REMOVAL OF METALS FROM WASTEWATER BY USING LOW COST BIO-ADSORBENTS

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ABSTRACT

The adsorption process is being widely used by various researchers for the removal of heavy metals from wastewater and activated carbon has been frequently used as an adsorbent. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. In the present investigation, feasibility of different non-conventional bio-adsorbents of plant and microbial origin waste carrot juice pulp, waste tea leaves, wood powder (saw dust), paper mill sludge and microbial bio-waste from fermentation industry were tested for the removal of metals Pb, Zn, Ni and Fe from wastewater in single metal state and multi-metallic state and were compared with activated carbon in order to develop inexpensive adsorbent.

Key Words: Low cost bioadsorbents, Microbial bio-waste, Heavy metals, pH, Contact time, Biomass concentration

INTRODUCTION

Contamination of environment by toxic heavy metals from industrial effluents is considered to be one of the serious problems, which gets aggravated due to their accumulation in the food chain and persistent nature1,2. Conventional wastewater treatment technologies have been developed to reduce metal concentration in wastewater3, which besides being cost intensive, impractical and uneconomical also causes damage to the environment. Therefore, cost effective and eco-friendly techniques are required for wastewater treatment4,5. Metal sorption by dead biomass is more effective than by living6 organisms. A multitude of biomass types7, comprising fungal biomass, bacterial biomass8, algae9, peat10 and so on have been studied for removal of heavy metals from solutions/industrial effluents. The particular amount of metal bound in the biosorbent depends however not only on the chosen biosorbent but also on the type of the metal ion, its concentration and other physiochemical parameter of the solution (e.g. pH, ionic strength). Earlier studies on metal biosorption were mainly restricted to solutions containing only one metal. In the present investigation feasibility of different non-conventional biosorbents of plant and microbial origin waste carrot juice pulp, waste tea leaves, wood powder (saw dust), paper mill sludge and microbial bio-waste from fermentation industry were tested for the removal of priority metals Pb, Zn, Ni and Fe from synthetic effluents in single metal state and multi-metallic state and were compared with activated carbon in order to develop inexpensive adsorbent.

MATERIAL AND METHODS

Preparation of adsorbents

Waste tea-leave and waste carrot pulp were collected from the cafeteria and juice corner, respectively. Wood powder was obtained as saw dust of Eucalyptus tree and paper mill sludge and microbial bio-waste were collected from Ukai Songarh pulp and paper mill and Fermentation industry, Surat, Gujarat, respectively. Activated carbon was obtained from S.D. Fine Chemicals Ltd., Mumbai, India. Waste biomass collected from different sources was dried at 70°C for overnight.
powderized using pestle and mortar and preserved in polythene bags for further adsorption experiments.

**Chemicals and reagents**

The stock solutions containing the 1000 mg l\(^{-1}\) concentration of Pb\(^{2+}\), Fe\(^{3+}\), Zn\(^{2+}\) and Ni\(^{2+}\) were prepared by dissolving the lead nitrate, ammonium ferrous sulphate, zinc sulphate and nickel nitrate in double distilled water. The salts of these chemicals were procured from S.D. Fine Chemicals Ltd., Mumbai, India.

**Batch equilibrium studies**

It was done in Erlenmeyer flask with a working volume of 100-200 ml. Dried biomass was added at different concentrations and metal concentrations (lead, nickel, iron and zinc) were kept near to 50 mg/L separately for each metal and pH 4.0 was maintained by dilute HNO\(_3\), agitated at 80 rpm at room temperature. Five milliliter samples were drawn at different time interval (0, 5,10,15, 30 and 60 min.), acidified by adding few drops of concentrated HCl, filtered using Whatman filter paper no.41 and residual metal content in the filtrate was analysed. Similarly, time course biosorption studies were carried out at varying pH and biomass concentration (2%,4%, 6% and 8 % of biomass) from two different metal ion concentrations (50 and 100 mg/L). Adsorption by mixed biomass of microbial bio-waste and paper mill sludge in the ratio of 4:1 from multi-metal solution containing lead : 13 mg/l, nickel : 6.9 mg/ l and zinc 14.2 mg/l) were also carried out.

**Metal analysis**

The residual concentration of lead, iron, nickel and zinc in the sorption medium was determined by Atomic absorption spectrophotometer. Specific metal uptake (q) by biomass (mg/g) was calculated as follows\(^{11}\):

\[
q = V \times \frac{(C_i - C_f)}{1000 W}
\]

Where, \(V\) is the volume of the solution in the contact batch flask, \(C_i\) is the initial concentration of lead in the solution (mg/g), \(C_f\) is the final concentration of lead in the solution and \(W\) is the mass of adsorbent (g). Similarly biosorption efficiency \(R\) % was calculated as :

\[
R = 100 \times \frac{(C_i-C_f)}{C_i}
\]

**RESULTS AND DISCUSSION**

Metal removal by different biomass from synthetic metal solution in batch mode was studied and Table 1 give the biosorption efficiency of different adsorbents at two different metal ion concentrations (50 mg/L and 100mg/L). For the same metal different adsorbents have different removal efficiency. The adsorption of metal ions reached equilibrium in 30-60 minutes of contact time at pH 4.0 and temperature of 28 ± 2°C by 2g of powderized biomass in 100 ml of synthetic metal solution and with continuous stirring at 80 rpm. Removal efficiency of lead by different wastes was in the order of paper mill waste (66%) > bio- waste (65%) > wood powder (37%) > waste tea-leaves (26%) > waste carrot pulp (2.4%). Similarly, the removal efficiency of zinc was in the order of waste carrot pulp (74%) > paper mill sludge (33%) > microbial bio-waste (28%) > waste tea-leaves (21%). Removal efficiency of nickel and iron was observed to be in the order of wood powder (33%) > waste carrot pulp (28%) > paper mill sludge (27%) > bio-waste (23%) > waste tea-leaves (13%) and paper mill sludge (47%) = microbial bio-waste (47%) > waste carrot pulp (38%) > wood powder (25%) > waste tea-leaves (10%) respectively. Except carrot pulp and tea leaves all other biomass types had highest affinity for Pb and thus high adsorption efficiency from 50-100 mg/l metal solution. The adsorption of Pb, Ni, Fe and Zn by activated carbon was carried out under similar conditions and was compared with other biomass types. Removal of zinc by waste carrot pulp was higher than the activated carbon whereas by wood powder and paper mill sludge it was nearly same as observed by activated carbon. Removal of lead by bio-waste and paper mill sludge was 65% and 66% whereas it was 77% by activated carbon. Removal of iron and nickel by activated carbon was 78% and 82% respectively, which was higher than any other adsorbent. These experiments showed that the removal of metal is rapid and paper mill sludge and bio-waste, which are available in large quantity, can effectively remove Pb, Fe and Zn from 50 mg/l to 100 mg/l of synthetic metal solution.

**Effect of pH**

Optimum removal of Zn and Pb by paper mill sludge and by microbial bio-waste was at pH 4.0. At pH 4.0, in 60 min. of contact 32% zinc and 36% lead were removed by 2% of paper mill
sludge (Fig. 1), whereas microbial bio-waste could remove 41% Zn and 77% Pb. Residual concentration and specific metal uptake from 50 mg l-1 metal solution indicated that at pH 4.0 to 5.0, there was maximum removal and uptake. pH of synthetic metal solution during biosorption of Zn, Ni, Pb had significant effect on metal uptake. It has been previously described that pH 4.0 is optimum for metal removal\textsuperscript{12,13}. There was no change in the pH of final solution after completion of adsorption. Adsorption of different metal species occurs differently at different pH, however pH of 4-5 was adequate from practical point of view for removal of various metal.

Table 1: Adsorption of metal ions from synthetic aqueous solution (pH 4.0) containing single metallic species by 2% dried waste biomass at 28±2°C and agitation at 80 rpm in 30 min of contact time

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pb</th>
<th>Fe</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Pb</td>
<td>Fe</td>
<td>Ni</td>
<td>Zn</td>
</tr>
<tr>
<td>concentration</td>
<td>C\textsubscript{i}</td>
<td>C\textsubscript{i}</td>
<td>C\textsubscript{i}</td>
<td>C\textsubscript{i}</td>
</tr>
<tr>
<td>Ci (mg/l)</td>
<td>C\textsubscript{f}</td>
<td>R</td>
<td>C\textsubscript{f}</td>
<td>R</td>
</tr>
<tr>
<td>Waste carrot pulp</td>
<td>48 2 82 17</td>
<td>31 38 79 17</td>
<td>34 58 56 42</td>
<td>12 74 66 32</td>
</tr>
<tr>
<td>Waste tea leave</td>
<td>36 26 80 8</td>
<td>41 10 78 20</td>
<td>43 13 73 24</td>
<td>38 21 73 27</td>
</tr>
<tr>
<td>Wood powder</td>
<td>32 37 65 35</td>
<td>37 23 89 10</td>
<td>33 33 76 24</td>
<td>31 35 79 22</td>
</tr>
<tr>
<td>Paper mill sludge</td>
<td>16 66 22 78</td>
<td>26 47 77 2</td>
<td>36 27 71 28</td>
<td>31 33 88 11</td>
</tr>
<tr>
<td>Bio-waste</td>
<td>17 65 51 48</td>
<td>26 47 49 50</td>
<td>38 23 92 7</td>
<td>36 28 96 2</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>15 70 22 77</td>
<td>11 78 34 64</td>
<td>9 82 51 48</td>
<td>31 36 68 31</td>
</tr>
</tbody>
</table>

(C\textsubscript{i} and C\textsubscript{f} are initial and final concentrations (mg/l) of metal in the solution; R is percent biosorption efficiency.)

**Fig. 1**: Effect of pH on uptake of Pb and Zn by paper mill sludge and microbial bio-waste

Optimization of biomass concentration for metal removal

Fig. 2 and Fig. 3 show the uptake of Ni, Zn and Pb from 51) mg/l of aqueous solution by different concentrations of paper mill sludge and microbial bio-waste respectively. Paper mill sludge exhibited increase in metal uptake (Zn, Ni, Pb) with increase in biomass concentration.
up to 4% and thereafter it decreased. Zn uptake decreased with further increase in biomass concentration, which was attributable to low metal concentration in the solution. Practically also it is not useful to increase the biomass beyond 2-4 g/100 ml for the uptake of metal\textsuperscript{19}. Similarly, microbial bio-waste showed increase in the uptake of Zn and Ni up to 2% and thereafter it decreased, whereas Pb uptake increased with increase in biomass concentration. Higher biomass concentrations were required as reported earlier\textsuperscript{15,16}, which may be because these wastes are directly obtained from industry and contain several impurities due to processing and handling and are not of pure plant or microbial origin. Optimum concentration of 2% was used in all experiments. Lower biomass concentration in the suspension at a given metal concentration enhances the metal/biosorbent ratio and thus increases metal uptake per gram of biosorbent, as long as the later is not saturated. All these results will have significance in scale up processes.

**Metal removal from multimetal solution by combination of adsorbents**

Many of the reported biosorption studies were conducted with single metal ion species in aqueous solutions while industrial effluents invariably contain more than one metal ion\textsuperscript{19}. Therefore, time course metal removal from multi-metallic solution (C\textsubscript{j} for Ni = 5.9 mg/l, Pb = 14.2 mg/l; Zn = 13.1 mg/l) by combination of 2 g of paper mill sludge and bio-waste/100 ml in the ratio of 4:1 at pH 5.0 was carried out (Fig. 4).

Time course experiment clearly indicates that there is rapid adsorption of all the three metal species in the initial 15-30 minute contact time where metal removal was in the order of Pb > Zn > Ni by 93%, 87% and 76% respectively. Metal uptake by non-living biomass is affected significantly in the presence of other cations in solution, depending on the chemical interaction of other chemical species (co-ions) with the metal of interest and the biomass\textsuperscript{17-21}. Many of the functional groups present on the surface are nonspecific and different cations compete for the binding sites. The results showed that it is possible to develop general-purpose biosorbers using bio-wastes that can remove a variety of metal cations. Paper mill sludge and microbial bio-waste (fermentation industry) can be used for such purposes. These adsorbents being powdery in nature can be useful in the treatment of wastewater using continuously stirred tank reactor. The metal loaded biomass due to its organic nature can be disposed off by incineration since the ash content in paper mill sludge and bio-waste was 40% and 8.5% respectively, which otherwise can be used for land filling or coupled with the possibility of feasible metal recovery. Non-living biomass for removal of metal ions from multi-metallic effluents by paper mill sludge and microbial bio-wastes in combination can have tremendous potential as an alternative to existing commercial adsorbents, which is cost effective as well as eco-friendly.\textsuperscript{22-28}

![Fig. 2: Effect of bio-mass concentration of paper mill sludge on metal uptake (q) of Ni, Zn, Pb (C\textsubscript{i} = 50 mg/L)](image-url)
Fig. 3: Effect of bio-mass concentration of bio-waste on metal uptake Ni, Zn, Pb. ($C_i = 50$ mg/L)

Fig. 4: Time course metal removal efficiency from mixed metal solution (Ni-5.9mg/L, Pb-13mg/L and Zn 14.2 mg/L) by mixed adsorbent (paper mill sludge + bio-waste)

CONCLUSION
Maximum uptake of Zn, Pb, Fe and Ni was found to be at pH 4.0 by 2% biomass. Most of the wastes had maximum biosorption efficiency for Pb among all metals. For the same metal different biomass has different removal efficiency. A combination of paper mill sludge and microbial bio-waste was effective in simultaneous removal of Pb, Zn and Ni from multi-metallic solution which was in the order of 93% Pb, >87% Zn, >76% Ni. These wastes are available in large quantity and can be used as an alternative to existing commercial adsorbents for removal of Pb, Zn and Ni from effluents.

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REFERENCES
24. Sarkar Angana and Sar Pinaki, Horizontal gene transfer of ARS genes : A possible
source of arsenic dissemination in subsurface environment, *J. Environ. Res. Develop.*, 9(3A), 803-812, \(2015\).

25. Raman Preet and Kaushik Anubha

