REMOVAL OF HEAVY METAL IONS FROM POLLUTED WATER USING ENVIRONMENTALLY-FRIENDLY MATERIALS

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Abstract

Ions such as Cr, Mn, Fe, Co, Cu, Zn, Cd and Pb can be effectively removed by burnt-brick, saw-dust and ball-clay packed glass columns. The removal efficiency is further enhanced by optimization of experimental parameters such as particle size, length of packing, flow rate, etc. Systematic investigation of standard solutions and mixtures of these metals within the working concentration range shows that brick-clay is the most efficient metal ion remover for many heavy metals.

Detailed investigation on the adsorption of lead ions on burnt brick particles between pH 4 and pH 6 results in the validity of the Fruendlich or Langmuir isotherm models. Ion-exchange phenomenon would also make a contribution to the lead ion removal process.

Key words: heavy metals, treatment, industrial effluent.

INTRODUCTION

Industrial development, urbanization and uncontrolled agricultural practices have resulted in severe environmental problems in Sri Lanka. Consequently, many rivers, water streams and lakes in the country have already been polluted with organic and inorganic pollutants, including coloured substances (azo dyes, anthraquinone, formazan and phthalocyanines), heavy metals, nutrients from sewage or fertilizers, pesticides and solid particles.[1-3] The presence of these contaminants changes physical, chemical as well as biological state of water. Consequently, harmful effects, such as unbalancing solution pH, death of aquatic life, increase in different pathogenic organisms and adverse effects to humans would result. Some specific toxicity problems associated with heavy metals that are found in biological systems include disruption of enzymes by forming metal-sulfur bonds, hindering transport properties by binding to cell membranes, formation of complexes with polysaccharides, bioaccumulation in tissues, and ability to combine or replace compounds which perform important physiological functions.[4-10]

Among many types of pollution, industrial pollution may be more significant. Although many industries require large quantities of water per unit weight of produce, a substantial portion of intake is thrown out as effluent which is contaminated with several substances. Textile industry, for instant, requires 12-65 litres of water for processing one meter of cloth. In Sri Lanka, garment/textile industry has rapidly developed in recent years. It plays an important role in the economy of the country as it is one of the major foreign exchange earners. However, the disposal of effluents of garment industry is posing serious problems as the receiving river or stream may become coloured due to inadequate effluent treatment. Sedimentation of heavy metals by association with organic and inorganic matter present in water body would be another undesirable process of textile effluent.

Industrial effluents usually consist of large amounts of dyes, cations, anions, organic substances, etc. These effluents should therefore be properly treated before discharged into water bodies. Many industries still use chemical procedures for treatment of effluents despite of environmental problems and economical factors. It is recommended that treated effluent should fulfil the specifications laid down by the Central Environmental Authority of Sri Lanka.

Removal of inorganic and organic pollutants from industrial effluents through chemical and biological means are well documented.[10-15] Among various methods available for metal ion removal, coagulation and precipitation, lime treatment, reverse osmosis, ion exchange and adsorption processes have been widely applied.[16-18]

Precipitation process of high metal ion concentrations in waste water are often the most economical. However, some complexing agents present in waste water may decrease the efficiency of the precipitation process. Although chemical precipitation methods have been traditionally used for removal of heavy metals, development of alternative approaches based on naturally occurring substances or their derivatives has become attractive during the past few years. It has been reported recently that many substances of biological origin are effective for removal of metal ions from waste waters; for instant, Salim and coworkers have conclusively demonstrated that several types of decaying leaves have shown an ability for removal of such metals as Al, Ni, Pb and Cd from aqueous solution.[10]

Another significant accomplishment in this area of research is to use immobilized cells including *Pseudomonas sp.*, *Cunninghamelle blakesleeana* and *Aphanocapsa pulchra* for removal of Ni, Cu, Cd, Zn and Co through specific binding processes.[11] Effect of other ions interferents on the removal efficiency, and the extent of recovery of such immobilized species have also been investigated.

Additionally, ion exchange and/or adsorption properties of many other natural substances have been extensively investigated[12]. Modified coconut coir dust has been shown to remove Pb, Cu and Ni successfully from aqueous solution, and it has been suggested that coconut coir has a good potential as an adsorbent of heavy metals present in industrial effluents.[11] Further, activated charcoal has been found to remove not only organic matter, but also heavy metals[13,14]. Metal speciation property of clay-based substances to extract metal ions from aqueous solutions has also been recently reported.[15,21]

High cost of construction, operation and maintenance, and generation of large amounts of unusable sludge have been a problem for effective treatment of industrial effluents, especially in developing countries.[19,20] Lack of environmental friendly attitudes, and poor collaborations between industries and national research institutes may have worsened the situation. As a result, pollution control and management are still at a very low level in developing countries.

It is the goal of this project to develop removal methods for heavy metals using naturally occurring substances which are low cost and readily available such as burnt-brick, different types of clay (ball-clay, kaolin, pot-clay, etc.), dolomite, saw-dust, rice-husk and aquatic plants. Extension of this methodology for removal of heavy metals from industrial effluents collected from various industries is also investigated.

METHODS AND MATERIALS

Materials: Burned brick (brick-clay) samples for all experiments were obtained from a kiln located in Kiribathkumbura, Sri Lanka. Other adsorbents tested; raw dolomite, burnt dolomite, activated charcoal, ball-clay, keolin and coir dust were obtained locally. Saw-dust of *Albizia Odoratissima* ('Mara' in Sinhala) was collected from a saw mill located at Pilimathalawa. All substances were powdered and separated into desired sizes.

Stock solutions of metal ions were prepared by dissolving analytical grade chemicals [NaCl, KCl, MgSO4, CaCO3, K_2CrO_4, $KMnO_4$, Fe(NH4)SO_4, $Co(NO_3)_2$, $CuSO_4$, $ZnSO_4$, $CdSO_4$ and $Pb(NO_3)_2$], purchased from the British Drug Houses Ltd., England, in deionized water. Small amounts of either concentrated HCl or concentrated HNO_3 were used when solubility problems were encountered. Diluted standard solutions of individual metal ions and mixtures of metal ions were prepared using appropriate volumes of each stock solution and deionized water.

Instrumentation: Atomic Absorption Spectrometer (Buck Instruments Model 200-A) was used to record absorbance measurements of each metal ion solution, in triplicate, at a selected wavelength using an appropriate hollow cathode lamp. Pure acetylene and air were used as the fuel and the oxidant, respectively. Brick particles and saw-dust particles were separated into desired sizes using a set of sieves attached to a vibrator.

Research design: Atomic absorption measurements of metal ion solutions before and after treatment with burnt-brick and saw-dust particles were recorded by passing standard solutions of individual metal ions of different concentrations (2.0, 4.0, 6.0, 8.0, and 10.0 mg/L) through burnt-brick/saw-dust packed glass columns (dynamic conditions). The predetermined optimized experimental/column parameters such as length of packing, diameter of column, amount of adsorbent, flow rate and volume of metal ion solution, were kept constant during all experiments. Same packing of adsorbents was used for each metal ion at all concentrations.

Since the working concentration range of a species depends on the linear dynamic range of atomic absorption detection, standard solutions and corresponding treated standards of **Mg, Ca, Mn, Fe, Cu, Zn** and **Cd** ions were diluted by an appropriate volume factor with deionized water until absorbences fell within the linear range. Absorbance measurements of solutions of **Cr, Co and Pb** ions were recorded without any further dilution as the concentration range of 2.0 to 10.0 mg/L is in the linear range of detection.

Further investigation on lead ion removal was performed by passing lead ion solutions of concentration ranging from 0.5 to 256 mg/dm^3 through brick-particle packed glass columns and absorbences were measured before and after treatment. The removal efficiencies and the variation of pH during the treatment process were monitored at many pH values varying from 3 to 9. Further, the eluent was tested for other metal ions. Desorption ability of lead was also tested after treatment process was completed.

RESULTS AND DISCUSSION

Preliminary Screening Experiments

Careful investigation on the efficiency of the removal process indicates that the optimum values for the ion removal process depend on the type of the adsorbent (Table 1). For detailed investigation of ion removal experiments, packed columns (dynamic systems) are preferentially selected over classical methods that use static conditions, as columns packed with suitable adsorbents would be considered as model systems to monitor the extent of ion removal from effluent/polluted water, when it is passed through water treatment plants.

Table 1. Optimum values of experimental parameters for heavy metal removal.

Parameter	burnt-brick	saw-dust
amount of adsorbent	25 g	15 g
volume of solution	100 cm^3	100 cm^3
particle size	0.4 mm	1.25 mm
length of packing	4.5 cm	---
flow rate	25-30 cm^3/min	30 cm^3/min
medium	water	water
pH	neutral	neutral

The percent efficiency of removal for each metal was calculated using the difference in concentrations, which were obtained by conversion of measured absorbencies to concentration units with the aid of calibration curves, before and after treatment with brick/saw-dust particles. Such calculations performed at each concentration lead to the extent of removal of heavy metals from aqueous solution. The series of standard solutions (of 2.00 to 10.00 mg/dm^3) of all metals with the exception of Cr gave a zero absorbance after treatment with brick particles, indicating that the concentration of these species in treated solutions was below the minimum detectable level, which depends on the type of the element and on the sensitivity of atomic absorption detection. Although zero absorbance was recorded only for Cd, Pb, Cu, Mn and Co at 2.00 mg/dm^3 level during the saw-dust treatment, only Pb showed a zero absorbance at 4.00 mg/dm^3 level.

Minimum detectable level of Cr, Mn, Co, Cu, Cd and Pb estimated from a different set of experiments yielded the results of 0.10 mg/dm^3 while that of Fe and Zn showed 0.50 mg/dm^3 and 0.05 mg/dm^3, respectively. Since these concentrations were used to calculate the percent removal of Cr, Mn, Co, Cu, Cd and Pb, actual percentages would be higher than the estimated values. Removal efficiency of Cr is also significant according to atomic absorption measurements although it is less than that of other metals at high concentrations.

The competition of heavy metal ions for adsorption sites depends on the stability of their complexes formed, order of complexing ability, valence of the metal ion, its ionic radius, and the ionization potential. The observed lower affinity of Cr for brick particles suggests that speciation of other metals in brick is stronger than that of Cr.

Columns packed with adsorbents of particle sizes different from what is stated in Table 1 can also be used for treatment of polluted water as the decrease in absorbance of heavy metal ions by many other sizes are not significantly different from that of the preselected value, and consequently, detailed studies of other sizes were not attempted. Nevertheless, sizes below 0.12 mm in diameter are not recommended as they introduce additional turbidity to the effluent. Additionally, experimental/column parameters were always kept constant at the values stated in the experimental section for comparative investigation of different metal ions.

Comparison of absorbance measurements, recorded using mixtures of pairs of metal ions which have close wavelengths of absorption with those of individual ion solutions at 2.0 mg/dm^3 concentration levels indicated that the interelement interferences are minimal with the exception of Zn and Pb which would interfere each other. Analysis of samples consisting of the ions investigated with the same column and experimental parameters, as used for individual ions, was conducted in order to check the possibility of extending the methodology developed in real situations (Table 2). The methodology was then extended for treatment of textile effluent samples obtained from garment industry. Treatment performed under identical conditions in five replicates reveals that levels of heavy metals present in textile effluents can be significantly decreased by brick-particle packed columns (Table 3), although the efficiency of removal is slightly less than that observed with laboratory prepared samples.

Table 2: Concentrations (mg/dm^3) of each metal in a matrix of ion mixtures before and after treatment, percent removal, and corresponding statistical parameters.

Metal	Initial con.(mg/dm^3)	Final con.(mg/dm^3)	% Removal
Cr	2.0	Undetectable	95.0
Mn	2.0	0.4	84.33
Fe	2.0	Undetectable	75.0
Co	2.0	Undetectable	95.0
Cu	2.0	Undetectable	95.0
Zn	2.0	Undetectable	97.0
Cd	2.0	Undetectable	95.0
Pb	2.0	Undetectable	95.0

Table 3: Average concentration values (mg/dm^3) of each metal in textile effluent samples before and after treatment.

Metal	Initial con.(mg/md^3)	Initial con.(mg/dm^3)
Cr	Undetectable	Undetectable
Mn	2.2	0.4
Fe	1.0	Undetectable
Co	Undetectable	Undetectable
Zn	0.7	Undetectable
Cd	Undetectable	Undetectable
Pb	Undetectable	Undetectable

Brick particles show a higher capacity of lead ion removal when compared to the other heavy metals such as Co, Cd, Fe, Mn, Cr and Cu. Mechanism of lead ion removal is complicated, and it is found to be a combination of chemisorption and ion exchange. Further, both the Fruendlich and the Langmuir isotherm models are followed by this removal process depending on experimental conditions. Nevertheless, this methodology, with some modifications, would be suitable for industries to treat their effluent.

CONCLUSIONS

Effective removal of Cr, Mn, Fe, Co, Cu, Zn, Cd and Pb from aqueous solution is achieved using glass columns packed with small burnt brick particles or saw-dust. Main group elements are more difficult to be removed from aqueous solution using these adsorbents. Extension of this methodology for treatment of textile effluents to decrease levels of above stated heavy metals below tolerance limits indicates the possibility of applying this procedure for treatment of industrial effluents. It is proposed that a filter packed with burnt brick particles would have a potential for removal of heavy metal ions present in industrial effluents. Environmental friendliness and cost effectiveness are added advantages of the proposed procedure.

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