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Groundnut Shell Powder as Low Cost Natural Adsorbent For Total Chromium in Spent Chrome Liquor

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ABSTRACT

The role of Groundnut Shell Powder (GNSP) to reduce the level of total chromium (Cr^{+3} and Cr^{+6}) in spent chrome liquor has been investigated. The maximum total chromium reduction was achieved by GNSP is 83.90% at pH of 7.70 with metal ion concentration of 100 ppm, adsorbent dose of 1.5g 100 mL^{-1}, contact time of 2 h and mesh size of 36 British standard sieve. GNSP has been successfully used as potential source of reducing load of pollutants in spent chrome liquor and treated effluent is highly suitable for use in various anaerobic reactors for biogas production.

Keywords: Spent chrome liquor, GNSP, Adsorption, BSS, Total chromium.

INTRODUCTION

Rapid advancement in terms of technology, industrialization and urbanization has severely posed a great threat to the quality of our atmosphere due to indiscriminate disposal of waste water. The industrial effluents contain a lot of toxic metal ions and variety of organic compounds which are harmful to different forms of life [1]. The discharge of these effluents restricts the multiple use of water and the opportunity to use the effluent as a source of energy is lost. Tanneries are considered most polluting industry due to release of chromium in water streams. Indian tanneries process sheep and goat skin, cow and buffalo hides using both vegetable and chrome tanning process. About 80% of the tanneries uses chrome tanning process as it provides heat, humidity resistant leather, superior finish and luster. Spent chrome liquor of tanneries waste mainly contains chromium in trivalent form which get further oxidized to its hexavalent form. The maximum levels permitted for trivalent chromium and hexavalent chromium in wastewater are 5 ppm and 0.05 ppm respectively [2]. Harmful effects of bothCr^{+3} and Cr^{+6} are well established. Cr^{+3} complexes are capable of bringing about apoptotic cell death in lymphocyte cell culture[3] and DNA damage due to its ability to cross link DNA[4] while Cr^{+6} is extremely toxic, carcinogenic and mutagenic in nature. Therefore removal of both Cr^{+3} and Cr^{+6} from spent chrome liquor become a cause of concern before its discharge into aquatic or agricultural streams. Various methods such as precipitation, solvent extraction, ion-exchange and HPLC have been reported but most of these methods create problems such as high operating cost or excessive use of reagents and secondary polluting effects. Hence there is a need of low cost natural biosorbent materials which can adsorb chromium as well as other harmful metal ions. Several attempts have been made for elimination of toxic Cr^{+3} and Cr^{+6} species using low cost adsorbents such as bark of several pine species[5], agricultural waste biomass[6], rice husk[7], rice bran[8], silica[9], tea wastes[10], maize tassel[11], commercial activated carbons [12], modified sugarcane bagasse[13], peanut hull[14-15], Terminalia catappa leaves [16], activated biocarbon [17].

The present study uses batch adsorption technique of Total chromium (Cr^{+3} and Cr^{+6}) on Groundnut shell powder in spent chrome liquor.

MATERIALS AND METHODS

The spent chrome liquor used for the experimental study was procured from leather complex Jalandhar, Punjab (India) at their common disposal site. The sample was collected three times within two hours interval in 15L capacity of plastic cans and stored in refrigerator. Groundnuts were collected from local market. Their shell were removed and powdered to obtain particles mesh size of 36 British standard sieves. All the analytical grade chemicals were used for the investigation. The pH of the solution was adjusted with 0.01M NaOH and 0.01 M HCl using century digital pH meter (model CP901). Procedure of APHA [18] was followed to determine concentration of total chromium. This procedure measures only hexavalent chromium and to measures total chromium (Cr^{+3} and Cr^{+6}) Cr^{+3} was converted to hexavalent state by oxidation using $KMnO_4$ and then determined Colorimetric ally by diphenyl carbazide in acidic medium.
Batch experiments were carried at pH (2.5-7.7), adsorbent dose (0.5-2.0g $100mL^{-1}$), contact time (60-150 min) and particle size (18-36 British standard sieve).

RESULTS AND DISCUSSION

Bioscavanging is undertaken to assess the efficiency of Groundnut shell powder as adsorbent for the removal of total chromium from spent chrome liquor. GNSP is composed of fats, ash, moisture [19], holocellolose, α–cellulose, hemicellulose, soluble carbohydrates, lignin [20] and proteins. Optimization of parameters such as pH, initial concentration of adsorbate and adsorbent, contact time, particles size have been investigated using batch equilibration process.

Effect of pH and Initial Concentration of Chromium: The removal of chromium from waste water by adsorption is highly dependent on the pH of the solution, which affects the surface change of the adsorbent, degree of ionization and speculation of adsorbate [21]. The role of hydrogen ion concentration on adsorption was observed in the pH range of 2.50-7.70, with initial concentration of total chromium ranging from 50-200 ppm, adsorbent dose of 1.5 g 100 mL^{-1}, particle size of 36 mesh and contact time of 2 h. As the tannery effluent contains more quantity of Cr^{+3} as compared to Cr^{+6}, with the increase in pH above 7.0 the precipitation of Cr^{+3} start taking place. But it was observed that precipitates are very light and do not settle. The precipitate starts settling in contact with GNSP. Adsorption of toxic substances also taking place on the surface sites of GNSP. Thus GNSP helps in removal of toxic substances by adsorption and settling of precipitates. With increase in pH of the solution, the percentage adsorption of chromium on GNSP increases. It has also been concluded that with increase in initial concentration of chromium, there is increase in the adsorption as observed in Langmuir's theory of adsorption isotherm. The maximum uptake of 83.90% total chromium by GNSP takes place at pH of 7.70 with metal ion concentration of 100 ppm, adsorbent dose 1.5g 100 ml, contact time of 2 h and mesh size of 36 British standard sieves. The results of variation of adsorption on GNSP with pH of the solution at constant metal ion concentration are given in Table 1

Table 1. Effect of pH on % Adsorption

Sr. No.	pH	Adsorbent dose (g 100mL^{-1})	Contact time (min)	Total chromium (ppm)	% Removal
1.	2.5	1.5	120	200	31
2.	2.5	1.5	120	150	40
3.	2.5	1.5	120	100	54
4.	2.5	1.5	120	50	57
5.	4.5	1.5	120	200	43
6.	4.5	1.5	120	150	48
7.	4.5	1.5	120	100	60
8.	4.5	1.5	120	50	67
9.	6.5	1.5	120	200	60
10.	6.5	1.5	120	150	74
11.	6.5	1.5	120	100	81
12.	6.5	1.5	120	50	79
13.	7.7	1.5	120	200	62
14.	7.7	1.5	120	150	75
15.	7.7	1.5	120	100	83.9
16.	7.7	1.5	120	50	80

Effect of Contact Time: The effect of contact time on the adsorption was studied by taking 2 L of the tannery effluent with initial chromium concentration of 100 ppm and with adsorbent dose of 1.5 g/100 ml and agitating time of 2 h. The contents were kept overnight for equilibration. Results indicated that metal removal reaches to 83.90% at contact time of 120 min. This was due to intra-particle diffusion of the metal ions on the surface of adsorbent. No appreciable adsorption increase was observed when contact time was further increased. The results are given in Table 2.

Table 2. Effect of Contact Time on % Adsorption

Sr. No.	Contact Time (Min)	% Adsorption
1	60	77
2	90	81
3	120	83.9
4	150	84

Effect of Adsorbent Dose: For this, initial chromium ion concentration was fixed at 100 mg/l and amount of adsorbent dose was varied from 0.5-2.0 g 100 mL^{-1} sample. The pH of the sample was kept at 7.70. Results indicated that with increase in adsorbent dose, the percentage removal of chromium increased to 83.90% at a dose of 1.5g 100 m L^{-1} sample. With the further increase in dose, no appreciable increase in adsorption was achieved. The result of the effect of adsorbent dose on chromium removal is presented in Table 3.

Table 3. Effect of Adsorbent Dose on % Adsorption

Sr. No.	Adsorbent dose (g 100mL^{-1})	% Adsorption
1	0.5	70
2	1.0	77
3	1.5	83.9
4	2.0	84

Effect of adsorbent particle size: Adsorbent particle size has significant influence on the kinetics of adsorption due to change in number of adsorption sites. The effect of chromium removal was studied by varying the adsorbent particle size between 18 to 36 mesh sizes. The treatment was given at pH of 7.70, amount of adsorbent dose 1.5g 100 m L^{-1}, chromium ion concentration of 100 ppm and contact time of 120 min. It was concluded that as the mesh size of particle increased from 18 to 36, the adsorption increased to 83.90%. This was due to the fact that with increase in the size of adsorbent, more and more surface was provided to adsorbate particles. When the mesh size was further increased, the particles become very light and separation of these by decantation becomes a difficult task. No doubt, with further increase in mesh size increased the adsorption but in order to attain settle ability of the particles of GNSP, mesh size was not further increased. The results observed are given in Table 4.

Table 4. Effect of Particle Size on % Adsorption

Sr. No	Particle size	% Adsorption
1	18	70
2	36	83.90

APPLICATIONS

GNSP is a low cost, excellent natural biosorbent which can be utilized to reduce the load of pollutants as well as to enhance the suitability of the treated effluent for anaerobic degradation. GNSP plays its role as both biosorbent as well as substrate. By the use of groundnut shell powder as an adsorbent, environmental pollution caused by tanneries can be reduced to considerable extent in terms of total chromium in both trivalent and hexavalent form.

CONCLUSIONS

From the above results, it was concluded that GNSP was found to be a suitable low cost natural adsorbent for the removal of total chromium from spent chrome liquor. As a result of this, it could be used not only for removing the toxic chromium but also to enable the effluent to undergo anaerobic degradation due to easy degradable components.

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