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Studies Of Carbonized Beet Root As A Selective Adsorbent For Cr (VI)



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ABSTRACT

In this work the carbonized beet root was used as an adsorbent for preconcentration of chromium(VI) in aqueous solutions. The carbonized beet was separated in two particle size. Results shown that the efficiency of recovery depend on the pH as well as particle size. The best recovery efficiency was obtained at pH=2 for both particle size of 0.5-0.6 and 1-1.1 mm in diameter. The effects of particle size, flow rate and dose of adsorbent have also studied in this work. © 2007 Trade Science Inc. -INDIA

KEYWORDS

Beet root;
Preconcentration;
Chromium(VI);
Selective adsorbent.

INTRODUCTION

Preconcentration/separation procedures for trace heavy metal ions in various environmental samples prior to their flame atomic absorption spectrometric determinations are generally necessity due to low levels of the analyte and high level of the interferic matrices^[1-5]. Due to the toxicological importance in the ecosystem, agriculture and human health, pollution by heavy metals has received wide spread attention in the recent years. Because of wide range of using chromium in industry such as tanning, metallurgy, plating and metal finishing, chromium finds way into soil and water through different wastes which

are disposed in environment. Chromium is a heavy metal and extensively used in tanning industries to obtain leather of desirable quality. Chromium is found in different forms, mostly as trivalent, Cr(III), and hexavalent, Cr(VI) forms. The trivalent form is less toxic and relatively immobile in nature; whereas the hexavalent form of Cr is readily soluble in water thus it is mobile and also has high toxicity that is known to be toxic with potential carcinogenic and mutagenic effects in nature^[6]. Chromium containing effluents find their way in the environment at disposal sites where Cr undergoes oxidation reactions and forms Cr(VI)^[7].

Mostly removal of Cr is achieved by various

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physicochemical processes such as oxidation/reduction, precipitation/filtration, coagulation, ion-exchange, membrane separation and reverse osmosis, but high cost and process complexity have limited their use in industries. In recent years, use of low cost adsorbents has been considered to removal heavy metal ions in this way several adsorbents have been examined by many scientists. Zhipei et al. reported the use of Chinese peat for the adsorption of Cr(VI) from solution^[8]. The, waste tea, exhausted coffee, nut and walnut shells^[9] rice husk^[10], and also commercially prepared adsorbents such as fly ash from thermal power plants^[11], palm pressed leaves^[12], agro waste^[13] and activated carbon are used for the removal of various heavy metal ions from solutions^[14-16].

Most of these methods suffer from drawbacks like high capital and operational cost and problems in disposal of the residual metal sludge^[17]. However, due to their high cost and sometimes low availability, their use is not as feasible as it should be. So there is a need mainly by developing nations to develop an easily available low cost adsorbent and to compare its adsorbent capacity with the commercially prepared one.

We used beet (also known as garden beet, blood turnip or red beet) as an adsorbent for preconcentration of chromium(VI) from aqueous solution, which is easily available and cheap.

EXPERIMENTAL

Materials

Beet was collected from north of Iran. Stock solutions were prepared from commercially available reagent-grade (Merck). Triply distilled water was used throughout. Solution of formaldehyde (10% v/v) was prepared by dissolving formaldehyde in distilled water.

Apparatus

Atomic absorption spectrometer (Perkin-Elmer A300) is used for metal analysis, also a Corning-250 pH meter used for adjusting the pH of sample solutions. Carbonizations of treated beet performed with an electrical muffle furnace (CSF-1200) in air atmosphere condition.

Procedure

The beet root was cleaned with water and finally washed by triply distilled water thoroughly. The external layer was removed and cut into the small slices (1-3 mm). 10 g of beet slices were soaked in the 80 mL formaldehyde solution (10 %v/v) for an overnight and then filtered through a Whatman paper. It was then subjected to carbonization at 300°C in electric furnace for 1 hour with air atmosphere (FTCP i.e. formaldehyde treated carbonized particles). The other part of beet slices was carbonized in the same condition without pretreatment with formaldehyde. It was then subjected to carbonization at 300°C in electric furnace for 1 hour in air atmosphere (NTCP i.e. non-treated carbonized particles). After carbonization the size of beet particles were reduced to ~ 0.5-1.5 mm. The carbonized beet particles were separated to various fractions of (I) 0.5 - 0.6 and (II) 1 - 1.1 mm in diameter using standard sieves.

Aqueous solution with the same concentrations of chromium ion (0.01 mgL⁻¹) has been prepared using stock solution at ambient temperature (ca. 22°C) in variable pH of 1-12. The adsorption processing has been carried out with two different carbonized beet particle sizes (i.e. 0.5 - 0.6 and 1 - 1.1 mm in diameter). The experiments have been performed in variable flow rates, dose of adsorbent (1-2 g of carbonized beet) and particle size.

The adsorption process has been performed with a glass column (10 × 2 cm) which was packed with 1.5 g of FTCP and NTCP particles. In order to preconcentration processing the flow rate was adjusted to 0.5 mL min⁻¹ and then elution was performed by 0.1 M HCl. The chromium composition of collected solutions has been analyzed by atomic absorption spectroscopy method.

RESULTS AND DISCUSSION

When solid potassium dichromate, K₂Cr₂O₇, is dissolved in water the resulting solution is orange. The color comes from the negative ions: CrO₄²⁻(aq) and Cr₂O₇²⁻(aq). However, in the solution these ions are actually in equilibrium as indicated by the equation:

$$2\text{CrO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O} \quad (1)$$

If we add H^+ to the chromate solution we will see change in color of the solution. From Le Chatellier's principle, we know the reaction will try to remove some of the H^+ that is added to the solution. The H^+ ion reacts with the CrO_4^{2-} , removing some of each, and making more $Cr_2O_7^{2-}$.

Activated carbon particles have macropores having diameters 30 to 100,000 Å and the micropores having diameters in the range of 10 to 30 Å. The adsorptive properties of activated carbon are due to its porous nature, the nature of carbon active and concentration of surface groups responsible for interaction with the ions^[18-23].

The selected adsorbent was cellulose based plant fiber having oxygen and hydroxyl groups. It is supposed that all of organic materials have been decomposed at temperature of 300°C. Formaldehyde pretreatment of beet root led to negative charge on the surface of carbonized beet (FTCP). At low pH a large number of hydrogen ions can neutralize the oppositely charged surface and thus enhance the electrostatic attraction between the adsorbent and adsorbent overcoming electrostatic repulsion between them. This can be explained that oxygen atoms from formaldehyde led to dipole-dipole interactions between water molecules and charged surface that in this case solvent can contact better with the pores on the surface of carbon^[24]. On the other hand experiments of adsorption with non treated beet (NTCP) indicate low recovery efficiency.

Results obtained from variation of pH of solution indicated that by increasing pH, the adsorption efficiency of Cr(VI) is decreased. Figure 1 illustrates plot of the adsorption efficiency against pH of the solution for Cr(VI) for FTCP and NTCP. Results indicate a very low recovery efficiency for NTCP and good recovery efficiency for FTCP. As can be seen the highest efficiency is at pH equal 2 and it decreases by increasing pH. At low pH the $Cr_2O_7^{2-}$ ion is predominant species in the solution, on the other hand at high pH the CrO_4^{2-} is the major ion in the solution (equation 1).

Figure 2 shows the molecular structure of $Cr_2O_7^{2-}$ and CrO_4^{2-} ions, as can be seen $Cr_2O_7^{2-}$ is a larger molecule rather than CrO_4^{2-} . It can be suggested that due to the large size of the dichromate ions, they are trapped by the cavities; on the other hand the chro-

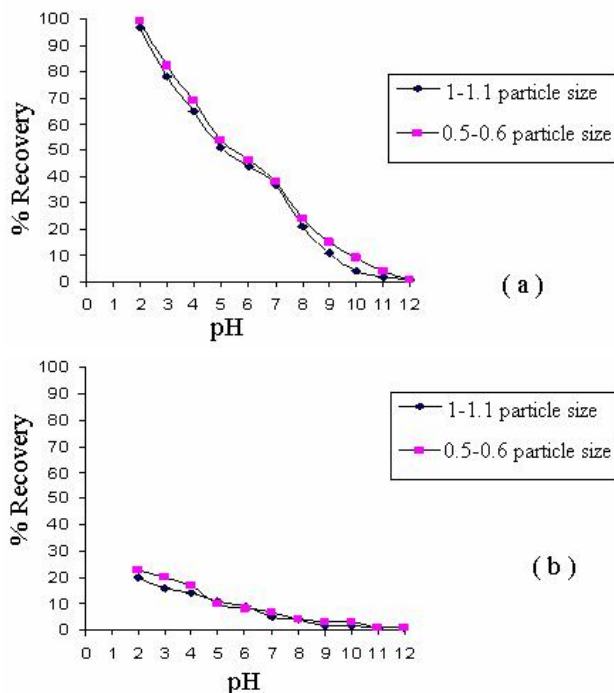


Figure 1: The effect of pH solution on Cr(VI) adsorption for (a) FTCP and (b) NTCP

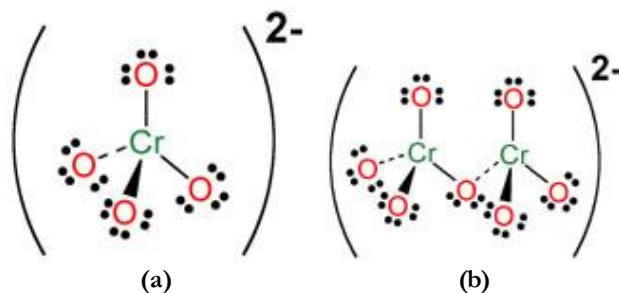


Figure 2: The molecular structure of (a) CrO_4^{2-} and (b) $Cr_2O_7^{2-}$ ions

mate ion is not retained in the cavities because of its small size. Consequently, the carbonized beet particles favorably adsorb the dichromate ion rather than chromate ion.

Figure 3 illustrates the plot of recovery efficiency of Cr(VI) against the dose of adsorbent. Results specify that 1.5 g of this adsorbent has the highest recovery efficiency for 200 mL of sample solution (flow rate = 0.5 mL min⁻¹).

Figure 4 illustrates the plot of recovery efficiency of Cr(VI) against the flowrate of sample solution. Results indicate that the recovery efficiency for FTCP and NTCP was increased by decreasing flowrate up to 0.5 ml min⁻¹. The recovery results are illustrated

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TABLE 1: Results of recovery efficiencies for FTCP and NTCP

Size of carbonized beet particles (FTCP)	% Recovery							
	Cu(II)	Ni(II)	Fe(II)	Co(II)	Zn(II)	NO ₃ ⁻	SO ₄ ²⁻	Cr(VI)
0.5-0.6 mm	3	2	1	1	2	4	3	100
1 mm	2	1	0.6	0.5	1	2	2	98.5

Size of carbonized beet particles (NTCP)	% Recovery							
	Cu (II)	Ni(II)	Fe(II)	Co(II)	Zn(II)	NO ₃ ⁻	SO ₄ ²⁻	Cr(VI)
0.5 mm	1	1	1.5	1	1	2	2	19
1 mm	0.8	1	1.1	1	0.7	1	2	14

Size of carbonized beet particles (NTCP)	% Recovery							
	Cu(II)	Ni(II)	Fe(II)	Co(II)	Zn(II)	NO ₃ ⁻	SO ₄ ²⁻	Cr(VI)
0.5-0.6 mm	1	1	1.5	1	1	2	2	19
1-1.1 mm	0.8	1	1.1	1	0.7	1	2	14

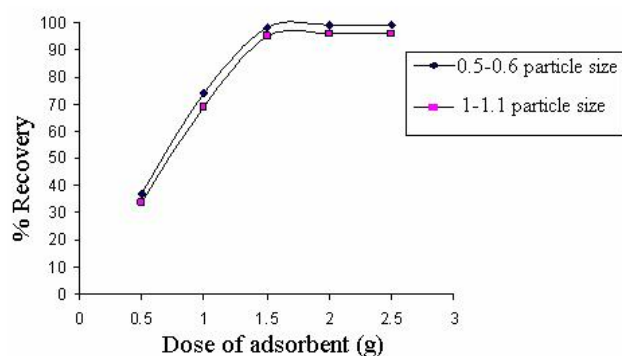


Figure 3: Effect of dose of adsorbent on the adsorption efficiency of Cr(VI) for FTCP

in TABLE 1, as can be seen in the recovery efficiencies for FTCP are very high and are comparable to the recovery results for NTCP.

Similar experiments have been carried out in the presence of solutions containing Cr(VI), Co(II), Zn(II), Cu(II), Fe(II) and Ni (II), NO₃⁻ and SO₄²⁻ ions. Results of this experiment are presented in TABLE 1, as can be seen in the presence of these interferences, the efficiency of the adsorption is not considerable suggesting this adsorbent can act a selective preconcentrate chromium(VI) ion in the solution.

CONCLUSION

In this work the carbonized beet has been considered to preconcentrate chromium(VI). In the separate experiments formaldehyde treated and non-treated beet particles were used. Results reveal that the formaldehyde treated beet can act as a selective

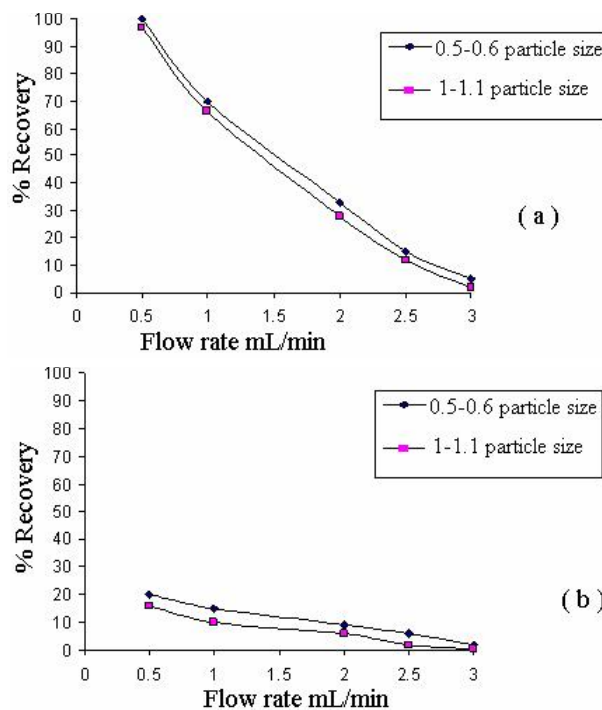


Figure 4: Effect of flow rate on the adsorption efficiency of Cr(VI) for (a) FTCP and (b) NTCP

adsorbent for the chromium(VI) ion but non-treated beet was not shown good recovery efficiency. Results indicated that by decreasing pH of the solution the adsorption efficiency is increased and the highest efficiency was at pH 2. The particle size of carbonized beet is also influence on the adsorption efficiency which the small particles execute better recoveries. The carbonized beet act as a selective adsorbent for preconcentrate chromium (VI) in the presence of other ions in the acidic pH

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