Novel biomaterial for decontamination of toxic metals from waste water

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Accepted 16 February, 2015

Azadirachta indica leaf powder leads to the formation of innovative biomaterial with increased sorption efficacy and environmental stability for the removal of Cd (II) and Ni (II) from its single metal solution. Synthetic strategy for strengthening the functional groups (COO) responsible for binding of metal species has been applied using acetylation, succination and graft co-polymerization processes. The resulting novel biomaterial was found to enhance the sorption efficiency (2-15%) and stability in terms of regeneration cycles (3 to 5). Characterization of the designed biomaterial was provided on the basis of SEM, FTIR and TGA. The results of the study show that the prepared material can be utilized as less expensive, environment friendly method with enhanced sorption efficacy and environmental stability for removal of toxic metal from contaminated water particularly for the rural and remote areas of the Country.

Key words: Innovative biomaterial, acetylation, succination, graft co-polymerization, structural modification.

INTRODUCTION

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, chromium, nickel, lead, mercury and zinc are often detected in industrial waste waters, which originate from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacturing, pesticides, pigment manufacture, printing and photographic industries etc (Kadirvelu et al., 2001). In view of its high toxicity, environmental mobility, non-biodegradability and stability, its removal becomes an absolute necessity. Traditional treatment techniques include chemical precipitation, membrane filtration, electrodialysis and ion exchange. Nevertheless, the application of such processes is sometimes restricted because of technical or economic constraints (Kurniawan et al., 2006).

Bioremediation is a method of environmental control and offers several advantages over conventional treatment methods including cost effectiveness, efficiency and minimization of chemical/biological sludge, no requirement of additional nutrients and regeneration of biosorbent (Afkhami, Madrakin and Karimi, 2008). Regeneration of the biosorbent increases the cost effectiveness of the process thus warrants its future success following the concept of Green Chemistry which is a new principle guiding the next generation products and processes (Pagnanelli, 2002). Recent realization, that biomaterials have also been associated with drawbacks related to stability and less sorption of wide range of toxic metals, restricting its commercial use (Nakano 2001). Agricultural wastes often, are also likely to transfer its respective color and odor to the water bodies. Therefore, biosynthetic modifications to improve the binding capacity and stability of natural biomaterials have attracted the keen attention of scientific community. In general, functional structural moieties like carboxylic acid, amino acids, phenolic, hydroxyl groups etc present in the biomaterials may constitute a physiologically active group of binding agents (working even at low concentration) to interact with metal ions and therefore, are supposed to be active sites for the sorption of metal ions. Strengthening of functional groups in the
biomaterial may lead to the designing of novel biomaterial with enhanced sorption efficacy and stability.

In continuation of our work (Goyal and Srivastava, 2008c; Goyal and Srivastava, 2009), the present communication reports modification onto Azadirachta indica leaf powder (AILP) an extremely free of cost agricultural waste owing to heavy leaves fall in autumn and spring season to improve its sorption efficiency and stability for possibility of its commercial use for abatement of cadmium and nickel from waste water.

MATERIALS AND METHODS

Biosorbent preparation, sorption and desorption studies

Biosorbent (Azadirachta indica) preparation, sorption and desorption studies dealing with metal solution has been carried out as mentioned in our earlier publications (Kardam et al., 2009; Goyal et al., 2011).

Synthetic modifications onto AILP

Acetylation

Acetylation of amino group on the biomaterial was achieved by washing 12.0 g of biomaterial first in 0.1 M HCl to remove any debris, followed by washing in sodium phosphate/sodium acetate buffer (0.1 M Na₃PO₄/1.0 M Na₂C₂H₃O₂) at pH 7.2. The biomaterial is reacted with 64.0 ml of acetic anhydride and stirred while maintaining the pH of 7.2 for 1 hr. The acetylated biomaterial was next centrifuged for 5 min at 3000 rpm. After removing the supernatant, the biomaterial was then resuspended in 1 M hydroxylamine to remove O-acetyl groups. The biomaterial was then washed with 0.1 M HCl to remove any more soluble materials and finally washed with de-ionised water.

Succination

The succination of the amino groups on the biomaterial was achieved by washing 12.0 g of biomaterial first in 0.1 M HCl to remove any debris, followed by washing in 0.1 M Sodium acetate at pH 8.0. The biomaterial was then resuspended in 500 ml of 1 M NaC₂H₃O₂·H₂O at pH 8.0. 16.0 g of succinic anhydride was added to the suspended biomaterial. An additional 16 g of succinic anhydride was added after 15 min intervals for the next one and half h (6 additions of 16.0 g succinic anhydride to the biomaterial). The biomaterial was then washed with 0.1 M HCl centrifuged and washed again with de-ionised water. Although the amino group is neutralized, it now forms an additional carboxyl group. By the addition of a carboxylate group, there should be an enhancement of metal binding by those metals that bind to carboxyl ligands.

Graft co-polymerization

Graft Co polymerization using standard practices were carried out as a function of AILP dosage (150, 200, 250, 300 mg), acrylic acid (1.0, 1.5, 2.0, and 2.5 ml), temperature (35±0.5°C) and time (60, 90, 120 and 150 min.). A required amount of Azadirachta powder was dispersed in a definite amount of water. Appropriate amount of Ceric Ammonium Nitrate (200 mg) and nitric acid (1.0 ml) were added slowly to the reaction mixture. Monomer Acrylic acid was added drop wise to the reaction mixture from the dropping funnel. The reaction flask was placed in a temperature controlled water bath at temperature (35±0.5°C) for various time periods under stirring by a magnetic stirrer. The reaction mixture was filtered and the homo-polymer was removed with excess water. The grafted sample was dried to a constant weight and used for sorption studies. Percentage of grafting was calculated from the increase in initial weight of AILP in the following manner: %G = (W₂-W₁)/ W₁ X 100, where Wᵢ denotes the weight of native AILP and W₂ the weight of grafted AILP after complete removal of the homo-polymer.

Characterization of the prepared biosorbents

Scanning electron microscopy (SEM)

The comparison of the surface morphology of unmodified and modified AILP was observed with a Scanning Electron Micrograph at bar length equivalent to 200 m, working voltage 20 KV with 200 x magnifications.

Fourier transform infrared spectroscopy (FTIR)

FTIR analysis in solid phase in KBr was performed using a Fourier Transform Infrared Spectrometer (FTIR- 8400, Shimadzu). Spectra of the sorbent before and after modifications were recorded.

Thermo gravimetric analysis

The TGA was performed using Thermo Gravimetric Analyzer (DTG-60, Shimadzu). The comparison of Initial Decomposition Temperature (IDT) and Final Decomposition Temperature (FDT) of unmodified and graft co-polymerized biomaterial was estimated with thermo grams.

Biosorption study

Sorption efficiency and number of regeneration cycles of the unmodified and chemically modified biomaterial was carried out in single metal [Cd (II) and Ni (II)] using the
procedure mentioned in our earlier publications (Kardam et al., 2009; Goyal et al., 2011; Goyal and Masram, 2012).

**Statistical analysis**

Batch experiments were conducted in triplicate (N=3) and data represents the mean value. Mean values, correlation coefficients, standard deviations were calculated using SPSS PC™ statistical package. For the determination of inter-group mean value differences, each parameter was subjected to the students-t test.

**RESULTS**

Sorption studies result into the standardization of the optimum conditions of biomass dosage [4g], particle size (105 µm), metal concentration (25 mg/l), contact time [30min.] and volume (200 ml) at pH 6.5. Maximum sorption for Cadmium and nickel ion was 81.36 and 73.65%.

**Mechanistic aspects of biosorption**

The aerial part of the plant *Azadirachta indica* possesses various organic chemical moieties prominently large proportions of low molecular weight amino acids (Ejoba, 2012). Amino acids have been found to constitute a physiologically active group of binding agents working even at low concentration, which because of ability to interact with metal ions is likely to be active sites for the sorption of metal ions. Carboxylate anion (COO⁻) of the acid group has enough potential for binding cationic metal ions and become active sites for the sorption of M⁺ ions. Enrichment of functional groups (COO⁻) responsible for sorption has been carried out as per following processes:

(i) In the acetylation of the biomaterial, the available amino ligands are blocked by acetic anhydride resulting into the increase in metal binding capacity. Acetylation brings about neutralization of the amino groups. It decreases the number of positively charged sites on biomaterial surface which causes a modest increase in metal uptake capacity (Figure 1).

(ii) Succination of the biomaterial is performed to add carboxyl group on to the nitrogen ligand (Figure 2): Another synthetic strategy of graft co-polymerization was also applied to increase the number of negatively charged carboxylate groups on the AILP biomaterial to enhance the ability to attract Metal [M⁺] ions (Figure 3). It was achieved by grafting of negatively charged functional groups using standard polymerization techniques.

Grafting of acrylic acid onto AILP biomaterial was calculated as a function of acrylic acid, time and biomass dosage at CAN (200 mg), temperature (35±0.5°C) and nitric acid (1 ml).
Biosorbents characterization

**Scanning electron microscopy (SEM)**

AILP represent large oval clusters in unmodified AILP while condensed, irregular type morphology in succinated, acetylated and graft co-polymerized AILP having pore area given in (Table 1). Observed aggregation and reduction in pore area of modified AILP may be ascribed to the modification onto AILP biomaterial.

**Fourier transform infra-red spectroscopy**

A perusal of the IR spectra of untreated and succinated biomaterial shows the presence of additional peak of carboxylate ion (1749.70 cm$^{-1}$) and conversion of amino to amide group (3285.77 cm$^{-1}$ to 3375.37 cm$^{-1}$) in succinated AILP confirming succination of the biomaterial.

The conversion of amino to amide group (3281.77 cm$^{-1}$ to 3369.14 cm$^{-1}$) confirmed acetylation process. The appearance of characteristic peak at 1725.2 cm$^{-1}$ (C=O) in the IR spectra of graft co-polymerized compared to its unmodified AILP confirms the formation of the grafted biomaterial.

**Evidence in support of improved environmental stability of the biomaterial**

**Thermo gravimetric analysis (TGA)**

Thermo Gravimetric analysis of untreated (native) and graft co-polymerized AILP biomaterial showed significant difference in the initial decomposition temperature (IDT) and final decomposition temperature (FDT). Upon grafting, temperature of AILP biomaterial is raised from (IDT: 37.94 to 49.32$^\circ$ C; FDT: 600 to 609.23$^\circ$ C), indicating that grafting of Acrylic acid improves the thermal stability of AILP biomaterial.

**Sorption efficiency of modified biomaterial**

All the three modified biomaterials were subjected for the assessment of sorption efficiency for cationic metals under previously standardized optimum conditions.

Increased sorption efficiency in all the three modified biomaterials has been observed at biomaterial dosage (2 and 4 g) (Table 2 and Table 3).
Table 2. Enhancement of sorption efficiency of different chemically modified AILP in case of single metal solution at 4g biomass dosage.

<table>
<thead>
<tr>
<th>Type of biomatrial</th>
<th>Sorption efficiency (%)</th>
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<tbody>
<tr>
<td></td>
<td>Cd (II)</td>
</tr>
<tr>
<td>Unmodified AILP</td>
<td>81.36</td>
</tr>
<tr>
<td>Succinated Biomaterial</td>
<td>88.42</td>
</tr>
<tr>
<td>Acetylated Biomaterial</td>
<td>87.54</td>
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<tr>
<td>Graft Biomaterial</td>
<td>91.23</td>
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</tbody>
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Table 4. Sorption of cationic metal ion on regenerated modified [Graft co-polymerized] biomaterial

<table>
<thead>
<tr>
<th>Cycles</th>
<th>% Sorption</th>
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<tbody>
<tr>
<td></td>
<td>Cd (II)</td>
</tr>
<tr>
<td>1</td>
<td>86.34</td>
</tr>
<tr>
<td>2</td>
<td>86.12</td>
</tr>
<tr>
<td>3</td>
<td>88.01</td>
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<tr>
<td>4</td>
<td>87.98</td>
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<td>5</td>
<td>87.23</td>
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<td>6</td>
<td>86.54</td>
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DISCUSSION

Increased sorption efficiency in the above three structural modifications can be assigned to the following facts:

Succination of the biomaterial results into the formation of additional carboxylate group along with the conversion of amine to amide group. Increase in carboxyl group results into the increase in sorption efficiency of biomaterial. Our finding is in agreement with the views of (Gardea-Torresday, 2008), who have reported that the succination not only decreases the number of positively charged sites in any biomaterial but also increases the number of negatively charged sites by contributing another carboxylic group.

In the case of acetylation the formation of amide group blocks the interferences of amino groups of the biomaterial. Our views find support from (Tsezos, 1985), stating that acetylation reaction is an exchange of positively charge substituted ammonium ion which does not contribute to the biosorption of metallic ions by an amide function (RNHCOCH₃) capable of coordination to the positively charged metal ion.

The enhanced sorption efficiency of graft co-polymerized biomaterial can also be explained on the basis of the fact that increase in the number of negatively charged ligands (COO⁻) increases sorption. (Saito, 1991) has indicated that graft co-polymerization is a promising technique for modifying physical and chemical properties of the adsorbent and to improve the adsorption property as well as prevent the leaching of organic substances.

The above experiment provides important information that structurally modified AILP is sufficient enough at the dose of 2 g to show good sorption efficiency compared to the 4 g dose of unmodified AILP. The fact exhibits the cost effectiveness of the present biomaterial when structurally modified.

Increased stability of the graft co-polymerized biomaterial was also monitored on the basis of increase in number of regeneration cycle. A perusal of the Table 4 clearly shows that structurally modified biomaterial (polymerized) can be used 6 times compared to only 4 times of unmodified biomaterial, exhibiting its increase environmental stability (Figure 4). It is inferred that out of 3 structural modifications considered for the study, graft co-polymerization not only increase the sorption efficiency but causes reduction in biomaterial dose highlighting its cost effectiveness.

Conclusion

The laboratory based findings open up new avenues in the abatement of Cd (II) and Ni (II) by altered Azadirachta indica leaf which is infact an agricultural waste owing to
heavy leaves fall in autumn and spring season. Thus, it introduces a less expensive, domestic and environment-friendly green method for the removal of metals from water bodies. Modifications resulted into the increased sorption efficacy and stability in terms of regeneration cycle (3 to 5) which in turn reducing the operational cost. Thus, it seems to be a promising technique for modifying physico-chemical properties of the biosorbent. The proposed novel biomaterial could be a low cost pretreatment step with enhanced sorption, stability and reusability before large chemical treatment for metal decontamination from waste water.

ACKNOWLEDGEMENT

The authors gratefully acknowledge Head, Department of Chemistry, University of Delhi for providing instrumental facilities. We are also thankful to University Grants Commission, New Delhi and SERB-DST New Delhi, India for providing financial assistance [F.15-54/12(SA-II)] and (SB/EMEQ-081/2014).

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