SELECTIVE REMOVAL OF RADIOISOTOPES BY NOVEL ACTIVE CARBONS

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Introduction

Sorption and ion exchange have been widely employed by the nuclear industry to decontaminate aqueous waste streams. Standard formulations of adsorbents are used world-wide to process radioactive liquid wastes. As discharge limits are lowered by regulatory authorities, it is more challenging for operators to comply with the governing principles of ALARP (as low as reasonably practicable) and BATNEEC (best available technology not entailing excessive cost)[1].

Sorption and ion exchange usually utilise costly inorganic or polymeric materials that are often affected by elevated levels of radiation and increased temperatures. They are also unstable in corrosive media and are not highly selective. The development of new sorptive materials that are free of the drawbacks mentioned earlier would make treatment and disposal much easier and safer.

Active carbons possess obvious advantages over other more conventional adsorbents (ion-exchange resins, inorganic ion-exchangers, zeolites, etc.) because of their high mechanical strength, chemical and radiation stability, high selectivity coupled with a cheap and simple manufacturing process[2-4]. Physical and chemical properties of these materials (i.e. surface area and porosity distribution, surface acidity, the presence of heteroatoms, etc.) may be controlled during the synthesis process. This is particularly applicable in the case of polymer-based carbons since most of these parameters can be preset during the resin-precursor manufacturing stage. The properties of carbonaceous adsorbents may be tailored to address the needs of a particular decontamination process.

In the current study, three active carbons derived from different precursors were tested for the removal of radioisotopes. The composition of waste streams was chosen to mimic discharges from nuclear power plants. Sorption experiments were carried out at the Harwell Laboratory, AEA Technology plc, Oxfordshire, UK. The objective of these experiments was to investigate the sorptive properties of these carbons towards radionuclides in complex waste streams.

Experimental

Active carbon derived from agricultural by-products (KAU-1.9) and commercially available F400 carbon were oxidised by nitric acid. Oxidation methodology can be found elsewhere[5-8]. A phosphorus-containing carbon (PGP-P) was prepared from a phosphorilated phenol-formaldehyde resin by refluxing in phosphorus oxychloride and toluene solution followed by pyrolysis[9].

The samples were analysed on a Perkin Elmer Series II 2400 elemental micro analyser. Phosphorus content in PGP-P was determined using the standard molybdate blue method[10]. The content of mineral admixtures was determined by ashing carbon samples in a furnace at $800^{\circ}C$. Elemental distributions of carbon ash were obtained by energy dispersive X-ray microanalysis (EDAX) using a Cambridge Stereoscan 360 scanning electron microscope

Surface area and pore size distribution of the adsorbents were determined from nitrogen sorption isotherms at 77 K measured by means of a Micromeritics ASAP2010 surface area analyser. The data was modelled using the DFT method[11].

The relative concentrations of different surface functional groups in oxidised carbons were determined using Boehm's method with sodium hydrogen carbonate, sodium carbonate, sodium hydroxide and sodium ethoxide[12].

Low activity reference waste streams were used in this study designated as NAEC S1, S3 and S5 (Novel Absorber Evaluation Club, AEA Technology, Harwell, UK). All waste streams contained 0.05M sodium nitrate to reduce peptisation of the adsorbent. The metal ion content of each stream was: (a) waste stream NAEC S1; ^{137}Cs, ^{60}Co, [65]Zn, ^{51}Cr, ^{59}Fe, [54]Mn, [106]Ru, [109]Cd, [110m]Ag, [203]Hg at the 100 Bq/ml level (b) waste stream NAEC S3; [239]Pu(IV) at 2 Bq/ml, [241]Am at 1 Bq/ml, ^{90}Sr at 5 Bq/ml (c) waste stream NAEC S5; [239]Pu(IV), [241]Am and [237]Np(V) at 1Bq/ml, 1g/l NaHCO₃.

The test solutions were adjusted to the required pH value and then kept for at least 24h at room temperature before

use to allow equilibration of ionic species. Stream NAEC S1 was analysed by gamma spectrometry (detection limit of 1 Bq/ml or less). Streams NAEC S3 and S5 were analysed by both alpha and beta scintillation counting.

Prior to use, adsorbents were conditioned by washing with weakly solution of sodium hydroxide. Washing was continued until the pH of the wash remained at its original value for 2-3h. The adsorbents were used wet after decanting the wash fluid and removing any excess moisture with a cellulose tissue.

1ml samples of the conditioned adsorbent was measured into 200ml screw-top plastic containers using a syringe that was modified as a 'full-bore' syringe. A known volume of a reference waste stream was added to the containers to make up the starting concentration of radioisotopes (100 Bq/ml). The containers were agitated using a constant temperature orbital shaker at 20°C. 1.5 ml aliquots of supernatant solution were extracted from the containers at intervals of 1, 2, 4, 6 and 24 hours, centrifuged and then 1ml was removed for analytical measurements. A blank experiment with no adsorbent present was also included. All the experiments were performed in duplicate, and results averaged.

All analytical results are presented as distribution coefficient (Kd) and uptake (mmol/g). The Kd is calculated using the expression:

$$Kd = (A_i/A_f - 1) \times V/m \ (ml/g),$$

where A_I and A_f are activities of a radionuclide in the solution before and after the sorption, respectively; V is solution volume (ml); and m is the mass (g) of carbon sample. The total Kd was determined for α- and β-emitting isotopes from NAEC S3 and NAEC S5 streams (calculated from total activity values).

Results and Discussion

Oxidised active carbons contain a relatively large amount of oxygen (Table 1). Oxygen-containing acidic surface groups formed during the nitric acid treatment are responsible for the increase in oxygen concentration.

Table 1. Surface area, pore volume and elemental analysis.

Adsorbent	KAU-1.9	F400(ox)	PGP-P
DFT S. Area, m^2/g	1100.4	850	278.4
DFT Pore Vol.,cm^3/g	0.73	0.26	0.13
Ash (wt%)	1.9	3.5	-
C (wt%)	83.21	83.64	75.49
H (wt%)	0.56	0.42	1.76
N (wt%)	0.61	0.73	1.15
P (wt%)	-	-	6.51
O*(wt%)	15.62	15.21	15.09

* Oxygen determined as residual

The molybdate blue method yielded a value of 6.51% phosphorus whereas direct elemental determination yielded 6.8 % of phosphorus. Elemental analysis revealed the presence of 1.15% of nitrogen in this material. This may be attributed to a nitrogen-containing modifying agent used in the preparation of the resin precursor. Oxidation of active carbons using nitric acid introduces very small amounts of nitrogen which was found in KAU-1.9 and F400(ox) samples.

Both unoxidised and oxidised F400 carbon samples contain relatively large amounts of mineral admixtures (4.78 % and 3.14 % respectively). The presence of silicon, aluminium, potassium, calcium, titanium and iron was detected by energy dispersive X-ray microanalysis in the ash samples of both samples. These impurities originate from bituminous coal which was the precursor of F400. Lower amount of ash in the oxidised sample suggests that a part of it was digested in nitric and hydrochloric acids during oxidation and subsequent washing procedures. The residual ash in the oxidised sample is likely to be attributed to silicate compounds that are not soluble in these acids. Similar observations regarding mineral impurities in F 400 were also reported by Alben and Jacobs [13] and Corapcioglu and Huang [14].

The pore-size distribution data clearly shows that the phosphorus-containing carbon is predominantly microporous (Fig. 1).
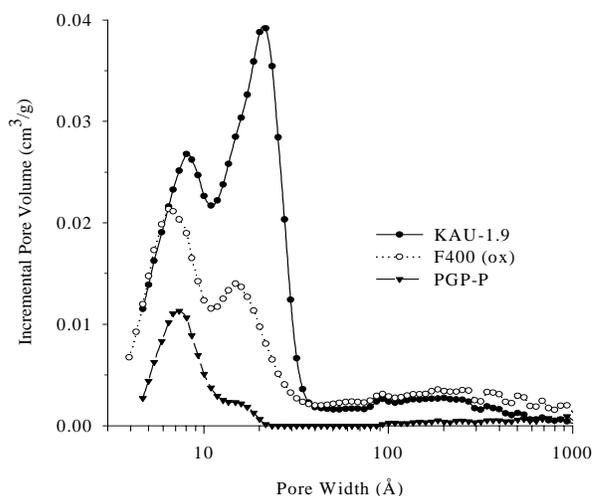

Figure 1. Pore size distributions for the carbons studied.

The mean micropore diameter of PGP-P is about 7Å. KAU-1.9 and F400(ox) possess a greater amount of small mesopores (~20 Å) in comparison to PGP-P. The pore volume of the phosphorus-containing carbon appears to be very low when compared with F400(ox) and KAU-1.9 (Table 1). The apparent bi-modal distribution of pores in the microporous region is caused by deficiencies of the DFT model [11]. The low surface area and pore volume

value of the PGP-P carbon can be attributed to the fact that surface phosphates tend to restrict catalytic gasification during thermal treatment of the carbon precursor[15,16]. The phosphates protect the surface from excessive burn-off thus yielding a low surface area carbon. Indirect evidence of this phenomenon was observed for the phosphorus carbon. It was extremely difficult to burn the PGP-P carbon in a pure oxygen atmosphere during phosphorus analysis.

The titration results show that the oxidised active carbons contain a relatively high concentration of oxygen-containing surface functional groups. Both samples have a similar quantity of carboxylic groups. However, the concentration of weaker functionalities (i.e. lactones and phenols) is different (Table 2). KAU-1.9 has a higher

exceeds that of some commercially manufactured sorptive materials specifically designed for the removal of heavy metals and radioisotopes[1].

Relatively low uptake was detected for Fe-59 and Cs-137. The result for Fe-59 is unusual since oxidised carbons normally exhibit higher selectivity towards iron in comparison with other metal ions[17]. The PGP-P carbon displayed better sorption for iron in comparison with the other carbons.

The uptake rate for radioisotope removal by carbons from NAEC S1 stream was fast. Within one hour between (85-95)% of metals were removed from the feed solution. However, there were some exceptions. Fe-59, Ru-106 and Cs-137 were removed relatively slowly compared to the

Table 2. Concentration of surface functional groups of KAU 1.9 and F400 (ox).

Carbon	Carboxyl groups mmol g^{-1}	Lactones mmol g^{-1}	Phenolic groups mmol g^{-1}	Total (non-carbonyl) mmol g^{-1}	Carbonyl groups mmol g^{-1}	Total capacity mmol g^{-1}
KAU 1.9	0.959	0.393	0.702	2.054	2.376	4.430
%[†]	46.69	19.13	34.18	100		
F 400 (ox)	0.719	0.439	0.427	1.586	1.356	2.941
%[†]	45.33	27.68	26.92	100		

[†] % of total non-carbonyl capacity

proportion of phenolic-type groups (in terms of acid strength) whereas F400(ox) possesses equal proportions of lactonic and phenolic-type groups. Both materials also contain a large quantity of carbonyl groups; these are capable of participating in donor-acceptor type interactions with heavy metal ions.

Radionuclide sorption studies performed with the carbonaceous adsorbents exhibit high distribution coefficients (Kd) for radioisotopes (Table 3 and Fig 2). The performance of the tested materials is comparable or

rest of the radionuclides. Within one hour only (45-55)% of iron, (60-70)% of ruthenium and (60-65)% of caesium were removed by the oxidised active carbons. Cs-137 uptake rate by PGP was similar to that of the oxidised carbons. Generally, after 24h (95-99.5)% of γ-emitters were removed from the feed solution.

KAU-1.9 and F400(ox) were also studied for the removal of α- and β-emitters (Pu, Am, Sr and Np) from NAEC S3 and NAEC S5 reference streams. The results for NAEC S3 indicate that KAU-1.9 yields much higher Kd values than

Table 3. Distribution coefficients and uptake values studied from NAEC S1 (γ-activity) and NAEC S3 (α-, β- activity).

Isotope	Kd values, ×10^4 ml/g / Uptake, ×10^{-8} mmol/g (pH 9)					
	F400(ox)		KAU 1.9		PGP-P	
Cd109	27.80	2.190	55.60	2.190	1.15	1.860
Hg203	5.64	0.048	7.28	0.048	1.00	0.038
Cr51	1.85	0.012	0.99	0.011	1.11	0.024
Ru106	2.89	0.284	1.30	0.276	2.11	0.479
Cs137	0.14	9.890	0.12	9.250	0.08	4.400
Mn54	3.24	0.342	14.00	0.348	3.68	0.183
Ag110m	3.72	0.229	1.74	0.224	2.68	0.240
Fe59	3.06	0.051	4.62	0.052	7.12	0.060
Zn65	14.10	0.286	56.60	0.287	9.38	0.285
Co60	9.88	2.720	69.50	2.740	1.38	3.300
Total Kd (α-activity)	2.84	—	12.70	—	—	—
Total Kd (β-activity)	0.28	—	0.78	—	—	—

F 400 (ox) (Table 3). Investigation of the effect of solution pH on Kd values for the NAEC S5 waste stream showed better sorption by KAU-1.9 with increase in solution pH whereas F400(ox) displayed the opposite behaviour (Table 4). α- and β-emitting isotopes were also rapidly removed from solution (90-95 % of radioisotopes were taken up during the first hour).
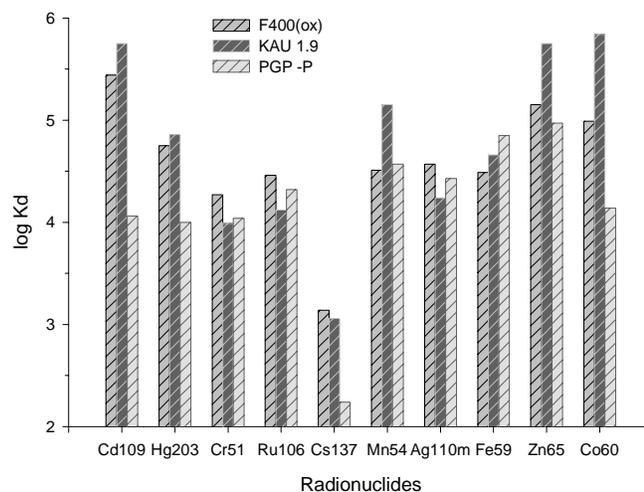

Figure 2. Log Kd for the materials studied.

Table 4. Batch contact test with selected carbons at different pH values using NAEC S5 reference waste stream (α-activity).

Sorbent	pH	Total Kd , $\times 10^4$ ml/g (α-activity)
KAU 1.9	7	0.48
KAU 1.9	9	1.62
KAU 1.9	11	1.80
F 400 (ox)	7	4.43
F 400 (ox)	9	3.53
F 400 (ox)	11	1.93

The removal of radioisotopes by active carbons may be attributed to the presence of inorganic mineral impurities and humic compounds present within the active carbons. The ash composition data showed that F 400 (derived from bituminous coal) contains considerable quantities of foreign components. These components included various metal oxides and silicates. These compounds themselves are known to be very good adsorbents for heavy metals and radioisotopes. The feed concentration of the radioisotope solution was very low 10-100 Bq/ml (10^{-8} – 10^{-10} mmol/l) and, therefore, metal oxide impurities present within carbon may selectively bind radioisotopes.

Sorption of α-emitters displayed by F400 (ox) may be partially related to the greater concentration of mineral admixtures within F400 (ox). Energy dispersive X-ray microanalysis of the ash obtained from F400 (ox) contained the elements Fe, Al, Ti and Si. Some of these oxides e.g. Fe, Al etc., may solubilise as the pH of the solution increases. This is reflected in the gradual reduction of Kd values for α-activity displayed by F400 (ox) as the pH of the solution increases (Table 4). Apricot stone derived KAU carbon contains less mineral admixtures as displayed by the low ash content values obtained for KAU-1.9 (Table 1). It is also quite likely that the elemental composition of ash derived from KAU-1.9 (mostly Na and Ca) differs from ash obtained from F400(ox) (mostly Al, Fe, Ti and Si). It is less likely that mineral admixtures in KAU-1.9 would have the same influence on radionuclide sorption as in F400 (ox). The increase in Kd values for α-activity displayed by KAU-1.9 is attributed to the effect of solution pH on the dissociation of weakly acidic functional groups. More of the acidic surface functional groups present in KAU-1.9 are dissociated at pH values of pH9 and pH11 respectively, consequently, increased metal sorption is observed as the pH of the solution increases.

Another possible reason for the enhanced sorption of radioisotopes by oxidised carbons may relate to the presence of humic substances that are formed during carbon oxidation due to a partial digestion of the carbon matrix. They tend to leach out from the carbon during contact with alkaline solutions. It was shown by Kuzin and Strashko[18] that the functionality of humic acid molecules are structurally similar to the surface functional groups present in oxidised activated carbons. Humic acids consist of flat networks of carbon rings with side radicals. Functional groups similar to those found on the surface of oxidised active carbons are distributed in the structure of humic compounds. An earlier investigation carried out by Chuveleva et al.[19-22] revealed that natural humic compounds (similar to those found in oxidised carbons) are capable of selectively binding radioisotopes. Humic acids as well as oxidised active carbons possess two major types of functional groups: carboxylic and phenolic. These groups associated with humic acids that are present within the pores of active carbons may be responsible for the improved selectivity displayed by these adsorbents towards radioactive metal species. The flexibility of these macromolecules may allow rotation of negatively charged acidic functional groups thereby facilitating the interaction of several neighbouring functional groups with a heavy metal ion. This can result in the formation of strongly bound metal chelates. This is in sharp contrast to the rigid structure of active carbons, where the possibility of metal ion interaction with multiple functional groups is restricted. Consequently, humic acids may contribute to

the overall metal sorption capacity and selectivity of oxidised carbons.

Performing sorption experiments in solution with alkaline pH may be important for the enhancement of the selectivity of active carbons. It was shown in earlier studies that the stability of carbon-metal surface complexes increases with pH (as inferred from stability constants) [23-25]. At high pH values, relatively weaker surface groups (i.e. phenolic), together with relatively stronger groups (i.e. carboxylic), dissociate and therefore participate in complexation reactions with metal ions in solution.

Conditioning of the adsorbents with alkaline solution (e.g. sodium hydroxide) effectively converts them into a cationic form. Cationic forms of carbonaceous materials may exhibit somewhat different sorptive properties compared to adsorbents in the hydrogen form. Mironov and Taushkanov[26] determined the exchange constants on oxidised carbons for a variety of binary systems such as nickel-sodium, nickel-hydrogen, zinc-sodium and zinc-hydrogen. They reported low apparent exchange constant values for Ni^{2+}-H^+, Zn^{2+}-H^+ and particularly for Na^+-H^+. Low values were thought to relate to a high affinity of the surface functional groups in active carbons towards hydrogen ions thereby resulting in poor metal uptake. On the other hand, the exchange constants between the divalent cations and sodium ions of the adsorbent surface attained high values i.e. good cation exchange[26]. The values of Me_1^{z+} - Me_2^{z+} exchange constants mostly depend on the extent of saturation of surface functional groups[17,23]. Highest values of the constants occur either at low surface saturation (e.g. at acidic pH) or at high saturation degrees in alkaline solutions. Medium saturation extent and near-neutral solution pH result in less pronounced differences of metal sorption i.e. reduced selectivity.

Conclusions

This study has shown that treatment of radioactive waste streams by active carbons can be used to substantially reduce the concentration of radioisotopes prior to discharge. Characterisation of adsorbents by a variety of physico-chemical methods confirms the presence of different surface functional groups containing heteroatoms (i.e. oxygen and phosphorus). The sorption results show that oxidised active carbons exhibit selectivity and rapid kinetics for the removal of radioisotopes. The presence of mineral admixtures, humic substances, the negatively charged adsorbent surface, a variety of surface functional groups in carbons as well as experimental conditions (solution pH, sorbent conditioning, etc.) influence the removal of radioisotopes.

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