fruit seed carbon (PPFSC) and commercial activated carbon (CAC) have been made by Kannan and Thambidurai²⁷. Different parameters like agitation time, pH and carbon dosage on the adsorption capacity are studied. The suitability of the Freundlich and Langmuir adsorption models is also investigated for each sorbent system. These sorbents could be regenerated by treatment with HCl and could be reused. The suitability of these materials is tested with metal plating industry²⁷. The modified nanometre-sized TiO₂ as a solid sorbent is prepared using impregnation method and characterized by SEM. The influence of co-ions on the adsorption studies of Ni²⁺ on this adsorbent is investigated by FAAS. When the test solution containing the sorbent is vibrated for 5 min and stationed for 12 h at pH 6.0, then 0.1 g of modified nanometre-sized TiO₂ could adsorb Ni(II) quantitatively and adsorbed Ni(II) could be desorbed with 10 ml of 4 mol/l HNO₃ as eluant. This method can be applied for the determination of trace amount of Ni(II) in the environmental water samples²⁸.

Co(II)

The modified nanometre-sized TiO₂ as a solid sorbent is prepared using impregnation method and characterized

using SEM. The adsorption properties of the sorbent to Co(II) in static system, main factors affecting the adsorption and desorption, adsorption isotherms and influence of co-existing ions on the determination of Co(II) are studied by FAAS and desorption experiments are carried out. When test solution containing the sorbent is vibrated for 5 min and stationed for 12 h at pH 8.0, 0.1 g of modified nanometre-sized TiO₂ could adsorb Co(II) quantitatively and Co(II) adsorbed onto the sorbent could be desorbed with 10 ml of 4.0 mol l⁻¹ HNO₃ as eluant. The sorbent possesses excellent adsorptivity. It can be applied for the determination of Co(II) in the environmental water samples²⁹. The application of a commercial natural bentonite (untreated NB) for the removal of Co(II) ions from aqueous solution has been tested by Mekhemer *et al.*³⁰. Different physical properties are characterized. The optimum pH for adsorption is 6.0. The data demonstrate that the adsorption of Co(II) increases linearly with time. The process is found to be spontaneous and endothermic under normal conditions. The adsorbed amount of Co(II) on washed bentonite (WB) increased by 100% compared to NB and bentonite calcined at 700°C (CB). The results indicate that WB can be considered as a potential adsorbent for Co(II) removal from aqueous solution. For desorption study, deionized water is used as desorbing agent. It is observed that only 4, 7 and 8 mg of Co(II) ions could be desorbed from NB surface loaded by 22.3, 24 and 30 mg Co(II)/g of NB (ref. 30). For assessment of human exposure to toxic metal of Co(II), environmental and biological monitoring are essential processes. The aim of this study is to achieve optimum factors necessary for the development of a sorbent for Co(II) present in urine, hair and nail samples. Solid phase extraction (SPE) using mini columns filled with Chromosorb 102 resin is optimized with respect to sample pH, ligand concentration, loading flow rate, elution solvent, sample volume (up to 500 ml), elution volume, amount of resins and sample matrix interferences. Co ion is retained on sorbent and is eluted with 2 M HNO₃ followed by determination using FAAS. Co recovery is more than 92%. This optimized method can be considered successful in simplifying sample preparation for trace residue analysis of Co(II) in different matrices when an occupational and environmental exposures is required³¹. A new chelating resin is prepared by coupling Amberlite XAD-2 with salicylic acid (SAL) using an azo spacer. Then the polymer support is coupled with iminodiacetic acid (IDA). The resultant resin is Amberlite XAD-2-SAL/IDA. The resulting sorbent has been characterized and studied for the pre-concentration and determination of trace Co(II) ion from human biological fluid and environmental water samples. The optimum pH value for sorption of the metal ion is 7.5. The sorption capacity of this resin is 87.4 mg/g. The chelating sorbent can be reused for 20 cycles of sorption-desorption without any significant change in sorption capacity. A recovery of

95.3% is obtained for the metal ion with 0.5 M nitric acid as the eluting agent. The equilibrium adsorption data of Co(II) on modified resin are analysed by Langmuir, Freundlich, Temkin and Redlich-Peterson models³². Following an effective accumulation of Co by non-living algal biomass of *Ascophyllum nodosum*, desorption of the metal from the biosorbent is examined using H₂SO₄, HCl, NH₄OH, KHCO₃, EDTA, KSCN, KCl and CaCl₂ solution. The 0.05 M CaCl₂ in HCl appeared to be the best eluant capable of desorbing more than 96% of the sequestered Co at the optimum pH 2–3. The effect of temperature on elution process and elution rate is not significant up to 60°C. The infrared (IR) spectra of the native and eluted biomass do not show significant difference. The electron micrographs of the algal biomass taken after washing it with the CaCl₂ (0.1 M) eluant solution indicate damage to the cells and cell walls, while strong acid, alkaline and KSCN treatment resulted in some changes in the cellulose structure. The kinetics of the Co stripping process is quite rapid. The required contact time for the complete removal of metal from the biomass is less than 2 h (ref. 8).

Cr(VI)

The adsorption of Cr(VI) ions from aqueous solution by en-modified cross-linked magnetic chitosan resin (EMCMCR) is studied in a batch adsorption system. Optimum pH and contact time for Cr(VI) adsorption are 2.0 and 6–10 min respectively. The adsorption kinetics is well explained by Langmuir and Temkin models. The maximum adsorption capacities obtained from Langmuir model are 51.81, 48.78 and 45.87 mg/g at 293, 303 and 313 K respectively. The adsorption is exothermic in nature and the Cr(VI) sorbents are successfully regenerated using 0.1 N NaOH solution³³. Different low-cost agro-based materials, namely *Tamarindus indica* seeds (TS), crushed coconut shells (CS), almond shells (AS), groundnut shells (GS) and walnut shells (WS) are evaluated for Cr(VI) removal. Batch tests indicate that hexavalent Cr(VI) sorption capacity (q_e) follows the sequence $q_e(\text{TS}) > q_e(\text{WS}) > q_e(\text{AS}) > q_e(\text{GS}) > q_e(\text{CS})$. Due to high sorption capacity, tamarind seed is selected for detailed sorption studies. Cr(VI) sorption by TS decreases with increase in pH and slightly reduces with increase in ionic strength. Cr(VI) sorption by TS is chemisorption in nature. Desorption of Cr(VI) from Cr(VI)-laden TS is less using distilled water and HCl, whereas with NaOH maximum desorption, i.e. about 15.3% is achieved³⁴. The magnetic polydivinylbenzene-1-vinylimidazole [m-poly(DVB-VIM)] microbeads are synthesized by copolymerizing divinylbenzene (DVB) with 1-vinylimidazole (VIM). The m-poly(DVB-VIM) microbeads are characterized by N₂ adsorption-desorption isotherms, ESR, elementary analysis, SEM and swelling studies.

Langmuir, Freundlich and Dubinin–Radushkovich isotherms are used as the model adsorption equilibrium data. Langmuir isotherm model is the most adequate. The activation energy is found to be 5.024 kJ/mol, which is characteristic of a chemically controlled reaction. This type of adsorption is endothermic in nature. Moreover, after use in adsorption, the m-poly(DVB–VIM) microbeads with paramagnetic property are separated via the applied magnetic force. The magnetic beads could be desorbed up to 97% by treating with 1 M NaOH. Therefore, m-poly(DVB–VIM) microbeads are a potential candidate for Cr(VI) removal under magnetic field³⁵. Polyaniline (PANI) and humic acid (HA) composite sorbents are prepared by adding different amounts of HA and PANI. The sorbents are characterized by SEM, FTIR and N₂ adsorption–desorption. Batch adsorption studies show that the sorbent PANI/HA1 has the best affinity for Cr(VI) in aqueous solution. The optimum contact time for adsorption is 120 min. The results of zeta potential measurement and batch experiments show that PANI/HA1 is stable in the pH range 4–7. Cr(VI) could be desorbed from the adsorbents more efficiently with NaOH in comparison to HCl. An adsorption mechanism is proposed on the basis of X-ray photoelectron spectroscopy (XPS) and zeta potential measurement results³⁶. Bai and Abraham³⁷ studied the Cr(VI) biosorption potential of immobilized *Rhizopus nigricans*. The biomass is immobilized by various mechanisms and the removal of Cr(VI) from aqueous solution, mechanical stability for desorbents and reuse in successive cycles are evaluated. The finely powdered biomass is immobilized in five different polymeric matrices, viz. calcium alginate, PVA, polyacrylamide, polyisoprene and polysulphone. Immobilization with polyurethane foam and coir fibre is less effective than polymer entrapment methods at different combinations (% w/v) of biomass dose. The Cr sorption capacity (mg/g) of all immobilized biomass is less than the native powdered biomass. The Cr sorption capacity decreases in the order free biomass (119.2) > polysulphone entrapped (101.5) > polyisoprene immobilized (98.76) > PVA immobilized (96.69) > calcium alginate entrapped (84.29) > polyacrylamide (45.56) at 500 mg l⁻¹ concentration of Cr(VI). The degree of mechanical stability and chemical resistance of the immobilized systems are in the order polysulphone > polyisoprene > PVA > polyacrylamide > calcium alginate. The bound Cr(VI) could be eluted successfully using 0.01 N NaOH, NaHCO₃ and Na₂CO₃. The adsorption data for native and immobilized biomass are evaluated using Freundlich isotherm model. The successive sorption–desorption studies employing polysulphone entrapped biomass indicate that the biomass beads could be regenerated and reused in more than 25 cycles and the regeneration efficiency is 75–78% (ref. 37). MWCNTs are used for the removal of Cr(VI). Different adsorption parameters are studied. Results show that pseudo second order kinetic model and BET isotherm are

found to correlate with the experimental data well. Study of thermodynamic parameters suggests the adsorption process to be spontaneous, physical and endothermic in nature. Desorption experiments show that the recovery percentage of Cr(VI) and MWCNTs regeneration strongly depend on regeneration solution pH, regeneration solution strength, contact time and temperature. The maximum desorption capacity is obtained by 0.2 M NaOH used as regeneration solution. Results show that after 10 cycles of successive adsorption/desorption process, MWCNTs can be reused well without any major decrease in its performance³⁸.

Pb(II)

Pb(II) adsorption from water is carried out using MWCNTs functionalized with tris(2-aminoethyl)amine and measured by FAAS. Effect of different parameters like pH, shaking time, initial metal ion concentration and adsorbent dosage on the adsorption process is studied via batch method. The results show that removal of Pb²⁺ is strongly dependent on pH. Maximum adsorption capacity of the sorbent at optimum condition is 43 mg/g. Desorption study reveals that Pb ions adsorbed could be desorbed at pH < 3 (using HNO₃) due to breakage of complexes formed on the sorbent surface. Adsorption–desorption cycles can be applied for four times³⁹. Adsorption features of *Cladophora fascicularis* are studied as a function of time, initial pH, initial Pb(II) concentration, temperature and co-existing ions. The maximum adsorption capacity is 198.5 mg/g at 298 K and pH 5.0. The adsorption processes are endothermic and the biosorption heat is 29.6 kJ/mol. Desorption studies indicate that among HNO₃, Ca(NO₃)₂, Na₂EDTA (0.1 and 0.01 M) and H₂O, 0.01 mol/l Na₂ EDTA is an efficient desorbent for the recovery of Pb(II) from the biomass⁴⁰. Pb(II) solution has been treated by a column packed with 5 mm diameter spheroids of poly(m-phenylenediamine) powder that has been entrapped in PVA via dynamic adsorption. The effect of operating conditions on the adsorbability and desorbability has been studied and optimized systematically. The highest adsorptivity reaches up to 75.9% for Pb(II) concentration of 500 mg l⁻¹ at the flow rate of 1 ml/min. The release of Pb(II) from Pb(II) adsorbing column has been carried out using 0.1 M HNO₃ as the eluant with an elution efficiency of 98.1% effectively regenerating the column. The regenerated column could be circularly used several times. The Adams–Bohart and Wolborska sorption models have been used to describe the dynamic sorption of Pb(II) through the packed column. It is interesting that Pb(II) adsorptivity onto the regenerated column is 20% higher than that onto as-prepared column, making the poly(m-phenylenediamine) spheroids attractive and cost-effective as a potential sorbent for continuous removal of Pb(II) in

large-scale operations⁴¹. Castaneda *et al.*⁴² studied the biosorption and desorption capacity of pretreated freshwater snail, *Melanoides tuberculata* shells as a biosorbent for the removal of Pb(II) from simulated wastewater and its ability to be regenerated after the process. The biosorption is carried out as a function of contact time and initial Pb(II) concentration at pH 5.5. Desorption of Pb(II) from the biosorbent is carried out using 0.1 M HCl at various contact times. The cycles of biosorption and desorption are carried out until the biosorbent is exhausted at a temperature range of 27–30°C. The Pb(II) concentration before and after each process is measured by FAAS. The optimum contact time for Pb(II) adsorption and desorption is found to be 80 and 60 min respectively. As the linearity for the two adsorption isotherm models is low, the results cannot be described by either Langmuir or Freundlich isotherms. Based on the data and the results obtained, pretreated freshwater snail shells are the potential biosorbent for Pb(II) removal from contaminated wastewater and can be regenerated after two cycles of adsorption⁴². Sorption/desorption reactions at the mineral/H₂O interface control the solution concentration of trace elements and their bioavailability in the natural environment. In this study, the influence of sorption density and residence time on the sorption–desorption kinetics of Pb on goethite has been examined. Pb sorption is rapid and almost complete in less than 1 h. Desorption of Pb is slow and is modelled best by the parabolic diffusion equation. At all sorption densities studied, desorption rate coefficients and the quantity of Pb desorbed are greater for the short-term experiments (5 days). This suggests that an insufficient desorption period caused by the high affinity of Pb for the goethite surface or the slow diffusion of Pb(OH)⁺ into crystal defects may be responsible for the absence of a residence time effect. Further studies are necessary to determine if the observed trends are real or are artifacts of the experiments⁴³. The adsorption and desorption equilibrium and kinetics of Pb ions for aqueous solution on a granular activated carbon (GAC) are examined. Based on the experimental results, a two-site adsorption model is proposed for the adsorption and desorption of Pb(II) under the study conditions. Pb(II) adsorption on the GAC is estimated to have simultaneously occurred on the strong and weak adsorption sites. The equilibrium and kinetics of the experimental results could be represented by the equations using one set of the common Langmuir parameters. Resultant kinetic parameters revealed that the adsorption equilibrium constant is two orders of magnitude greater for strong adsorption sites than for weak adsorption sites, though the maximum number of weak adsorption sites is 1.5 times more than that of strong adsorption sites. The strong adsorption equilibrium constant resulted from a small desorption rate constant. Here deionized water is used for desorption⁴⁴.

Zn(II)

Zn adsorption is carried out in the soils of three nuclear power plant sites in India. ⁶⁵Zn is used as a radiotracer to study the sorption characteristics of Zn(II). The sorption of Zn is determined at 25°C and 45°C at pH 7.8 ± 0.2 in a solution of 0.01M Ca(NO₃)₂ as the supporting electrolyte. The effect of organic matter and other physico-chemical properties on the uptake of Zn is also studied in all the soil samples. The results show that the cation exchange capacity, organic matter, pH and clay content are the main contributors to zinc sorption in these soils. The maximum adsorption is found in the Kakarpara Atomic Power Plant site soils having high organic matter and clay content. The zinc supply parameters of these soils are also discussed. In the desorption studies, the sequential extraction of the adsorbed zinc from the soils shows that the diethylene triamine penta acetic acid extracts maximum amount of adsorbed Zn than CaCl₂ and Mg(NO₃)₂. The Zn sorption on the soil and Zn retention after desorption show a positive correlation with vermiculite and smectite mineral contents present in the clay fraction of the soils. The effect of strong base, i.e. NaOH and demineralized water as eluant is almost negligible from soils of all the sites, whereas desorption by strong acid, i.e. HNO₃ is 75–96% of the adsorbed Zn (ref. 45). Water-insoluble starch phosphates (SPs) with different contents of phosphate groups are used as adsorbents of Zn(II). Different adsorption parameters are thoroughly studied. The optimum pH for adsorption is found to be 4.0 and the maximum adsorption capacity basing on Langmuir isotherm model is found to be 2.14 mmol/g. Furthermore, the desorption process and reusability of the adsorbents are studied. Also, 0.5 N HCl is found to be an appropriate desorbing agent. After three adsorption/desorption cycles, the Zn(II) adsorption capacities of three SP samples decrease from 0.92, 1.23 and 1.44 to approximately 0.72, 1.02 and 1.29 mmol/g respectively, and all the desorption percentages are greater than 93% (ref. 46). Solid waste such as palm fibre and shell produced by the palm oil industry is used by palm oil mills as boiler fuels to produce steam for electricity generation. The ash produced after combustion creates a disposal problem for the palm oil industry. This study aims to use oil palm ash as an adsorbent material for the removal and recovery of Zn ions from the solution. The optimum pH for adsorption ranges from 3 to 6 and a maximum adsorption capacity of 0.163 mmol/g of ash at pH 6. The affinity constant of oil palm ash is found to greatly exceed that of a commercial ion exchange resin, suggesting that oil palm ash may find potential application in treating dilute Zn-containing waste streams. Four isotherm models are used to fit the constant pH equilibrium isotherms obtained at four different pH values. The entire dataset is successively simulated using two of the isotherm models: a Langmuir model with pH dependent parameters and an

extended Langmuir–Freundlich model with pH independent parameters. The rates of adsorption and desorption for Zn are measured using a stirred-batch contactor. The contact time required to reach apparent adsorption equilibrium is found to decrease with increasing adsorbent dosage. Both the rate and extent of Zn desorption are affected by pH of the desorbing solution. The adsorption and desorption rates are consistent with simple first-order rate models⁴⁷. The blank alginate beads and the immobilized dead green algal cells are used for removal of Zn ions from aqueous solution. It is found that the adsorption on both the sorbents increases with increasing pH and pH 5 is found to be optimum. In both cases, approximately 90% of the maximum Zn uptake takes place within the first 30 min. In both cases for blank alginate and immobilized algal cells, the presence of Cu and Ni in aqueous solution is found to suppress the sorption process. Sorption and desorption of Zn on immobilized algal cells and blank alginate beads are studied by conducting three repeated cycles of sorption and desorption. Further, 0.1 M HCl is used as the eluting agent. The regenerated sorbents are then used for Zn sorption and Zn uptake is found to improve after the first cycle. This may be attributed to the fact that the acid used in desorption could remove some contaminants that might have been bound previously by the algal cells⁴⁸. Biosorption of Zn ions on *Spirulina platensis* both in free and immobilized forms is studied in batch systems with respect to pH, metal ion concentration, algal dosage and time. Optimum pH and contact time for adsorption are found to be 8.0 and 90 min respectively. The immobilized *S. platensis* in calcium alginate matrix is the better biosorbent. Also, 0.1 M EDTA is used as the eluant, which allows the reuse of biomass in sorption–desorption cycles thrice without considerable loss in biosorption capacity. Further, 89–95% of Zn is desorbed with EDTA. The functional groups involved in Zn biosorption are identified using Fourier transform infrared spectroscopy. Spectroscopic study of algae shows that the presence of carboxyl, hydroxyl, amino, amide and imine groups is responsible for biosorption of Zn ions⁴⁹.

Adsorption–desorption through column

Continuous process or column study is preferred over batch process for large-scale applications owing to consistent product quality and low capital and operating costs per unit of product. The adsorption–desorption of copper ions and a mixture of five metal ions (Cd, Cu, Ni, Pb and Zn) in aqueous solution by a spruce sawdust column has been reported by Marin and Ayele⁵⁰. An ion exchange mechanism seems to explain the removal of Cu by the natural components of sawdust, i.e. Ca, Mg and Mn accounting for 71%, 13% and 5.5% respectively, of the Cu binding on sawdust. Regeneration of the sawdust

column is carried out by H^+ , Ca^{2+} and Na^+ and follows the sequence: $H^+ > Ca^{2+} > Na^+$, where protons are the most efficient regenerating agents. Adsorption–desorption cycles show that Cu-binding capacity of sawdust, after a decrease of 23% between cycles 1 and 2, is stabilized at 3.1×10^{-2} m eq/g for the following cycles. Adsorption of a mixture of five metal ions indicates that Ni breaks through first when saturation of sawdust is reached, followed by the other metal ions in the order Zn, Cd, Cu and Pb. The effects of competitive ion exchange, because of difference in affinity between the metal ions for sawdust, results in the metals having the lower affinity being displaced by those having higher affinity⁵⁰. The ability of *Pycnoporus sanguineus* for the removal of heavy metals from aqueous solution has been investigated in fixed-bed column studies by Zulfadhly *et al.*⁵¹. The experiments are conducted to study the effect of important design parameters such as column bed height, flow rate and initial concentration of solution. A mathematical model based on external mass transfer and pore diffusion is used for the prediction of mass transfer coefficient and effective diffusivity of metals in macro-fungi bed. Experimental breakthrough profiles are compared with the simulated breakthrough profiles obtained from the mathematical model. Bed depth service time (BDST) model is used to analyse the experimental data and evaluates the performance of biosorption column. The BDST model parameters needed for the design of biosorption columns are evaluated for Pb, Cu and Cd removal in the column. The columns are regenerated by eluting the metal ions using 0.1 M HCl after the adsorption studies. The columns are subjected to repeated cycles of adsorption of the same metal ions and desorption to evaluate the removal efficiency after adsorption–desorption⁵¹. Adsorption and regeneration of ion exchange resins are studied using a subcritical solution of a CO_2 – H_2O mixture and a fixed bed column. The commercial Amberlite IRC-50/IRC-86 cation exchange resin and Amberlite IRA-67 anion exchange resin are tested for heavy metals (Pb, Cu, Cd) adsorption from a solution with different initial metal concentrations at different temperatures. After adsorption, the loaded resins are regenerated with water and carbon dioxide at different temperatures and pressure of 25 MPa. The efficiency of the IRC-50 resin is lower than that of the IRC-86 resin for the adsorption of metals like Cd, Cu and Pb. Results obtained for desorption of these metals indicate that the process could be used for Cd and in principle for Cu. Mathematical modelling of the metal desorption process is carried out successfully as an extraction process. For this purpose, the VTII model, which is applied to extract ion from solids using supercritical solvents is used in this work⁵². Batch and column sorption studies to remove Cu(II) from aqueous solution are tested using marine alga *Sargassum tenerrimum*. Maximum Cu uptake is 174.23 mg/g at an initial pH of 6.0. The Cu-loaded biomass is eluted using 0.1 M HCl and

no damage is caused to the biosorbent. Effect of operating parameters such as bed height and flow rate is studied in a packed column and the metal uptake decreases with increase in flow rate. The BDST and the Thomas models are used to analyse the experimental data and model parameters. During regeneration, a loss of sorption performance is observed during seven cycles of sorption–desorption indicated by a shortened breakthrough time and a broadened mass transfer zone⁵³. Metal biosorption behaviour of raw seaweed *Sargassum filipendula* in ten consecutive sorption–desorption cycles has been studied in a packed-bed flow-through column during continuous removal of Cu from a 35 mg l⁻¹ aqueous solution at pH 5.0. The eluant used is a 1% (w/v) CaCl₂/HCl at pH 3.0. The sorption and desorption are carried out for an average of 85 and 15 h respectively, representing more than 41 days of continuous use of the biosorbent. The weight loss of the biomass after this time is 21.6%. The Cu biosorption capacity of the biomass remains constant at approximately 38 mg Cu/g. The loss of sorption performance is indicated by a shortening breakthrough time and broadening mass transfer zone. The critical bed length representing the mass transfer zone increases almost linearly from 28 to 34 cm. Life factors for *S. filipendula* are found to be 0.0008 h⁻¹ for breakthrough time and 0.008 cm/h for critical bed length using an exponential decay and linear fitting functions, respectively. Regeneration with CaCl₂/HCl at pH 3.0 provides elution efficiencies up to 100%. Maximum concentration factors are determined to be in the range 16–44. A decreasing tendency is observed with an increasing exposure time⁵⁴.

Adsorption–desorption through immobilization

Native biomass consists of small particles with low density, poor mechanical strength and less rigidity. Immobilization of biomass provides increased resistance to changes in conditions such as pH and temperature. Immobilization can also yield beads and granules that can be stripped of metals, reactivated and reused in a manner similar to ion-exchange resins and activated carbon. Sodium alginate extracted from the brown algae *Laminaria digitata* is used to prepare metal-sorbing beads. Their metal-binding properties are investigated with respect to Cu and Cd ions in single and binary metal solutions. The experiments are carried out both in batch and column scale. Alginate is found to be a promising material for heavy-metal removal, while it has to follow a competitive mechanism in multi-metal solutions. The maximum adsorption capacities for Cu²⁺ and Cd²⁺ are 1.5 and 2.09 m mol/g respectively. The calculated diffusion coefficients are (2.8–3.0) × 10¹⁵ cm²/s for Cu and (4.4–4.5) × 10¹⁵ cm²/s for Cd ions respectively. Finally, the obtained diffusion coefficients are used for the simulation of the breakthrough curves on column filtration experiments.

Linear adsorption driving force model is used to provide a rough estimation of the operational and design parameters in flow column adsorption processes⁵⁵. Adsorption–desorption of metal ion Cu(II), Cd(II) and Pb(II) on *S. duplicatum* biomass immobilized by silica-gel are carried out with a continuous method using a set of adsorption equipment controlled automatically. Adsorption of Cu(II), Cd(II) and Pb(II) on silica-gel immobilized *S. duplicatum* is optimum at pH 5.0, with the adsorption capacities of 280.112, 130.513 and 113.660 μmol/g respectively. On the competition adsorption, the Cu(II) ion is more readily adsorbed on immobilized *S. duplicatum* with adsorption selectivity coefficient (α) > 1. The recovery percentage of Cu(II), Cd(II) and Pb(II) is 98, 84 and 70 respectively, with 2.0 m mol/l HCl as eluant⁵⁶. Immobilized *Zoogloea* and *Zooglan* in calcium alginate silica matrix are shown to have a high adsorption capacity for Cu and Cd ions. The Cu ion uptake in the presence of calcium and magnesium ions can be enhanced using immobilized *Zoogloea* and *Zooglan*. Heavy-metal ion adsorption efficiency decreases in the following order: Cu > Cd > Zn > Cr. The adsorbed metal ions are desorbed completely using H₂SO₄. Immobilized *Zoogloea* and *Zooglan* can be used repeatedly for heavy-metal sequestration without loss of adsorption capacity⁵⁷. Cu, Ni and Pb from aqueous solution can be removed using chitosan immobilized on bentonite (ChB). The presence of Na⁺ ions suppresses the adsorption capacity in the order Ni > Cu > Pb. The kinetics of this type of adsorption is found to be pseudo second-order in nature. It signifies that the rate-determining step is chemisorption by nature and the covalent bonds are formed through sharing of electrons between ChB and metal ions. The values of Langmuir constant (q) for Cu, Ni and Pb are 12.6, 6.1 and 15.0 mg/g respectively. The preferential adsorption of Pb(II) over Cu(II) and Ni(II) onto ChB is due to properties such as electronegativity, hydrolysis constant and softness values. In the desorption studies, 0.1 M HCl provides the highest desorption capacity in comparison to 0.1 M NaCl and 0.1 M NaOH, but with the most material damage to ChB. After three cycles of adsorption–desorption, % desorption using HCl is 79, 70 and 81 for Cu(II), Ni(II) and Pb(II) respectively⁵⁸. Loofa sponge (LS) immobilized biomass of *C. sorokiniana* (LSIBCS) isolated from industrial wastewater is utilized as a new biosorbent for the removal of Cr(III) from aqueous solution. A comparison of biosorption of Cr(III) by LSIBCS and free biomass of *C. sorokiniana* (FBCS) from 10 to 300 mg Cr(III)/l aqueous solution shows increase in uptake of 17.79% when the microalgal biomass is immobilized on LS. Maximum biosorption capacity for LSIBCS and FBCS is found to be 69.26 and 58.80 mg Cr(III)/g biosorbent respectively whereas the amount of Cr(III) ions adsorbed onto naked LS is 4.97 mg/g. Optimum contact time for adsorption is 15 and 20 min for LSIBCS and FBCS respectively, and optimum pH is found to be 4.0.

Desorption studies show that 98% of the adsorbed Cr(III) could be desorbed with 0.1 mol/l HNO₃, whereas other desorbing agents are less effective in the order EDTA > H₂SO₄ > CH₃COOH > HCl. The regenerated LSIBCS retains 92.68% of the initial Cr(III) binding capacity up to five cycles of reuse in continuous flow fixed bed columns⁵⁹.

Adsorption/desorption processes used in field

Heavy metals from heavy metal-loaded chelating resins are recovered with recyclable soluble complexing agents. The scale-up of desorption is then conducted at mini pilot scale. The scale-up criteria tend to minimize desorption time and used soluble polymer quantity⁶⁰. The adsorption potential of activated carbon prepared by phosphoric acid treatment of tamarind seeds (PTC) and commercial activated carbon (CAC) in removing heavy metals such as Cd and Cu has been studied using fixed-bed adsorption column. There are plans to extend this idea to large-scale effluent treatment. The aim of carrying out the continuous flow studies in fixed-bed column is to assess the effect of pH, flow rate, bed height, the influence of common cations/anions on metal adsorption and its regeneration capacity. Phosphorylated tamarind seed carbon is found to be superior to common activated carbon in removal of metal ions⁶¹. Humic substances present on peat provide negatively charged adsorption sites on which metals get adsorbed through various mechanisms like physical, ion exchange and complexation. The main objective of this pilot study is to establish the physical and chemical processes involved in the adsorption of heavy metals on peat, with emphasis on the competition and displacement behaviour of Cd, Pb, Cu, Ni and Zn (ref. 62). Atkinson *et al.*⁶³ have extended biosorption technology to treat metal-contaminated industrial effluents. They have suggested that the effectiveness of the technology should be tested both on cost and performance basis before implementation. They have also suggested that factors like process design, capital expenditure, biosorptive capacity, cost, immobilization, commercial biosorbents, biomass surface charge, biomass regeneration and reusability must be considered when bioremediation is selected as the clean-up technology⁶³. Interaction of microbial cells and soluble heavy metal ions occurs both in passive and active processes using metabolically inactive and active biomass. Biosorption is generally used to describe passive interaction of microbial cells. During 1980 and 1990s, pilot installations and few commercial-scale units have been constructed in USA and Canada. These pilot plants help researchers to realize the limitations associated with the use of inactive microbial biomass in the industrial application of biosorption. Presence of co-ions has a negative effect on the recycling and reuse of the biosorbents^{64,65}. The most recent pilot and

industrial application of immobilized biomass reactors used in mining and metallurgical wastewater is a novel type moving bed sand filter with immobilized biofilm. Here the sand grains act as immobilizing material for the biofilm. Here, sand is continuously circulated to the reactor, washed and the produced biomass along with the sequestered metal ions is continuously removed. The metal removal mechanisms are through biosorption, bio-precipitation and bioreduction⁶⁶.

Conclusion and future plan

The knowledge of both adsorption and desorption capacity of a material in a continuous adsorption/desorption cycle is an important factor in designing large-scale applications. It has been found that both sorption/desorption properties depend on the structure of the adsorbents or their surface properties. It is interesting to note that the desorption properties depend comparatively more on the adsorbates. No matter what type of adsorbent is used, a common eluant is used to desorb the same metal ion (adsorbate) in most of the cases. Although much research has been done on the sorption/desorption field, there are still some gaps to be filled. Laboratory-scale experiments should be applied in the field. In adsorption study, quantitative relationship between pore size distribution of the adsorbent, size of the adsorbate molecule, functional groups present on the adsorbent surface, column or batch conditions, particle size of the adsorbents and sorption capacity help in predicting and selecting adsorbents in field applications. In the adsorption study, multi-component system should be given more priority because the aqueous system contains various metal ions as the contaminants and interaction between different metal ions play an important role in sorption efficiency of different metal ions. The choice of low cost, effective and recyclable adsorbents important. The adsorbents should have high sorption capacity, with easy separation from aqueous solution, low cost and recycling use. Similarly, in the desorption study, choice of suitable eluant is important. The eluant should be metal-selective, economically feasible and desorption rate should be high. Successful adsorption studies will transpire through collaboration and technology transfer with/from experts in the respective fields.

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