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Column and batch studies for bioremediation of chromium (VI) from aqueous and industrial wastewater

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ABSTRACT

The column and batch removal of Cr (VI) from aqueous solution and industrial effluent using low-cost adsorbents such as saw dust (*Dalbergia sisso*), walnut (*Juglans regia)* and almond shell (*Prunus dulcis)* under different experimental conditions was investigated in this study. The influences of initial Cr (VI) ion concentration (10 to 100ppm), pH (2 to 9), flow rate (0.5-1ml/minute), contact time (60-180 minute), sorbent dosage (5-10gm), agitation speed (80-160rpm) have been reported. The results indicate that the optimum pH, flow rate, sorbent dosage, agitation speed for the removal was found to be 2, 0.5ml/min.,10gm, 120rpm respectively for all types of carbon. The comparative chromium (100ppm) removal efficacy of three adsorbents is in the order of walnut shell (82.2%)>sawdust (71%)>almond shell (70%) from both aqueous solution and industrial effluent. Continous column studies are more efficient in Cr (VI) removal as compared to batch studies.

KEYWORDS

Bioremediation;
Biosorbents;
Heavy metals;
Column studies;
Bioscavengers.

INTRODUCTION

Heavy metals are the natural components of Earth's crust. As trace elements, some heavy metals (copper, selenium, zinc) are essential to maintain metabolism of human body. However, at higher concentration they can lead to poisoning. These heavy metals once discharged into the waste streams, get accumulated throughout the food chain, thus becoming a serious threat to the environment. Heavy metals like Ni, Zn, Cu, Cd, Cr, and Hg are toxic even in the minute quantities. Chromium, a common pollutant get introduced into natural waters from the textiles, leather tanning, electroplating and metal finishing industries, cement, mining, dyeing and fertilizer and photography industries. Chromium effects human physiology by accumulating in food chain and cause several ailments. Researchers have recently reported that vitamin C reacts inside human lung cells with chromium (VI), causing massive DNA damage, low doses of chromium (VI) combined with vitamin C produce upto 15 times as many chromosomal breaks and upto 10 times more mutations, compared with cells lacking vitamin C. Adverse effects of hexavalent form on skin include ulceration, dermatitis and allergic skin reactions, perforation of mucous membranes of nasal septum, irritation of pharynx and larynx, asthmatic bronchitis, edema, coughing and wheezing, shortness of breath and nasal itch.

According to Indian standards the permissible limit of Cr (VI) for industrial effluents to be discharged to surface water is 0.1mg\l[1]. The tolerance limit for Cr (VI) for discharge into inland surface waters is 0.1mg/l and in potable water is 0.05mg/l. Chromium contaminated wastes are usually discharged to the environment as hexavalent chromium in the form of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anions which are thermodynamically stable over a wide pH range[2]. Therefore removal of Cr (VI) from industrial effluents is important before discharging them into the aquatic environment or on to land. A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly reduction, ion exchange, electrodialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption[3]. Most of these methods suffer from drawbacks such as high capital and operational costs associated with energy and chemical consumption or the disposal of the residual metal sludge. Many reports have appeared on the development of low-cost activated carbon adsorbents developed from cheaper and readily available materials[4-6] Activated carbons with their large surface area, microporous character and chemical nature of their surface have made them potential adsorbents for the removal of heavy metals from industrial wastewater. A new technology alternative has been pioneered to remove toxic heavy metals from industrial effluents, called biosorption. It is effective, simple and cheap[7]. The adsorption of chromium (VI) by a number of materials such as leaf mould[8], activated groundnut husk carbon[9,10], coconut husk and palm pressed fibres[11], coconut shell activated carbon[12], coconut shell, wood and dust coal activated carbons[13], coconut jute carbon[14], coconut tree sawdust carbon[15], sawdust and used tyres carbon[16], phosphate treated sawdust[17], cactus, olive stone/cake, wool, charcoal and pine needles[18], rice husk carbon[19,20], moss[21], coconut fibre compost, maize cob, sugar beet pulp and cane bagasse[22], hazelnut shell carbon[23], almond shell carbon[24], corncob[25], quaternized wood[26], cow dung carbon[27], waste slurry[28] and carbon slurry[29] have been reported in the literature.

In this study, three biosorbents, namely walnut, almond shells and sawdust are used to remove chromium (VI) from aqueous solution. In process application, the most effective apparatus for continuous operation is a column reactor, much like that used for ion exchange. Thus, many researchers have used a column packed with various biomasses capable of removing heavy metals[30,31]. Meanwhile, many mathematical models have been used to study column systems, and their dynamic behavior has also been well established[32]. All these models have been mainly originated from research on activated carbon sorption, ion exchange or chromatographic applications. However, in the case of Cr (VI) removal in the column, a few studies have been reported, but no theoretical model has been proposed to predict the experimental breakthrough data[33]. The search for new and innovative treatment technologies has prompted to exploit the biosorptive properties of biologically derived materials that can be produced at low cost. This project work is based on removal of chromium (VI) from aqueous as well as from industrial effluent.

MATERIAL AND METHODS

All the chemicals used were of analytical grade. Synthetic stock solution of 1000ppm of Cr (VI) was prepared using potassium dichromate dried at 378K for 24 hours in double distilled water. The working solutions were prepared just before using from the stock solution by dilution with double distilled H_2O. pH of the solutions were adjusted using NaOH and HCl. The concentration of chromium was determined spectrophotometrically by using diphenyl carbazide method.

Preparation of Biosorbent Biosorbents used are walnut (*juglans regia)*, almond (*prunus dulcis)* and sawdust (*Dalbergia sisso*) collected from natural resources and local market. A known amount of each of three biosorbents were dried at 120°C in hot air oven for 24 hours, grinded and sieved. The sieved biosorbents were treated with 50ml of concentrated H_2SO_4 and formaldehyde solution to remove colour leaching problem. Finally they were given subsequent washings with distilled water and acetone, dried and then loaded in a packed bed reactor.

Procurement of Effluent The chromium bearing wastewater samples were collected from electroplating unit of D.C International, F-205, Phase-VIII, Focal point, Ludhiana. The highest chromium concentration was found to be 180ppm at pH 4.0- 5.0.

Initial characterization of industrial effluent

Various parameters like Cr (VI), pH, Total Solids, Total dissolved solids, Total suspended solids, Alkalinity, Hardness, Dissolved Oxygen, Chemical and Biological oxygen demand were studied for initial characterization of industrial effluent [34]. All parameters expressed in mg/l except pH is as follows: Cr 100ppm, pH, 4.5; TS, 1000; TDS, 200; TSS, 800; Alkalinity, 106; Hardness, 650; COD, 540; BOD, 330; chlorides, 450.

Batch sorption experiments

The Cr (VI) stock solution was prepared by dissolving their corresponding analytical grade salt of $K_2Cr_2O_7$ in distilled water. Further dilution with a concentration of 20ppm was prepared from the stock solution of chromium. 250ml of Erlenmeyer flasks containing heavy metal solution (100ml) of known concentration was taken for batch biosorption experiments. 10gm each of powdered sawdust, walnut and almond shells were added to the flasks separately. The mixtures were agitated on a rotary shaker for half an hour. The pH of sample solutions were adjusted by using 0.1M HCl or 0.1M NaOH at the obtained optimal values for each of biosorbent. The experiments were performed at room temperature (32$\pm$2°C). The contents were centrifuged and supernatant was measured for Cr (VI) content by diphenyl carbazide method spectrophotometrically at 540nm. The effects of various parameters on the rate of adsorption process were observed by varying contact time, t (60, 90 and 180 min), initial concentration of chromium ion, C_o (10-200ppm), adsorbent dosage, W (5, 8 and 10g/100ml) and initial pH of solution (2, 5, 7, 9). The solution volume (V) was kept constant (200ml). The chromium removal (%) at any instant of time was determined by the following equation:

$$\% \text{ Cr removal} = \frac{(C_0 - C_t)}{C_0 \times 100\%}$$

where, C_o and C_t are the concentration of chromium (mg/l) at initial condition and at equilibrium respectively. To increase the accuracy of the data, each experiment was repeated three times[35].

Continous column equilibration studies

Continous reactor used in this study consists of 14cm long and 1.3mm internal diameter glass column. The column was densely packed with a known amount of 10gm each of sawdust, walnut and almond shell dried powder. Glass wool was added on top and bottom of packing to prevent the adsorbent particles from floating and separating. Flow rate was maintained at minimum with the help of stop cock. Aqueous solution (100ml) of chromium for known concentrations (20-200ppm) were allowed to flow into the column and collected the filtrate and chromium contents were then estimated by diphenyl carbazide Method. Industrial effluent with known concentration of chromium (100ppm) was subsequently passed through column.

TABLE 1 : Effect of initial Cr (VI) concentration on %removal efficiency of sawdust (*Dalbergia sisoo*), walnut (*Juglans regia*) and almond shell (*Prunus dulcis*)

Sr. no.	Initial Cr (VI) concentration (ppm)	% Cr(VI) removal with saw dust	% Cr(VI) removal with walnut shell	%Cr(VI) removal with almond shells
1	10	40.8	50.0	34.0
2	20	57.1	59.5	41.3
3	40	61.1	69.7	56.1
4	50	64.7	76.0	64.1
5	100	71.6	81.6	70.6
6	100(Effluent)	69.5	78.7	67.0

Analytical methods

The concentration of Cr (VI) in the liquid samples was determined colorimetrically by the reaction with 1,5-diphenylcarbazide in acid solution. The absorbance of the resulting red–violet sample was measured at 540 nm using a spectrophotometer. To determine the total concentration of chromium, all the chromium was converted into the hexavalent state by oxidation with potassium permanganate at high temperature (120-130°C). Thereafter, the oxidized chromium was analyzed by the above-mentioned method for Cr (VI) analysis. Since chromium in solution is mostly in the hexavalent or trivalent states, the concentration of Cr (III) can be obtained from the difference in concentration between the total and hexavalent chromium[34].

RESULTS AND DISCUSSION

Optimized conditions: pH 2, flow rate 0.5ml/min., sorbent dosage 10gm

From TABLE 1 and figure 1, it is evident that the

TABLE 2 : Effect of pH on %Cr (VI) removal efficiency for three adsorbents

pH	% Cr (VI) removal with sawdust	% Cr (VI) removal with walnut shell	% Cr (VI) removal with almond shell
2	72.0	80.5	70.0
5	68.0	75.7	62.0
7	57.5	67.7	58.8
9	50.7	58.4	51.8

uptake capacity increased with increase in initial concentration, which may be due to availability of more number of chromium (VI) ions in solution for sorption. Higher initial adsorbate concentration provided higher driving force to overcome all mass transfer resistances of metal ions from aqueous to solid phase, resulting in higher probability of collision between chromium (VI) ions and the active sites.The percentage removal of Cr (VI) from the industrial effluent is nearly equal to that from aqueous solution. The Cr (VI) is present in the form of negatively charged $HCrO_4^-$ and $Cr_2O_7^{2-}$ at pH 2. Because of protolysis of surface sites by H^+/H_3O^+ on surface of biosorbents by adsorbing H^+/H_3O^+ which are of smaller size and more mobile at pH 2, result in stronger electrostatic force of attraction between sorbent and acid chromium ion and consequently resulting in higher adsorption capacity.

Effect of pH

The effect of various pH values of 2, 5, 7, and 9 on the uptake capacity of three selected biosorbents at 100ppm initial Cr (VI) concentration was investigated as seen in TABLE 2.

It was observed that at lower pH values, $Cr_3O_{10}^-$ and $Cr_4O_{13}^{2-}$ species are formed. The optimum pH for biosorption of hexavalent chromium on to sawdust, walnut and almond was observed at pH 2. This indicates the formation of more polymerized chromium oxide species with decreased pH. As illustrated in TABLE 2, 72.0%, 80.5% and 70.0% of chromium ions were adsorbed from a solution of 100ppm concentration whereas reduction to 50.7%, 58.4% and 51.8% removal was determined as the pH shifted from 2-9. The behavior of chromium adsorption with varying pH may be due to various mechanisms such as electrostatic attraction/ repulsion, chemical interaction and ion exchange which are responsible for adsorption on adsorbent surfaces.

TABLE 3 : Effect of contact time on %Cr (VI) removal efficiency for three biosorbents

Concentration (ppm)	Biosorbents	60 mins	90 mins	180 mins
100	Sawdust	70.0%	68.7%	52.8%
100	Walnut shell	68.8%	80.0%	51%
100	Almond shell	58.8%	65.0%	70.2%

Effect of flow rate

A minimum flow rate was adjusted i.e 0.5ml/min for sawdust, 0.4ml/min for walnut and 0.5 ml/min for almond. It has been seen that minimum flow rate helps in maximum adsorption.

Effect of contact time

Contact time of 60 min, 90 min and 180 min was optimized at 100ppm concentration for the three biosorbents i.e. sawdust, almond and walnut.

From the TABLE 3 it was found that at 100ppm concentration, the three biosorbents i.e. sawdust, walnut and almond shells have shown maximum removal of 70% at a contact time of 60 minutes, 80% removal at contact time of 90 minutes and 70.2% at contact time of 180 mins respectively. It is evident that equilibrium time is dependent on adsorbate concentration. It was estimated that rate of uptake was rapid in early steps but gradually decreased and become constant when equilibrium was reached. After a certain time of contact, desorption might occur. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

Effect of sorbent dosage

The study for the sorptive removal of chromium (VI) with respect to sorbent dose was done over the range 5-10g, at pH 2, temperature 300 K, optimized contact time, stirring rate 120 rpm and initial chromium (VI) concentration 100ppm. The results shown in TABLE 4 demonstrate that the rate of sorption of chromium (VI) ions increases when mass of three adsorbents increased from 5-10g/100ml and attains equilibria. Sorption increases from 48 % to 71% (saw dust), 52.4% to 82.2% (walnut shell) and 47% to 70% (almond shells) while the increase in the removal efficiency on introducing an additional 5g/100ml of selected biosorbent was not so significant. The optimum biosorbent dosage was 10g/100ml for the wastewater under study. It is apparent that the removal percent of chromium (VI)

TABLE 4 : Effect of sorbent dosage on %Cr (VI) removal efficiency for three biosorbents

Amount of biosorbent	% Cr (VI) removal with sawdust	% Cr (VI) removal with walnut shell	% Cr (VI) removal with almond shell
5g	48.0	52.4	47.0
8g	67.5	71.2	66.8
10g	71.0	82.2	70.0

increases rapidly with increase in the dose of three biosorbents due to the greater availability of the sorption sites or surface area. The concentration of both the metal ions and the biosorbent is a significant factor to be considered for effective biosorption as it determines the sorbent/sorbate equilibrium of the system.

It was found that sawdust, walnut and almond shells have shown maximum chromium removal of 71%, 82.2% and 70% at 10 g of adsorbent dosage for 100ppm Cr (VI) concentration respectively.

Effect of agitation speed

Agitation speed was optimized at different rpm i.e 80, 120, 160 rpm for the three biosorbents i.e. sawdust, walnut and almond.

The adsorption capacity of all the three biosorbents increased with increase in agitation speed and an optimum was achieved at 120 rpm (TABLE 5). On increasing the agitation speed further, there might occur some desorption. Agitation facilitates proper contact between metal ions in solution and biomass binding sites and promotes effective transfer of sorbate ions to the sorbent sites. The contact between solid and liquid is more effective at moderate agitation[36].

Chromium removal in batch process

Removal of industrial chromium from aqueous as well as from electroplating industrial effluent has been done in batch process in order to compare it with continuous treatment technology. In Batch process at 10ppm Cr (VI) concentration saw dust, walnut & almond show 34.7, 47% & 27.4% removal at an optimum pH 2, agitation speed 120 rpm, sorbent dosage10gm & contact time 60-180minutes. At 20ppm Cr (VI) concentration, they show 54.2%, 56.4% & 32.3% removal. It can be estimated that percentage Cr (VI) removal from aqueous solution in batch studies is less as compared to continuous treatment technology.

TABLE 5 : Effect of agitation speed on %Cr (VI) removal efficiency for three adsorbents

Agitation speed (rpm)	% Cr (VI) removal with sawdust	% Cr (VI) removal with walnut shell	% Cr (VI) removal with almond shell
80	66.4	74.6	57.1
120	72.2	80.9	69.0
160	69.1	78.3	67.4

CONCLUSIONS

The selected biosorbents i.e. sawdust, walnut and almond (10gm) shows 71%, 82.2% and 70% removal of Cr (VI) ions (100ppm) by column experiment at an optimized pH 2, flow rate 0.5ml/min, contact time of 60, 90 and 180 minutes respectively. The comparative Chromium removal efficacy of three adsorbents is in the order of walnut shell>sawdust>almond shell from both aqueous solution and industrial effluent. Optimization of agitation speed shows that adsorption capacity was increased with increase in agitation speed and an optimum was achieved at 120 rpm for all the three selected biosorbents. Continuous column studies are more efficient in Cr (VI) removal as compared to batch studies. The property of biosorption is independent of life functions since dead substrate exhibited this property as well or even better than live ones. The use of dead substrate is more advantageous for water treatment as it is not affected by toxic wastes[37]. Since optimum conditions in laboratory environment are reproducible in real working environment as well, the findings of the present study may be very useful for assessing the process at industrial scale. Each of the three biosorbents can be successfully employed for the removal of chromium (VI) ions from wastewater. From this study it can be concluded that biological methods hold an advantage over chemical methods for the removal of heavy metals by precipitation and adsorption[38].

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