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Adsorption of Cesium, Thallium, Strontium and Cobalt Radionuclides Using Activated Carbon

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Adsorption studies of Cs^+, Tl^+, Sr^{2+} and Co^{2+} on activated carbons from aqueous solutions was reported. The carbon samples were characterized using different techniques. The chemical nature of the surface of the activated carbon was studied. Optimal conditions for adsorption of the metal ions have been identified. The comparative study for the metal ions was also considered in the presence of different anions. The data suggest the possible use of activated carbons for preconcentration and separation of some cations.

Key Words: Radionuclides, Activated carbon, Batch technique, Adsorption.

INTRODUCTION

Adsorption is a significant phenomenon in many physical, biological and chemical processes. It is a process in which the molecules or atoms of one phase interpenetrate nearly uniformly those of another phase to form a solution with it. The material that concentrated or adsorbed to surface is called the adsorbate while the adsorbing phase is termed the adsorbent. There are many substances which can be used as adsorbents such as fly ash[1], metal oxides, zeolites, biomass[2], oethite, pyrite fines, hydroxides[3], clays, peanut hulls[4], sand and active carbon[5,6]. Because of their large surface area and their high degree of surface reactivity, active carbons are regarded as very good adsorbents for the removal of both organic[7-9] and heavy metal contaminants and can be used in a number of possible technological and analytical applications. The presence of heavy metals in the environment is a major concern due to their toxicity to many life forms. In the past few years there has been a manifest interest in the adsorption process in solution because these processes play an important role in phenomena such as the environmental transport of heavy metals[10,11], analytical separations[12] and preconcentration of metals present in trace amounts[13]. With the increase in the number of nuclear power reactors, the radioactive pollution of water is growing, this problem could be alleviated by means of suitable adsorption processes, also activated carbons are used extensively as adsorbents of different compounds[14]. Factors affecting the adsorption process *e.g.*, pH, activated carbon dosage, contact time, initial metal concentration and solution temperature were studied[15]. Single copper and nickel adsorption from aqueous solutions onto a granular activated carbon were reported. The present paper reports the results of a study of the adsorption of Cs^+, Tl^+, Sr^{2+} and Co^{2+} radionuclides from aqueous solutions on three activated carbons, two of them were obtained from almond shells and the other one (sample M) was obtained from commercial sources.

EXPERIMENTAL

Adsorbents: Two of the three activated carbons used as adsorbents in this study (samples A-8 and A-14) were prepared using almond shells as raw material. The activation step was carried out in a flow of carbon dioxide (75 cm^3 min^{-1}) during heating at 1123 K (heating rate = 5 K min^{-1}) for 8 h (sample A-8) and 14 h (sample-14). The activated carbons were characterized using various techniques, such as surface area, pore volume and base neutralization capacity. Their textural properties were determined from adsorption measurements of CO_2 at 298 K. From adsorption data, surface area and micropore volume were obtained with the help of the Dubinin-Radushkevich equation[16]. The volume of mesopores and that of the macropores were determined independently using a Carlo Erba mercury porosimeter, model 200.

The pH of the three carbon samples was measured in a suspension of 1 g of the carbon in 20 cm^3 of CO_2 free distilled water, the contact time was 48 h and the temperature was 298 K. The base neutralization capacity of the carbons was determined with a 0.1 M NaOH solution. Ash contents were obtained after burning in air at 973 K for 3 h.

Adsorption measurement: The adsorption of metal ions by the activated carbons was followed by adding 0.1 g of carbon to a vial containing 4 cm^3 of an aqueous solution of the corresponding radioisotope. The radioisotope (^{60}Co) used in this study were supplied by Hot Laboratories Centre-Egyptian Atomic Energy Authority and ^{82}Sr and ^{202}Tl radioisotopes was supplied by Cyclotron Project-Egyptian Atomic Energy Authority and in this study, we used inactive CsCl solution with concentration of 7 M. The amount of carbon and the volume of aqueous solution in all adsorption measurements were kept constant except where otherwise specified.

The concentration of metal ions, was in all cases, 10^{-7} M and the pH of the solutions was equal to 6 and it was adjusted either with sodium hydroxide or nitric acid. The vials were kept in thermostat shaker bath at 298 K. After different periods of time the radioactivity of the solution was measured. For radioactivity measurements, the aliquots (0.05 cm^3) were first dried on planchets under an infrared lamp and then counted under identical geometrical conditions, with a Geiger-Muller counter, model Philips PW-4355. The percentage adsorption was calculated from the relationship percentage adsorption = $(A_0 - A)/A_0 \times 100$, where A_0 = initial radioactivity of the solution and A = solution radioactivity after adding the carbon, the distribution coefficient (K_d) was computed from the expression:

$$K_d = \frac{\text{Radioactivity of the adsorbed ion g}^{-1}\text{ of carbon}}{\text{Radioactivity of equilibrated solution cm}^{-1}}$$

$$= \frac{[A_0 - A]\times[V]}{W\times A}$$

where W = amount of carbon (g) and V = volume of aliquots (cm^3).

RESULTS AND DISCUSSION

Carbon samples characterization: Table-1 shows some characteristics of the activated carbon samples. The apparent surface area of the activated carbons from almond shells (A-8 and A-14) increases with increasing activation time and their surface areas are higher that obtained for sample M. The microporosity of these carbon samples varies in the same order, M < A-8 < A-14. However, the results obtained by mercury porosimetry indicate that in sample M, meso-and macroporosity is more developed than in A-8 and A-14. At the same time, the chemical nature of their surfaces is also different. Thus, as deduced from pH measurements and the NaOH neutralization capacity values (Table-2), whereas sample M exhibits acidic functional groups, A-8 and A-14 show basic functional groups.

TABLE-1
DATA FOR THE CARBON SAMPLES

Sample	S_{CO2}[a] (m^2g^{-1})	V_{mic}[b] (cm^3 g^{-1}) CO_2 at 298 K	V_p[c] (cm^3g^{-1})	Ash content (%)	pH	mEq[d] NaOH (g^{-1})
A-8	1150	0.47	0.27	0.20	8.56	0.00
A-14	1288	0.53	0.35	0.21	8.79	0.00
M	0710	0,29	0.60	2.41	6.66	0.30

[a]Apparent surface area from CO_2 adsorption at 298 K. [b]Micropore volume. [c]Volume of pores that have diameters greater than 7.5 nm, determined by a mercury porosimetry. [d]Base neutralization capacity.

Effect of contact time: The adsorption of Cs^+, Tl^+, Sr^{2+} and Co^{2+} on the three samples of activated carbon was investigated as a function of equilibration time, the results are shown in (Figs. 1-3). In general, in the beginning, the adsorption increases sharply with increasing equilibration time. After 20 min, the adsorption increases smoothly, attaining constant value around 40 min. However, in order to be sure that adsorption equilibrium between metallic ions and activated carbon was reached, 60 min equilibration time was employed in all sequent measurements.

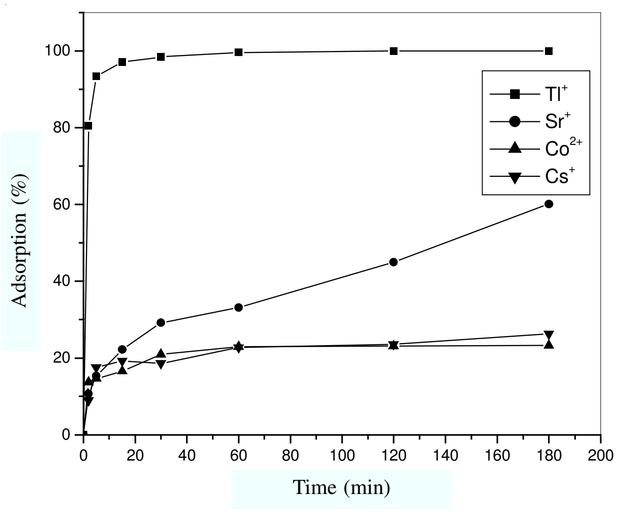

Fig. 1. Adsorption of the cations as a function of equilibration time (sample 1-8)

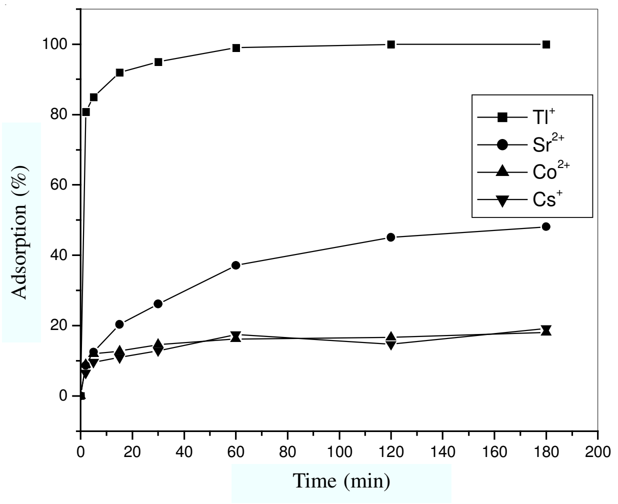

Fig. 2. Adsorption of the cations as a function of equilibration time (sample 1-14)

It is important to note the small adsorption capacity of these carbon samples against Cs^+; it may be due to the low polarizing power of Cs^+ as deduced from its charge: radius ratio.Thus, the carbon Cs^+ interaction forces are too weak and therefore the cesium ions are retained only on those surface centers which show a high density of negative charge[13].

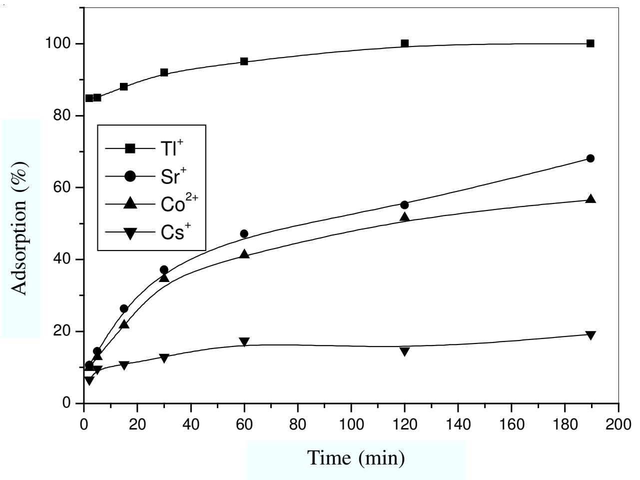

Fig. 3. Adsorption of the cations as a function of equilibration time (sample-M)

On the other hand, the amount of Tl^+ adsorbed by the three carbon samples is too high. Although Tl^+ is similar to Cs^+ with respect to its ionic radii ($Tl^+ = 0.144$ nm, $Cs^+ = 0.169$ nm), hydrated radii ($Tl^+_{aq.} = 0.330$ nm, $Cs^+_{aq.} = 0.169$ nm)[12] and charge, it is difficult to explain why both cations behave so differently and why the amount of Tl^+ removed from the solution is higher than the amounts of Sr^{2+} and Co^{2+}. This may possibly be because of the precipitation of thallium under such conditions. This fact is confirmed by the adsorption values obtained for Tl^+ which are independent of the carbon sample used. In this case it is very hard to differentiate the amount of Tl^+ adsorbed from that precipitated.

These results indicate that the most preferable adsorbent is A-8, it is possible to separate Tl^+ from Cs^+ in a solution where they are present in trace amounts. Thus, while Ti^+ is removed from the solution up to 98 % and Cs^+ remains in it. Furthermore, this adsorption process could be used for Tl^+ preconcentration. Figs. 1-3 show that, except in case of Tl^+, the percentage adsorption increases with increasing meso-and macroporosity are in order M < A-8 < A-14 as shown in Table-1. Therefore, these results indicate that the surface corresponding to micropore is not accessible to these cations, not only because of their size, (hydrated radius (nm): $Cs^+ = 0.329$, $Tl^+ = 0.330$, $Sr^{2+} = 0.412$ and $Co^{2+} = 0.423$) but also because some electrostatic interactions can take place[12].

Effect of pH: Figs. 4-6 show the effect of pH on the adsorption of the four metal cations on the three activated carbon samples, in case of A-8 and A-14, the uptake of Cs^+ reaches to about 90 %, while only about 20 % of other metal cations are adsorbed.

In case of adsorption of cations on sample M, the uptake of Cs^+ and Tl^+ reaches to 85 % and the uptake of Sr^{2+} and Co^{2+} reaches to about 25 %, so the separation of Cs^+ from other cations occur on samples A-8 and A-14. As pH dropped, the cation exchange capacity of samples A-8 and A-14 are increased, this can be explained by the fact that at low pH, higher concentrations of H^+ ions are present in the solution and therefore increase the exchanging capacity.

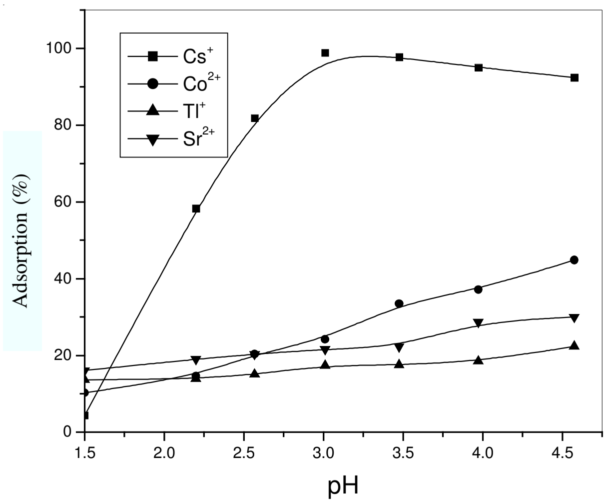

Fig. 4. Effect of pH value on uptake of the cations, using A-8

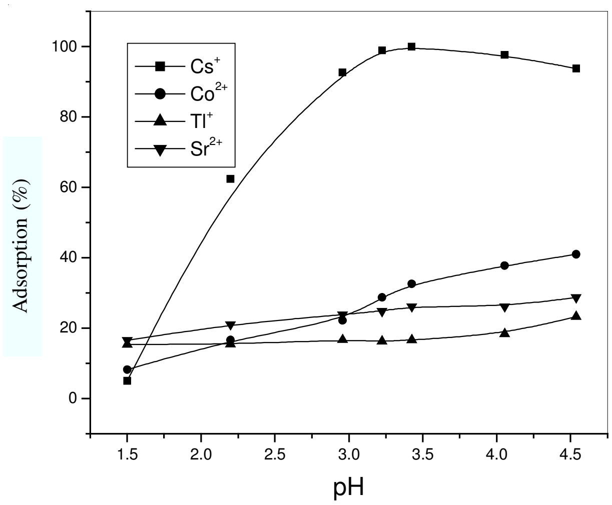

Fig. 5. Effect of pH value on uptake of the cations, using A-14

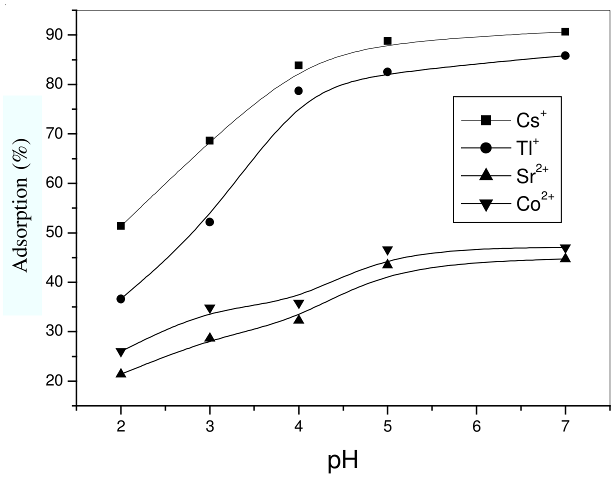

Fig. 6. Effect of pH value on uptake of the cations, using M

Effect of adsorbent weight: The influence of amount of activated carbon on the adsorption of metal cations has been tested in the range 50-1000 mg. The results are given in Figs. 7-9. The plots of adsorption percentage *versus* amount of carbon indicate that initially, adsorption increases sharply with increasing amounts of carbon up to a given value, depending on cation used and then attains an almost constant value. This may be due to a decrease in the effective surface area resulting from conglomeration of the carbon especially at higher adsorbent concentrations.

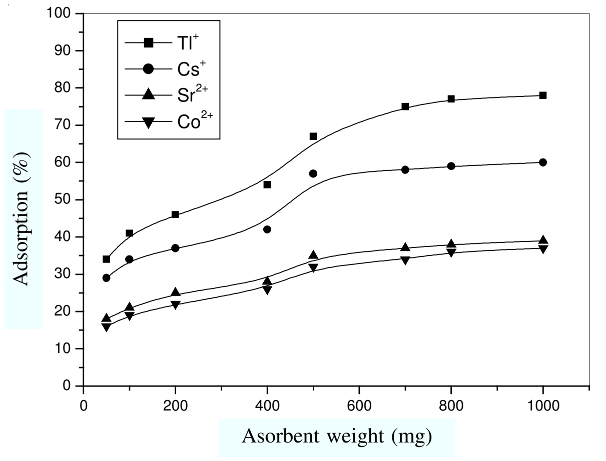

Fig. 7. Effect of adsorbent weight on the adsorption of the cations on A-8

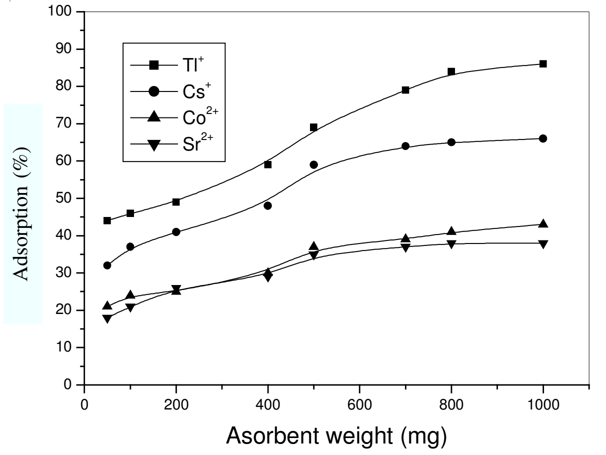

Fig. 8. Effect of adsorbent weight on the adsorption of the cations on A-14

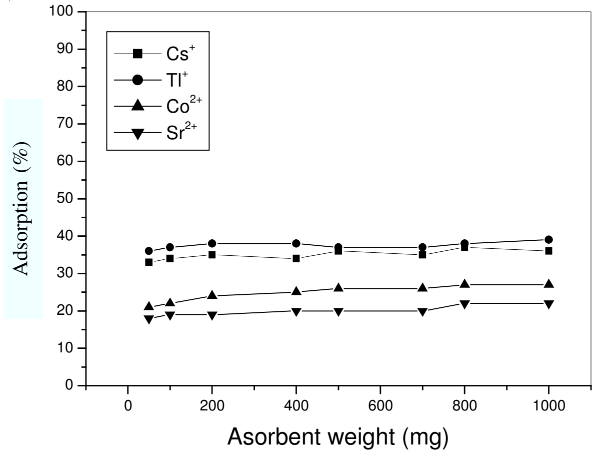

Fig. 9. Effect of adsorbent weight on the adsorption of the cations on M

Since the distribution coefficient K_d, is a measurements of the adsorption yield, it is clear that the optimal amount of adsorbent is that corresponds to the maximum value of K_d. As shown in Figs.7-9, this optimal amount is a function of each adsorbent cation system. It is noteworthy that the adsorption yield in the case of sample (M) is independent of the amount of adsorbent in the range investigated (Fig. 9).

Effect of presence of a number of anions on the adsorption of metal cations: It was considered to carry out some processes of adsorption in the presence of a number of different anions to determine the effect of these anions on the adsorption of the metal cations by the activated carbon samples. The concentration of anions was of the order of 10^{-2} M and most of them were added in the form of sodium salts.

The results obtained using M and A-14 are listed in Table-3. It is evident from this table that there are many anions which increase the adsorption of the different cations with respect to the process without such anions. This fact can be interpreted in terms of electrostatic and chemical processes. Thus, the anions can be adsorbed on the carbon surface, increasing the density of negative charge on it and therefore its capacity to attract cations. On the other hand, the presence of additional ions in solution leads to a higher ionic force and both the activity coefficient and the activity itself increase, therefore, the equilibrium constant of each adsorption process also increases.

However, at the concentration levels mentioned above, anions such as tartrate, citrate and the ligand ethylene-diamine, significantly reduce the adsorption of metal cations. It can be seen (Table-3) that in several cases this reduction takes place only when using the sample A-14. The suppression of adsorption in the presence of these complexing ligands can be explained on the basis of the formation of stable complexes with these cations, which may not therefore undergo adsorption to the same extent on the carbon surface. Since sample A-14 has less meso- and macroporosity than sample M, the latter shows a fraction of sample accessible to these complexes greater than that shown by A-14.

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TABLE-2

ADSORPTION OF DIFFERENT CATIONS ON THE ACTIVATED CARBONS (A-14 AND M) IN PRESENCE OF ANIONS AND LIGANDS

Ion	Sample	No anion	Chloride	Ethylene diamine	Acetate	Nitrate	Thiosulphate	EDTA	Tartrate	Citrate
Cs$^+$	A-14	06.25	10.21	0.00	16.37	08.33	09.06	00.91	2.85	00.36
	M	12.63	11.29	5.93	16.26	14.83	18.37	18.84	5.18	13.05
Tl$^+$	A-14	98.05	98.43	98.09	98.76	99.01	99.05	98.50	98.62	98.52
	M	97.20	97.52	97.73	98.32	98.32	98.20	97.32	97.83	99.01
Sr^{2+}	A-14	60.00	57.96	33.88	68.59	74.31	82.07	67.40	67.84	50.92
	M	67.45	75.53	40.58	77.89	83.50	94.28	90.76	69.63	71.56
Co^{2+}	A-14M	52.73	85.92	17.97	85.90	93.85	97.19	90.76	21.28	66.23
		82.25	90.11	92.81	93.18	96.02	98.88	94.66	93.33	90.53

This is the main reason that both samples behave differently in relation to the mentioned adsorption processes but, of course, the chemical nature of their surfaces must also play an important role.

Conclusion

It may be concluded from the data that by using activated carbons with a determined porosity it is possible to separate a given ion from a number of elements; at the same time it can also be preconcentrated. Moreover, the separation and preconcentration processes can be improved by adding a suitable anion.

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