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A COMPARATIVE STUDY ON THE REMOVAL OF URANYL IONS FROM ARTIFICIALLY ENRICHED RADIOACTIVE WATERS USING CLAYS FROM ROMANIA

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Abstract

The present work evaluates the results of the experiments performed with three different clay minerals from Romania (Nereju (N) - Vrancea County, Valea Chioarului (V.C.) – Maramures County and Marsid (M) – Salaj County), so as to establish their potential to be used in the treatment of radioactive wastewaters. The sorption behaviour of uranyl ions from artificially enriched radioactive waters samples on clays sampled from Romanian regions has been studied, in the absence of any ionic competition, as a function of the contact time, effect particle size, temperature and concentration of the radioactive solution. Thermodynamic parameters, the Gibbs free energy, enthalpy and entropy were also calculated. The positive values of both ΔH^o and ΔS^0 and the negative value of ΔG^o indicate an endothermic and a spontaneous adsorption process, respectively. Out of all three clay types, the one sampled from Masid (Salaj County) is the best one as far as the purposes of the present study are concerned.

Keywords: uranyl ions, clays mineral, removal of uranyl ions.

Introduction

The content of radioelements and their distribution in rocks, soil and surface waters is still a current research topic of great importance. Uranium, one of the most studied radioelements, is a heavy element that could exist in natural samples under several

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oxidation states but the major ones are U(IV) and U(VI). These two main oxidation states are geochemically and hydrogeochemically relevant. However, depending on the environmental conditions, this radioelement exists in both oxidation states in natural matrixes. A major percent of U(IV) under anoxic conditions and more U(VI) under oxic conditions will normally exist (Burns and Finch, 1999).

The presence of radionuclides in wastes is a major environmental concern. Removing radioactive ions from wastewater is an important issue in liquid waste treatment because these ions are hazardous with respect to the environment and human health given both their high toxicity even at low concentrations and their half-life time (long half live times). The occurrence of these pollutants in water is directly related to industrial activities such as mining, nuclear power generation plants, nuclear weapon production and various laboratory activities (Kaygun et al., 2007). The system here suggested has been preferred as uranium is the most abundant constituent of nuclear wastes.

The adsorption of toxic ions from aqueous solutions onto clay minerals is a very important issue in different areas of science. The treatment of radioactive liquid waste is aimed at both decontamination and volume reduction (so as to simplify its storage). The sorption of heavy and radioactive metal ions from effluents proved to be very efficient, numerous sorbents being used for the removal of uranium and thorium from the wastewaters, such as: natural and modified clays (Popovici et al., 2006; Humelnicu et al., 2009), microorganisms (Tsuruta, 2002), activated carbon (Someda et al., 2008), different types of cellulosic materials (Bontea et al., 2006), zeolites (Akyil et al., 2003; Aytas et al., 2004) etc.

One of the most effective methods in the treating of radioactive wastewaters is based on adsorption and ion-exchanger processes. In recent years, inorganic ion exchangers have emerged as an increasingly substituting or/and additional means for conventional organic ion exchangers, particularly in low radioactive wastewaters. Among natural inorganic exchangers, clays play an important role. Both the significant cation exchange capacity of clay minerals and their availability at low cost recommend them for radionuclide immobilization and decontamination of radioactive wastewaters.

Among the radioelements, uranium is one whose mobility in clays and soils may vary widely, depending on the type of clay or soil and on their physico-chemical properties (Megouda et al., 2007).

In many countries, natural or modified clay materials are used in the removal of heavy metals and radionuclides off low-level radioactive effluents (McKinley et al., 1995; Prikryl et al., 2001; Turner et al., 1996; Vengris et al., 2001, Yu et al., 2007).

The aim of the present work is to determine whether some clays sampled from several Romanian regions may act as effective uranium adsorbents under different conditions of temperature, particle size, and concentration of radioactive ions.

Materials and Methods

The uranium aqueous solution was prepared by dissolving an appropriate amount of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (Merck) in distilled water. The total U(VI) concentration of the aqueous solution was determined spectrophotometrically, using Arsenazo III as

complexing agent (Savvin, 1961) at 665 nm. All the spectrophotometrical analyses have been done by using a CECIL 1020-type spectrophotometer. The calculated standard error of the measurements was below 4 %.

Three different clays sampled from Nereju (N) (Vrancea County), Valea Chioarului (V.C.) (Maramures County) and Marsid (M) (Salaj County) have been used for the present study. Table 1 presents the chemical composition of all three clay types used herein (Barbat et al., 1989; Popovici et al., 2002; Vuza et al., 2004).

Tab. 1 Chemical composition of the selected clay minerals (%)

Clay	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	P.C.
N	68.38	12.20	1.39	3.24	0.52	2.03	2.52	0.25	9.46
V.C.	69.61	19.70	1.27	0.90	2.41	0.18	1.31	-	5.35
M	69.00	12.68	1.13	3.57	0.75	2.64	0.60	0.13	9.50

The samples of clay minerals were ground and dry-sieved to obtain different sized particles. Prior to their application, the clays were sieved and the particle fractions of 0.09 and 0.063 mm were selected for the adsorption experiments, without any further purification or pre-treatment. The specific surface area of the sorbent, measured through nitrogen adsorption based on BET equation (Brunauer et al., 1938), was found to be of 16.82 $m^2 g^{-1}$ for the Nereju (N) sample, 27.94 $m^2 g^{-1}$ for the Valea Chioarului (V.C.) sample and of 33.38 $m^2 g^{-1}$ for the Marsid (M) sample. The experiments were carried out through batch techniques, at pH 3. Around this pH value the UO_2^{2+} ions start to hydrolyze resulting in the formation of hydroxocomplexes such as $UO_2^{2+}(OH)^+$, $UO_2^{2+}(OH_2)$ and $UO_2^{2+}(OH)_3^-$. At higher pH values, UO_2^{2+} ions will undergo much more complicate hydroxylation and carbonate complexation (Mahramanlioglu, 2003; Misaelides et al., 1995).

However, based on equation 1 the distribution coefficient (K_d) has been calculated for all three clay types (Kilincarslan et al., 2005; Unuabonah et al., 2007).

$$K_d = \left[(C_i - C_e)/C_e\right] \cdot V/m, \text{ (mL g}^{-1}\text{)} \quad (1)$$

where:

m – the mass of solid phase (g);

V – volume of UO_2^{2+} solution contacted with clay (mL);

C_i – initial concentration of the radioactive solution;

C_e – equilibrium concentration of the radioactive solution.

Results

Effect of contact time

The sorption of uranium ions on the clay materials was studied as a function of contact time, at 303±3 K, at an established concentration of radioactive solution (0.5 mg mL^{-1}) by modifying the contact time from 24 h to 120 h. The plot of the obtained results in figure 1,

shows that the distribution coefficient increases with the contact time, reaching equilibrium after 72 h, for all three clay types.

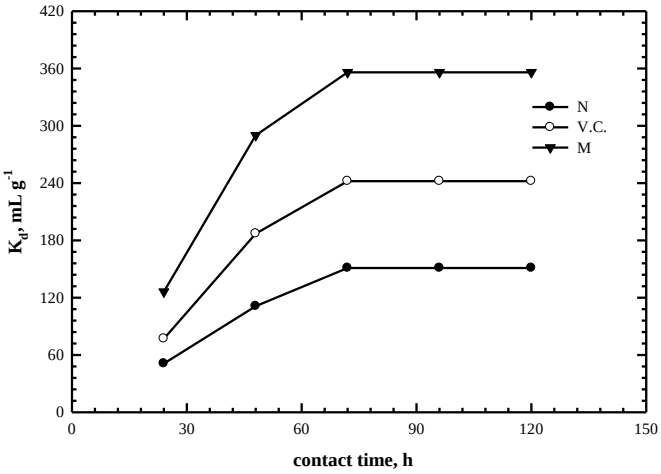

Fig. 1 Effect of contact time on the distribution coefficient of uranium on clays (C_i = 0.5 mg mL^{-1}, M/V ratio = 0.004 g mL^{-1}, pH = 3)

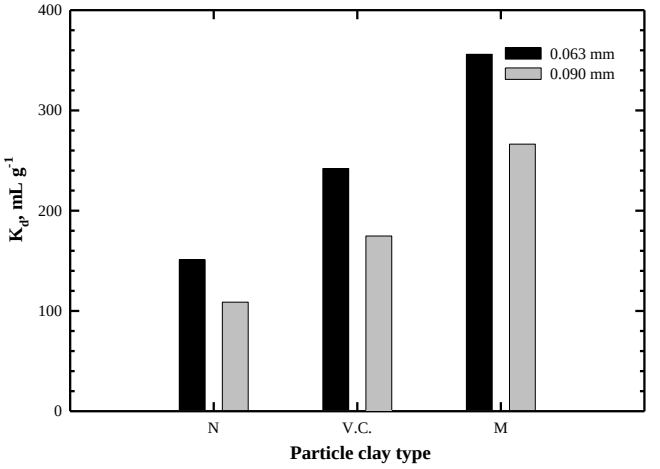

Fig. 2 Effect of particle size on the sorption of uranium on clays. (C_i = 0.5 mg mL^{-1}, pH = 3)

Based on the results obtained on this parameter, it can be concluded that the clay sampled from Marsid (M) has the highest sorption capacity of uranium ion, compared to those sampled from Nereju (N) and Valea Chioarului (V.C.). After 72 h contact time, the Marsid clay has retained with a factor of 2.3 more uranium compared to the Nereju (N) clay and with a factor of 1.5 more that the clay from Valea Chioarului.

Effect of particle size

The sorption of uranium on all three types of clay was studied on 0.09 and 0.063 mm size samples. The obtained data are shown in figure 2. An increasing trend may be observed with the decrease of particle size, as the surface involved increases with the decreasing particle size.

Marsid clay shows the highest retention in both size samples, compared to the other two clay types used in the present study, namely Nereju (N) and Valea Chioarului (V.C.).

Effect of initial concentration of the radioactive solution

The adsorption of uranyl ions on clays as a function of the radioactive solution concentration was studied at 293 ±3 K, varying the concentration of the radioactive solution between 0.25 and 0.75 mg mL^{-1}, and keeping all the other parameters constant (0.063 mm clay particle size and 72 h contact time). Figure 3 shows the distribution coefficients for U(VI) on clays.

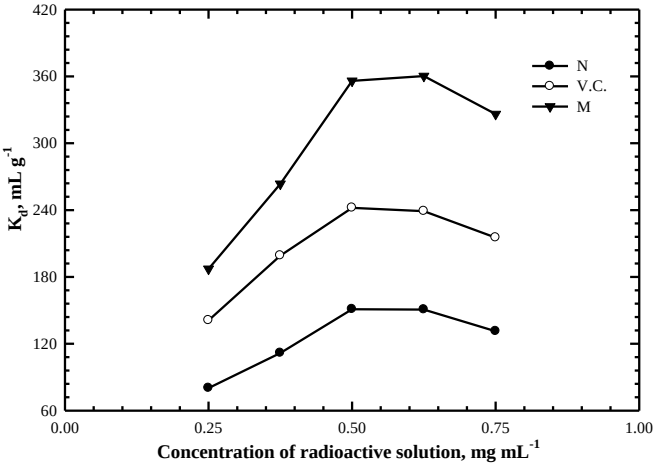

Fig. 3 Variation of K_d with modification of the initial concentration of the radioactive solution.

The depletion of the uranium uptake at higher initial concentrations (C > 0.5 mg mL^{-1}) is probably due to surface precipitation, inducing the blockage of micropores (Abusafa et al., 2002; Aytas Olmez et al., 2004).

Effect of temperature

The sorption of U(VI) ions onto clay materials was studied as a function of temperature, over the range 293-333 K. Figure 4 plots the distribution coefficient as a function of temperature. The results obtained support the conclusion of Kreston et al., according to whom the interaction between clay and the uranyl ions is a physical one.

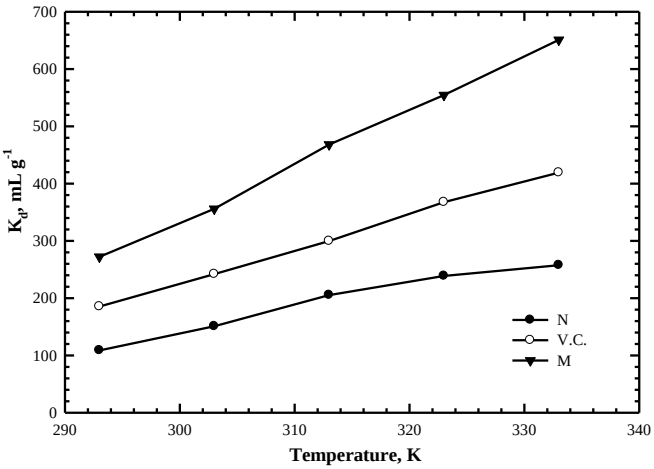

Fig. 4 Variation of distribution coefficient versus temperature

The thermodynamic parameters – standard enthalpy (ΔH^0) and standard entropy (ΔS^0) – were calculated from the slopes and intercepts of the linear variation of $\ln K_d$ *versus* 1/T (fig. 5), through the following equation (2):

$$\ln K_d = \left(\Delta S^0 / R\right) - (\Delta H^0 / RT) \quad (2)$$

where K_d is the distribution coefficient, T is the absolute temperature (K) and R is the ideal gas constant.

The Gibbs free energy values were calculated through the following equation (3):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

The thermodynamic parameters calculated for the uranium sorption process on clay materials are summarized in table 2.

The positive values of both ΔH^o and ΔS^0, and the negative value of ΔG^o, indicate an endothermic and a spontaneous adsorption process, respectively.

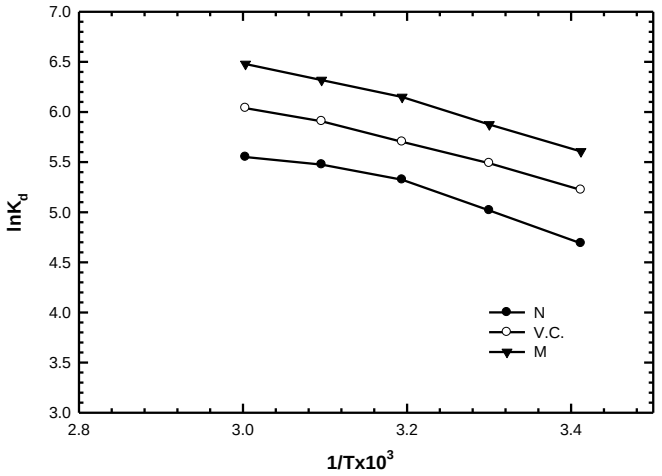

Fig. 5 Relation between lnK_d and sorption temperature.

Tab. 2 Thermodynamic parameters for the sorption of U(VI) on the clayey materials

Clays type	ΔH^o, J/mol	ΔS^o, J/mol·K	ΔG^o, kJ/mol				
			293 K	303 K	313 K	323 K	333 K
N	17.885	95.867	-10.204	-11.163	-12.122	-13.080	-14.039
V.C.	16.721	100.690	-12.781	-13.788	-14.795	-15.802	-16.809
M	17.843	107.674	-13.705	-14.782	-15.859	-16.936	-18.012

Conclusions

The present work indicates that the adsorption of uranyl ions from aqueous solutions depends on contact time, particle size, concentration of radioactive solution and temperature. Out of the three clay types, the one sampled from Masid (Salaj County) is the best one as far as the purposes of the present study are concerned.

The temperature was varied so as to evaluate the values of ΔH^o, ΔS^o and ΔG^o. Based on the positive values of both ΔH^o and ΔS^o and the negative ΔG^o obtained after the study of the effect temperature, it can be suggested that the endothermic and spontaneous nature of sorption can occur for all three clay types.

The adsorption efficiency of the clays used is not as high as in the case of other adsorbents (*e.g* aluminosilicates or titanosilicates). However, their abundance and low cost recommend them in radioactive wastewaters decontamination, as this would decrease the

cost of a possible technological application of this method in the treatment of radioactive wastewaters.

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