Biosorption of heavy metals by paper mill waste from aqueous solution

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ABSTRACT

In the present study the removal of lead, cadmium, nickel and copper from aqueous solution was carried out using paper mill sludge. Time course studies were carried out with these metals and effect of pH (4-9), metal concentration (5-100mg/l), biomass concentration (1-5%) were evaluated in batch sorption system. Optimum results obtained at pH 4.5 with 1% biomass concentration (w/v), biosorption was rapid, more than 70% of metal ion adsorbed within 15 minutes even at a concentration of 100mg/l of metal. Langmuir and Freundlich sorption isotherm were overall applicable and showed that physico-chemical adsorption and ion exchange interactions simultaneously play a role in binding of the metals. The significance of this paper is the utilization of low cost sorbent available in abundance for the removal of metals from dilute aqueous solution.

Keywords: Heavy metal, biosorption, paper mill waste, Langmuir-Freundlich isotherm

1. Introduction

Today, with the rapidly increasing population, water resources becoming scarcer, there is a strong need to reconsider the patterns of our consumption and the way we use our water resources. Contamination of the environment with toxic heavy metals from industrial wastewater is a major problem (Volesky, 2003). Metal ions are serious environmental pollutant frequently encountered in industrial waste water (Klimmer et al., 2001). An accelerated release of heavy metals into the aquatic environment poses serious water pollution problems because of their toxicity, persistence and bioaccumulation in food chains. Metals and pesticides, in particular, have an inclination to accumulate and undergo food chain magnification (Klavins et al., 2009). It is thus important to check the metals at source of discharge to not to allow them to enter the aqueous system.

A number of physico-chemical protocols are being used world-wide to depollute water loaded with heavy metals. However, these methods are inherently problematic in their application and are not economically feasible (Volesky, 2001: Sharma, 2003: Okoronkwo et al., 2007). Biological processes like bioaccumulation, biosorption have acquired due attention owing to number of advantages and engaged the scientists from all over the world to identify the potent biomass type (Khan et al., 2009: Al-Masri et al., 2010: Xiao et al., 2010).

The term, biosorption is used to describe the passive non- metabolically mediated process of metal binding to living or dead biomass (Rangsayatorn et al., 2002: Wang and Chen, 2009). Since most conventional methods are neither effective nor economical, especially when used for the reduction of heavy metal ions to low concentrations, new separation methods are
required to reduce heavy metal concentrations to environmentally acceptable levels at affordable cost. A variety of low-cost biomass has been studied by various workers for controlling pollution from diverse sources in different parts of the world (Kar and Misra, 2004). They include anaerobically digested sludge (Tokcaer and Yetis, 2006), bacteria (Lu et al., 2006), fungi (Garcia et al., 2005) and algae (Elifantz and Tel-Or, 2002). Agricultural materials have also been used. These include rice bran, soybean and cottonseed hulls, crop milling waste (Saeed et al., 2005), groundnut husk, maize cob meal, coir, jute and sawdust (Shukla and Pai, 2005), canola meal, coconut shell (Ogunsuyi et al., 2001) and spent tea leaves (Lavecchia et al., 2010; Ahluwalia and Goyal, 2005) amongst others. Fruit waste of Gular used by Rifaqat et al., 2010 “a”, for the removal of Cr (VI), Foeniculum vulgaris for Cd (Rifaqat et al., 2010 “b”).

Most cellulosic materials investigated have been found to be good adsorbents for heavy metals (Opeolu et al., 2010). Diverse plant parts such as coconut fiber pith, coconut shell fiber, plant bark (Acacia arabica, Eucalyptus), pine needles, cactus leaves, neem leave powder have also been tried for chromium removal showing efficiency more than 90–100% at optimum pH (Dakiky et al., 2002: Manju and Anirudhan 1997: Mohan et al., 2006: Sarin and Pant, 2006: Venkateswarlu et al., 2007). Paper industry generates a considerable amount of wastes, considerable amount of solid wastes generated by the paper and pulp industry are deposited directly in landfill (Mendez et al., 2009). Present study aims to make use of paper mill sludge to remove the heavy metal ions from waste water instead of the conventional techniques that are difficult to control, and require mostly expensive equipments.

2. Materials and Method

2.1 Chemicals and reagents

The stock solutions containing the 1000 mg l\(^{-1}\) concentration of lead, cadmium, nickel and copper were prepared by dissolving lead nitrate, cadmium iodide, nickel sulphate and copper sulphate respectively in milli Q water. The salts of these chemicals were of analytical grade, procured from s.d.fine-chem Limited, Mumbai.

2.2 Metal analysis

The residual concentration of metals was determined by atomic absorption spectrophotometer using an air-acetylene flame and single element hollow cathode lamps (GBC 932AA, Australia). The stock reference material (1000 mg l\(^{-1}\)) was procured from Acros organics, New Jersey, USA and the appropriate dilution from these stock solutions was done as per GBC catalogue.

2.3 Preparation of Biosorbent

Paper mill sludge mainly as primary clarified sludge (Kraft pulp & paper based mill) used in this study was collected from filter bed of effluent treatment plant from Shri Gopal unit of Ballarpur industries Limited, Yamunanagar (Haryana). The sludge was washed with distilled water to remove the particulate matter before carrying out the metal adsorption experiments. The sludge was then oven-dried at 100°C overnight, powderized and stored in the polythene bag for further studies.

2.4 Effect of pH
Effect of pH was studied with batch biosorption, using biomass concentration of 1.0% w/v separately for each metal with a metal concentration of about 50 mg l⁻¹ of varied pH (2.0, 3.0, 4.0, 4.5 and 5.0). Biosorption experiments were conducted in Erlenmeyer flasks (500ml), a volume of 150ml metal solution with different pH adjusted with dilute HNO₃ was taken in different flasks, were agitated at 100 rpm at room temperature. Sample was drawn at different times (up to 5 hrs), acidified using 2-3 drops concentrated HCl, filtered using qualitative filter paper (equivalent to grade 1) and residual metal content in sorption medium were analyzed.

2.5 Effect of biomass concentration (w/v)

Biomass concentration was optimized with batch biosorption studies using different concentration of biomass i.e. 0.5-2.0% separately for each metal with a metal concentration of about 50 mg l⁻¹ and a pH 4.5, experiments were conducted as described earlier.

2.6 Effect of contact time and initial concentration of metal ions

Time-course profile of adsorption of single metal species of lead, nickel, cadmium and copper from of aqueous solution (pH 4.5) of different concentration (5 – 100 mg l⁻¹) by 1% dried paper mill sludge was studied up to five hours at 28±2°C and agitation at 100rpm. Sample was drawn at different time interval i.e. 15 min, 30 min, 1h, 2h, 3h, 4h and 5h, analyzed for the residual metal concentrations.

2.7 Equilibrium studies

Batch biosorption experiments were conducted in Erlenmeyer flasks (500ml), 150ml solution of different metals of pH 4.5 adjusted with dilute HNO₃ was taken in different flasks with 1.5g of dried biomass (i.e.1.0% w/v), were agitated at 100 rpm at room temperature. Initial concentration of metals (Cᵢ) was kept about 150 mg l⁻¹. Preliminary studies showed that equilibrium attained at 10hrs, therefore sample was drawn after 10 hrs and analyzed as described earlier. The amount of metal adsorbed at equilibrium qₘₐₓ was calculated using following equation: 

\[
q_{\text{max}} (\text{Adsorption capacity}) = \frac{V}{w} (C_i - C_f)
\]

Where Ci and Cf are the liquid phase concentrations of the metal at initial and equilibrium respectively, V is the volume of the solution and w is the dry weight of biomass/adsorbent.

2.8 Assessment of sorption performance

Different type solid-liquid sorption systems are preliminarily examined on two types of investigations, a) equilibrium batch sorption test and, b) dynamic flow continuous–flow sorption studies. In the present study sorption is studied with equilibrium batch sorption test. The degree of biosorption of a metal ion on a biosorbent is a function of equilibrium between metal-ion concentration in solution and that of adsorbed onto the surface of biosorbent material at constant pH and temperature. The equilibrium of the biosorption process is described by fitting the experimental data with models (Gadd et al., 1988) usually used for the representation of the equilibrium adsorption isotherm. The two widely accepted and linearized equilibrium adsorption isotherm models have been used in the present study given by Langmuir and Freundlich adsorption isotherm.

\[
q_{\text{eq}} = \frac{K b C_{\text{eq}}}{1 + b C_{\text{eq}}}
\]

Langmuir model
Where $q_{eq}$ is metal accumulated per unit mass of the biosorbent material, $C_{eq}$ is the metal residual concentration in solution, $K$ is the maximum specific uptake corresponding to the site saturation and $b$ is the ratio of adsorption and desorption rates representing the affinity of the sorbate to binding site. Langmuir model has few assumptions such as a) the surface consists of adsorption sites, b) all adsorbed species interact only with the sites and not with each other, c) adsorption is limited to monolayer, d) adsorption energy of all sites is identical and independent of the presence of adsorbed neighboring species. Another empirical model for monolayer adsorption is Freundlich model

$$q_{eq} = K_f C_{eq}^{1/n}$$  
Freundlich model

Where $q_{eq}$ and $C_{eq}$ means the same as in Langmuir while $K_f$ and $n$ are Freundlich coefficients

3. Results and Discussions

3.1 Effect of pH on the removal of the heavy metal ions

Results presented in Figure 1 show that maximum removal took place at pH 4.5; indicates that the maximum adsorption affinities take place in moderately and slightly acidic medium.

![Figure 1: Effect of pH on the %removal of different metals by paper mill waste (Dry biomass: 1.0%, Temp.28±2°C; Agitation 100 rpm for 1 hr, Initial conc. (Ci) 50 mg l⁻¹)](image)

3.2 Effect of Biomass concentration

Behavior of all the metals was found to be similar with change in biomass concentration. Biosorption of each metal was found to be better with 1% concentration of biomass with each metal the pattern of different metal adsorbed is shown in Figure 2.

![Figure 2: Effect of Biomass concentration (w/v) on the %removal of different metals by paper mill waste (Temp.28±2°C; pH 4.5, Agitation 100 rpm for 1 hr, Initial conc. (Ci) 50 mg l⁻¹)](image)
3.3 Effect of contact time and initial concentration of metal ions on % removal

The results shared common characteristics; adsorption was quick enough and up to 70%-89% of the metal ions adsorbed within 15 minutes from 100mg l\(^{-1}\) and 5 mg l\(^{-1}\) initial concentration respectively. Though Cd, Cu at 50 mg l\(^{-1}\) and Pb, Ni at 20 mg l\(^{-1}\) showed a decrease in absorption in the first 15 minutes, with increase in contact time the adsorption increased. At equilibrium, adsorption was 99.8% of Ni, 98.0% of Pb, 99.2% of Cu and 99.8% of Cd by dried paper mill sludge with an initial conc. of about 5 mg l\(^{-1}\) of aqueous solution. Although at higher initial conc. i.e. from 10 - 100 mg l\(^{-1}\) of metals, the adsorption was decreased but it has been well above 90% (Figure 3-6).

![Figure 3](image1.png)

**Figure 3:** Effect of initial concentration (Ci) of Cd with time of agitation on residual concentration. (Temp.28±2°C; pH. 4.5, Agitation 100 rpm, Biomass conc. 1% w/v)

![Figure 4](image2.png)

**Figure 4:** Effect of initial concentration (Ci) of Cu with time of agitation on residual concentration. (Temp.28±2°C; pH. 4.5, Agitation 100 rpm, Biomass conc. 1% w/v)
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Figure 5: Effect of initial concentration (Ci) of Pb with time of agitation on residual concentration. (Temp.28±2°C; pH. 4.5, Agitation 100 rpm, Biomass conc. 1% w/v)

Figure 6: Effect of initial concentration (Ci) of Ni with time of agitation on residual concentration. (Temp.28±2°C; pH. 4.5, Agitation 100 rpm, Biomass conc. 1% w/v)

Adsorption isotherm

Biosorption of heavy metals is a rapid process and equilibrium is established between the adsorbed metal ions on the surface of the adsorbent (q<sub>eq</sub>) and unadsorbed metal ions in solutions (C<sub>eq</sub>). Langmuir and Freundlich isotherm represents this equilibrium and are widely used to analyze the data for water and wastewater treatment applications.

Langmuir and Freundlich adsorption constants evaluated from isotherms and correlation coefficients (R<sup>2</sup>) are given in Table 1. It is quite clear that both physico-chemical adsorption and ion exchange interaction plays a role in binding of lead, copper, nickel and cadmium from aqueous solution simultaneously. Paper mill sludge consists of both organic and inorganic constituents therefore mechanism of adsorption involves both ion exchange interaction as well as physico-chemical adsorption.
A good correlation between experimental data and Langmuir and Freundlich adsorptions models for lead, nickel, copper and cadmium ($R^2 > 0.9$) shows that Freundlich sorption model fitted well as compared to Langmuir adsorption model throughout the concentration range of Pb, Ni, Cu and Cd with a correlation coefficient of more than 0.9 with each metal. However Cd has favored Freundlich model relatively more than the Langmuir.

**Table 1:** Values of Langmuir and Freundlich adsorption constants evaluated from isotherms and correlation coefficients ($R^2$)

| Metal | Equilibrium Constants | Langmuir Model | Freundlich Model |
|-------|-----------------------|----------------|------------------|
|       | $K$ | $b$ | $R^2$ | $n$ | $K_f$ | $R^2$ |
| Pb    | 1.0768 | 7.3736 | 0.8905 | 1.57 | 3.17 | 0.97 |
| Ni    | 7.8612 | 2.5625 | 0.8566 | 1.95 | 2.42 | 0.96 |
| Cd    | 1.8602 | 4.3449 | 0.7702 | 2.44 | 4.47 | 0.93 |
| Cu    | 3.6309 | 5.3575 | 0.9814 | 1.71 | 4.09 | 0.98 |

Interestingly, in comparison with the study carried out earlier by Lister & Line (2001) with paper mill waste where biosorption capacity of 5.5 mg/g is reported for Cu at an initial concentration of 76.7 ppm, present study showed far better results in terms of % removal and biosorption capacity. The answer for the difference may lie in the fact that paper-mill waste is jumble of de-inked fiber sludge, primary fiber sludge, secondary sludge and mixtures. Their composition mainly depends on the type of paper produced and the origin of cellulose fibers (Mendez et al., 2009). Different classes of metals favor different ligands present in biological system; there are different functional groups and classes of organic compounds in different biomass e.g. hydroxyl carboxyl amino ester sulphydryl carbonyl terminal & carbonyl internal etc. that are related to biosorption (Wang and Chen, 2009). In the present study it is revealed that biosorbent was almost equally favored by all the metals under study (i.e. Cd, Ni, Cu, & Pb). Table 2 gives a brief comparison of biosorption capacity of some of the excellent biosorbent reported earlier with present study.

**Table 2:** Selected heavy metal adsorption capacities for selected low cost adsorbents

| Metal | Adsorbent | Uptake (mg g$^{-1}$) | Isotherm model | pH | Reference |
|-------|-----------|----------------------|----------------|----|-----------|
| Ni    | waste biomass (P. chrysogenum) | 56.2 | ----- | ----- | Su et al., 2006 |
|       | surface imprinted (P. chrysogenum) | 82.5 | ----- | ----- | Su et al., 2006 |
|       | Red mud | 10.9 | L | 5.6 | Lopez et al., 1998 |
|       | Hazelnut shell | 10.1 | L | 3.0–7.0 | Demirbas et al., 2002 |
|       | Orange peel (citrus reticulate) | 80.0 | L, F | 6.0 | Ajmal et al., 2000 |
|       | Grape stalk waste | 10.6 | L | 5.5–6.0 | Villaescusa et al., 2004 |
|       | Paper Mill Waste | 13.7 | F | 4.5 | Present study |
| Cu    | Red mud | 19.7 | L | | Lopez et al., 1998 |
|       | Waste of fermentation, autoclaved at 120 °C (S. cerevisiae) | 4.93 | | | Bakkaloglu et al., 1998 |
|       | Whiskey distillery spent wash lyophilized (S. cerevisiae) | 6.4 | | | Al-Saraj et al., 1999 |
|       | mycelial waste (A. terreus) | 160 | | | Gulati et al., 2002 |
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| Material                        | Pb Content (mg/L) | Pb Adsorption (%) | Source                           |
|---------------------------------|-------------------|-------------------|----------------------------------|
| Paper Mill Waste                | 180               | 5.5               | Lister and Line, 2001            |
| Paper mill sludge               |                   |                   | Calace et al., 2003              |
| Tree bark                       | 21.6              | 5.5               | Gaballah and Kilbertus, 1998     |
| Peanut hulls                    | 65.6              | L 5.0             | Periasamy and Namasivayam, 1996  |
| Grape stalk waste               | 10.1              | L 5.5–6.0         | Villaescusa et al., 2004         |
| Iron slag                       | 88.5              | L 3.5–8.5         | Feng et al., 2004                |
| Wheat Bran                      | 24.5              | L,F 4.5           | Singh et al., 2011               |
| Paper Mill Waste                | 13.9              | L,F 4.5           | Present study                    |
| Whiskey distillery spent wash,  | 189.0             |                   | Bustard and McHale, 1998         |
| lyophilized (S. cerevisiae)     |                   |                   |                                  |
| Grape stalk waste               | 49.9              | L 5.5             | Martinez et al., 2006            |
| Sugar beet pulp                 | 73.8              | L 5.5             | Reddad et al., 2003              |
| sugar cane bagasse              | 133.6             | 6.0               | Peternele et al., 1999           |
| Wheat Bran                      | 20.2              | L,F 4.5           | Singh et al., 2011               |
| Paper mill waste                | 14.1              | L,F 4.5           | Present study                    |
| Waste yeast from brewery (S.   | 14.2              |                   | Zhao and Duncan, 1997            |
| cerevisiae)                     |                   |                   |                                  |
| Paper mill sludge               |                   |                   | Calace et al., 2003              |
| Scolecite                       | 70                | F 4.5–7.0         | Dal Bosco et al., 2005           |
| Paper mill waste                | 14.8              | F 4.5             | Present study                    |

### 4. Conclusion

A biosorption technology in which living or dead biomass is used to accumulate heavy metals find a major drawback of cost of growing a sufficient quantity of bacterial fungal or algal biomass. Waste biomass of another industry represent good candidate for the development of inexpensive biosorbent, present study conclude that paper mill waste can be used efficiently in the removal of heavy metal ions (Pb\(^{2+}\), Cu\(^{2+}\), Cd\(^{2+}\) and Ni\(^{2+}\)) from aqueous solutions. Though adsorption of metal ions was affected by pH, adsorption was above 70% for all the metal ions covering a range of pH from 2 to 5. Adsorptions of metal ions studied were fitted with both Langmuir and Freundlich isotherms; though Cd favored the Freundlich model while others were fitted with both the models. Paper mill waste did not require any pretreatment, the experimental studies showed that paper mill waste is a competent biosorbent to remove high amount of toxic heavy metal ions from aqueous system; may prove to be the best management/utilization of the waste. Further physico-chemical characterization of biomass and application in continuous system are among the plans for future research.
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