Sorption of ^{226}Ra from oil effluents onto synthetic cation exchangers

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ABSTRACT

Increasing environmental awareness is being urged for the safe disposal of ^{226}Ra-contaminated production water generated in the oil industry. Birnessite, antimony silicate and their cationic derivatives were studied for the take-up of ^{226}Ra using the batch-type method under experimentally determined parameters, viz. contact time, solution-solid ratio and ^{226}Ra concentration. Data was expressed in terms of distribution coefficients. Sorption experiments were performed in different concentrations of nitric acid in order to speculate the mechanism of ^{226}Ra uptake. Variation in the magnitude of sorption efficiency of the materials in the presence of the major components of waste streams, i.e. Na$^+$, K$^+$ and Ca^{2+}, revealed that K$^+$ was the greatest competitor and Na$^+$ the least. The application of the materials to sorb ^{226}Ra from actual oil co-production water samples, collected from Der Ezzor and Al Fourat petroleum companies (DEZPC and AFPC), was interpreted in terms of the exchange properties of the materials and water characterisation. Of the parameters studied, the selectivity of materials was shown to be greatly dependent on the pH of wastewater to be treated.

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1. Introduction

Like most production activities in modern civilisation, oil production and decontamination facilities generate large volumes of liquid waste. In some cases wastewater from oilfields, which contains radium nuclides, can exceed the amount of oil produced. Decontamination facilities, particularly those using high pressure water jetting for wet abrasive decontamination of equipments, also generate huge volumes of ^{226}Ra contaminated wastes, i.e. water, sludge and scales (IAEA, 2004). The presence of radium-226 in high concentrations in radioactive waste from the oil industry makes it of a major concern from an environment viewpoint because of its toxicity and long half-life (1620 years). Levels of activity in oil-produced water can attain several hundred becquerels per litre, depending on the source rocks of the oil reservoirs and the associated brine water (Al-Masri, 2006; IAEA, 2004; Jonkers et al., 1997; Swann et al., 2004). Discharging this type of wastewater may cause environmental pollution as surface and ground waters as well as in soil, and thus exposure to the public.

Safe treatment and management of radioactive wastes recognises the importance of using inorganic exchange materials to achieve selective removal of radioisotopes prior to discharge to the environment. Crystalline inorganic ion exchangers, especially those

with an open and rigid framework structure become preferable to zeolites (Clearfield, 1995) since they have higher selectivity and better chemical and thermal stabilities. In this context, an antimony silicate material has recently become of commercial interest as it has been found to take up efficiently a number of radionuclides (Al Attar et al., 2003a,b; Koudsi and Dyer, 2001). Birnessite is the most stable layered manganese oxide and was first reported in the Birness region of Scotland. It is the main Mn-bearing phase in soil, marine manganese nodules and macro nodules. Birnessite can behave as an ion-sieve material with an effective pore diameter of 3 Å (Feng et al., 1995; Shen et al., 1993). Previous work illustrated the superior uptake behaviour of birnessite for thorium-234 (Al Attar and Budeir, 2011), uranium (Al Attar and Dyer, 2002) and other radioisotopes present in radioactive waste effluents (Al Attar et al., 2003a,b) in comparison to titanosilicates (Al Attar and Dyer, 2001; Al-Attar et al., 2000) and antimony silicate (Al Attar et al., 2004).

Recently, a programme of research was commenced to treat oil co-produced streams using inorganic exchangers in order to comply with beneficial reuse and discharge limits. This work includes studies on the efficiency of birnessite and antimony silicate to take up ^{226}Ra under carefully chosen parameters, such as contact time, solution volume-to-exchanger mass ratio and ^{226}Ra activity. The original forms and M-derivatives of the materials (where M = H, Na, K, and Ca) were studied to take up ^{226}Ra in four different media, representing chemical conditions in wastewaters. Application to the sorption of ^{226}Ra from actual oil production waters was

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included. Experiments were carried out using a batch-type method and data was expressed in terms of distribution coefficients.

2. Ion exchange theory

2.1. Distribution coefficient (Harjula et al., 1992)

The remediation of nuclear waste effluents using inorganic ion exchangers ideally involves column exchange. The batch distribution coefficient (K_d) for a given radionuclide is a useful quantity since it represents the maximum processing capacity obtainable in column operation in terms of solution volume (V in L or mL) that can be treated with a given mass (M in kg or g) of an ion exchanger. Under ideal conditions, K_d is calculated from the following equation,

$$K_d = \frac{(A_i - A_t)}{A_t} \times \frac{V}{M} \qquad (1)$$

where A_i and A_t are, respectively, the initial and equilibrium solution activities of the radionuclide of interest. The distribution coefficients obtained in this study were the mean of two independent experiments, based upon the hydrated mass of the exchanger.

2.2. Binary ion exchange system (Harjula, 2000)

In a typical binary cation exchange reaction, the solid with the exchangeable cation (B^{z_B}) is contacted with a solution containing another cation (A^{z_A}), and the exchange process may be written as follows,

$$z_B A^{z_A} + z_A \overline{B}^{z_B} \leftrightarrow z_B \overline{A}^{z_A} + z_A B^{z_B} \qquad (2)$$

where A^{z_A} and B^{z_B} refer to the ions in solution, $\overline{A}^{z_A}$ and $\overline{B}^{z_B}$ refer to the ions in the exchanger, z_A and z_B are the respective ion charges.

Ion exchange is a stoichiometric reaction and each ion removed from the exchanger is replaced by an equivalent amount of another ion to retain charge neutrality. Various equilibrium quantities are used to estimate the efficiency of the ion exchanger for a given separation task. The most common of these is the selectivity coefficient ($k_{A/B}$), which can be defined as in equation (3);

$$k_{A/B} = \frac{\overline{C}_A^{z_B} C_B^{z_A}}{\overline{C}_B^{z_A} C_A^{z_B}} \qquad (3)$$

where $\overline{C}_A$ and $\overline{C}_B$ are the concentrations of the ions in the exchanger, C_A and C_B are the concentrations of the ions in solution.

Both selectivity and distribution coefficients depend on the ionic composition of the exchanger and the ionic strength of the external solution. However, under special condition $k_{A/B}$ value is constant. By substituting equation (3) in (2), K_d can be represented by equation (4);

$$K_d = k_{A/B}^{1/z_B} \left(\frac{\overline{C}_B}{C_B}\right)^{z_A/z_B} \qquad (4)$$

when A is present in solution and exchanger at a much lower concentration than B (e.g. when A is a trace ion and B is a macro-ion ($\overline{C}_B \ll \overline{C}_A, C_A \ll C_B$), $k_{A/B}$ and ($\overline{C}_B$) are essentially constants ($\overline{C}_B \approx Q$, the ion exchange capacity of the exchanger). Taking the logarithm of this gives equation (5), which can be used in identifying the mechanism of the ion uptake by an exchanger,

$$\log K_d = \frac{1}{z_B}\log\left(k_{A/B} Q^{z_A}\right) - \frac{z_A}{z_B}\log(C_B) \qquad (5)$$

Under these circumstances, K_d depends only on the concentration of ion B in solution. Plotting $\log K_d$ as a function of $\log C_B$ should give a straight line with a slope of $-(z_A/z_B)$ when ion A has an equivalence of exchange for ion B. Graphs of $\log K_d$ versus $\log C_B$ can be used to study exchange mechanisms, the charges of the exchanging species and to estimate the performance of an exchanger. Great care should be taken in the interpretation of data to make sure that the assumptions leading to equation (5) are valid.

The overriding condition for linear dependence becomes apparent if, for simplicity, a uni-univalent exchange ($z_A = z_B = 1$) is considered. Inserting $\overline{C}_B = Q - \overline{C}_A$ into equation (3), and combining with $K_d = \overline{C}_A/C_A$ gives equation (6).

$$K_d = \frac{Q}{\dfrac{C_B}{k_{A/B}} + C_A} \qquad (6)$$

This equation shows that the condition for linear dependence of K_d on C_B is in fact $C_B/k_{A/B} \gg C_A$. When the exchanger is highly selective ($k_{A/B}$ is very high, e.g. >50,000), even if $C_B \gg C_A$, the dependence may not be linear and deviations from the slope $-(z_A/z_B)$ may be observed at low C_B with increasing the selectivity.

In dilute solutions (i.e.<10^{-2} M), such as in nuclear wastes in which the concentration of the radionuclide is ca. 10^{-10} M, the K_d of the trace ion A depends only on the concentration of ion B in solution; so the selectivity coefficient is essentially independent of the ionic strength of the dilute solution and no activity correction is necessary (i.e. the deviation of γ_A/γ_B from unity is insignificant).

3. Experimental

3.1. Chemicals

^{226}Ra tracer, with 187.3 kBq mL^{-1} in 0.1 M HNO$_3$ (carrier content 10 μg Ba mL^{-1}), was supplied by Isotope Products (California, USA). Antimony silicate material (batch number 59/9/C) was provided by Crosfield Ltd. (now INOES Silicas Ltd.), Warrington, UK. Oil co-produced waters were sampled from Der Ezzor (DEZPC) and Al Fourat Petroleum Companies (AFPC) in Syria. Chemicals used were analytical grade reagents.

3.2. Preparation of materials and their cationic derivatives

Birnessite is produced by alkaline oxidisation of manganese chloride as stated by Golden et al. (1986a). H-birnessite was used as a precursor to synthesise the cationic derivatives of birnessite according to the method described earlier (Al Attar and Budeir, 2011); symbolised as M–H-birnessite, where M = H$^+$, K$^+$, Na$^+$, or Ca^{2+}. Similarly exchanged forms of antimony silicate were prepared (i.e. M-SbSi) in the manner explained in the literature (Al Attar et al., 2003a).

3.3. Characterisation of the ion exchange materials

Examination of the powder X-ray diffraction (XRD) patterns of the studied materials was performed at ambient temperature, over the angular range (2θ) 3–50°, with step of 0.5° and counting time of 0.5 s step^{-1}. The Stoe Transmission diffractometer (Model STADI-P) source consists of mono chromatic Cu-K$_\alpha$ radiation, $\lambda = 1.54060$ Å, generated in a tube operating at 30 mA current and voltage of 50 kV.