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REMOVAL OF HEAVY METAL IONS FROM TEXTILE EFFLUENTS USING BURNT BRICK PARTICLES

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ABSTRACT

Burnt brick-particle packed columns have a strong ability for removal ofheavy metal ions including Cr, Mn, Fe, Co, Cu, Zn, Cd and Pb from aqueous solution. Higher removal efficiencies of Fe, Co, Cu, Cd and Pb from mixtures of metal ions suggest the preferential speciation/adsorption ability of these metals over Cr, Mn and Zn. This methodology can be successfully applied for treatment of textile effluents, and consequently, the amount of heavy metals after treatment falls well below the tolerance limits. Environmental friendliness, readily availability and low cost are other attractive features of these columns.

1. INTRODUCTION

Heavy metals are considered to be environmental pollutants because most of them create harmful effects to the environment. Some 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.[1-3]

Industrial effluents usually consist of large amounts of dyes, cations, anions, organic substances, etc.[4,5] 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.[1,6] Although analytical chemists play a major role in providing with accurate and precise methodology for detection of water quality parameters, it is the responsibility of environmental chemists to adapt environmentally friendly procedures which would decrease magnitudes of these parameters in treated waters below the tolerance levels.

Methods used for treatment of waste water, especially industrial effluents, should be economical, effective and simple. Although chemical precipitation methods have been traditionally used for removal of heavy metals,[7] development of alternative approaches based on naturally occurring substances and 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 instance, 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.[8]

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.[3,9,10] Effect of other anions commonly present in water, and interference effects 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 other naturally occurring adsorbents have been extensively investigated. 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[12,13]. Metal speciation property of clay-based substances to extract metal ions from aqueous solutions has also been recently reported.[14,15]

Although low cost sand and charcoal filters are employed for removal of colour and organic matter, in latter stages of the purification process of industrial effluents, expensive chemical procedures are still in use in metal ion removal. It is the goal of our research to explore possibility of using brick-particle filters in place of chemical procedures for removal of heavy metals. Brick was specially selected as it is commonly available at a low cost, and textile industry is selected as it is a continuously expanding industry in Sri Lanka.

Investigation of in-vitro removal of heavy metal ions including Cr, Mn, Fe, Co, Cu, Zn, Cd and Pb, from solutions of individual ions and from mixtures consisting of metal ions was initially performed. This methodology was successfully extended for removal of heavy metal ions present in textile effluents, with a reasonably high efficiency.

2. EXPERIMENTAL

Materials: Burnt brick samples for all experiments were obtained from a kiln located in Kiribathkumbura, Sri Lanka. They were powdered and separated into desired sizes. Stock solutions of metal ions were prepared by dissolving the analytical grade chemicals [K_2CrO_4, $KMnO_4$, $FeSO_4$, $Co(NO_3)_2$, $CuSO_4$, $ZnSO_4$, $CdSO_4$ 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. Untreated, blue coloured textile effluent samples were obtained from Osprey Garment (Pvt) Ltd., Ranala, Sri Lanka, while the plant was in operation.

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 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 brick 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/dm^3) through brick-particle packed glass columns. 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 Mn, Fe, Cu, Zn and Cd ions were diluted by an appropriate volume factor with deionized water until absorbencies 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/dm^3 is in the linear range of detection. The experimental/column parameters such as length of packing (4.5 cm), diameter of column (3.0 cm), amount of adsorbent (25 g), flow rate (25-30 cm^3/min) and volume of metal ion solution (100 cm^3) were kept constant during all experiments. Same packing of brick particles was used for each metal ion at all concentrations.

Five replicate analyses of ion mixtures consisting of all eight heavy metals at 2.0 mg/dm^3 concentration level were performed by passing them through five different columns packed identically with the parameters stated above, and the results were treated statistically. Textile effluent samples were also analyzed in five replicates under identical conditions, and the same statistical treatment, as performed for laboratory prepared samples, was applied.

3. RESULTS AND DISCUSSION

Absorbencies of heavy metal ions (Cr, Mn, Fe, Co, Cu, Zn, Cd and Pb) in the concentration range of 2.0 to 10.0 mg/dm^3 are drastically reduced when they are passed through glass columns packed with burnt brick particles of diameter 0.40 mm (Fig. 1 and Fig. 2). This clearly demonstrates the ability of brick particles for removal of heavy metal ions from aqueous solution. Packed columns (dynamic systems) are preferentially selected over classical methods that use static solutions, as columns packed with suitable adsorbents would be considered as model systems to investigate the extent of ion removal from effluent/polluted water, when passed through water treatment plants. Similar heavy metal ion removal studies by other types of clay and carbon-based substances, such as activated carbon and coconut coir, have already been reported recently.[14-18]

Grounded particles of burnt brick of 0.40 mm diameter were especially selected, as this size offers the best efficiency for colour removal of textile effluents obtained from the same company.[19,20] Columns packed with 0.40 mm diameter particles would then be effectively employed for both heavy metal ion and colour removal of textile and other types of industrial effluents. The decrease in absorbance of heavy metal ions by many other sizes ranging from 0.12 mm to 1.00 mm is how ever 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 investigations of different metal ions.

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 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 all metals with the exception of Cr gave

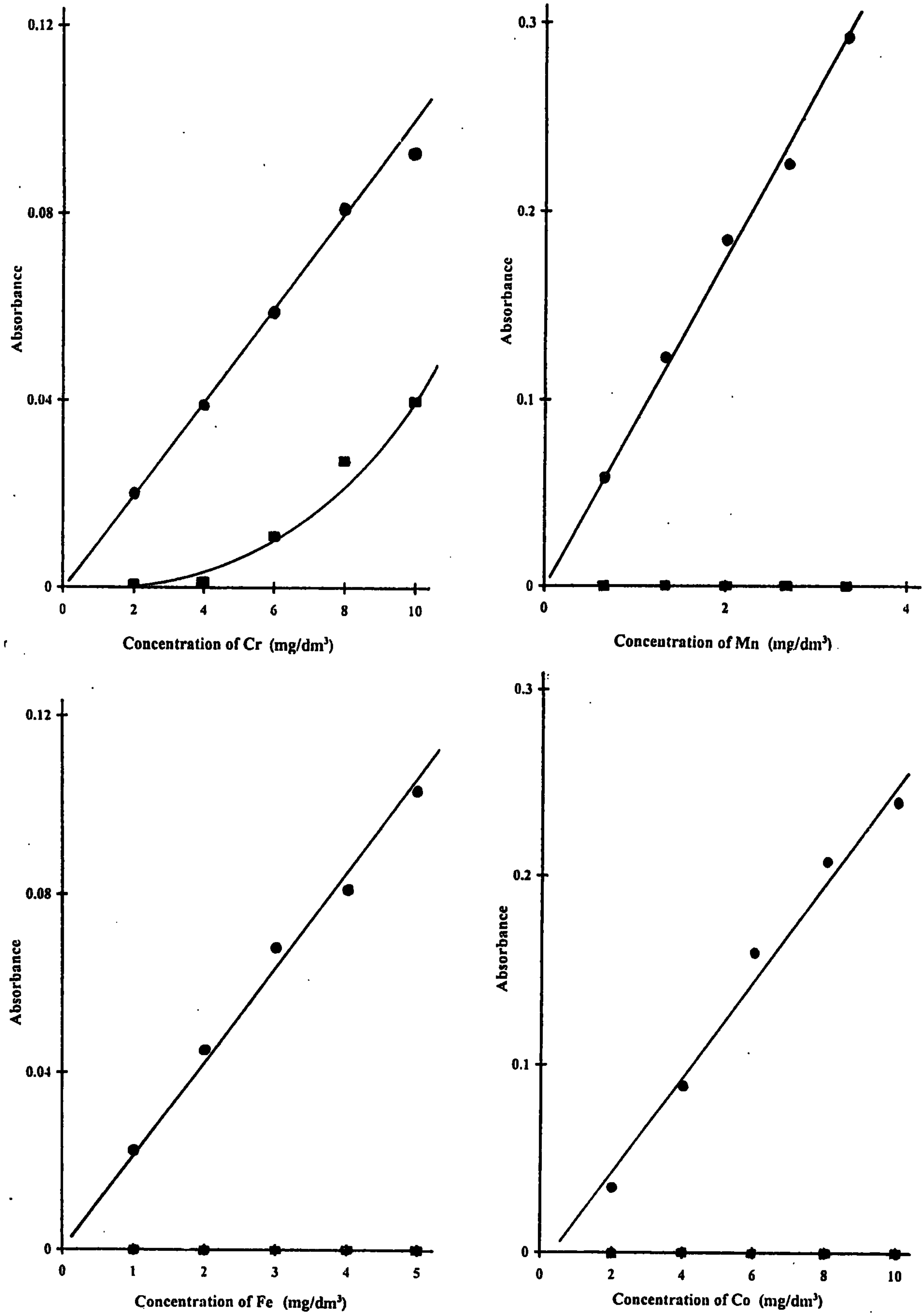

Fig. 1 Absorbance of standard metal ion solutions before (●) and after (■) treatment with brick-particle packed columns

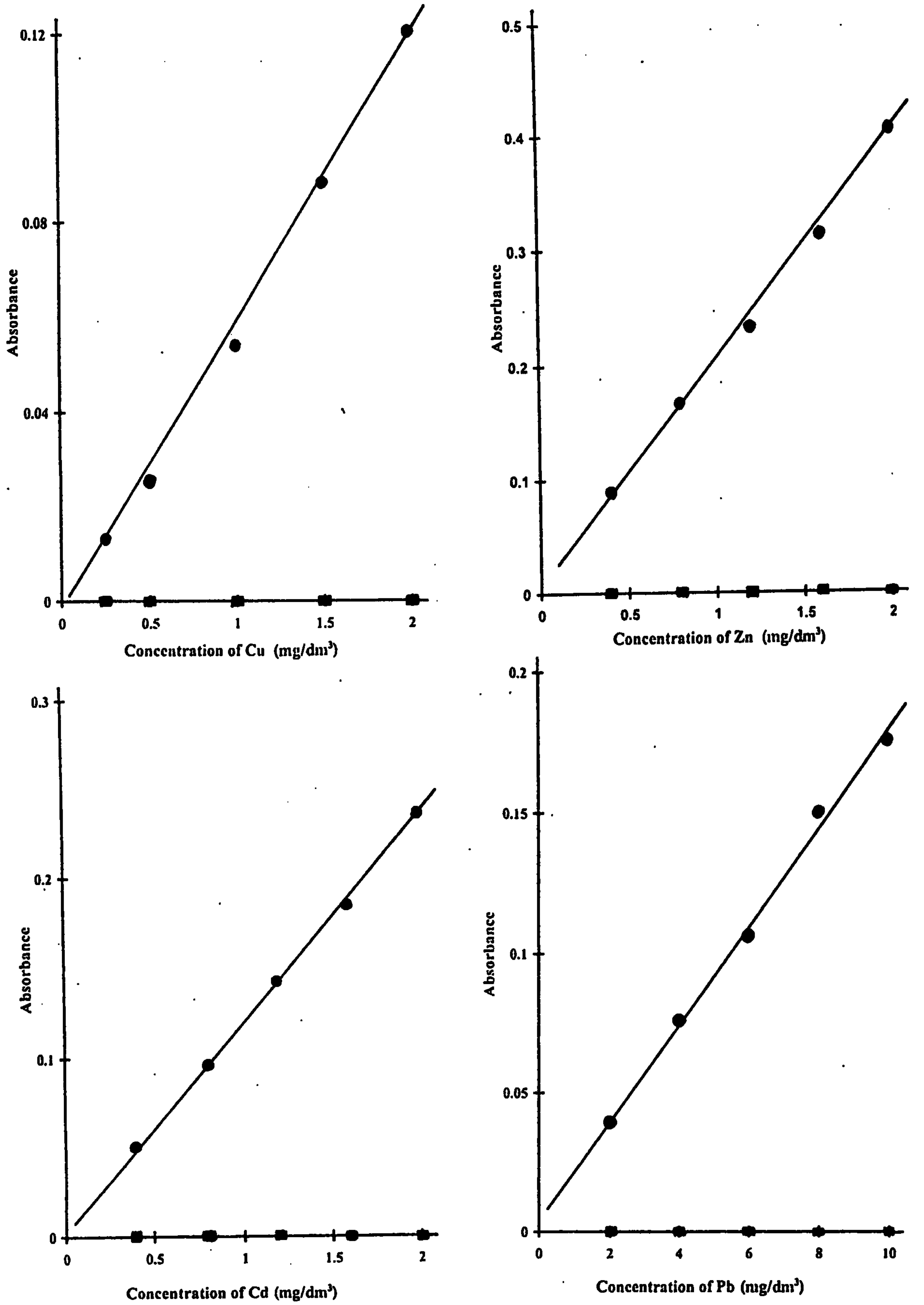

Fig. 2 Absorbance of standard metal ion solutions before (●) and after (■) treatment with brick-particle packed columns

a zero absorbance after treatment, 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. 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 percent removal estimated for the lowest and the highest concentrations of each metal are shown in Figures 3 and 4. A lower percent removal for Fe, as seen in Fig. 3, is due to higher minimum detectable level of 0.50 mg/dm^3 compared to lower values of other metals.

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. The report on the conversion of speciated Cr to residual Cr in red mud supports this observation.[18] How ever, detailed mechanistic investigation was not attempted as it is not the goal of this research.

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. How ever, preventive measures to avoid the effect of Zn on Pb were not attempted.

Removal efficiency of an individual metal ion at 2.0 mg/dm^3 is higher than that of the same metal in a matrix of other ions at the same concentration. Although Fe, Co, Cu, Cd and Pb are removed up to undetectable levels from the mixture, other ions are less effectively removed. Selective adsorption of certain ions by adsorbents would decrease the extent of removal of other ions, while interelement interferences would lead to an increase in absorbance resulting in positive analytical errors. Relative magnitudes of these two opposing effects are difficult to be estimated and hence the direction of the error in the final result cannot be predicted.

Analysis of five replicate 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 reproducibility of the treatment process. Confidence limits of the percent removal of each ion was calculated using the student's t-test at 90% confidence level after application of the Q-test at the same confidence level[21] indicated that the proposed methodology is reproducible and effective (Table 1).

The methodology developed for ion removal from complex mixtures prepared in the laboratory using brick-particle packed columns was extended for treatment of textile effluent samples obtained from Osprey Industries (Pvt.) Ltd. Treatment performed under identical conditions in five replicates reveals that levels of heavy metals present in textile effluents can be significanly decreased by brick-particle packed columns (Table 2), although the efficiency

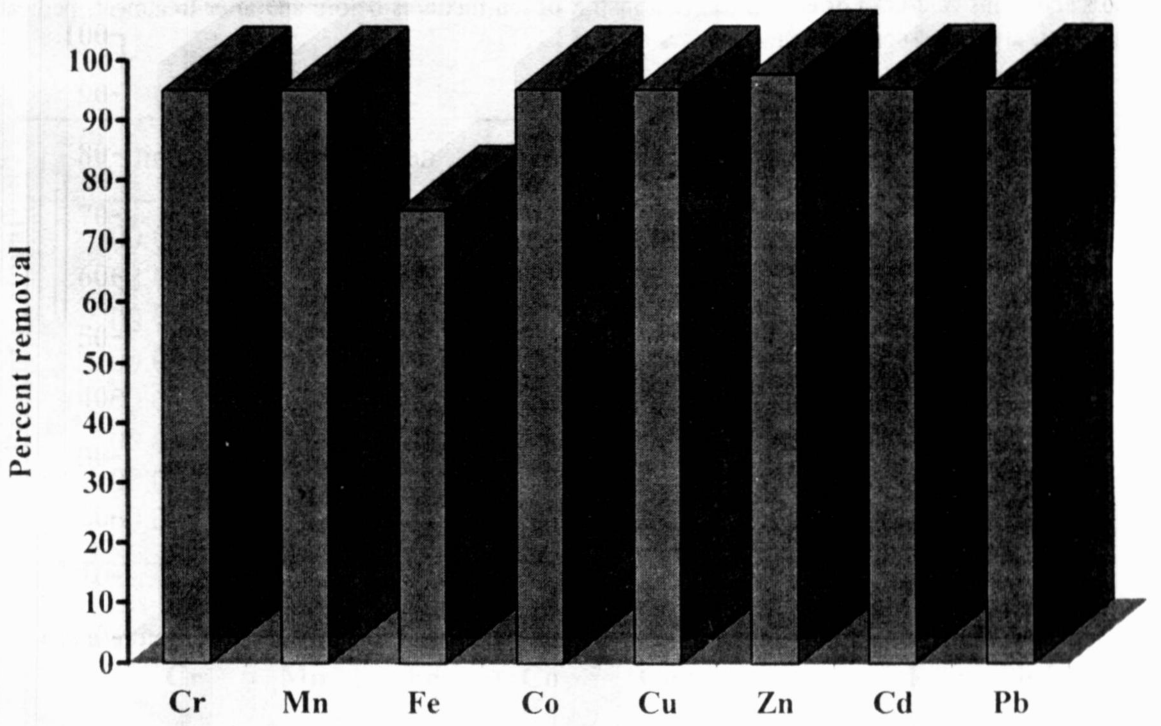

Fig. 3 Removal efficiencies of 2 mg/dm^3 metal ion solutions.

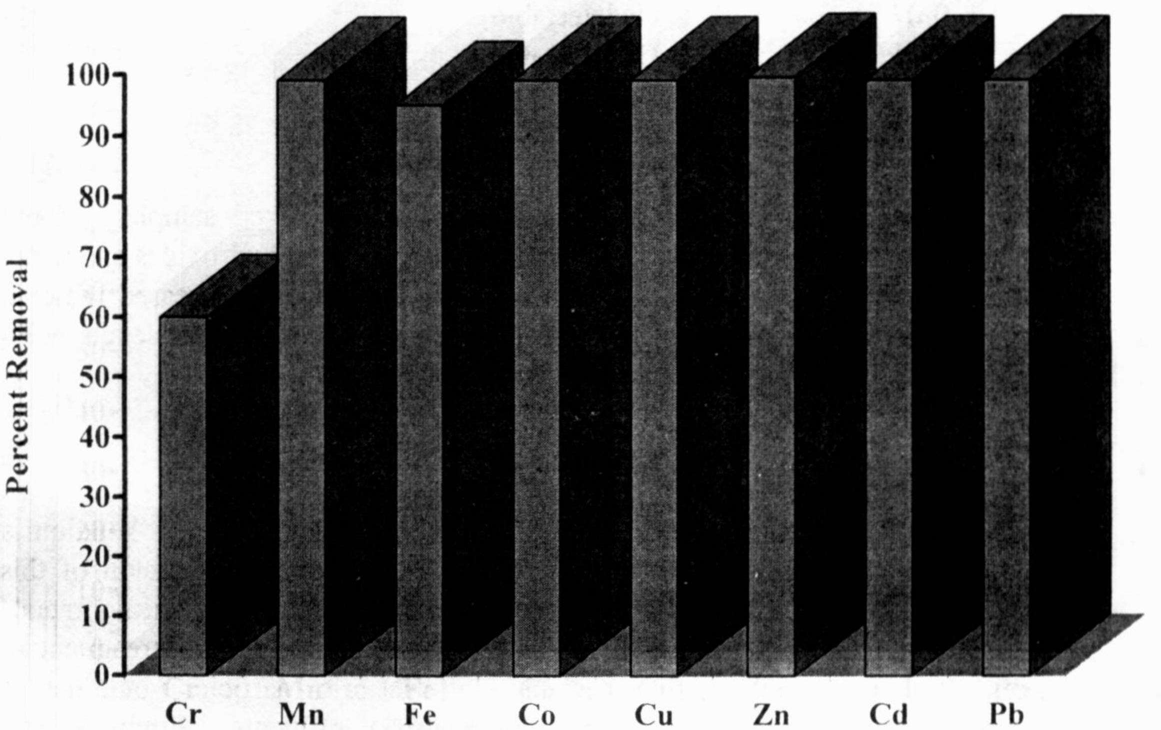

Fig. 4 Removal efficiencies of 10 mg/dm^3 metal ion solutions.

Table 1: 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.	Final con.	% Removal	Std. dev.	Confidence limit
Cr	2.0	Undetectable	95.00	0.00	95.00 +0.00
Mn	2.0	0.4	84.33	0.98	84.33 +0.89
Fe	2.0	Undetectable	75.00	0.00	75.00 +0.00
Co	2.0	Undetectable	95.00	0.00	95.00 +0.00
Cu	2.0	Undetectable	95.00	0.00	95.00 +0.00
Zn	2.0	Undetectable	97.50	0.00	97.50 +0.00
Cd	2.0	Undetectable	95.00	0.00	95.00 +0.00
Pb	2.0	Undetectable	95.00	0.00	95.00 +0.00

Table 2: Average concentration values (mg/dm^3) of each metal in textile effluent samples before and after treatment.

Metal	Initial con.	Final con.
Cr	Undetectable	Undetectable
Mn	2.2	0.4
Fe	1.0	Undetectable
Co	Undetectable	Undetectable
Cu	Undetectable	Undetectable
Zn	0.07	Undetectable
Cd	Undetectable	Undetectable
Pb	Undetectable	Undetectable

of removal is slightly less than that observed with laboratory prepared samples. Band interference due to the formation of less volatile substances such as metal hydroxides and metal phosphates would probably decrease absorbencies which would result in decreased removal abilities. Further, the interference of Pb on Zn determination was not explored in details as Pb was not detected in the textile effluents obtained.

4. CONCLUSION

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. 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. Use of other natural substances such as saw-dust, dolomite, aquatic plants and plant materials for treatment of polluted waters and industrial effluents is the next logical step this research.

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