

Multi Metal Removal from Aqueous System Using Agricultural Wastes: A Novel and Cost Effective Water Treatment Technology

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ABSTRACT: Intensive industrialization generates hazardous wastes prominently comprising of toxic metals that needs to be tackled in a safe manner. Human population needs method and technologies to clean water and diminish the environmental dangers related to technological progress. Abatement of heavy metals from aqueous system is now shifting from the use of conventional adsorbents to the use of biosorbents. Biosorption can be one such solution to clean up heavy metal contamination. The present piece of work reports the competitive biosorption of Cd (II), Cr (III) and Ni (II) on unmodified Shelled *Moringa Oleifera* Seeds (SMOS) present in ternary mixture and was compared with the single metal solution. The extent of adsorption capacity of the ternary metal ions was low (10-20%) as compared to single metal ions. SMOS removed the target metal ions in the selectivity order of Cd (II) > Cr (III) > Ni (II). Biosorption capacity of ternary metal ions was found to be pH dependent and the maximum sorption occurred at pH 6.5. Kinetic studies revealed that the present adsorption system follows Lagergren first order rate equation. Regeneration of exhausted biomass was also attempted for several cycles with a view to restore the biosorbent to its original state. The findings open up new avenues in the decontamination of multimetal ions from aqueous system using SMOS as domestic and ecofriendly safe technology under the domain of green chemistry.

INTRODUCTION

For the first time in his entire cultural history, man is facing one of the most horrible ecological crises-the problem of environment pollution, especially with presence of toxic metals in aqueous system, which sometimes in the past was pure, undisturbed, uncontaminated and basically quite hospitable for him. Today the cry of "Water Pollution" is heard from all the hooks and corners of the globe and it has become a major threat to the very existence of mankind on the planet earth. Toxic metal pollution can be much more serious and insidious problem, as these are intrinsic components of the environment. Among the toxic heavy metals, cadmium, chromium and nickel called "The Big Three" are in the limelight due to their major impact on the environment. Consequently, all these toxic effluents need to be assessed and require integrated solution documentation and removal strategies. The chemical process viz. ion exchange, reverse osmosis, precipitation etc. that exists today for metal abatement are not economical for treating a large volume of water bodies of dilute metal concentration and often not feasible. In this endeavor, biosorption has emerged as an option for developing economic and ecofriendly wastewater treatment process. Biosorption offers advantages of low operating cost, minimizes the

volume of chemical sludge, is highly efficient in dilute effluents and has no nutrient requirement. These merits have served as potential incentives for promoting biosorption as a viable clean up technology for heavy metal pollution (Volesky, 2003).

Although actual wastewater treatment systems often have to deal with a mixture of heavy metals, most research activities are single metal sorption oriented and therefore not realistic. Relatively less work has been done to elucidate the details of the biosorption behavior in multimetal systems, which are normally the composition of industrial effluents. In continuation of our work (Sharma *et al.*, 2007, 2006 and 2005) on the biosorption of toxic metals present as single solute metal ions in aqueous system, the present communication reports the competitive sorption of multi metal solution containing Cd (II), Cr (III) and Ni (II) on unmodified Shelled *Moringa Oleifera* Seeds (SMOS).

METHODOLOGY

Biosorbent Preparation

Moringa oleifera seeds were collected from the near by areas of Dayalbagh Educational Institute. Seeds

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collected were washed extensively with double distilled water to remove the adhering dirt and other particulate matter, dried at 65°C for 24 hours, crushed and sieved through 105, 210 and 420 μ copper sieves. Shelled *Moringa Oleifera* Seeds (SMOS) were used as biosorbent. No other chemical or physical treatments were used prior to adsorption experiments.

Sorption Studies

Batch experiments were carried out as a function of biomass dosage (2.0 to 6.0 g), particle size (105 to 420 μ), contact time (10 to 60 min.), metal concentration (1 to 100 mg/L) and pH (2.5 to 8.5). Appropriate metal salts of AR grade were used to prepare stock solutions. After proper pH adjustments, known quantity of biosorbent was added and finally metal bearing suspensions were kept under magnetic stirring. After shaking, suspension was allowed to settle down (10 min.). The residual biomass sorbed with metal ions was filtered using Whatmann 42 filter paper. To the filtrate metal estimation was carried out. Cd (II) and Cr (III) were estimated using radio assay over a planar NaI (TI) detector coupled to 4K MCA (Canberra Accuspec Card with PC AT 386) while, Ni (II) was estimated using flame Atomic Absorption spectroscopy (Perkin Elmer, 2380). Percent metal sorption by the sorbent was computed using the equation,

$$\% \text{ Sorption} = (C_0 - C_e) / C_0 \times 100 \quad \dots (1)$$

where, C_0 and C_e were the initial and final concentration of metal ions in the solution.

Biosorption Kinetics

The concentration of both the metal ions and the biosorbent is a significant factor to be considered for effective biosorption. It determines the sorbent/sorbate equilibrium of the system. Lagergren plots were obtained by conducting kinetic studies (batch) at initial Cd (II), Cr (III) and Ni (II) ions concentration. SMOS (4.0 g) was suspended in 200 ml of metallic solution of known initial sorbate concentration at the appropriate pH values mentioned above, where maximum sorption was recorded. The mixture was continuously stirred using a magnetic stirrer. Samples were withdrawn at pre-determined time intervals in the range of 10 to 60 minutes, filtered and analyzed for residual metal ions concentration.

Biomass Regeneration and Reusability

Regeneration and reusability of the biosorbent material must also be considered when assessing the efficiency

and feasibility of a treatment process. If the active agent can be regenerated through desorption cycle without destroying the integrity of the cell wall and hence, surface metal binding sites, the process will become more lucrative. With this aim in view, desorption studies (batch process) were conducted to desorb the ternary metal ions from loaded biomass as a function of concentration of different stripping agents [Soft acids: citric acid, 0.5 M; Hard acids: hydrochloric and nitric acids, 0.01 to 0.05 M]. Metal loaded biosorbent obtained from our sorption experiments, were transformed to Erlenmeyer flasks and shaken with 50 ml of each acid for 40 minutes. The filtrate was analyzed for desorbed metal ions.

Data Analysis

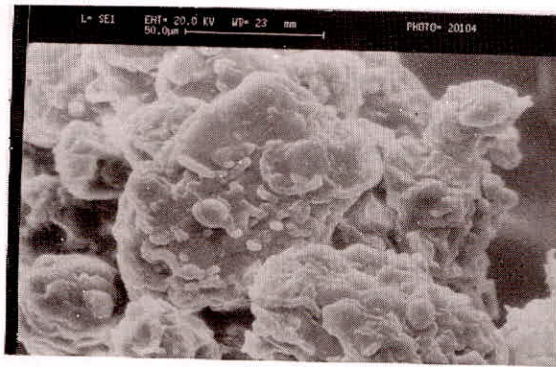
Batch experiments were conducted in replicates ($N = 5$) and data represent the mean value. Mean values, correlation coefficients, standard deviation were calculated using SPSS⁺ statistical package (SPSS, 1983). For the determination of inter group mean value differences, each parameter was subjected to student's t-test for significance level ($p < 0.05$).

RESULTS AND DISCUSSION

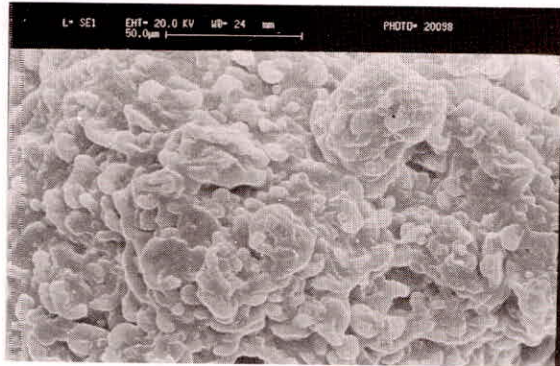
Cd (II), Cr (III) and Ni (II) biosorption on SMOS

Single Metal Situation

Previous experiments performed on the biosorption of Cd (II), Cr (III) and Ni (II) in single metal ion solution using unmodified SMOS indicates that maximum metal binding occurred at pH 6.5 for all the cationic metallic species. Morphological changes observed in Scanning Electron Micrographs of native and exhausted biomasses indicate the existence of biosorption phenomenon. Comparison of SEM of untreated (Figure 1 a) and metal treated SMOS represents large spherical clusters having a pore area of 8.66 μm^2 in case of native SMOS, while dense agglomerated, etched dendrite type morphology having a pore area of 2.66 μm^2 in Cd (II) (Figure 1b), 0.80 μm^2 in Cr (III) and 3.84 μm^2 in Ni (II) in exhausted SMOS. Observed aggregation and reduction in pore area of native and exhausted samples could be ascribed to the liquid phase concentration of metal ions at experimental pH confirming the phenomenon of biosorption. Fourier Transform Infrared spectroscopic analysis performed on untreated and metal treated biomass highlighted Amino acid-metal interactions responsible for sorption phenomenon.



(a) Untreated SMOS



(b) Cd (II) treated SMOS

Fig. 1: Scanning Electron Micrographs of Untreated and Cd (II) treated SMOS Multi metal situation

Table 1: Soluble Metal Ion Concentration (μM) of Target Ternary Metals [Cd (II), Cr (III) and Ni (II)] on Unmodified SMOS at Optimum Conditions

Target Multi Metals	Sorption Efficiency (μM)
Cd (II)	10.39 \pm 0.52
Cr (III)	30.54 \pm 1.46
Ni (II)	33.68 \pm 1.71

The maximum percentage sorption calculated for each ion present in ternary mixture at pH 6.5 [Cd (II): 76.59%; Cr (III): 68.85% and Ni (II): 60.52%] (Figure 2) was lowered (10–20%) as compared to single metal ions. Similar trends of effect of metal concentration, biomass dosage, particle size, contact time and pH on biosorption efficiency were observed in ternary metal solution as compared to solution of single metal ions.

The fall in sorption capacity of the target biomass in multi metal solution than that of single metal ions may be ascribed to the less availability of binding sites. In case of multi metal solution, the binding site is competitively divided among the various metal ions. The combined action of competitive biosorption of Cd (II), Cr (III) and Ni (II) seems to be antagonistic in nature. The most logical reason for this action was claimed to be screening effect by the metals present in the solution (Sag and Kutsal, 1996). It is generally complicated to find a common rule to identify how metal properties affect the competitive sorption. Among various factors that affects the biosorption preference of a sorbent, binding of metal ions on biomaterials largely depend on physicochemical properties of metals. It has been reported that in general,

Table 1 presents the soluble ion concentration of Cd (II), Cr (III) and Ni (II) present as multi metals after biosorption on SMOS using optimum particle size (105 μ), biomass dosage (4.0 g), metal concentration (25 mg/L), contact time (40 min.), volume (200 ml) at pH 6.5. In each case data were evaluated at significance value ($p < 0.05$).

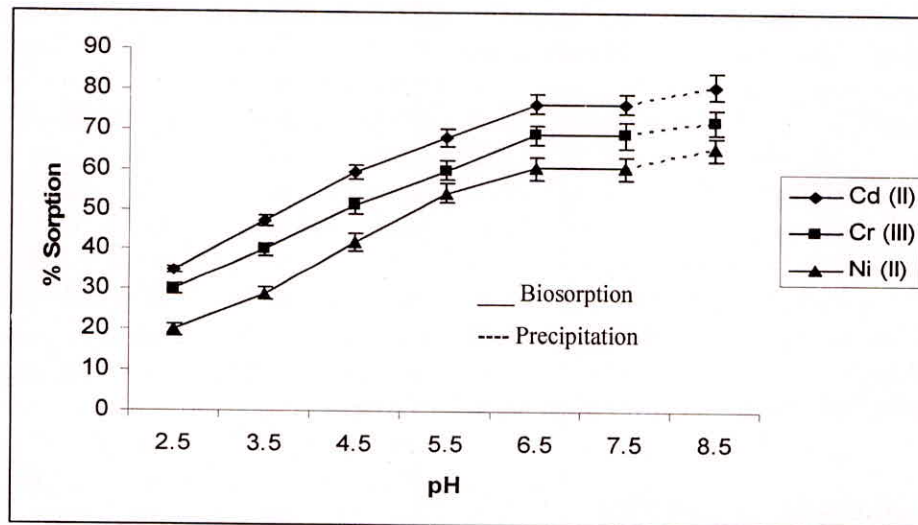


Fig. 2: Effect of pH on sorption behavior of Cd (II), Cr (III) and Ni (II) on SMOS in multi metal solution. Error bars represent standard deviation of five replicate determinations

the greater the electro negativity, electrode potential and ionic size, the greater will be the affinity for sorption (Mattuschka and Straube, 1993; Sag *et al.*, 2002). The order of sorption [Cd (II) > Cr (III) > Ni (II)] for the SMOS, obtained was consistent with the physicochemical properties of cationic metal ions under study. Thus, in present tri-metallic combination, sorption of metals is a competitive process between ions in solution and those sorbed onto the biomass surface.

Kinetics of adsorption, which governs the residence time, in terms of solution uptake rate, is one of the important characteristics defining the efficiency of biosorption. Kinetics experiments showed that the adsorption of target multi metal ions increases with the lapse of time. Initially, the sorption of Cd (II), Cr (III) and Ni (II) on SMOS was found to be rapid during 10 to 40 minutes after which the rate slowed down as the equilibrium approached at 40 minutes of contact time. No further increase in sorption was observed with increase of contact time up to 60 minutes. The order of the sorption of sorbates onto sorbent is determined by subjecting the data to the linearized form of Lagergren equation,

$$\log (q_e - q_t) = \log (q_e) - (K_{ad}/2.303)t \quad \dots (2)$$

where, K_{ad} is the first order rate constant of sorption, while q_e and q_t are the maximum amount sorbed at equilibrium and at time t respectively. The linear plots of $\log (q_e - q_t)$ versus t yield straight line. The Kinetics profiles of target trimetallic species are shown in Figure 3.

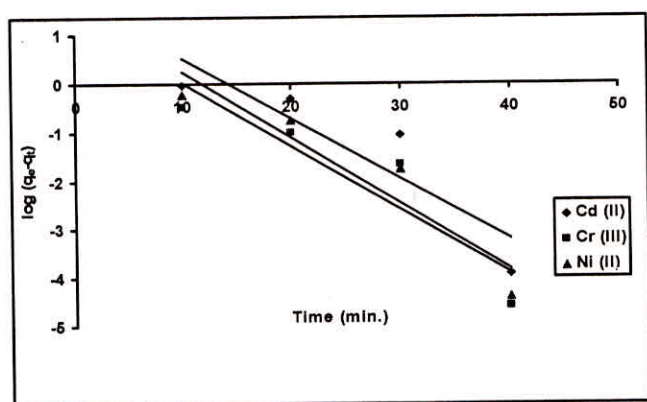


Fig. 3: Lagergren plots for the adsorption of multi metal ions at SMOS

The lower adsorption rate constant for multi metal ions [Cd (II): 0.37 min^{-1} ; Cr (III): 0.30 min^{-1} and Ni (II): 0.28 min^{-1}] compared to single metal ions [Cd (II): 0.51 min^{-1} ; Cr (III): 0.40 min^{-1} and Ni (II): 0.34 min^{-1}] might be explained that metal ions

compete for vacant sites and with in the shortest possible time uptake by binding sites.

It is well known that desorption of sorbed heavy metals and repeated usability of the exhausted biosorbent are of significance from the view point of practical application for the water treatment. With this aim in view, desorption behavior of ternary metals from metal loaded biomass was observed after eluting with different stripping agents (citric, hydrochloric and nitric acid). Residual seed biomass was subjected for desorption followed by further resorption up to several cycles. Results showed that citric acid can recover the metals up to five cycles but at the same time rate of desorption is very less. Whereas, the maximum desorption [Cd (II): 94.02%; Cr (III): 91.20%; Ni (II): 92.10%] was observed at hydrochloric acid (0.05 M). However, better desorption [Cd (II): 99.24%; Cr (III): 99.15%; Ni (II): 99.10%] could be achieved with the same strength of nitric acid as eluant (Table 2). Multi metal sorption on regenerated shelled *Moringa oleifera* seeds remained constant to the value [Cd (II): 76.59%; Cr (III): 68.85%; Ni (II): 60.52%] up to three regeneration cycles and then started decreasing [Cd (II): 69.26%; Cr (III): 61.10%; Ni (II): 56.51%] in the fourth cycle.

Table 2: Sorption of Multi Metal [25 mg/L: Cd (II), Cr (III) and Ni (II)] Ions on Regenerated Biomass

No. of Cycles	Sorption (%)		
	Cd (II)	Cr (III)	Ni (II)
1.	76.03	68.10	60.21
2.	76.20	68.26	60.30
3.	76.59	68.85	60.52
4.	69.26	61.10	56.51

CONCLUSIONS

Biosorption process may hold the greatest promise in the future because, if properly used, they can provide the most effective and economical approach to dealing with challenging environmental problems. Biosorption observations on the ability of Shelled *Moringa Oleifera* Seeds (SMOS) indicate the biomass of having potential to sequester multi metal ions [Cd (II), Cr (III) and Ni (II)] effectively from the aqueous system. The adsorption of target metals on the seed biomass was found to be competitive where the adsorption capacities of metals were lowered (10 to 20%) with those of single metal ions. The selectivity order of sorption for tri metallic combination was found to be Cd (II) > Cr (III) > Ni (II). Kinetic studies showed that uptake of metal ions increases with time and maximum

sorption was obtained with in the first 40 minutes of the process. Spent biosorbent was regenerated and effectively reused making the process more economical.

SIGNIFICANCE

The present piece of work adds a new dimension to the designing of novel water treatment process as low cost, safe, domestic and ecofriendly technique based on biosorption using non toxic *Moringa oleifera* seeds. Wonderful **bio tablets, bio cakes and bio filters** can be developed based on the information.

ACKNOWLEDGEMENTS

Authors are grateful to Prof. V.G. Das, Director Dayalbagh Educational Institute, Agra for providing necessary research facilities. Parul Sharma is thankful to Council of Scientific and Industrial Research, New Delhi for Senior Research Fellowship.

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