

Pertechnetate Removal from NaCl Solution using Activated Carbon Modified with Oxidizing and Reducing Agents

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The surface of activated carbon (AC) was modified using various oxidizing agents, such as hydrogen peroxide, potassium permanganate and nitric acid, and also reducing agents such as ascorbic acid, tin(II) chloride and hydroxyl amine. The performance of treated active carbons for pertechnetate removal from 0.1% NaCl solution was investigated in batch-type experiments. The oxidative treatment led to an increase in carboxyl groups, identified by FT-IR spectrum measurement. The pertechnetate removal performances of each treated AC were presented comparing the values of distribution coefficient (K_d). The active carbons modified with reducing agents showed better pertechnetate removal efficiency than untreated AC, whereas those modified with oxidizing agents showed worse efficiencies. This means that the removal performance of pertechnetate depends on the reducing ability of AC surface. A new technology for more effective removal of pertechnetate using AC has being developed.

I. INTRODUCTION

Technetium has been needed to be separated from environmental samples, contaminated groundwater for remediation, and nuclear fuel reprocessing wastes. The major separation techniques are co-precipitation, solvent extraction, anion exchange and adsorption onto AC. Among them, AC is a widely used. AC in character has well developed pore structures, large specific surface areas, and is easy to modify the surface. Several studies[1-2] for the removal of pertechnetate using AC have been reported, the mechanism of pertechnetate removal by AC surface is not clear.

In this study, it is aim to modify the surface of active carbon using oxidizing and reducing reagents, and to investigate the performance of modified active carbons for the removal of pertechnetate. Furthermore, the removal mechanism is to be studied, presenting a new technology for more effective removal of pertechnetate using AC.

II. EXPERIMENTAL

A commercial AC(Merck 102186) was used and modified with oxidizing reagents(30% H₂O₂ with 0.1 M HCl, 8 M HNO₃, KMnO₄ with 1 M HCl), and with reducing reagents(0.1 M SnCl₂ with 1 M HCl, 0.1 M NH₂OH.HCl with 0.1 M HCl), respectively. The modified AC was repeatedly centrifuged, and washed with 0.001 M NaOH or water until the pH of supernatant reached the value more than 4, and then dried at 110 °C. The dried AC-KBr(ratio=1:500) mixtures were used for measuring FT-IR spectra from 4000 to 400 cm⁻¹.

For each adsorption experiment, 4 ml of 0.1 % NaCl solution containing 550 Bq of ⁹⁹Tc and 0.02 g of AC were put in a PE vial. The suspension was equilibrated for 2 days at room temperature slowly rotating the PE vial and then centrifuged. 1 ml of the supernatant was taken to the LSC vial and mixed with 14 ml of LSC cocktail, and finally its activity was measured. The remaining solution was used for the pH measurement. The K_d values were determined from the ratio(=⁹⁹Tc activity sorbed on CA per gram/⁹⁹Tc activity dissolved in solution per ml) with a unit of ml/g.

III. RESULTS

FT-IR spectra of AC shows several absorption bands between 4000 and 400 cm⁻¹. The spectral change for CA by the

oxidative modification was observed conspicuously at a band centered around 1720 cm^{-1} which is corresponding to carboxylic C=O bond[3]. The absorption peak intensity around 1720 cm^{-1} was increased with increasing the concentration of oxidative reagent, showing more production of carboxylic groups on the AC surfaces by oxidative modification. On the other hand, the reductive modification gave little spectral changes. The effect of mixing time on the adsorption was also investigated. Thereafter, the equilibration time for all experiments was almost the same to be 48 h.

The effect of pH on the adsorption of pertechnetate onto modified AC surfaces was investigated. For all the AC modified with oxidative or reductive reagents, all the K_d values decreased with increasing pH in the pH region investigated from 3 to 8, as displayed in Table 1. This shows that deprotonated carboxylic groups at higher pH prevent pertechnetate from sorbing on the AC through the negatively-charged repulsion between the two. This also suggests that the major functional group on the surfaces be carboxylic groups from comparing pK_a values of carboxylic and phenolic groups, as reported[2].

It is expected that more carboxylic groups on the surface lead to more adsorption of pertechnetate at a given pH. Unexpectedly, in this work, the contrary result was obtained: the adsorption for oxidative modification was less than that for reductive modification. It suggests that alternative understandings for this observation be needed. In other study[4] on adsorption of Cr(VI) onto AC surface, reductive adsorption mechanism was presented. That is, Cr(VI) is first reduced to Cr(III) by the functional groups and then Cr(III) adsorbs on the surface. Based on this mechanism, our experimental results can be explained with better understandings. Pertechnetate (Tc(VII)) could be reduced to Tc(V) or Tc(IV) by accepting electron from the graphite lattice of AC. In cases of oxidative modification, the electrons to provide for pertechnetate would be much more consumed during the treatment, causing an decrease in adsorption. There are two major factors for more adsorption. One is the number of carboxylic groups on the surface of CA. the other is that of electrons to be donated by CA. The method satisfying these two conditions has being developed.

TABLE I. The values of pH and K_d on adsorption of pertechnetate with modified AC

AC	Modification											
	Oxidative						No		Reductive			
	H_2O_2		HNO_3		KMnO_4		water		SnCl_2		NH_2OH	
	pH	K_d	pH	K_d	pH	K_d	pH	K_d	pH	K_d	pH	K_d
Merck	3.29	23000	3.13	2200	2.99	7900	5.40	41000	4.94	65000	5.55	43000
102186	3.43	21000	3.27	1900	3.10	6500	5.86	29000	5.40	40000	5.90	29000
	4.53	6900	4.16	540	3.98	1700	7.77	4700	7.69	5000	7.60	5600

IV. CONCLUSIONS

Active carbons for technetium removal from 0.1% NaCl solution were treated with various oxidative and reductive reagents to modify their surface functional groups. Contrary to the expectation that the oxidative treatment leads to an increase in pertechnetate adsorption due to the increase of carboxylic groups interacting with pertechnetate, the oxidative treatment decreased it, compared to untreated active carbons, while the reductive treatment increased it. This was explained as an adsorption of reduced technetium species. This study could contribute to develop new technologies for the effective removal of technetium from aqueous solution.

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