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Removal of Chromium (VI) by Biosorption of Eucalyptus Bark

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Abstract: Adsorption of Chromium (VI) on the Eucalyptus Bark has been studied with the variation in parameters. Different parameters like particle size of adsorbent, concentration of adsorbate, amount of adsorbent, stirring speed, time, temperature and pH were studied. The adsorption has been carried out in batch process. The adsorption capacity increases with decreasing the particle size of adsorbent. The optimum conditions for the maximum adsorption are attained with 2.0g of adsorbent, 40 ppm metal ion concentration, at room temperature (10°C), with 90 min contact time, with 300 rpm agitation speed and at pH 2.

Key words: Eucalyptus bark · Chromium (VI) · Adsorption · Removal of Chromium

INTRODUCTION

Rapid industrialization is the major cause of inclusion of heavy metals in environment especially in the water bodies all over the world. The heavy metal contamination of aqueous streams is becoming a serious threat to aquatic ecosystem because of their high toxicity even at very low concentrations. Heavy metals are not susceptible to biological degradation and usually accumulated in living tissues after entering through the food chain. Chromium is considered as one of the top sixteen toxic pollutants because of its carcinogenic characteristics for humans [1, 2].

Chromium is released into the environment by both natural and anthropogenic sources. Three main strategies can be considered for Cr (VI) removal from water are as reduction of hexavalent Chromium to trivalent with subsequent immobilization as the hydroxide [3] sorption onto various materials, including ion-exchange and biosorption [4, 5] membrane filtration [6, 7]. Other then these wide ranges of physical and chemical processes are also available for the removal of Chromium (VI) from water, such as electrochemical precipitation, ultra filtration, ion-exchange and reverse osmosis [8, 9]. A major draw back with precipitation is sludge production. Ion-exchange is considered a better alternative technique for such purpose. However, it is not economically appealing because of high operational cost. These high technology processes have significant disadvantages, including incomplete metal removal, requirements for expensive equipments and monitoring systems, high reagent or energy requirement systems, or generation of toxic sludge or other waste products that require disposal [10].

Chromium is an essential nutrient for the maintenance of normal glucose, fat and metabolism and cholesterol level in human body include weight loss, impaired glucose tolerance, increase serum cholesterol, faster hyper glycemia and increased triglycerides. An adequate health is daily dose of 50-500 micrograms of Chromium per day. It is estimated the safe quantity for human body. People using diets containing large amount of highly processed food especially unite bread and refined sugar and sometimes, consume less than the suggested dietary level of Chromium [11]. Following are three main forms of Chromium which have different effects on health to different extent. Chromium (III) does not result in hazardous effects as Chromium (VI) unless ingested in very large amount. Chromium in food is mainly in the form of trivalent Chromium. Metallic Chromium is the second major form of Chromium. This has zero oxidation state. Exposure of this form of Chromium is less common and no health hazards are associated with it. Hexavalent Chromium is irritating and high exposure level for short term can result in adverse effects at the site of contact as ulcer, initiation of the nasal mucosa and irritation of the gastrointestinal track. It also causes the adverse effects in kidney and liver. Inhalation exposure to Cr (VI) may

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results in addition adverse effects of perforation of the nasal septum, lungs cancer and skin ulcer and affects the immune system [12-15]. As Cr (VI) is more toxic than other forms so we will discuss the toxicity of Cr (VI) in detail as follow:

Hexavalent Chromium is known to be a toxic pollutant. Most recently several medical studies have evidenced the capacity of Cr (VI) to produce cancer in workers who manipulates chromates [16]. Skin contact with certain Cr (VI) compounds can cause skin ulcer. Some people are extremely sensitive to Cr (VI) and Cr (III). Allergic reactions consisting of several problems like severe redness and swelling to the skin have been noted [17]. Chromium has the potential to cause many health effects from long term exposure at level above the MCL e.g., damage to liver, kidney, circulatory and nerve tissues, dermatitis. The US EPA (Environmental pollution agency) has set the maximum contaminate level for chromium in drinking water at 0.1mg/L these standards are based on the total concentration of trivalent and hexavalent form of dissolved chromium [18]. The WHO guidelines [19] the Spanish legislation of 2003 limits to 0.5mg/L the concentration of Cr(VI) in water destined for domestic consumption [20]. The treatment of waste water to reduce the presence of Cr (VI) is a capable requirement prior to the discharge and reuse of water. The present work investigates the possible use of eucalyptus bark powder as biosorbent for the industrial effluent treatment.

MATERIALS AND METHODS

Experiments were carried out to investigate the parameters for the optimization of the extraction of Cr (VI) from the sample solution by using, Balance ER-120A (AND), pH Meter Hanna pH 211 (with glass electrode), Electric Grinder. Perkin and Elmer Analyst 100 Atomic Absorption Spectrometer.

Preparation of Adsorbent (Eucalyptus Bark Powder): After the separation of Eucalyptus bark from tree, it were washed with distilled water and dried in an oven at 105 °C overnight. Dried bark was ground to fine powder in a grinder.

Preparation of Solutions: 1000 ppm of stock solution of $K_2Cr_2O_7$ (Riedel-de Haen) was prepared by dissolving 2.82 g of $K_2Cr_2O_7$ in distilled water. Successive dilutions of stock solutions were carried out to set up standard solutions ranging 5-50 ppm.

Selection of Best Adsorbent: Sample solution of Chromium having 40 ppm concentration and 50 ml volume was taken at room temperature (10°C) in six different beakers. The one gram amount of different adsorbents e.g. Eucalyptus bark, Bagasse, Rice husk, Bombax Ceiba shells, Wheat straws and Ficus Religiosa leaves were added in different beakers for one hour and stirred them gently. Then after one hour all the solutions were filtered and subjected to the Atomic absorption spectrometer to measure the absorbance of Chromium (VI) and % absorption was calculated for each sample using standard solutions.

Effect of Particle Size of Adsorbent: Sample solution of 50 ml of 40 ppm of Chromium was treated at room temperature (10°C) in three different beakers. The one gram amount of different mesh sizes of eucalyptus e.g. 10-30, 30-50, 50-80 Mesh were added in different beakers for one hour and stirred them gently. Then after one hour all the solutions were filtered and subjected to the Atomic absorption spectrometer to measure the absorbance of Chromium (VI) and % absorption was calculated for each solution using standard solutions. And the 50-80 mesh size was found to be the best among them.

Effect of Amount of Adsorbent: Sample solution of 50 ml of 40 ppm of Chromium was treated in nine different clean and dry beakers at room temperature (10°C). The effect of adsorbent dose was studied by adding finely powdered eucalyptus bark in different amounts ranging from 0.5g to 4.5g. All flasks were agitated on orbital shaker at 150 rpm for an hour. The solutions were filtered to remove the adsorbent and filtrates were subjected to atomic adsorption spectrometer (Aanalyst 100) to measure the absorbance of Cr (VI) at 340 nm. The percentage adsorption were calculated for each solution using standard solutions.

Effect of Increasing Concentration of Metal Ions: Sample solutions of 50 ml of having 10, 20,30,40,50,60,70,80 ppm concentrations and 50 ml volume of each was treated in eight different beakers at room temperature (10°C). The 2 g of adsorbent were taken in each beaker and stirred them gently. Eight sample solutions of Potassium dichromate were prepared having concentration range 10, 20, 30, 40, 50, 60, 70, 80 ppm, 50 ml volume each were placed in 8 different beakers with 2g adsorbent in each beaker at room temperature. These were stirred gently by using glass rods for few times. These were filtered after 1 hour and their absorbance were noted by using Atomic Absorption Spectrometer.

Effect of Contact Time on Adsorption: The extraction process was carried out with sample solutions of chromium of 50 ml of 40 ppm with 2 g of adsorbent in each beaker and allowed to stand for different time e.g. just to pass (0 minute), 30 minute, 60 minute, 90 minute, 120 minute,150 minute,180 minute at room temperature with gentle stirring. The adsorbents were separated by filtration through whatman filter paper and filtrate was subjected to atomic absorption spectrometer. The percentage adsorption was calculated for each sample.

Effect of Temperature on Adsorption: 50 ml of 40 ppm sample solutions of Chromium with 2 g of adsorbent in each beaker were allowed to stand for different temperature in e.g. 0°C, 10°C (room temperature), 20°C, 30°C, 40°C and 50 ° c with gentle stirring. After 90 minutes the solutions were filtered. %age adsorption was calculated for each sample by Atomic Adsorption Spectrometer.

This revealed that best temperature for adsorption is 10°C (room temperature) and high temperature had no positive influence on the extraction of Cr (VI) from the sample solution.

Effect of Agitation Speed on Adsorption: Experiments were carried out under the similar conditions of as mentioned in above experiments. Sample solutions of Chromium were allowed to agitate at different agitation speeds e.g. 100, 200, 300, 500, 700, 900 rpm. After 90 minutes the solutions were filtered. The percentage adsorption was calculated for each sample by Atomic Adsorption Spectrometer. This revealed that best stirring rate for adsorption 300 rpm.

Effect of pH of Adsorption: Similar experiments were carried out to investigate the effect of pH with the sample solutions of Chromium having 50ml of 40 ppm with 2 g of adsorbent in each beaker, at 10°C for 90 minutes and 300 rpm with adjusted different pH ranging from 2,3,4,5,6,7,8,9,10. After 90 minutes the solutions were filtered. The percentage adsorption was calculated for each sample by Atomic Adsorption Spectrometer. This revealed that best pH for adsorption is 2.

Blank experiments were run regularly in all experiments. Each experiment was repeated five times and results given are the average value of all.

RESULTS AND DISCUSSION

The release of toxic metals has disastrous effects on the ecosystem. Various chemical and physical methods are being used presently for the removal of toxic heavy metals from the effluents but these methods are either cost prohibited or not practicable on account of operational shortcomings. Now a day, various plants and several other biological materials are being investigated for the removal of heavy metals by adsorption process. Agro wastes have proved to be costs effective adsorbents for the removal of heavy metals from the aqueous streams. In the present study, powder of eucalyptus bark has been used as adsorbent for the removal of Cr (VI).

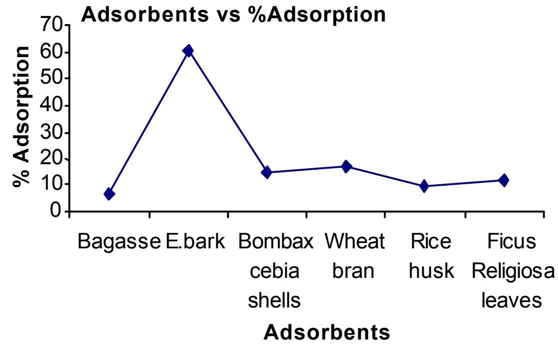

Fig. 1: Selection of Adsorbent

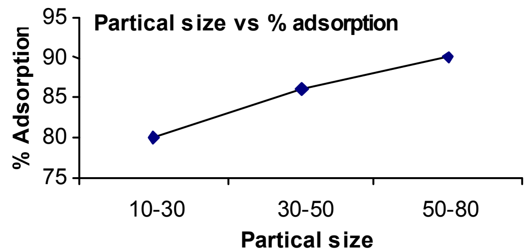

Fig. 2: Effect of mesh size on Adsorption of Cr (VI)

The selection of adsorbent is an important factor. This helps in the selection of best adsorbent among the different adsorbents. Eucalyptus bark was found to be the best as shown in the Figure 1.

The minimum mesh size showed the best results i.e. the maximum adsorption of the metal from the sample solution. It may be so because the equal quantity of different mesh size provides different number of particles and thus different surface area and binding sites. Larger particles provide minimum number of binding sites exposed to the solution molecules and the smallest particle size provides largest surface area and more binding sites are available for metal ions to get bind. This can be shown in the Figure 2.

The amount of adsorbent is clearly an important parameter that affects the adsorption process as shown in the Figure 3. As illustrated by the figure metal removal

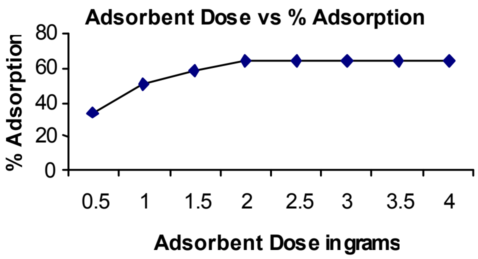

Fig. 3: Effect of amount of Adsorbent on the Adsorption of Cr (VI)

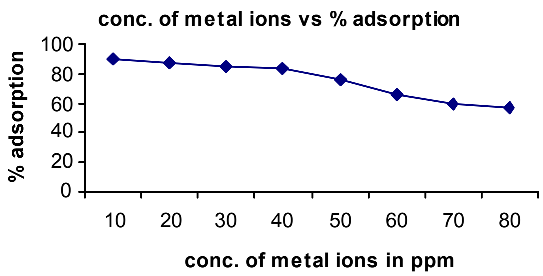

Fig. 4: Effect of increasing concentration of Metal Ions on the Adsorption of Cr (VI)

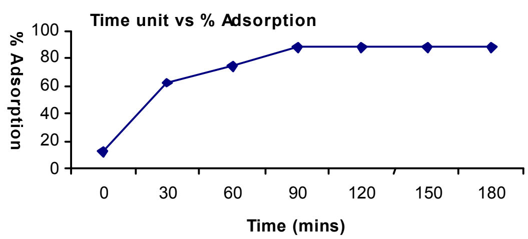

Fig. 5: Effect of contact time on the Adsorption of Cr (VI)

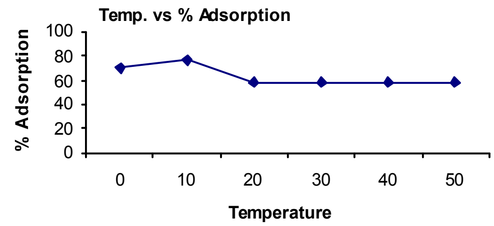

Fig. 6: Effect of temperature on the Adsorption of Cr (VI)

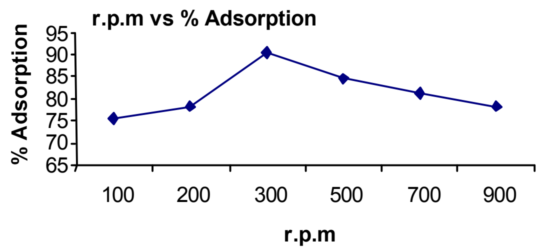

Fig. 7: Effect of agitation speed on the Adsorption of Cr (VI)

efficiency increases with increase in adsorbent dose, since contact surface of adsorbent particles is increased. Maximum removal was found to be 64.64% for the optimum dose of 2.0g for Cr (VI).

From the graph in Figure 4 it was observed that as the concentration increased from 10 to 80 the rate of adsorption decreased. In this way metal concentration showed an inverse relation with adsorption, i.e. maximum adsorption occurs at minimum concentration of metal ions; it may be so because greater number of ions in the solution causes more number of collisions and thus leading to desorption of metal ions from the binding sites of adsorbent particles where as with limited number of ions there are limited number of collision between the metal ions that is why low concentration showed higher rates of adsorption.

Contact time is another important factor in batch adsorption process. Effect of contact time on adsorption was studied and the results are given in Figure 5. As the time period for which the adsorbent was kept in contact with metal solution was increased, the % adsorption went on increasing up to 90 min and it was remained constant up to 180 min because the active binding sites of adsorbent fully bind the metal ions up to 90 minutes and after this time there was no change in % adsorption. So 90 minutes is best time for adsorption.

Effect of temperature during a biosorption studies is shown in Figure 6 At low temperature i.e. at 0 °C the kinetic energy of the metal ions is low and less metal ions reached the adsorbent's active sites so less percentage adsorption was observed as the temperature increased the kinetic energy of the metal ions in the solution also increases so maximum number of metal ions reached to the adsorbent surface. But further increase in the temperature caused the desorption because the kinetic energy of the metal ions in the solution increased so much that they start to unbind by the adsorbent surface. So the maximum adsorption occurred at 10 °C. This was the best temperature for adsorption.

As the number of revolution per minute (rpm) was increased the percentage adsorption was increased and reached to its maxima at 300 rpm. It can be shown in Figure 7 onward it starts to decrease it may be due to greater number of collisions between the metal ions to metal ions and metal ions to adsorbent particles. These increased number of collision leads to the desorption of metal from the active binding sites of adsorbent. It may be possible that the number of revolution per minutes up to 300 rpm gives productive collisions (i.e. collisions effective for binding of metal ions with binding sites of adsorbent) resulting in greater adsorption and further

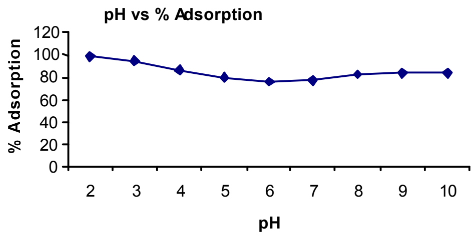

Fig. 8: Effect of pH on the Adsorption of Cr (VI)

increase in rpm leads to destructive collision (i.e. collision causing detachment of metal ions from binding sites) causing desorption.

The pH of aqueous Solution of Cr (Vl) seemed to be very important in biosorption studies. The original pH of the solution was slightly acidic. The results showed that adsorption decrease with increase in the pH of the solution. Maximum adsorption 98.4% is shown in Figure 8.

It was observed that as the pH goes on increasing, the adsorption decreases. This is because of the fact that under acidic conditions the metal surface is highly protonated that favors the uptake of Cr (Vl) in anionic form. As we increase the pH of the solution surface protonation of adsorbent reduces gradually and hence adsorption decreases. pH dependence of metal adsorption may be also related to dissociation of functional group on adsorbent. Further more as pH increases there is a competition between $OH^-$and chromate ions. The former is the dominant species at higher pH values. The net positive surface potential of the adsorbent decreases which results in the weakening of electrostatic forces between adsorbent and metal ions, which leads to the reduction in adsorption capacity.

CONCLUSION

From the present study, it is concluded that powder of eucalyptus bark has successful application as an adsorbent and shows high efficiency for the removal of Cr (VI) from aqueous solution. Eucalyptus bark is easily available in Pakistan. Optimize conditions for Cr(VI) removal with eucalyptus bark are 2g adsorbent, 90 min time, 300 rpm agitation rate, 10°C room temperature at pH 2.

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