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Adsorption of Chromium(VI) on Chitosan-Coated Perlite

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ABSTRACT

Chitosan-coated perlite beads were prepared by drop-wise addition of a liquid slurry containing chitosan and perlite to an alkaline bath. The beads were characterized by SEM and EDS x-ray microanalysis. The chitosan content of the beads was 23%, as determined by a pyrolysis method. Adsorption of hexavalent chromium from aqueous solutions on chitosan-coated perlite beads was studied under both equilibrium and dynamic conditions. The effect of pH on adsorption was also investigated. The data were fitted to the Langmuir adsorption isotherm.

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The adsorption capacity of chitosan-coated perlite was found to be 104 mg/g of adsorbent from a solution containing 5000 ppm of Cr(VI). On the basis of chitosan, the capacity was 452 mg/g of chitosan. The capacity was considerably higher than that of chitosan in its natural and modified forms, which was in the range of 11.3 to 78 mg/g of chitosan. The beads loaded with chromium were regenerated with sodium hydroxide solution of different concentrations. A limited number of adsorption-desorption cycles indicated that the chitosan-coated beads could be regenerated and reused to remove Cr(VI) from waste streams.

Key Words: Chitosan; Perlite; Chromium; Adsorption; Desorption.

INTRODUCTION

Pollution of the environment by heavy metals has received a great deal of attention due to their toxicological effect to the ecosystem, agriculture, and human health.[1] Waste streams from industries, such as chrome plating and processing units, tanneries, and electronic device manufacturing facilities, contain significant quantities of chromium and other trace metals. A number of studies have been carried out for the removal of chromium using various types of adsorbents from different waste streams[2–5] with a varying degree of success. Also, microbial reduction of Cr(VI) to Cr(III) as a means to remove chromium has been investigated by a number of researchers.[6–10] Factors that affect microbial Cr(VI) reduction includes biomass concentration, initial Cr(VI) content, carbon source, pH, and temperature. A review of microbial chromium(VI) reduction is provided by Chen and Hao.[10]

A number of investigators used zero-valent iron for removal of Cr(VI) from groundwater.[11–15] The studies indicated that chromate removal contributes to passivation of the iron surfaces. The mechanism for chromium removal appears to be Cr(VI) reduction accompanied by hydroxide precipitation. Chromium can exist both in tri- and hexavalent forms, making its removal from a stream rather difficult. In most of the methods, first Cr(VI) was reduced to Cr(III) and then precipitated out. However, this technique is not very cost effective. Cr(VI) is typically present as an anion and its direct precipitation is not usually practical. A number of techniques such as ion exchange, adsorption, and electrodeposition, are being used to remove chromium(VI) from effluent. All these methods have their inherent advantages and limitations. However, it appears

that adsorption can be an effective process if a low-cost adsorbent having high capacity for Cr(VI) is available. The adsorption capacity of various adsorbents for Cr(VI) is summarized in Table 1. It may be noted from the table that activated carbons have a higher capacity for Cr(VI) compared to other adsorbents. However, activated carbon is costly and desorption of Cr(VI) from activated carbon is rather difficult. A number of studies focused on chitosan as an adsorbent due to its nontoxicity, chelating ability with metals, and biodegradability. Chitosan is a low-cost adsorbent compared to activated carbon, however, its adsorption capacity is low. In this study, chitosan was coated on an inert substrate, perlite, to enhance its adsorption capacity for Cr(VI).

Chitosan is a partially acetylated glucosamine polymer encountered in the cell walls of fungi.[16] It also results from the deacetylation of chitin, which is a major component of crustacean shells and available in abundance in nature. This polymer is very effective in adsorbing metal ions because of its ability for complexation and high content of amino functional groups. In their natural form, these materials are soft and have a tendency to agglomerate or form gels. Often, the specific binding sites of these biosorbents in their natural form are not readily available for sorption. It is necessary to provide physical support and increase the accessibility of the metal binding sites for process applications. A number of attempts have been made to modify chitosan to increase its capacity for chromium by synthesizing polyaminated chitosan,[16] *N*-benzyl sulfonated chitosan,[17] glutaraldehyde cross-linked chitosan,[18] crown ethers grafted chitosan,[19,20] metal ion imprinted chitosan,[21] and emulsion impregnated chitosan.[22] The adsorption capacity of these modified adsorbents is also given in Table 1. To overcome some of the problems associated with the use of pure chitosan, in this study, chitosan was coated on perlite, an inorganic porous aluminosilicate, and formed into beads. It was expected that the more active sites of chitosan would be available due to the coating, thus, enhancing the adsorption capacity. Perlite is a siliceous volcanic glassy rock with an amorphous structure. It was used to a limited extent as an adsorbent for methylene blue,[23] trivalent chromium,[24] and as solid support in chromatography.[25,26] The characterization of chitosan-coated perlite beads and evaluation of their adsorption capacity for Cr(VI) are reported in this article. Characterization of the beads is accomplished by scanning electron micrograph (SEM), energy dispersive spectroscopy (EDS) x-ray microanalysis, and Fourier Transform InfraRed (FTIR) spectroscopy. Adsorption experiments were conducted under both equilibrium and dynamic conditions. In addition, the effect of pH on the uptake of Cr(VI) and the regeneration

Table 1. Adsorption capacities of different adsorbents for chromium(VI).

Adsorbent	Maximum adsorption capacity (mg/g)	pH	Maximum initial concentration (mg/L)	Reference
Activated carbon (Filtrosorb 400)	125.5	6.0	260.0	4
Sawdust	3.3	6.0	50.0	30
Coconut shell activated carbon	20.0	2.5	—	31
Activated carbon (Filtrosorb 400)	145.0	2.5	1000.0	5
Sphagnum moss peat	119.0	1.5	1000.0	5
Compost	101.0	1.5	1000.0	5
Leaf mold	43.0	2.0	1000.0	5
Sawdust	39.7	2.0	1000.0	32
Sugar beat pulp	17.2	2.0	500.0	32
Maize cob	13.8	1.5	300.0	32
Sugar cane bagasse	13.4	2.0	500.0	32
Coconut husk fibers	29.0	2.1	—	33
Palm pressed-fibers	15.0	2.0	—	33
Pinus sylvestris bark activated by 0.05-N NaCl	19.5	4.5	20.0	34
Leather-based activated carbon	241.0	3.0	1000.0	35
Chitosan	78.0	5.0	1000.0	35
Cross-linked chitosan	50.0	5.0	1000.0	36
Metal ion imprinted chitosan	51.0	5.5	1000.0	21
Chitosan cross-linked with epichlorohydrin	52.3	5.5	1000.0	21
Metal ion imprinted chitosan cross-linked with epichlorohydrin	51.0	5.5	1000.0	21
Chitosan cross-linked with ethylene glycol diglycidyl ether	56.8	5.5	1000.0	21
Chitosan cross-linked with epichlorohydrin	11.3	3.0	100.0	37
Chitosan coated on perlite	153.8	4.0	5000.0	Present study

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of the bed following an adsorption run using sodium hydroxide were also investigated.

EXPERIMENTAL

Materials

The expanded form of perlite was obtained from Silbrico Corporation, IL, USA. Medium molecular weight chitosan and potassium dichromate were procured from Aldrich Chemical Corporation (Wisconsin, USA). All chemicals used were of analytical grade. Oxalic acid and sodium hydroxide were purchased from Fischer Scientific Company. A stock solution containing 5000 ppm of Cr(VI) was prepared using distilled deionized water. All the working solutions were obtained by diluting the stock solution with distilled deionized water.

Preparation of Chitosan-Coated Perlite Beads

Perlite, which is composed mainly of alumina and silica, was used as a substrate for the preparation of the beads. Perlite was first mixed with 0.2-M oxalic acid and the mixture was stirred for 12 hours at room temperature. The acid from the mixture was filtered using Whatman 41 filter paper. The filtered perlite was washed with deionized water until the filtrate pH was between 6 and 6.9. After washing, the perlite was dried overnight at 70°C, and sieved through a 100-mesh sieve. The perlite particles were next stored in a desiccator. About 30 g of chitosan were slowly added to 1-L of 0.2-M oxalic acid solution under continuous stirring at 40 to 50°C to form a viscous gel. About 60 g of acid-treated perlite powder were mixed with 0.5-L deionized water and slowly added to the gel and stirred for 4 hours at 40 to 50°C. The highly porous beads were then prepared by drop-wise addition of perlite-gel mixture into a 0.7-M NaOH precipitation bath.[17] Maintaining this concentration of NaOH was critical in forming the beads and in subsequent washing of the beads. The purpose of adding an acidic perlite-chitosan mixture to the NaOH solution is to assist rapid neutralization of oxalic acid so that the spherical shape could be retained. If the concentration of NaOH in the bath was lower than 0.7-M, the beads tend to disintegrate and not retain the spherical shape. The beads were separated from NaOH bath, and washed several times with deionized water to a neutral pH. The wet beads were next divided into three batches and were dried in three different ways: in a freeze dryer, in a oven under vacuum, and in air. The freeze-drying

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method appears to maintain the spherical shape better than the other two methods.

Adsorption Experiments

Equilibrium adsorption studies were carried out at 25°C by exposing the beads to an aqueous solution containing Cr(VI) ions in 125-mL Erlenmeyer flasks. Potassium dichromate, 100 mL, ($K_2Cr_2O_7$) solutions of different concentrations were poured in the flasks and then a 1-g bead was mixed with the solution. While studying the effect of pH on the adsorption capacity, the initial pH of the solutions was adjusted to the desired value by adding either 0.2-M sulfuric acid or 0.2-M sodium hydroxide solution. The flasks were then placed in a temperature-controlled shaker bath maintained at 25 ± 0.5°C for a specific time period. Following the exposure of the beads to Cr(VI) to the solution in a flask for a predetermined period of time, the solution was filtered and the filtrate was analyzed for chromium ion by atomic absorption spectroscopy. The adsorption isotherm was obtained by varying the initial concentration of chromium ions in the

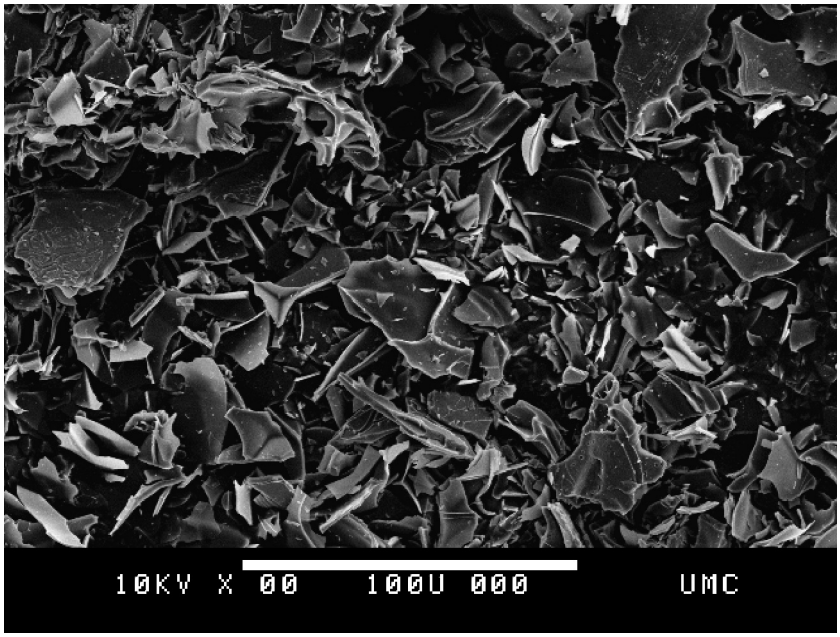

Figure 1. The SEM micrograph of pure perlite powder.

solution. The amount of Cr(VI) adsorbed per unit mass of adsorbent (q_e) was calculated using the equation,

$$q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

where C_i and C_e represent initial and equilibrium concentrations in mg/L, respectively, V is the volume of the solution in liters (L), and M is the mass of the adsorbent in g.

A glass column of 12.7 mm (0.5 in) ID was used for studying adsorption of chromium ions under dynamic conditions. About 35 g of beads were packed in the column that provided a bed height of about 254 mm (10 in.). A flow rate of 10 mL/min was used during a run. Each run was continued for 150 to 180 minutes. It was noted that the bed became saturated during this time period as indicated by the outlet Cr(VI) concentration. Following an adsorption run, the bed was regenerated using NaOH solution. Different concentrations of NaOH solution were used to determine the optimum concentration range and volume required for complete regen-

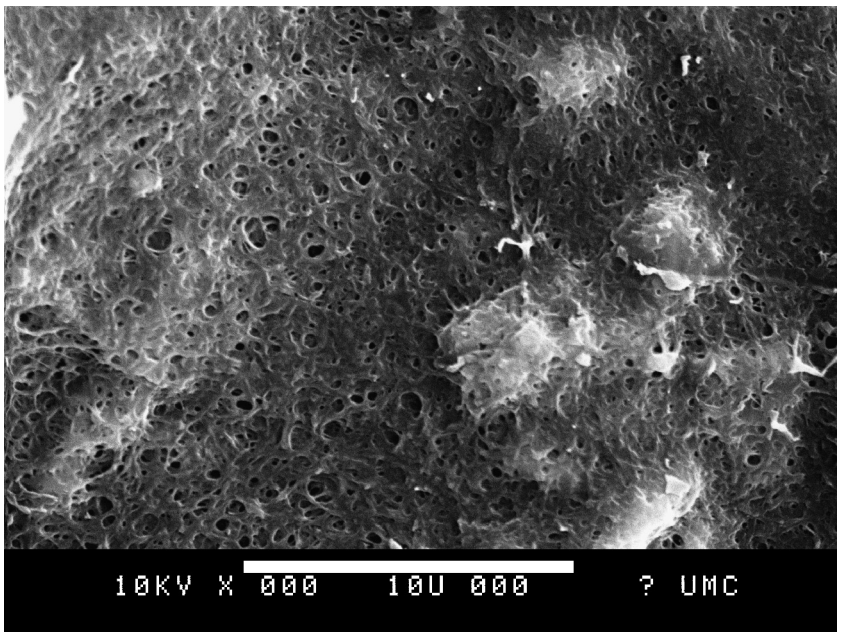

Figure 2. The SEM of the outer surface of chitosan-coated perlite beads produced by freeze-drying.

eration of the bed. Four adsorption-regeneration cycles were conducted using the same bed to check the sustainability of the bed for repeated use.

RESULTS AND DISCUSSION

Characterization of Bead

The amount of chitosan present in the beads was determined by heating the beads at 800°C in the presence of air. Two ceramic crucibles, one containing acid-washed pure perlite and the other one containing chitosan-coated perlite, were placed inside a furnace heated to 800°C. Chitosan was burnt out at this temperature and the chitosan content was determined from the weight difference. It was found that 23% of chitosan was coated on perlite.

The SEM of various samples was taken to study the surface morphology. The SEM of pure perlite powder showed no particular shape

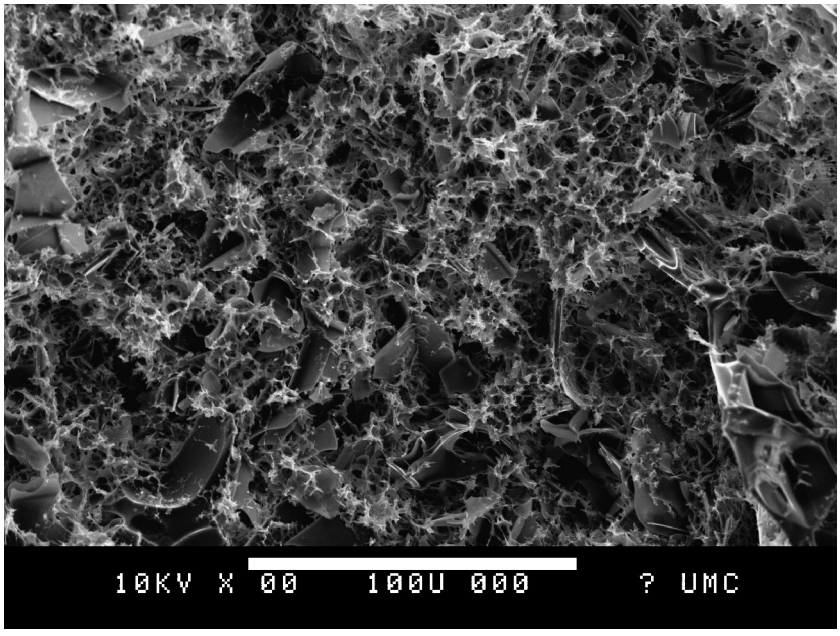

Figure 3. The SEM of the cross-section of the chitosan-coated perlite beads shown in Figure 2.

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or crystalline structure and it rather appeared like flakes (Figure 1). The surface morphology of the pure perlite appears to change significantly following coating with chitosan. The SEM micrograph of the outer surface of perlite coated with chitosan is shown in Figure 2. The porous nature of the outer surface is evident from this micrograph. The beads were cut into half and then the SEM of the internal surface was taken. The SEM of the cross sections of the beads is shown Figure 3. The inside of the beads are also found to be porous in nature. The surface morphology and texture of coated perlite were completely different compared to uncoated perlite. The inner surface appears to have a similar type of texture and surface morphology as the outer surface. Figure 4 shows the surface characteristics and morphology of the beads after their exposure to chromium(VI) solution. It can be observed that there is a drastic change in the morphology of the beads after adsorption.

The EDS x-ray microanalysis was performed to identify the elements present on the chitosan-coated beads before and after their exposure to chromium solution. The EDS analysis of chitosan-coated unexposed perlite

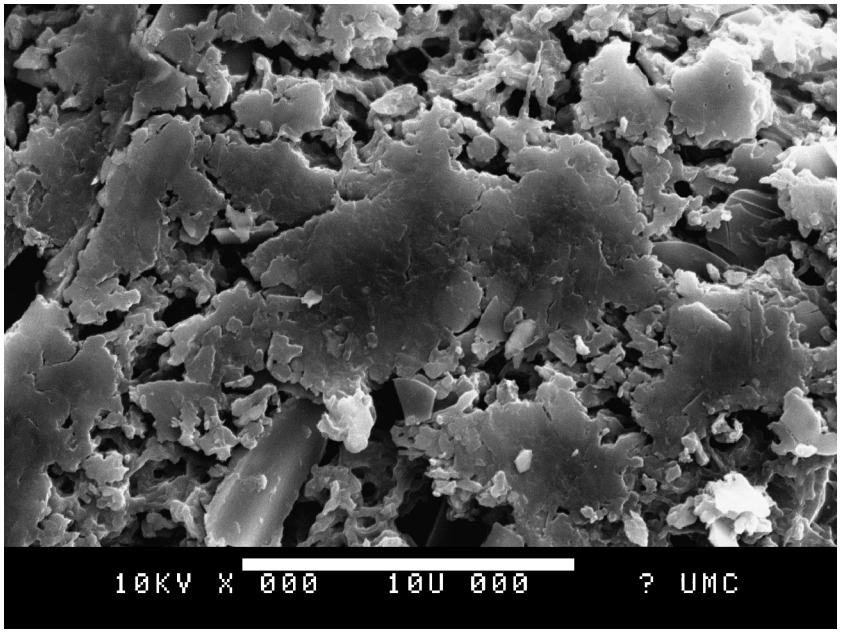

Figure 4. The SEM of the cross-section of the chitosan-coated perlite beads exposed to Cr(VI).

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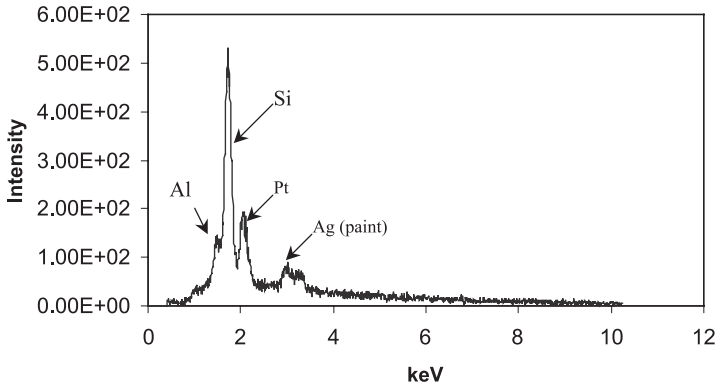

Figure 5. EDS x-ray microanalysis of unexposed chitosan-coated perlite beads showing the presence of Si and Al. (Pt and Ag were due to the sputter coating of the sample for electrical contact.)

beads is shown in Figure 5. The EDS x-ray microanalysis shows peaks for both aluminum and silicon. It may be noted that these are the two major constituents of perlite. The EDS of the beads that were exposed to Cr(VI) ion is presented in Figure 6. A strong peak around 5 keV for Cr and another peak around 3 keV for K can be observed in this spectrum. Chitosan is capable of bonding with both cations and anions. Potassium dichromate dissociates into chromate (anion) and K (cation) in water, which is dependent on pH of the solution. Therefore, both types of ions are present in the solution to bind to chitosan.

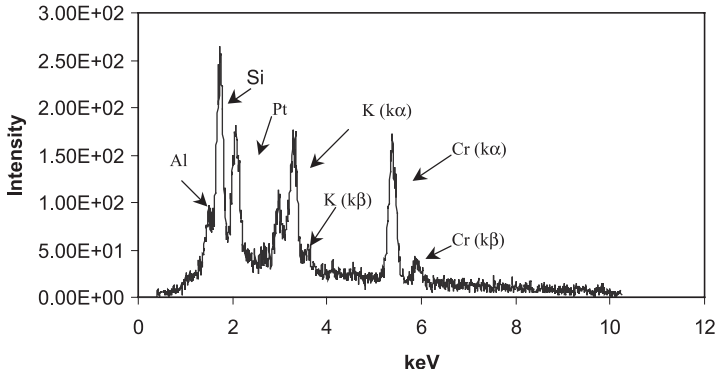

Figure 6. EDS x-ray microanalysis of chitosan-coated perlite beads following exposure to $K_2Cr_2O_7$ solution.

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Effect of pH on Adsorption

The effect of pH on the adsorption of Cr(VI) from aqueous solutions was studied by determining the adsorption capacity at different pH values. The concentration of Cr(VI) in the solution was maintained at 5000 ppm in all the runs. The pH of the solution was adjusted to a desired value by addition of either 0.2-M H_2SO_4 or 0.2-M NaOH. Following the addition of the beads into the solution, it was observed that the pH of the solution changed. The initial pH of the solutions was varied from 1 to 6. The adsorption capacities at different pH values indicated that the extent of adsorption was not strongly dependent on the pH of the solution up to a pH of about 4.0. At a pH higher than 4.0, only a small decrease in the capacity was noted. The adsorption capacity of the beads for chromium(VI) at different pH is given in Table 2. Chromium(VI) forms stable complexes, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, and $HCr_2O_7^-$, depending on the pH of the solution. The fraction of any particular species depends on the chromium concentration and pH of the solution.[2,27] Speciation studies of Cr(VI) in aqueous solution, on the basis of spectrophotometry, electrochemistry, freezing point depression, and NMR, indicated the existence of the following equilibria:

$$H_2CrO_4 = H^+ + HCrO_4^-$$

$$HCrO_4^- = H^+ + CrO_4^{2-}$$

$$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$$

The equilibrium between the species in the solution is dependent on pH, with $Cr_2O_7^{2-}$ and $HCrO_4^-$ existing primarily in acidic media and CrO_4^{2-} being the lone species of Cr(VI) above pH 7.0. Ramsey et al.,[28] using Raman spectroscopic analysis of dilute chromate solutions, concluded that at pH 4.0 and below 0.007 moles of Cr(VI), the predominant species was $HCrO_4^-$ rather than $Cr_2O_7^{2-}$. Thus, the chelation is expected to be dependent on pH. Kaminski and Modrzejewska[29] suggested that chitosan can form chelates with metal ions with the release of hydrogen ion, which, therefore, suggests that the adsorption of a metal ion on chitosan should depend strongly on the pH of the solution. The extent of adsorption of Cr(VI) increased with a decreasing pH of the solution. At lower pH values, the amine group of chitosan undergoes protonation, leading to the increased electrostatic attraction between NH_3^+ and sorbate anion. As the pH increases, deprotonation of amino group occurs, resulting in a decrease of adsorption.

Table 2. The effect of pH on adsorption of Cr(VI) from aqueous solution of potassium dichromate by chitosan-coated perlite beads.

Initial concentration (mg/L)	Amount of beads (g)	Volume of the solution used in the study (mL)	pH of the starting solution	pH of the solution following exposure	Amount of Cr(VI) adsorbed (mg/g of adsorbent)	Amount of Cr(VI) adsorbed (mg/g of chitosan)
4950.0	1	100	0.92	1.15	137.0	595.6
4950.0	1	100	1.8	2.19	135.0	586.9
4950.0	1	100	4.5	6.05	134.0	582.6
4950.0	1	100	5.18	6.12	114.0	495.6
4950.0	1	100	5.9	6.34	125.0	543.4

Equilibrium Adsorption Results

From the pH study, it was concluded that the chitosan-coated beads had a maximum adsorption capacity at a pH of 4.0. Therefore, equilibrium adsorption capacity of beads for chromium at different concentrations was determined at pH 4.0 and 25°C. The data are shown in Figure 7a. As expected, the adsorption capacity was dependent on the concentration. The higher the Cr(VI) in the solution, the higher was the adsorption capacity. It may also be noted that the equilibrium was reached within 5 hours of exposure. The Langmuir equation was used to predict the saturation adsorption capacity of the beads. As can be seen Figure 7b, the Langmuir

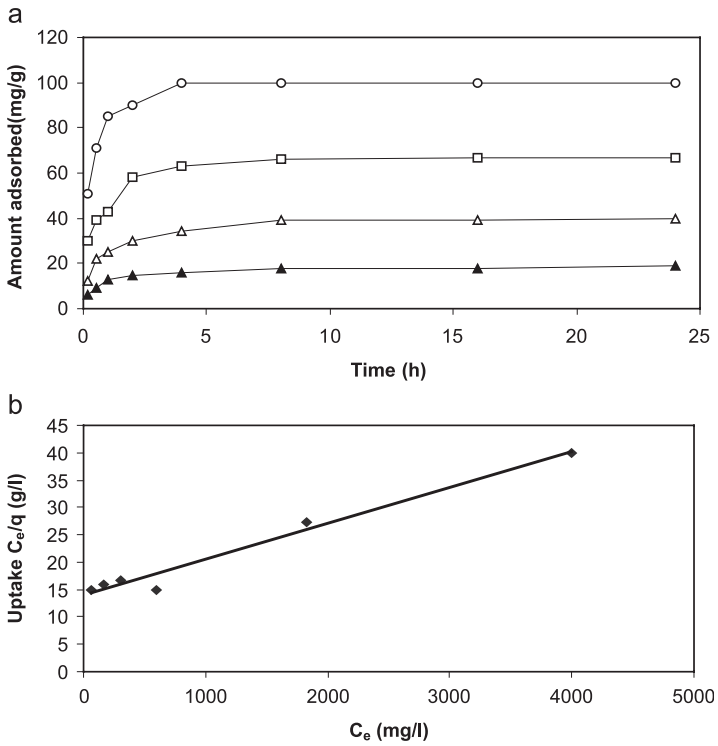

Figure 7. a. Effect of time and concentration on Cr(VI) removal by chitosan bead. The initial concentrations of the solution were (○) 5000, (□) 2500, (△) 1000, and (▲) 500 mg/L respectively. b. Langmuir iostherm for adsorption of chromium(VI) on chitosan-coated perlite beads [C_e = mg of Cr(VI) per L of solution; q = mg of Cr(VI) adsorbed per g of adsorbent].

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isotherm adequately represents the adsorption behavior of Cr(VI) on chitosan-coated perlite and predicted the saturation adsorption capacity of chitosan-coated perlite for Cr(VI) to be 153.8 mg/g of bead. A comparison of adsorption capacities of various adsorbents is presented in Table 1. The adsorption capacity of the chitosan-coated beads is found to be considerably greater than other chitosan-based adsorbents. The increase in the uptake is due to better dispersion of chitosan, exposing more adsorption sites or amine groups.

Dynamic Studies

About 35 g of beads were used to make a 254-mm (10-in.) column. A flow rate of 10 mL/min was maintained during the run. Each run was continued for about 150 to 180 minutes. It was noted that the bed became saturated during this time period, as indicated by the outlet metal concentration. Although chromium broke through the column rather quickly, by adjusting the bed volume or the amount of adsorbent in the bed, the breakthrough time can be increased to obtain a final effluent concentration that will meet the regulatory limit. Breakthrough curves for Cr(VI) from a potassium dichromate solution for four cycles are shown in Figure 8. As can be seen from the outlet concentration profile, a steady-state value was reached in about 50 minutes, when inlet Cr(VI) concentration was about 3000 ppm. Following an adsorption run, the bed was regenerated using NaOH solution. Different concentrations of NaOH solution were used to determine the optimum concentration range and

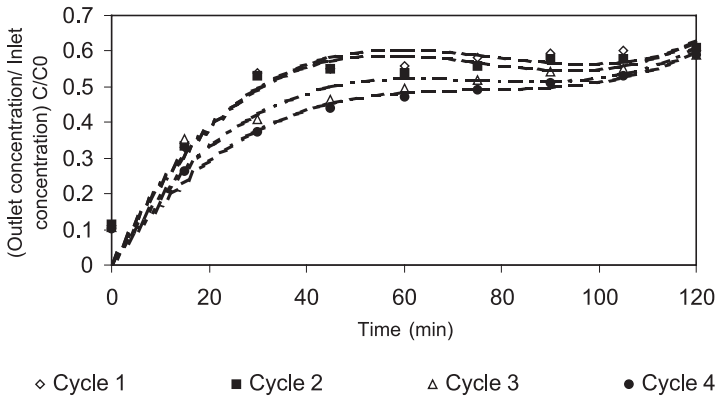

Figure 8. Breakthrough curves for chromium(VI) adsorption on chitosan-coated perlite beads.

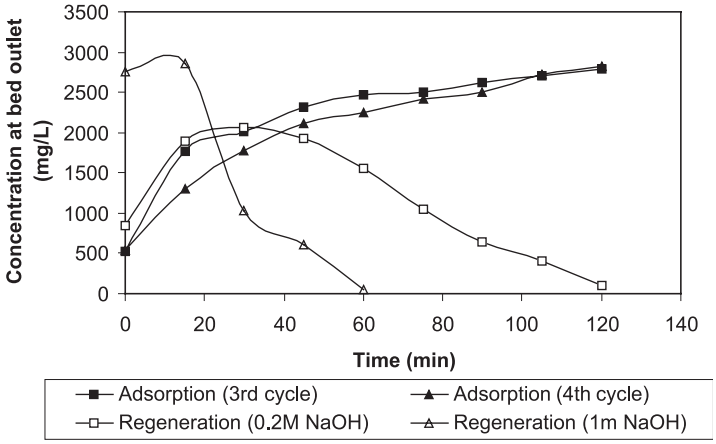

Figure 9. Effect of concentration of NaOH for regeneration of the bed following exposure to Cr(VI) solution.

volume required for complete regeneration of the bed. Four adsorption-regeneration cycles were conducted using the same bed to check degradation of the bed due to repeated use. As can be seen from Figure 8, the bed did not lose its capacity for Cr(VI) after four cycles. However, it should be noted that four cycles is not enough to make a definite conclusion regarding the degradation of the adsorbent due to repeated use. A 0.1-molar solution of NaOH was used to regenerate the column for the first and second cycle. A flow rate of 10 mL/min was also used during regeneration. Approximately 1-L NaOH solution was required to regenerate the column. It took about 4 hours to regenerate the bed. In the third cycle, 500 mL of 0.2-M NaOH solution was used to regenerate the same column. As can be seen from Figure 9, about 120 minutes were required. The use of a more concentrated NaOH solution further reduced the amount and the time for regeneration of the same column. As shown in Figure 9, the regeneration time reduced to 60 minutes when 500 mL of 0.5-M NaOH solution was used.

CONCLUSION

Chitosan was effectively coated on an inert substrate, perlite, and was made in the form of spherical beads. Pyrolysis results indicated that 23% of chitosan was coated on perlite. The SEM micrographs of chitosan-coated

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adsorbent showed that these beads were highly porous. The equilibrium adsorption data showed that chitosan-coated beads adsorbed a significant amount of chromium compared to chitosan or other chemically modified chitosan, as reported in published research. It appears that by coating chitosan on perlite, more active sites could be effectively exposed for adsorption. The adsorption capacity was dependent on the pH of the solution and increased with a decrease of pH. The equilibrium adsorption data were correlated by the Langmuir equation. The regeneration of the bed loaded with Cr(VI) was accomplished by using 0.1-M NaOH solution, however, the volume necessary to regenerate the bed could be decreased significantly using a higher NaOH concentration. The adsorption capacity of chitosan-coated perlite remained unchanged after four adsorption-desorption cycles. However, more adsorption-desorption cycles should be repeated to determine the life cycle of this adsorbent.

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