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Adsorption of Uranium from Aqueous Solutions Using Activated Carbon

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ABSTRACT

The adsorption of uranium from aqueous solution has been investigated using conventional commercially available activated carbons. It was found that treatment with hot nitric acid oxidized the surface of activated carbon and significantly increased the adsorption capacity for uranium in near-neutral and slightly acidic nitrate solutions. Equilibrium data were fitted to a simplified Freundlich isotherm for the purpose of comparison of oxidized and as-received samples. The decontamination of aqueous solutions was investigated in small column experiments. An ion-exchange mechanism of uranium sorption from aqueous solution is discussed.

INTRODUCTION

There is increasing concern about the level of toxic metals in the environment. This has led to more stringent legislation and has prompted industry to seek more effective methods of pollution control as the permissible limits are reduced. In order to meet these rigorous demands, researchers are faced with the challenge of improving the performance of existing processes and developing new separation processes. Adsorption processes have long been used in the water and wastewater industry for

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the removal of color, odor, and organic pollution (1). These processes are usually based on the use of activated carbon. Activated carbon has a strong affinity for organic molecules and contains oxygenated functional groupings on the entire surface which are capable of sorbing metal ions from aqueous solution. Furthermore, high chemical, radiation, and thermal stability, rigid porous structure, and mechanical strength impart considerable advantages over polymeric materials. Despite this, little work has been done on the use of activated carbon for the sorption of heavy metals (2, 3) and radionuclides (4–8) from aqueous solutions. In particular, the sorption of uranium by activated carbon has attracted little attention, though Goodrich (9) has investigated uptake from solutions prepared with a number of uranium salts. Some work is reported in the analytical literature, where uranium exists in solution in the presence of organic ligands (10–14). Saleem et al. (15) studied uranium sorption from buffered solutions fixed at pH 4. Janowska et al. (16) studied uranium sorption from sulfuric acid solutions on ammonia-modified activated carbons. Bone char has been investigated for the removal of uranium and plutonium from aqueous effluents at Monsanto Research Corporation, Ohio, USA (17–19). The recovery of uranium from seawater (20–23) and nuclear wastewater (24) has been studied with activated carbon loaded with metal oxides and hydroxides.

Uranium arises in waste streams generated by the nuclear industry (25) and also in surface and groundwaters in some parts of the world (26, 27). The sorption of uranium from near-neutral and mildly acidic aqueous solutions onto activated carbon is the subject of this work.

EXPERIMENTAL

Several varieties of commercial activated carbon were tested in this work. The results presented here are for two varieties of commercial grade coconut shell activated carbon, i.e., sample C2 (manufactured by Sutcliffe-Speakman and coded 208C) and sample C6 (supplied by BDH and coded 33034). As-received samples of both these activated carbons were screened into the size range 355–600 μm and washed exhaustively with distilled water. The samples were first air-dried and then kept in a vacuum desiccator at ambient temperature. Oxidized samples of activated carbon were produced by heating in nitric acid at a temperature of 80–90°C for 8 hours in a round-bottomed flask fitted with a reflux condenser. The oxidized activated carbons were then exhaustively washed with distilled water and dried. Oxidized activated carbons are designated by indicating the type of activated carbon and the concentration of oxidizing nitric acid.

For example, C6(7N HNO_3) indicates as-received carbon C6 (BDH 33034) oxidized in 7 N HNO_3 for 8 hours at 80–90°C.

The surface area and Dubinin–Radushkevich micropore volume of the activated carbon samples were determined by nitrogen sorption at 77 K using a fully automatic Micromeritics ASAP 2000 surface area analyzer.

Uranium solutions were prepared using depleted uranyl nitrate hexahydrate, $UO_2(NO_3)\cdot 6H_2O$, BDH reagent grade. The uranium-235 content of this salt was determined as 0.33%. Nitric acid was FSA Laboratory Services analytical grade. Uranium was determined by the "BromoPadap" method using 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol reagent using a Perkin-Elmer UV/visible spectrophotometer at 530 nm (28) and by ion chromatography based on postcolumn derivitization with PAR reagent [4-(2-pyridylazo resorcinol] (29, 30). All the reagents used in uranium analysis were analytical grade.

Batch equilibration studies were carried out by agitating known amounts of activated carbon and uranium solution at room temperature for at least 24 hours. The amount of uranium sorbed was calculated by the difference in the initial uranium concentration and the equilibrium solution concentration.

The mass of uranium sorbed per unit mass of activated carbon (x/m) is expressed in mg U/g of activated carbon and is given by the relationship:

$$x/m = \frac{C_0 - C_e}{m/V} = \frac{(C_0 - C_e)V}{m} = \frac{F_0 C_0}{m/V}$$

where C_0 (mg/L) and C_e (mg/L) are the initial and equilibrium uranium concentrations, m/V is the ratio of the mass of activated carbon (mg) to the batch volume of uranium solution (mL), and F_0 is the fraction of uranium sorbed, $[1 - (C_e/C_0)]$.

The batch equilibrium isotherms are fitted by a simplified Freundlich equation of the form

$$x/m = kC_e^n$$

k and n are the Freundlich constants characteristic of a particular adsorption isotherm and can be evaluated from the intercept and slope of the linear plot of log (x/m) versus log C_e.

The kinetic studies were performed by the finite bath method (30). Uranium solution of known initial concentration and volume (500 mL) was agitated in a round-bottomed flask with an accurately weighed sample of activated carbon at room temperature. The agitation speed was 1100–1200 rpm. Uranium samples were taken by syringe for analysis at regular intervals.

Packed bed experiments were performed with a sample of oxidized activation carbon (C6 7N HNO_3) in a 1-cm diameter glass column. Activated carbon was thoroughly prewetted by agitating in distilled water for 5–6 hours to remove trapped air from the pores prior to packing into the column. The uranyl nitrate solution was pumped in downflow using a constant feed peristaltic pump. Effluent samples were collected in an automatic fraction collector at timed intervals.

RESULTS AND DISCUSSION

The pore characteristics of as-received and oxidized activated carbons were obtained from nitrogen adsorption isotherms. The general shape of the adsorption isotherm (Type 1) was retained, but there was a decrease in the nitrogen adsorption capacity after oxidation and flattening of the curve at the knee of the isotherm, suggesting the formation of mesopores. This is confirmed by the reduction in the Langmuir surface area and Dubinin–Radushkevich micropore volume of the oxidized samples (see Table 1). The reduction in surface area may well be compensated by improved accessibility of ionic species within the pore structure of the adsorbent.

The sorption of cations from aqueous solution depends upon the nature of the functional groups located at the surface and within the pores of activated carbon. The oxygenated groups that have been identified are normally weakly acidic in character, e.g., phenolic, carboxylic, quinone, and lactone groupings (31–36). The exact nature of these surface groups is not known but there is strong evidence to suggest that oxidative treatment significantly increases the proportion of weakly acidic groups (37–42).

Figure 1 indicates that uranium sorption falls as the pH drops from 4.3 to 2. Four separate aqueous solutions were prepared at the same initial uranium concentration and contacted with C2(7N HNO_3). One sample was kept in an aqueous uranyl nitrate solution (pH 4.3) and the remaining three were adjusted to pH 2 using HCl, HNO_3, and H_2SO_4. Saleem et al.

TABLE 1
Pore Properties of As-Received and Nitric Acid Oxidized Active Carbon Samples

Active carbons	Langmuir surface area (m^2/g)	DR micropore volume (cm^3/g)
C2(as-received)	1689	0.586
C2(7N HNO_3)	1167	0.369
C2(9N HNO_3)	975	0.324
C6(as-received)	1166	0.407
C6(7N HNO_3)	1020	0.363

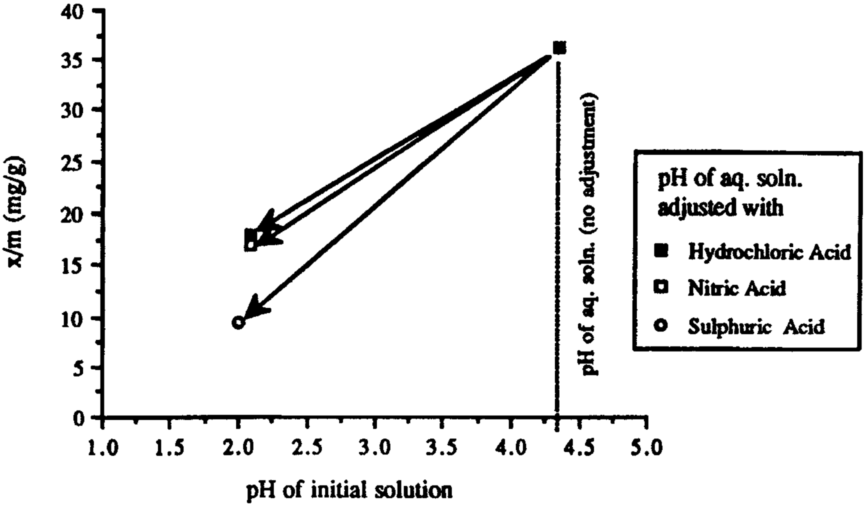

FIG. 1 Influence of pH adjustment with acids on uranium sorption [C2(7N HNO_3); C_0 = 43.50 mg/L, m/V = 25 mg/25 mL].

(15) reported a similar observation while sorbing uranium from different pH buffer solutions.

In neutral and near-neutral solutions, uranium exists in hydrolyzed form, and the following ionic species have been identified (43): UO_2^{2+}, $[(UO_2)_2(OH)_2]^{2+}$ dimer, $[(UO_2)_3(OH)_5]^+$ trimer. The cation forms of the uranyl ion exist in the pH range 2–4, and it is these species that are exchanged at the functional groups on the surface of activated carbon. It is likely that carboxylic groups with a p*K* value of 4–5 are largely responsible for the ion exchange of uranium from near-neutral aqueous solutions. The mechanism of uranium sorption is predominantly by cation exchange at the weakly acidic functional groups, and this can be described by the following equilibrium reaction for divalent uranyl ions:

$$2(R—COO^-H^+) + UO_2^{2+} \underset{pH<4}{\overset{pH\sim4}{\rightleftharpoons}} (R—COO^-)_2UO_2^{2+} + 2H^+$$

Similar ion-exchange reactions can be postulated for the other hydrolyzed ionic species of uranium. Other oxygenated weak acid groups, e.g., phenolic and lactone-type groups, are capable of ion exchange provided that the pH of the solution exceeds the dissociation p*K* value of the functional group. Lowering of the pH value by the addition of acid will tend to protonate the surface groups and lead to desorption of cationic uranium complexes. Acidification with dilute nitric acid will form the neutral

$UO_2(NO_3)_2$ species which is not sorbed by an ion-exchange mechanism. Equilibrium adsorption isotherms are given in Figs. 2–5 for uranium sorption in near-neutral aqueous solution and in the presence of dilute nitric acid for both as-received and oxidized samples of activated carbon. There is clear evidence of the enhancement of uranium uptake with surface oxidized activated carbons (see Figs. 2 and 3). The reduction of uranium sorption in the presence of nitrate ion in solution is shown in Figs. 4 and 5. These isotherms are readily fitted to a simple Freundlich-type isotherm as can be seen in Fig. 6. This suggests that uranium is sorbed by a simple ion-exchange-type mechanism at the fixed cationic sites within the adsorbent structure. A Langmuir type of fit was less satisfactory in the concentration ranges investigated here. Figure 7 shows the isotherms of uranium sorption from dilute nitric acid on three samples of activated carbon that have been oxidized at increasing nitric acid concentration. There is a marked increase in uranium capacity as the acid concentration is raised from 5 to 9 N HNO_3. These data are also fitted to a simple Freundlich-type adsorption isotherm (see Fig. 8).

The rate of uranium uptake is dependent on the pore structure of the adsorbent and the particle size of the material. We have measured the rate of uptake of uranium on oxidized carbons in the size range 250–600

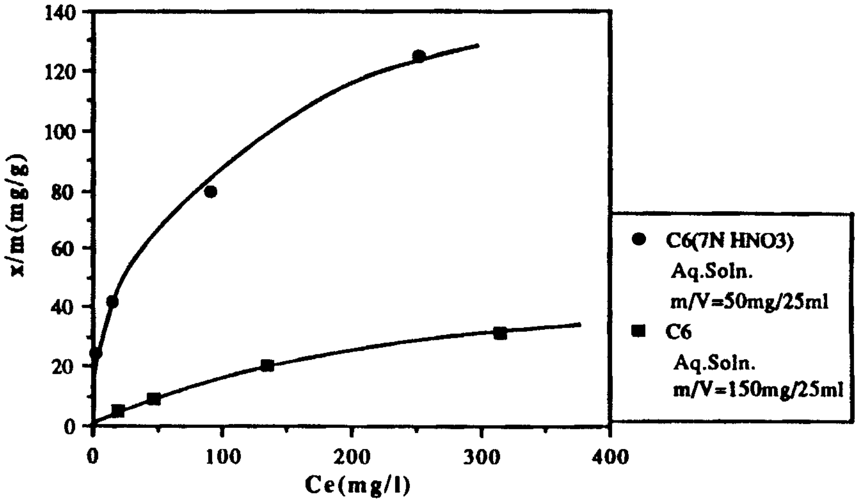

FIG. 2 Sorption isotherms of uranium with C6(7N HNO_3) and C6 active carbons from aqueous solution.

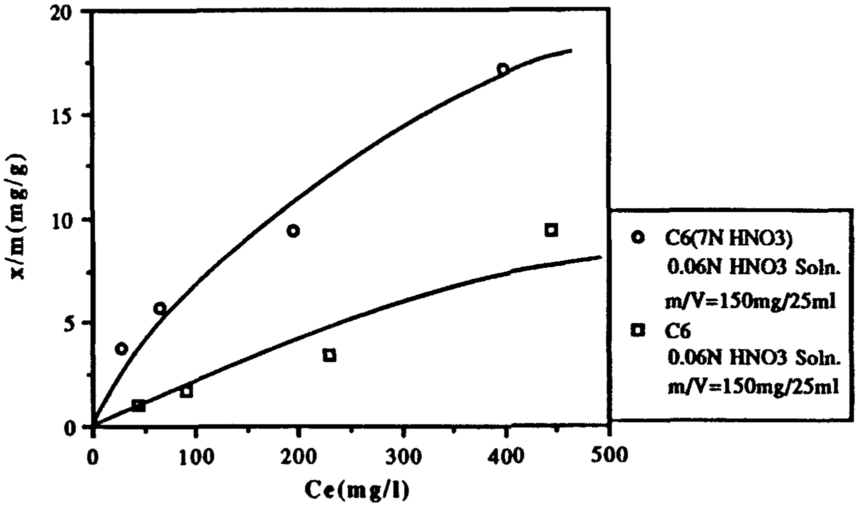

FIG. 3 Sorption isotherms of uranium with C6(7N HNO_3) and C6 active carbons from 0.06 N HNO_3 solution.

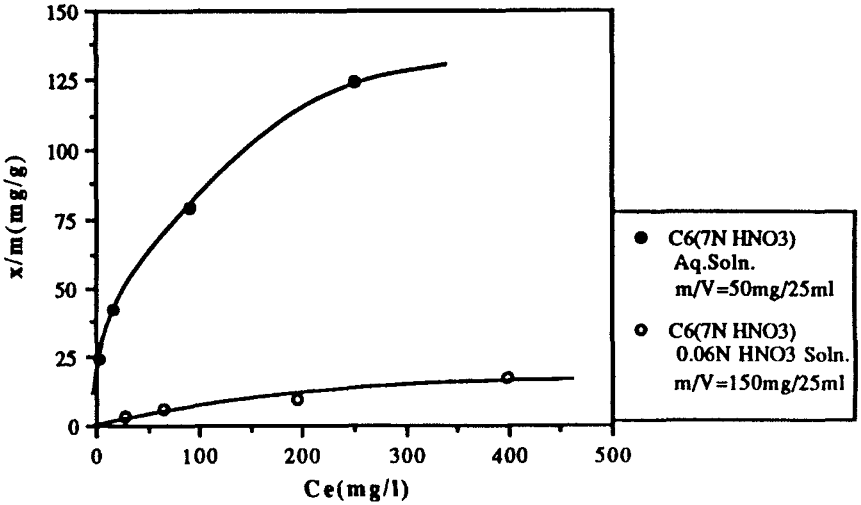

FIG. 4 Sorption isotherms of uranium with C6(7N HNO_3) active carbon from aqueous solution and 0.06 N HNO_3 solution.

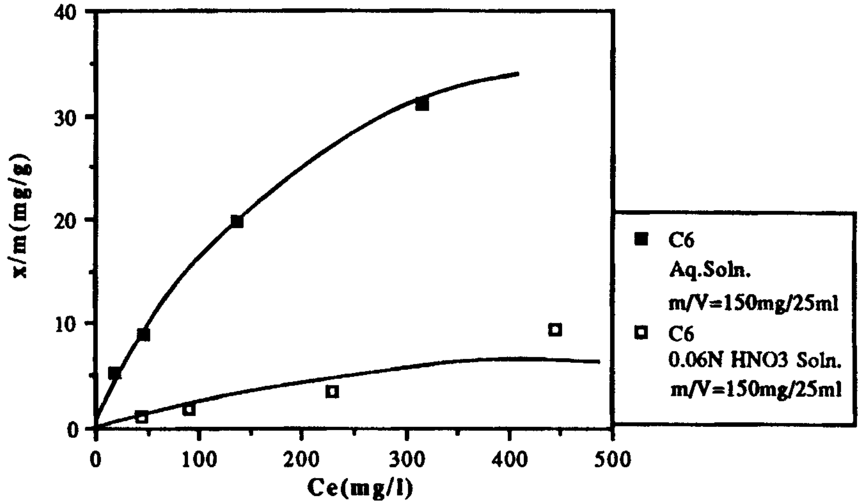

FIG. 5 Sorption isotherms of uranium with C6 active carbon from aqueous solution and 0.06 N HNO_3 solution.

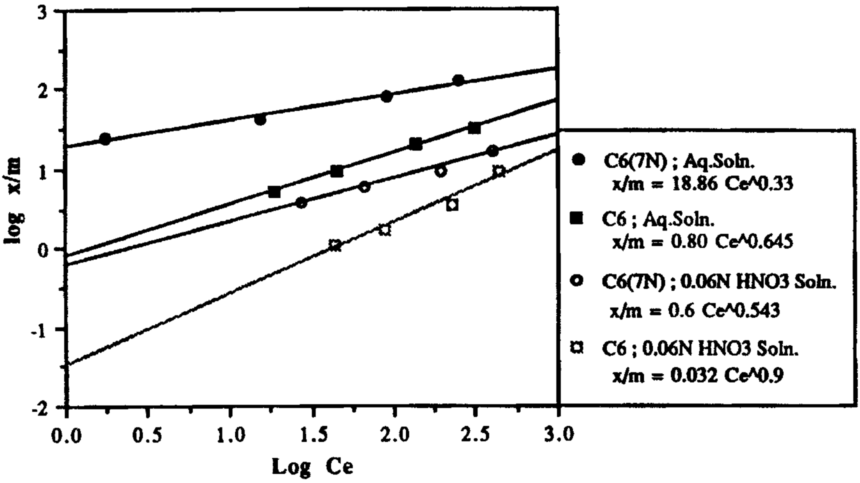

FIG. 6 Freundlich fit of uranium sorption isotherms with C6 and C6(7N HNO_3) from aqueous solution and 0.06 N nitric acid solution.

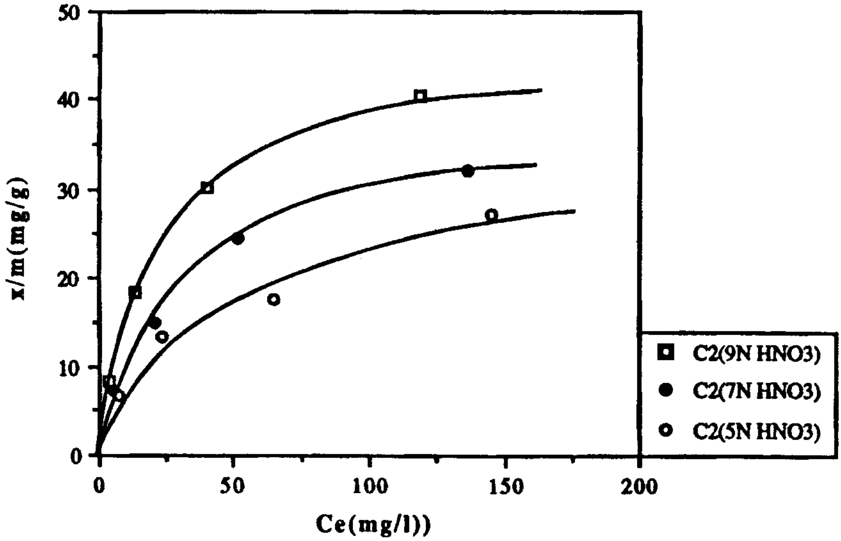

FIG. 7 Uranium sorption isotherm with C2(5N HNO_3), C2(7N HNO_3), and C2(9N HNO_3) in 0.012 N HNO_3 solution [*m*/*V* = 50 mg/25 mL].

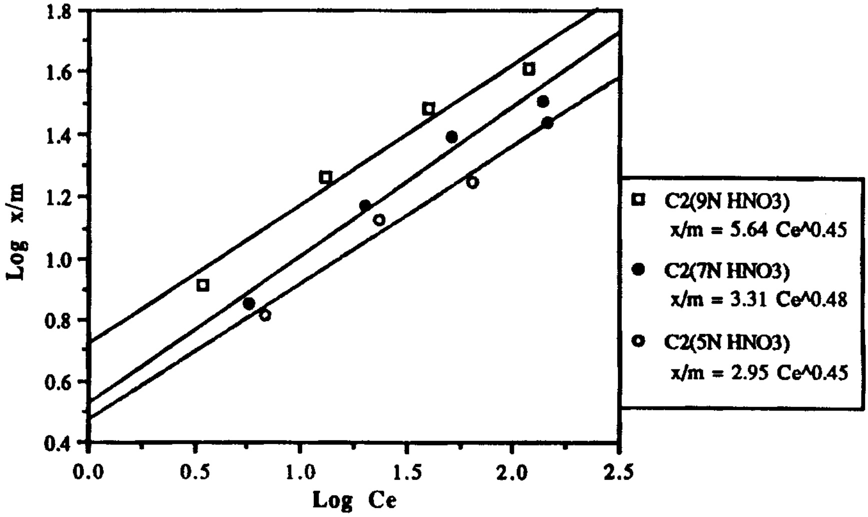

FIG. 8 Freundlich plot of uranium sorption isotherm with C2(5N HNO_3), C2(7N HNO_3), and C2(9N HNO_3) in 0.012 N HNO_3 solution.

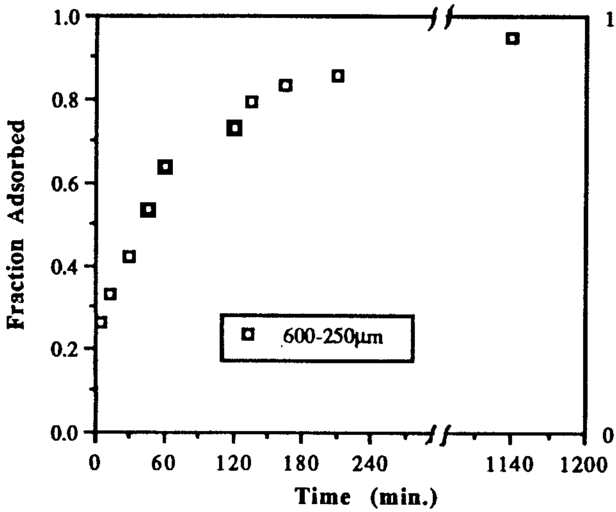

FIG. 9 Kinetic curve of uranium batch sorption from aqueous solution with C6(7N HNO_3) [m/V = 500 mg/500 mL; C_0 = 50 mg/L U in aqueous solution].

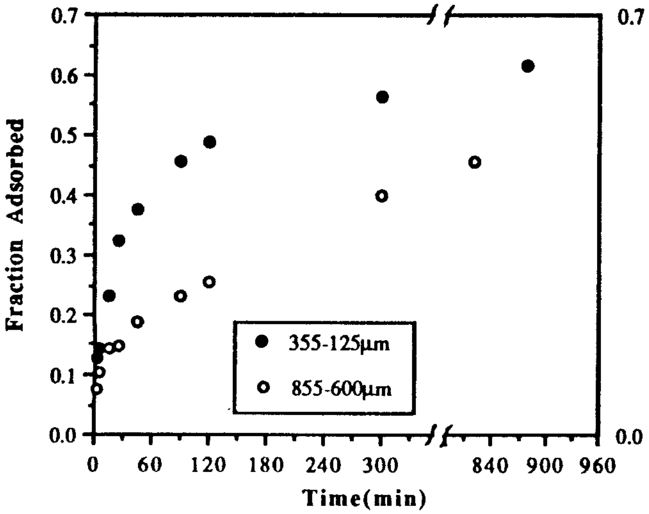

FIG. 10 Kinetic curve of uranium batch sorption from dilute nitric acid solution with C6(7N HNO_3) of two particle sizes [m/V = 1000 mg/500 mL; C_0 = 50 mg/L U in 0.012 N HNO_3 solution].

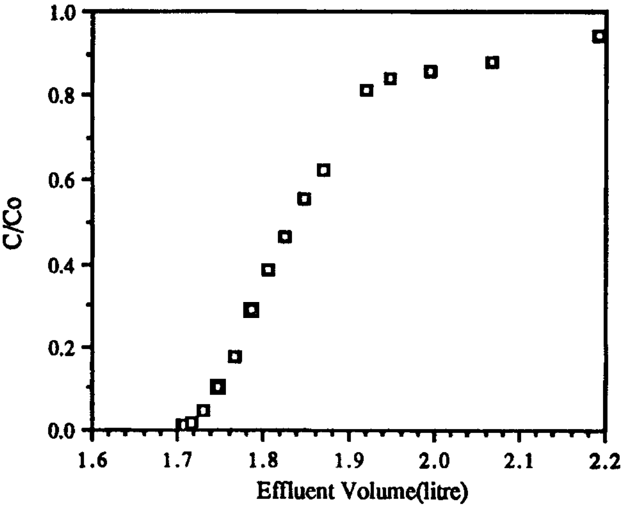

FIG. 11 Uranium breakthrough curve from dilute nitric acid solution with a bed of oxidized active carbon, C6(7N HNO_3, 355–125 μm). Solution: 50 mg/L U in 0.012 N HNO_3. Flow rate: 0.48–0.2 mL/min. Column: 1 cm diameter. Bed height: 7.75 cm. Weight of active carbon: 3.2 g. Breakthrough capacity = 25 mg/g.

μm, and a typical kinetic curve is shown in Fig. 9. The rate of adsorption is initially rapid, indicating some surface sorption. However, the gradual uptake of uranium is diffusion controlled within the porous structure of micro- and mesopores, and therefore the attainment of equilibrium is slow. About 90% sorption is reached in about 4 hours, but thermodynamic equilibrium in batch contact is not attained after 20 hours of contact. Confirmation of the diffusional mechanism is seen in Fig. 10 which shows the rate of uptake at two different particle sizes of adsorbent, i.e., 855–600 and 125–355 μm.

We have investigated the breakthrough behavior of activated carbon in a small-scale packed column using a granular size 125–355 μm. The expected relatively sharp S-shape breakthrough curve was obtained provided the flow rate was sufficiently low to overcome dispersion due to the slow diffusion of uranium species into the pore structure of the adsorbent phase. This experiment serves to confirm the feasibility of uranium removal in a packed bed of activated carbon, and a loading of 25 mg/g uranium was achieved from a dilute nitric acid solution containing 50 mg/L uranium in the feed solution (Fig. 11).

CONCLUSION

The application of activated carbon to the removal of uranium from near-neutral and acidic aqueous solutions has been successfully demonstrated. The effectiveness of surface oxidized forms of activated carbon are shown, and these improvements are achieved by chemical oxidation of the carbon surface. A simple Freundlich-type adsorption isotherm fits the batch equilibration data, and it is found that an ion-exchange mechanism based on the exchange of cationic hydrolyzed complexes of uranium with weakly acidic functional groups explains the sorption mechanism. The rate of sorption is diffusion controlled within the pore structure of the adsorbent and is relatively slow. Classical breakthrough curves are obtained in small-scale packed column trials, suggesting that the conventional application of activated carbon is possible for the decontamination of trace levels of uranium in aqueous solutions.

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