Removal of Cr (VI) Ion by Modified Bean Husk

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Abstract: In this work, bean husk (BH) was used to remove Cr (VI) ion from synthetic aqueous solution. Batch experiments using closed plastic beakers were designed to obtain Cr (VI) ion sorption data. Bean Husk was modified by using citric acid. The parameter for modification was selected by trying different parameters such as time, temperature and citric acid quantity. In batch experiments, the influences of contact time, pH, adsorbent dose and initial chromium concentration was researched on adsorption process performance and adsorption isotherm for the equilibrium was studied on modified bean husk (MBH). The results showed that adsorption of Cr (VI) by (MBH) reached to equilibrium after 90 min and after that a little change of Cr (VI) removal efficiency was observed. Higher chromium adsorption was observed at lower pH such as pH around 2. The (MBH) in this study showed very good promise for practical applicability and can be an alternative biosorbent for the removal of Cr (VI) from aqueous solution.

Introduction

The presence of Cr (VI) ion has become a major concern today due to its deleterious effects on health and environment (Khezami and Capart, 2005). Chromium is extensively used in pigments and paints, leather tanning, fungicides, electroplating, cement, steel, ceramic and glass industries (Kocaoba and Akcin, 2005). The use of other alternative techniques (such as adsorption, ion exchange, membrane and biological processes) based on physical, chemical and biological mechanisms is advisable in order to protect the environment and at the same time recovering at least available metal (Hu et al, 2003).

As Cr (VI) is carcinogenic, a maximum permissible concentration for total Cr of 0.5 mg/L and for Cr (VI) of 0.05 mg/L is legally prescribed in wastewater after treatment (Gao et al, 1999). Therefore, the control of the chromium level in wastewater is essential (Petruzzelli et al, 1996). Several approaches have been studied and developed for the effective removal of Cr (VI) ion using biosorbents like peat, brown coal and humic acids, chitosan, hazelnut shell.

Lignocelluloses have widely been used as biosorbents for heavy metals because of substances inherently associated with cellulose such as lignin, tannin and pectin, which contains phenolic and aliphatic hydroxyl and carboxylic groups. Lignocelluloses all contain, as a common property, polyphenolic compounds, such as tannin and lignin, which are believed to be the active sites for attachment of heavy metal cations (Shin and Rowell, 2005). Laszlo and Dintzis have also shown that lignocelluloses have ion-exchange capacity and general sorptive characteristics, which are derived from their constituent polymers and structure (Laszlo and Dintzis, 1994). Lignocelluloses are hygroscopic and also have an affinity for water. Natural materials that are available in large quantities, or waste products from industrial or agricultural operations, may have potential as inexpensive sorbents.

Biosorption can be represented as a sorption process that means the transfer from a bulk fluid to a surface. The biosorbent obtained from biomass leads to interesting possibilities to use low-cost materials for industrial wastewater. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase containing a dissolved species to be sorbed. Biosorption is assumed to arise from two basic mechanisms: an initial rapid metal ion uptake due to physical adsorption and a subsequent slow uptake due to chemisorption. It has been reported that most metal biosorption of divalent metals occurs in a short time interval after solid–liquid contact in the batch reactors (Volesky, 2001). Biosorption is a fast and reversible reaction of the heavy metals with biomass matrix.

Conventional methods utilized to remove the Cr (VI) from industrial wastewaters include reduction followed by chemical and electrochemical precipitation, activated carbon adsorption, chemical oxidation/reduction, ion-exchange, solvent extraction, membrane separation, ultra filtration, reverse osmosis (Rengaraj et al, 2003; Sapari et al, 1996; Arslan and Pehlivan, 2007). Conventional techniques have their own limitations such as less efficiency, sensitive operating conditions, incomplete metal removal, high cost and producing toxic chemical sludge or disposal of other waste products in the clarification systems.

The aim of this study was to develop a new economic technique for (MBH) exploitation and utilization and to enhance the treatment of aqueous solution. (MBH) was chosen since it is cheap and easily available by products from the agricultural materials. This study reports the use of citric acid modified (BH) as a biosorbent to remove hexavalent chromium from aqueous solutions. The effects of solution pH, contact time, adsorbent concentration, and initial metal concentration on Cr (VI) adsorption were investigated in detail way in the submitted paper.

Materials and Methods

Materials

(BH) was collected from vicinity of Konya-Turkey. Straws were ground with Retsch RM 100 model grinding machine. They were ground and sieved to obtain size of 100 μm. Before the use, all the sorbents were washed thoroughly with deionized water and dried in air oven at 100 °C for 24 h. All chemicals were of analytical grade. Double distilled water was used to prepare all solutions throughout the experiments. Cr (VI) stock solution (from Merck) was prepared by dissolving $K_2Cr_2O_7$ salt in double distilled water. Solutions were stored in plastic sealed beakers. Solutions of 0.01 M NaOH and HCl (from Merck) were used for pH adjustment.

Experimental Methods

A series of standard Cr (VI) solution were prepared by appropriate dilution of the stock solution. A thermo stated shaker of GFL 3033 model was used for adsorption experiments. The pH measurements were performed with Orion 900S2 Model pH meter. For Cr (VI) ion sorption studies, 40 mg (MBH) was brought in contact with 25 mL of Cr (VI) solution at constant speed using orbital shaker at 25 °C. After filtration, the concentration of Cr (VI) in the filtrate was analyzed spectrophometrically. The amount of unabsorbed Cr (VI) was calculated by taking the difference of initial concentration and total Cr (VI) concentration in the filtrate. The concentrations of Cr (VI) ions in initial and final solutions were determined spectrophotometrically at 540 nm by UV-visible Spectrophotometer (Shimadzu UV-1700) using 1,5 diphenyl carbazide as a complexing agent. Diphenylcarbazide gives reaction with Cr (VI) in acid medium and Cr (III)–diphenylcarbazone complex occurs (Equation 1).

$$2 \, CrO_4^{2-} + 3 \, H_4L + 8 \, H^+ \rightarrow Cr \, (HL)_2^+ + Cr^{3+} \, H_2L + 8 \, H_2O \tag{1}$$

H_4L: 1,5-Diphenylcarbazide
H_2L: Diphenylcarbazone

Scheme 1. Reaction between Cr (VI) ion and diphenylcarbazide

Contact time adsorption experiments were conducted at room temperature (25±1 °C) in a well-mixed Pyrex glass vessel with a cover. The effect of (MBH) amount for adsorption was studied in the batch vessel by varying the resin from 0.01 to 0.3 g for optimum contact time. The effect of pH on Cr (VI) ion sorption was evaluated by adjusting the initial pH of the initial solution within the range of 1.5- 7. The pH of each solution was adjusted to the desired value with 0.01 M NaOH and HCl. The solutions were agitated in the shaker for 2 h. In addition to these, the effects of concentration were also investigated in order to determine the optimum conditions for these parameters.

Biosorbent Characterization

Modification of (Bh) Wwith Citric Acid (Ca)

First citric acid (5-10 g) was dissolved in water (50 ml), added to 10 g (BH) having particle size over 100 μm and allowed to soak for 24 hours at 60 °C in the oven. At this period, all surface moisture was removed and (BH) particles were coated with CA. Then, the dry sample was reacted for 2 hours (optimum time) by elevating oven temperature to 100 °C (optimum temperature). The reaction time was raised to for 2 to 24 hours at constant temperature (100 °C) and mixtures were allowed for reacting. Reaction products were mixed with distilled water for 30 min, filtered and washed with water and the product was dried in the oven. Finally, the modified shells were vacuum oven dried for 16 h at 45 °C. The thermally treated sample was then cooled to room temperature and then ground again to the desired particle size.

Ir Spectra of Bh and Mbh

To decide whether citric acid was esterified into (BH), IR spectroscopic analysis of both untreated (BH) and (MBH) were studied. The two major changes in the IR spectrum of (MBH) could be observed by comparing it with that of (MBH): a) a quite evidently increase in the carbonyl (C=O) stretching vibration absorbance in the range of 1730-1750 cm^{-1}; b) a reduction in the hydroxyl (O-H) stretching band in the range of 3430-3440 cm^{-1}. It reflected the result of citric acid esterification. For high amounts of introduced free carboxyl groups, it can be concluded that CA modified (MBH) presented an adequate physical and chemical characteristics to adsorb Cr (VI) ions.

Carboxyl Determination

0.25 g dry sample was added in water and 0.1 N NaOH was added and stirred for 24 h. The mixture was back-titrated with 0.1 M HCl until the phenolphthalein end point. Conversion factors were determined using citric acid as standards. Untreated BH was used for comparison in carboxyl determination. Carboxylic acid (%) has been calculated as 5% for (BH) and 14 % for (MBH) respectively.

Results and Discussion

Effect of Solution Initial Ph on The Cr (Vi) Adsorption

Earlier studies have shown that solution pH is an important parameter influencing the biosorption of Cr (VI) ions (Gupta et al, 2001). Cr (VI) removal was investigated as a function of solution pH and the result is indicated in Fig. 1. The biosorption of Cr (VI) onto (MBH) is strongly pH-dependent. 93 % of the Cr (VI) adsorbed onto (MBH) from the solution when the optimum pH was around 2.0. The capacity of (*MRS)* reached in this study is 0.91 mmol Cr(VI) per gram of (MBH) at pH 2.0. There is a sharp decrease in the removal when the solution pH is raised from 2.0 to 3.0 and thereafter the effect becomes negligible. The decrease in the adsorption with the increase in solution pH may be due to the decrease in electrostatic force of attraction between the adsorbent and the adsorbate ions. The interactions of Cr (VI) ions with (MBH) surface molecules are complex, dominated by adsorption, electrostatic attraction, ion exchange and chelation. The binding of Cr (VI) involved two mechanisms, the first of these being simple adsorption and the second through the formation of complexes, which may be chelates. According to the mechanism and the discussion of pH effect, the adsorption will lead to a decrease in pH as equivalent H$^+$ will be released along with the adsorption. Hexavalent chromium existing as negative species in solution may release hydroxide (OH$^-$) instead of proton (H$^+$) when they are adsorbed by (MBH), and therefore result in an increase in pH (Raji and Anirudhan, 1997). This is the case for most Cr (VI) adsorption, but there is always exception. Because of the complexity of most biomaterials, it is very likely that both of these processes of binding will take place in a system at the same time. The following Equation (2) describes the chemical adsorption involving exchange with hydroxyl ions:

$$R–CO + H_2O + HCrO_4^- \leftrightarrow R–COHO_3Cr^+ + 2OH^- \qquad (2)$$

pH in solution has been identified as the most important variable governing Cr (VI) uptake on (MBH). This is partly because hydrogen ions themselves are strongly competing adsorbate and the solution pH influences the ionization of surface functional groups. It can therefore be assumed that the more the pH decreases, the higher the affinity of sorbent for Cr (VI) ion. As the pH is lowered <2, the overall surface charge on (MBH) will become increasingly less negative, which reduces the attraction of positively charged metal cations. Increasing the initial pH of the solution therefore increases the interactions of Cr (VI) with (MBH). As the maximal binding level can be reached when all of the carboxyl functions are neutralized, the binding assays were performed at pH around 5.0. It was evident from the plots (Fig. 1.) that the maximum uptake of Cr (VI) occurred at around pH 2.0

for (MBH) and the other sorption experiments were performed at these pH values. The decrease in Cr (VI) ion removal capacity (MBH)   at pH > 2.0 may be caused by hydrolysis accompanying by precipitation of metal hydroxides. Metal hydroxides are amphoteric, i.e., they are increasingly soluble at both low and high pH, and the point of minimum solubility (optimum pH for precipitation) occurs at a different pH value for every metal. At a pH at which the solubility of one chromium hydroxide may be minimized, the solubility of another may be relatively high.
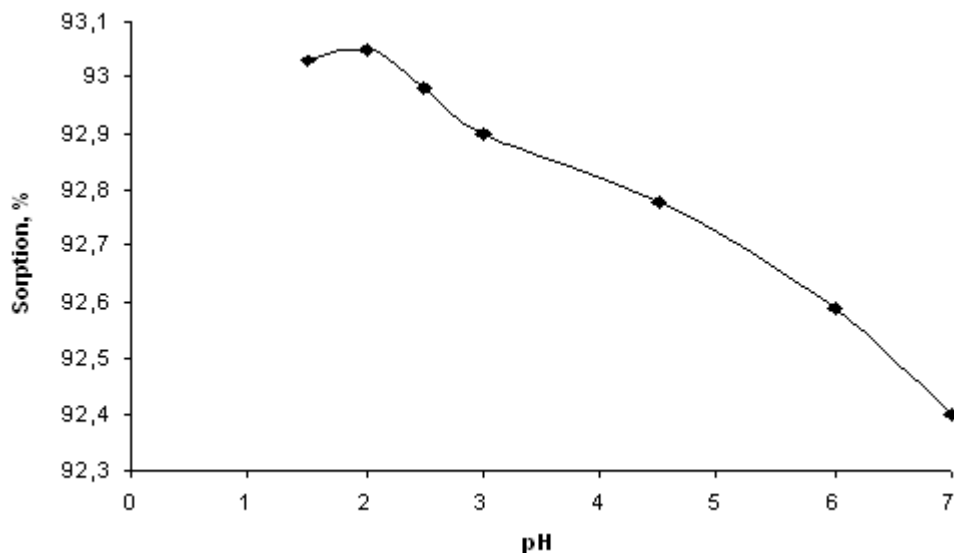

Fig. 1. Effect of pH on the adsorption of Cr (VI)

This pH dependence of the binding showed that adsorption, chelation, electrostatic interactions and other phenomena is involved in the binding mechanism of Cr (VI) by (MBH). Indeed, adsorption and/or chelation involving hydroxyl functions, close to carboxylated, may increase the binding level of Cr (VI) ions in addition to the electrostatic interactions taking place. In the complexation mechanism, Cr (VI) ion sequestration is viewed as the coordination of chromium ions to surface functional groups. It was confirmed that (MBH) is dominated by negatively charged sites that are largely carboxylated groups with some weaker acidic groups. The extent of Cr (VI) adsorption from aqueous solutions is strongly influenced by the chemistry and surface morphology of the (MBH), for example; the interaction of Cr (VI) ions on surface carboxyl groups (RCOOH); hydrogen bonding of hydrated metal ions with glucose from mostly cellulose and formation of complexes with surface. At pH values higher than 3-4, carboxyl groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced. At low pH, the surface of (MBH) would also be surrounded by hydronium ions, which decrease the chromium ion interaction with binding sites of the sorbent by greater repulsive forces.

Effect of Contact Time
The effect of time on the adsorption of Cr (VI) ions by the (MBH) was studied by taking 0.1 g sorbent with 50.0 ml of 0.002 M Cr (VI) solution in different plastic beakers. The beakers were shaken for different time intervals in a temperature-controlled shaker. Fig. 2 shows the effect of contact time on adsorption of Cr (VI) ions using (MBH). The results show that the percentage of Cr (VI) ion adsorption by (MBH) increased with increasing time of equilibration and it reached the plateau value at about 90 min for the Cr (VI) ions.
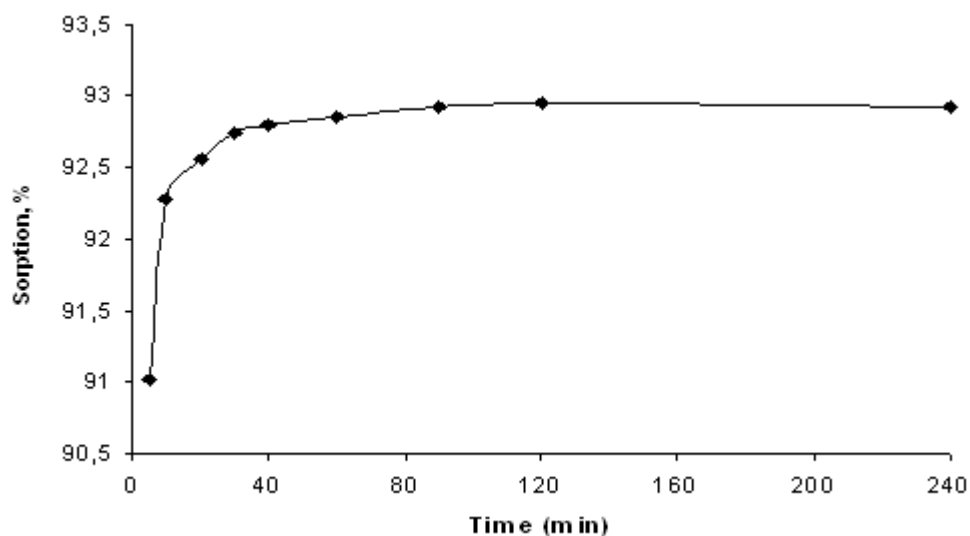
Fig. 2. Effect of contact time on the sorption of Cr (VI)

Effect of Amount on Adsorption

The effect of the (MBH) amount on the removal of metal ions is shown in Fig. 3. Adsorption increased from 92.53 to 93.07 % for (MBH) with increase in adsorbent dose from 0.01 to 0.3 g in the case of chromium ion and then became almost constant.
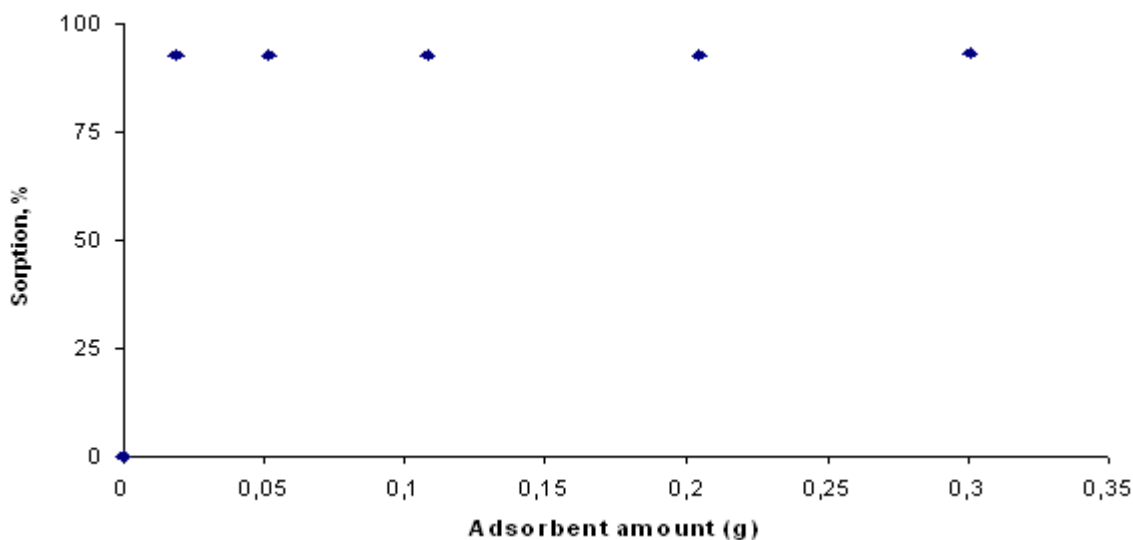

Fig. 3. Effect of sorbent dosage on the sorption of Cr (VI)

Effect of Initial Cr (Vi) Concentration

The initial Cr (VI) concentration provides an important driving force; hence, a higher initial concentration of Cr (VI) ions will increase the sorption rate. The effect of changing the initial concentration of Cr (VI) on adsorption, while keeping the dosage of (MBH) constant at room temperature. Cr (VI) ion adsorbed increased sharply in the beginning and then slowly towards the end of the run. For the different initial concentrations, adsorption equilibrium was rapidly achieved. For (MBH), sorption increased with increasing initial Cr (VI) concentration. At low Cr (VI) concentrations, steep isotherms were obtained which are highly desirable as they indicate high affinity of the sorbent for the given sorbed species. The process may contribute to the binding phenomenon in addition to adsorption, which may include electrostatic interactions and even chelation in the case of the more strongly bound Cr (VI) ion.

The Langmuir and Freundlich isotherms were both used to describe observed sorption phenomena of Cr (VI) on different adsorbents (Gode and Pehlivan, 2005; Ajmal et al, 1998). The Langmuir isotherm applies to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. For a

single solute, it is given by the Freundlich model, which is an empirical model used to describe adsorption in aqueous systems, was also used to explain the observed phenomena of Cr (VI) adsorption on (MBH). The sorption data of Cr (VI) have been correlated with Langmuir and Freundlich models [Eqs. (3) and (4)].

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_S} + \frac{C_e}{A_S}$$

(3)

where C_e is the equilibrium concentration (mg/L), q_e the amount of adsorbed material at equilibrium (mg/g), K_b the "affinity" parameter or Langmuir constant (L/mg), and A_s the "capacity" parameter (mg/g).

Freundlich equation:

$$q = K_f. C_e^n$$

(4)

where, n is Freundlich constant and K_f is the adsorption coefficient, q is the weight adsorbed per unit weight of adsorbent and C_e is the equilibrium Cr (VI) concentration in fluid. Taking logs and rearranging the equation (4), the equation (5) was obtained. The adsorption data in the linear forms gave satisfactory correlation coefficients for a part of the covered concentration range.

$$\log q = \log K_f + n \log C_e$$

(5)

The effect of sorbate concentration is studied and in the case of low Cr (VI) concentrations, the ratio of the initial number of moles of metal ions to the available surface area is larger and subsequently the fractional adsorption becomes independent of initial concentrations. However, at higher concentrations, the available sites of adsorption become fewer, and hence the percentage removal of metal ions depends upon the initial concentration. The amount of Cr (VI) ions adsorbed per unit mass of the (MBH) increased with the initial Cr (VI) concentration as expected. The Langmuir described the sorption data adequately. We found the Langmuir isotherm, to have the highest correlation coefficients above 0.98 for (MBH). It was found that more than 90% removal of Cr (VI) was achieved using (MBH).

Conclusions

Biosorption is a relatively new process that has shown significant contribution for the removal of contaminants from aqueous effluents. In this study, the toxic Cr (VI) ion biosorption on inexpensive and efficient biosorbents from agricultural waste materials have been investigated as replacement strategy for existing conventional systems. The use of these low cost biosorbents is recommended since they are relatively cheap or of no cost, easily available, renewable and show highly affinity for Cr (VI) ions. Literature also reveals that in some cases the modification of the adsorbent increased the removal efficiency. (BH) both untreated and treated is effective in removal of Cr (VI) ion from aqueous solutions. Adsorption of Cr (VI) is dependent on its initial concentrations and pH of the metal solution. The results indicate that the optimum pH for the removal of Cr (VI) ions by (MBH) is around 2. Cr (VI) removal is built up; equilibrium conditions are attained after nearly 90 min. Isothermal data of Cr (VI) sorption on (MBH) can be modeled by Langmuir isotherm. The capacity of (*MRS)* reached in this study is 0.91 mmol Cr(VI) per gram of (MBH) at pH 2.0.

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