Management of hexavalent chromium from industrial waste using low-cost waste biomass

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Abstract

Hexavalent chromium because of its unique properties finds large number of industrial applications. Consequently, these industries discharge large quantities of chromium containing effluents. Since chromium is a known mutagen and carcinogen, the prevalent pollution laws in most countries require its complete removal from waste streams before discharge. There are several methods employed for chromium removal. However, most of these methods are unsustainable in nature and economically unattractive. It is therefore necessary to look for a new practical, economic, efficient and sustainable alternative for the management of chromium bearing industrial effluents. Bio-management approaches are gaining immense creditability worldwide across in the recent years. Chromium being non-renewable and finite natural resource, the argument is not limited only to their removal from the effluents, but also extends to finding an efficient and economical ways of recovery/recycling. The present study explores the possibility of using saw dust for the removal of hexavalent chromium from industrial waste.

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1. Introduction

Chromium metal exists in environment both in trivalent and hexavalent forms. It is known that Cr(VI) is 500 times more toxic than the Cr (III) form. Hexavalent chromium has got unique properties of corrosion resistance, hardness and colour and therefore finds large number of applications in industries like chrome-plating, automobiles, steel and alloys, paints, leather tanning and ammunition factories (Raji & Anirudhan, 1998). Consequently, these
industries discharge large quantities of chromium containing effluents. Since chromium is a known mutagen and carcinogen (Oguz, 2005), the prevalent pollution laws in most countries require its complete elimination from waste streams before emancipation. The most commonly used method for chromium removal method is reduction followed by chemical precipitation (Baral et al. 2006). However, this process has many disadvantages like high installation costs, high energy-intensive, consume large quantities of chemicals and difficulty of handling the later produced solid waste and hence are economically unattractive. Therefore, it is necessary to look for a new practical, economic, efficient and sustainable alternative for the management of chromium bearing industrial effluents. Bio-management practices are gaining immense creditability world over in the recent times (Vinodhini & Das, 2009). Chromium being non-renewable and finite natural resource, the argument is not limited only to their removal from the effluents, but also extends to finding an efficient and economical ways of recovery/recycling. The researchers in the present study explores the possibility of using biosorption process for the removal of hexavalent chromium from industrial waste using treated and untreated saw dust, a low-cost biomaterial.

2. Methodology

2.1. Sample collection and methods employed

All the biosorption experiments were conducted as per the method prescribed by the following researchers (Itankar et al., 2013; Patil, 2012; Patil and Paknikar, 1999). Analysis of chromium from experimental solutions were carried out as per APHA (1998). All the chemicals employed in the present study were of analytical grades. Borosilicate glassware was used. All the apparatus after acid treatment were rinsed thoroughly with tap water followed by rinsing with deionized water. The biomaterial employed in the present study was sawdust. It was obtained from local sawmill. Sawdust sample was collected in polythene bags and transported to the laboratory and washed several times with tap water followed by distilled water until a colourless solution was detected spectrophotometrically i.e., the discarded water ran clear. Washed saw dust was subjected to oven drying at 50°C for 2-3 days till constant weight was obtained. Dried biomaterial was powdered using electric mixer and sieved with vibratory sieves so as to obtain particle size ≤ 500 μm (0.5mm). Conventional sorbents like activated charcoal was used as reference material. Stock solution of hexavalent chromium (1000 mg/l) was prepared by dissolving 3.735g potassium dichromate (K₂Cr₂O₇) in 1000ml of deionized distilled water (APHA, 1998). Desired concentration 50 mg/l of Cr (VI) for experimental purpose was prepared from stock solution. Solution pH was adjusted using 0.01 -1M of HCl and/or NaOH. Reagents prepared for analytical use were stored under refrigerated conditions (9-10°C). Negligible change in working volume was observed due to addition of HCl or NaOH. Cr(VI) from the solution was analysed by 1,2-diphenylcarbazide (DPC) method at λ max of 540 nm according to the method prescribed in Standard Methods (APHA, AWWA, WEF 1998). pH was determined using digital pH meter.

2.2 Preparation of L cysteine treated saw dust biosorbent

To prepare 100 ml solution of L cysteine 1g powder was dissolve in required amount of concentrated HCl followed by adding DW. 4g of washed and cleaned saw dust was treated with 100ml L-cysteine solution at 50°C for 4 hours at 80 rpm on a rotary orbital shaker. The mixture was filtered through ordinary filter paper, washed several time with distilled water and subjected to drying in hot air oven at 30°C for 24 hours. The subsequent material obtained was placed in airtight container for further use.

2.3 Batch equilibrium studies using biomass

Batch equilibrium studies were conducted using SD, TSD and AC. 1g of biomaterial was contacted with 25 ml of 50 mg/l of Cr (VI) solution in a set of 250 ml capacity of Erlenmeyer flasks at 30°C for 1 hour. Contents of the flasks were filtered and analyzed for residual Cr (VI) concentration. All experiments were performed in duplicates and repeated twice to confirm the results. Appropriate controls were run simultaneously. In order to evaluate the influence of pH on biosorption of Cr (VI), powdered unconditioned biomass was contacted with Cr (VI) solution of different pH ranging from 2 to 10 prior to sorption. Cr (VI) ion loading capacity was determined by contacting 1g biomaterial several time with fresh solution of 25 ml of 50mg/l of Cr (VI) solution till saturation was achieved. In order to determine the influence of biosorbent quantity on biosorption of, varying amount ranging from (0.1-5%...
w/v) was contacted with 50 mg/l of chromium solution. To study the influence of chromium solution concentration 1g of biomass was treated with different concentration of chromium solution under optimum condition.

2.4 Adsorption isotherm models

Cr (VI) solutions of varying concentrations (5 to 500 mg/L) were used to study the effect of initial Cr (VI) concentration on it adsorption. The amount of Cr (VI) sorbed at equilibrium, Q (μmol/g), which represents the Cr (VI) uptake, was calculated from the difference in Cr (VI) concentration in the aqueous phase before and after adsorption, according to the following equation:

\[ Q = V (C_i - C_f)/1000 m \]  

Where, Q is the Cr (VI) uptake (μmol per gram biomass); V is the volume of Cr (VI) solution (ml); C_i is the initial concentration (mg/l); C_f is the final concentration (mg/l); m is the mass of biosorbent (g). To examine the relationship between sorbed and aqueous concentration at equilibrium, sorption isotherm models viz. Freundlich (1926) and Langmuir (1918) were used for fitting the data.

\[ \ln Q = \ln K + \frac{1}{n}C_{eq} \]  Freundlich equation

\[ \frac{C_{eq}}{Q} = \frac{1}{bQ_{max}} + \frac{C_{eq}}{Q_{max}} \]  Langmuir equation

Where, C_{eq} is the liquid phase concentration of Cr (VI); b is the Langmuir constant; K is the constant; 1/n is the intensity of adsorption and Q is the specific metal uptake; Q_{max} is the maximum chromium uptake.

3. Result and discussion

3.1 Impact of pH on Cr(VI) sorption

Biosorption study on heavy metals in past have shown that most important characteristic to affect the biosorption process is pH (Vinodhini & Das 2010). Impact of H⁺ ions concentration on the biosorption of Cr (VI) ions was studied on TSW, SW and AC in the pH range of 1 to 10. It was observed that the maximum sorption of Cr (VI) occurs at initial pH ranging from 2 to 4 (97%) for TSD, 93% AC and 70% for SD respectively and decreases at lower and higher pH values as depicted in (Fig 1).

Under acidic conditions, the biosorbent is positively charged due to protonation and dichromate ion exists as oxyanion leading to an electrostatic attraction amid them (Boddu et al., 2003). Sharp decrease in biosorption above pH 4 may be due to occupation of the adsorption sites by oxyanionic species like HCrO₄⁻, CrO₄²⁻, CrO₄²⁻, etc., which hinders the approach of such ions further toward the sorbent surface (Vinodhini and Das, 2009). Results attribute that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biomaterial (Popuri et al., 2007). Cr (VI) containing industrial wastewaters generally has acidic pH. Obviously, no pH adjustments would be required prior to biosorption, thereby reducing the cost of Cr (VI) biosorption process.

3.2 Impact of adsorbent dose

The effect of SD, TSD and AC on the biosorption of Cr (VI) is illustrated in fig 2. To study the ratio between solute and biosorbent, Biomaterial quantity in the range of 0.3g - 5g, at fixed volume of 25 ml of Cr (VI) solution having concentration 50 mg/l was contacted at 30°C, 100 rpm in rotary shaker for 1 hour at optimal pH. The result indicated that as the biomass quantity increased the percentage biosorption of Cr (VI) also increased and become constant after saturation point is reached. At lower value 0.3g/l of biomass quantity of TSW, AC and SW percentage sorption was 90%, 80% and 75.9% respectively. The mechanism can be explained as with rise in biomass quantity, number of binding site and surface area increases which in turn result in higher removal of Cr (VI) ions (Bai and Abraham 2001). However as the quantity of biomass further increased the Cr (VI) sorption did not increased but
remain constant which is very well depicted in Fig 2. Various interpretation given includes competition between chromium ion, electrostatic interaction, agglomeration of adsorption site, less available binding site, inappropriate mixing due to higher density of biomass. (Tewari et.al 2005).

![Fig.1. Effect of pH on Cr (VI) removal by TSD, SD and AC](image1)

**3.3 Impact of loading capacity**

Table 1 depicts the data on Cr (VI) loading capacity of SD, TSD and AC unconditioned biosorbents. It was found that TSD had maximum loading capacity for Cr (VI) (7.63 μmol/g) sorption followed by AC (7.04 μmol/g) and SD. Loading capacity of activated charcoal was found relatively lower when compared with the TSD.

![Fig.2. Effect of Biosorbent dose on Cr (VI) removal by TSD, SD and AC](image2)
Table 1. Chromium loading capacity of biosorbent under study

| Biosorbent          | Loading capacity in mg/g of biomass |
|---------------------|-------------------------------------|
|                     | Unconditioned biomass               |
| Treated saw dust    | 15.42                               |
| Saw dust            | 11.2                                |
| Activated charcoal  | 16.58                               |

3.4 Impact of concentration of Cr (VI) on biosorption

The sustainability and efficiency of biosorption process mainly depends on concentration of sorbent as well as metal ion. For the cost effective management of industrial wastewater for Cr (VI) removal, it is necessary to know the solute/sorbent ratio required. Cr (VI) solution with concentration ranging from 10mg/l to 500mg/l was prepared. Biomass was treated with these solutions for 1 hour at 100 rpm and 30° C temperature. As observed in Fig 4) that at lesser concentration (10mg/l), percentage adsorption in TSW was 99.96%, AC 100% whereas in SW it was 89% which implies that at lower concentration, metal ions interact with reactive site better while increase in concentration from 50mg/l to 500mg/l shows a decline. This change is because with rise in chromium ion concentration in solution number of ions competing for available binding site on the biomaterial increases which leads to insufficient site for complex formation.

4. Adsorption isotherm models

The effect of initial concentration provides an important driving force to overcome all mass transfer resistance of target ion between the aqueous and solid phases. The biosorption of Cr (VI) was carried out at different initial concentrations ranging from 5 to 300 mg/l at pH 4.0 using 1 g/25ml of Saw dust biomass. It was found that the equilibrium sorption capacity of the sorbent increased with increasing initial concentration of Cr (VI) from 5 to 300 mg/l. This was due to the increase in the number of ions competing for the available binding sites in the biomass. The concentration on biosorption uptake of Cr (VI) by the sorbent reached to a plateau at 300 mg/l. There was a significant increase in the specific uptake of Cr (VI) up to 300 mg/l. Later the specific uptake of Cr (VI) decreased with increased concentration (data not shown). This might be due to the saturation of binding sites, which clearly showed that Cr (VI) uptake by Saw dust biomass was a chemically equilibrated and saturation phenomenon. To
examine the relationship between sorption, isotherm models are widely employed for fitting the experimental data. Langmuir and Freundlich models were used to describe the equilibrium between the Cr (VI) sorbed on Saw dust biomass and Cr (VI) ions in the solution. It was also observed that Cr (VI) uptake values could be well fitted to the Langmuir and Freundlich isotherm models with regression value of >0.97. Linear transformation of the adsorption data using Freundlich and Langmuir models ($R^2 ≥ 0.97$) allowed computation of the Cr(VI) adsorption capacities. Experimental data obtained in the studies were found to obey basic principles underlying these models, that is, heterogeneous surface adsorption and monolayer adsorption at constant adsorption energy respectively (Freundlich, 1926; Langmuir, 1918). Further studies on loading capacity, adsorption and desorption and scale up studies for chromium removal and recovery is under progress.

5. Conclusion

The presence of L-cysteine in saw dust biomass enhanced Cr (VI) biosorption from chromium solution. Cr adsorption in the presence of L-Cysteine is preferred at lower pH. At pH 3, the Cr uptake by TSW increased to 99%. SD is easily available countrywide, by making simple chemical modification its adsorption capacity can be enhanced. Small scale industries like electroplating industries having low concentration of Cr(VI) in waste water can use it in batched or stirred tank flow reactors. From the foregoing results and discussion it could be concluded that low cost waste biomass viz. TSD, SD was highly efficient and has immense potentials as “biomaterial” for the removal of hexavalent chromium from aqueous industrial wastes. Recovery of chromium from waste and recycling it back to the industry would lead to the conservation of non-renewable resources.

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