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General Article

Use of natural products as biosorbent of heavy metals ó An overview

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Abstract

Industrial effluents loaded with heavy metals are a cause of hazards to human and other forms of life. Conventional methods such as precipitation, evaporation, electroplating, ion exchange, membrane processes, etc. used for removal of heavy metals from waste water however, are often cost prohibitive having inadequate efficiencies at low metal ion concentrations. Biosorption can be considered as an alternative technology which has been proved as more efficient and economical for removal of heavy metals from the industrial waste water. The most frequently used biosorbents are bacteria, fungi, algae and yeasts. But more recently, low cost natural products have also been searched as biosorbent. This paper presents an overview of the potential use of some natural products as biosorbent which could serve as a cost effective means of treating effluents charged with toxic heavy metals.

Keywords: Biosorbent, Heavy metals, Waste water, Industrial effluent, Natural products.

IPC code; Int. cl.^{8} — C02F 1/28, C02F 1/62, C02F 3/00, C02F 3/32

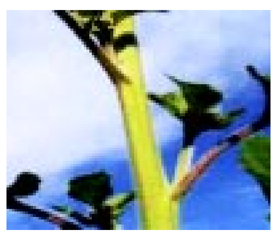
Introduction

Heavy metals are a group of pollutants which occur as natural constituents of the earth's crust. Serious consequences of biological hazards caused by metal toxicity cannot be ruled out. A high degree of industrialization and urbanization has substantially enhanced the degradation of aquatic environments through the discharge of industrial waste water and domestic wastes. This has resulted in significant amount of heavy metals being deposited into natural aquatic and terrestrial ecosystems. It has also increased the biological cycling of toxic heavy metals. In view of this, there is an urgent need for removal of heavy metal contaminants.

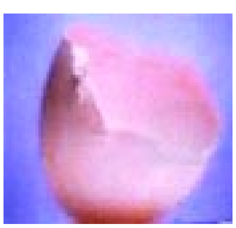
Conventional methods for heavy metal removal from aqueous solution include chemical precipitation, electrolytic recovery, ion exchange/ chelation and solvent extraction/liquid membrane separation[1]. But these methods are often cost prohibitive having inadequate efficiencies at low metal concentrations, particularly in the range of 1-100 mg/l[(Ref.2)]. Some of these methods, furthermore, generate toxic sludge, the disposal of which is an additional burden on the techno-economic feasibility of treatment procedures. These constraints have caused the search for alternative methods that would be efficient for metal sequestering. Such a possibility offers a method that uses sorbents of biological origin[3-5] for removal of heavy metals from dilute aqueous solutions. The most frequently studied biosorbents are bacteria, fungi and algae[6-10]. But more recently, the search for new cost effective


Rice Husk


Fruit waste


Sunflower stem


Crab shell


Egg shell


Coconut copra meal


Sugar beet pulp


Coconut shell carbon

biosorbents involving removal of toxic metals from waste water/effluents has directed attention and natural sorbents are searched among many waste materials from food and agricultural industry. These materials can be considered as low cost sorbents[11] and require little processing, abundant in nature or are a by-product or waste material from some industry[3].

Natural Products as Biosorbents

Crab shell

Utilization of crab shell for biosorption of copper (II) and cobalt (II) was investigated by Vijayaraghavan *et al*[12]. At optimum particle size (0.767 mm), biosorbent dosage (5g/l) and initial solution *p*H (*p*H 6), crab shell recorded maximum copper and cobalt uptakes of 243.9 and 322.6mg/g, respectively. Among the several eluting agents, viz. HCl, H_2SO_4, HNO_3, $CaCl_2$, NaCl, NH_4Cl, NH_4OH, NaOH, EDTA(Na) and EDTA(Na)/HCl, EDTA (*p*H 3.5, in HCl) performed well and caused low biosorption damage. The biosorbent was successfully regenerated and reused for five cycles.

The carapace of the crab (*Cancer pagurus* Linn.), a waste material disposed of by the seafood industry, could serve as a viable, cost effective biosorbent for the removal of metals from aqueous media. In sequential-batch process Zn^{2+} uptakes of 105.6 and 67.6 mg/g were recorded for 0.25-0.8mm and 0.8-1.5mm particles, respectively, while values of 141.3 and 76.9 mg/g were recorded in fixed-bed column studies[13].

Coconut copra meal

Coconut copra meal is a by-product of coconut production and is characterized by functional groups such as alcohols, hydroxyls, carboxylic acids, etc. on its surface. Its effective use as a biosorbent for the removal of heavy metals like cadmium was investigated by Hofomaja and Ho[14]. Cadmium biosorption by coconut copra meal was found to be dependent on the initial solution *p*H and initial cadmium concentration. Mathematical relationships were drawn to relate the change in the solution hydrogen ion concentration with equilibrium biosorption capacity, initial cadmium concentration and equilibrium biosorption capacity.

Egg shell

The crushed egg shells possess relatively high sorption capacity of Cr (III) ions[15]. When compared with other sorbents, it was found that sorption capacity increased with the increase of Cr (III) concentration, temperature and sorbent concentration. Egg shells were able to remove the concentration of Cr (III) ions below the acceptable level i.e. at 40°C, at the initial metal ion concentration 100mg/kg, at sorbent concentration 15g/l.

Papaya wood

Papaya wood was evaluated as a new biosorbent of heavy metals[16]. On contacting with 10mg/l copper (II), cadmium (II) and Zinc (II) solutions with 5g/l papaya wood, during shake flask contact time of 1h, the respective metal removal was noted to be 97.8, 94.9 and 66.8 %. Sorption was most efficient at *p*H 5 and metal ion biosorption increased as the ratio of metal solution to the biomass quantity decreased. At equilibrium, the affinity of papaya wood to biosorp metals was in order of copper (II) >cadmium (II) >Zinc (II), which remained the same during the testing of variables of different factors.

Sunflower stem

The sorption potential of sunflower stem for Cr (III) ions was investigated in detail by Malik *et al*[17]. The stem was washed with water and dried in air and inner soft tissue was removed and outer hard tissue was chopped up to 1 cm length, washed and deionized with water, dried in oven at 105 + 5°C and ground in a blade mill. The powder was sieved into different fractions (180-300 µm). The maximum sorption (>85%) of Cr (III) ions (70.2 µm) has been accomplished using 30 mg of high density sunflower stem in 10 min from 0.001 M nitric and 0.0001M hydrochloric acid solutions.

Rice bran

The capacity of raw rice bran for chromium and nickel removal from aqueous solutions was investigated by Oliveira *et al*[18]. The Langmuir and Freundlich adsorption models, which are in common use for describing sorption equilibrium for wastewater treatment applications, were used to represent the experimental data and equilibrium data fitted well to the Freundlich isotherm model. Cr (VI) and Ni (II) were sorbed due to strong interactions with active sites of the sorbent.

Husk of Bengal gram

The potential to remove Cr (VI) from aqueous solutions through biosorption using the husk of Bengal gram

(***Cicer arietinum* Linn.**) was investigated in batch experiments by Ahalya *et al*[19]. The results showed removal of 99% of chromium in the 10mg/l chromium solution, the biomass required at saturation was 1g/mg. The biosorptive capacity of the sorbent was dependent on the *p*H of the chromium solution, with *p*H 2 being the optimal. The adsorption capacity increased with the increase in agitation speed and optimum was achieved at 120 rpm. The biosorption of Cr (VI) was studied by Fourier transform infrared spectroscopy (FTIR). Husk of Bengal gram was proved to be an excellent material for biosorption of Cr (VI) to treat waste water containing low content of metal.

Husk of Black gram

Black gram husk [***Vigna mungo* (Linn.) Hepper**] efficiently remove heavy metal ions from aqueous solutions with selectivity order of Pb> Cd> Zn> Cu> Ni. The biosorption increased as the initial metal concentration increased. Biosorption equilibrium was established within 30 min, which were well described by Langmuir and Freundlich adsorption isotherms. The maximum amount of heavy metal adsorbed at equilibrium was 49.97, 39.99, 33.81, 25.73 and 19.56 mg/g biomass for Pb, Cd, Zn, Cu and Ni, respectively. The biosorption capacities were found to be *p*H dependent and the maximum adsorption occurred at the solution *p*H 5[Ref. 20].

Sugar beet pulp

Dried sugar beet (***Beta vulgaris* Linn.**) pulp, an agricultural solid waste by-product, was used as an biosorbent for the removal of copper (II) from aqueous solution[21]. The results indicated that at 250 mg/l copper (II) concentration dried sugar beet pulp exhibited the highest copper (II) uptake capacity of 28.5 mg/g at 25ºC and at an initial *p*H value of 4.0. The Langmuir model was found to be best.

Black tea leaves

Sorption of Cr (VI) on used black tea leaves as a low-cost adsorbent was studied by Kumita *et al*[22]. Batch experiments were conducted to evaluate the effects of Cr (VI) concentration, solution *p*H and temperature on the removal process. The maximum Cr (VI) adsorptive conditions, with a minimum reduction, were achieved from the dynamics of operational parameters: the initial Cr (VI) concentration <150mg/l; the initial solution *p*H 1.54-2.00 and the processing temperature <50ºC, for the possibility of its practical application.

Wheat shell

The biosorption of copper (II) by wheat shell was reported by Basci *et al*[23]. Maximum biosorption of copper onto wheat shell occurred at 240 rpm agitation speed and at *p*H between 5 and 6. The biosorption values of copper (II) were increased with increasing *p*H from 2 to 5 and decreased with increasing copper/wheat shell sorption capacites from 0.83 to 10.84 mg Cu (II)/g wheat shell. The biosorption efficiencies at these ratios were 99 and 52%, respectively.

Cork biomass

Cork oak tree is very abundant in several countries which develop bottle cork for the wine industry. The effect of pretreatment of cork biomass on the biosorption of heavy metals, viz. Cu, Zn and Ni was studied by Chubar *et al*[24]. The pretreatment of the cork biomass with 0.5 M sodium chloride solution led to an increase of 30% of cork sorption capacity for copper, while the pretreatment with 0.5 M calcium chloride solution did not improve significantly the performance of biomass. The use of oxidizing agents (NaClO and $NaIO_3$) in the pretreatment step allowed an increase of the sorption capacity of the biomass[24].

Rice husk

The ability of rice husk to adsorb Cd (II) from water has been explored by Ajmal *et al*[25]. The extent of removal depends on concentration of the solution, *p*H, temperature and contact time. The adsorption model followed the Langmuir isotherm. Removal efficiency by column process is better than by batch process.

Petiolar-felt-sheath of Palm

The petiolar-felt-sheath of Palm (PFP) was reported as a new biosorbent for the removal of heavy metals from contaminated water[26]. Biosorption of heavy metals such as Pb(II), Ni(II), Cd (II), Cr (III) and Zn (II) by PFP was examined and efficient removal of all the toxic metals ions with selectivity order of Pb> Cd> Cu> Zn> Ni> Cr was found. The uptake was rapid, with more than 70% completed within 15 minutes. The bound metal ions were successfully desorbed and the PFP biomass remained effective after several adsorption desorption cycles.

Coffee beans

The biosorption of metals such as copper (II), zinc (II), lead (II), iron (III) and cadmium (II) is reported by using discarded coffee beans[27]. Using dropped and degreased (DCB) coffee beans as an adsorbent batch adsorption experiments were carried out at various *p*H in order to elucidate the selectivity of metal ions. All metals were adsorbed at low *p*H region (3.0-5.0). Of particular interest was the adsorption characteristics of cadmium (II) on DCB. The reaction mechanism was found to be an ion exchange reaction between metal ions and DCB.

Arca shell

The biosorption potential of pretreated arca shell biomass for lead, copper, nickel, cobalt and cesium was explored from the artificially prepared solution containing known amount of metals[28]. At equilibrium, the maximum total uptake by shell biomaterial was 18.33±0.44, 17.64±0.31, 9.86±0.17, 3.93±0.11 and 7.82±0.36 mg/g for lead, copper, nickel, cesium and cobalt, respectively under the optimized condition of *p*H, initial concentration, biosorbent dose and contact time.

Table 1 : Natural products used as biosorbents for removal of heavy metals from aqueous solutions

Biosorbents (Natural products)	Metals	Adsorption Capacity (mg/g) / Efficiency (%)	References
Black tea leaves	Cr(VI)	364 mg /g	22
Cocoa shells	Pb, Cr, Cd, Cu, Fe, Zn, Co, Mn, Ni, Al	Pb 95, Cr 53, Cd 81, Cu 70, Fe 45, Zn 64, Co 57, Mn 53, Ni 50, Al 15(%)	30
Coconut copra meal	Cd	1.70 mg/g	14
Coconut shell carbon	Zn	90%	29
Coffee beans	Cu (II), Zn (II), Pb(II), Fe(III) and Cd(II)	5.98×10^{-2} mmol /g	27
Crab shell	Cu Co	243.9 mg/g 322.6 mg /g	12
Egg shell	Cr(III)	160 mg/g	15
Husk of Bengal gram	Cr(VI)	99%	19
Husk of Black gram	Pb, Cd, Zn,Cu,Ni	49.97, 39.99, 33.81, 25.73, 19.56(mg /g)	16
Papaya wood	Cu, Cd, Zn	97.8, 94.9, 66.8 (%)	20
Sugarbeet pulp	Cu(II)	28.5mg /g	21
Sunflower stem	Cr(III)	85%	17
Waste fruit residues	Hg (II), Pb (II), Cd (II), Cu (II), Zn (II), Ni (II)	Hg 85, Pb 90, Cd 86, Cu 96, Zn 87, Ni 85(%)	31
Wheat shell	Cu (II)	99%	23

Coconut shell carbon

The biosorption of Zn from aqueous solution by a composite adsorbent (chitosan-coated acid treated coconut shell carbon) is reported[29]. Coconut shell carbon was modified with chitosan and/or oxidizing agent (phosphoric acid) to produce composite adsorbent. The removal efficiency was controlled by solution *p*H, adsorbent concentration and agitation times, initial ion concentration and particle size.

Cocoa shells

The efficiency with which cocoa shells remove heavy metals from acidic solutions (*p*H 2) and how the composition of these solutions influence the heavy metal uptake efficiency is reported[30]. The removal of metals from aqueous solutions followed a specific order of Pb >Cr> Cd = Cu = Fe > Zn = Co > Mn = Ni = Al.

Waste fruit residues

Biowaste obtained from fruit juice industry was evaluated as a new biosorbent for removal of toxic heavy metals, Hg (II), Pb (II), Cd (II), Cu (II), Zn (II) and Ni (II)[31]. The removal efficiency of phosphated fruit residues (P-FR) was higher than fruit residue (FR) especially at low *p*H values. The order of removal of heavy metal by P-FR was Cu (II)> Pb (II)> Ni (II) ≥ Zn (II)> Hg (II) = Cd (II).

Fish scales

The feasibility of using fish scale as an adsorbent to remove heavy metals was examined by Mustafiz[32]. Biological effects on adsorption of heavy metals such as lead, arsenic and chromium were studied using Atlantic Cod scale. The difference in results between non-sterilized and sterilized experiments showed the microbial contribution to heavy metal removal.

Table 1 summarizes the bio-sorption capacities/efficiencies of natural products discussed above.

Conclusion

The research reports summarized in this article have highlighted the potential use of natural products as biosorbent of heavy metals which represents a cost effective excellent tool for removing heavy metals from aqueous environment. Mathematical modelings are definitely helpful for biosorption process optimization.

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