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DEPOLLUTION OF URANYL POLLUTED WATERS USING PILLARED CLAYS

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This paper reports on the use of clays pillared with copper polyhydroxycations in the depollution of waters polluted with radioactive elements. The pillared clays have very good surface properties which recommend them for use in cationic depollution. The article includes a kinetic study on the depollution of radioactive polluted waters, studying the influence of temperature on the process. The pillared clays are prepared from Romanian clay originally from Valea Chioarului deposits; the experiments have used an autochthonous material in an unconventional performant depollution technology.

Keywords: *depollution, pillared clays, programmed thermodesorption, radioactive pollution*

Introduction

The goal of this article is to study the use of montmorillonitic structures pillared with copper polyhydroxycations in decontamination of radioactive polluted waters. Based on the EU 96/29 Euratom – 2000 directive, the EU politics is to reduce in time the radioactive affected surfaces and to reintroduce them into the 'clean' surfaces circuit. A series of studies concerning especially rehabilitation of radioactive polluted waters from barren gangues in uranium ore exploiting areas were performed.

The processing areas of uranium radioactive ore (in Romania there are Banat, Bihor, Moldova) represent a risk factor for the environment, flora and fauna, but especially for the population. The radioactive elements generate serious diseases, often incurable. This is why depollution of radioactive polluted waters is a priority in the environment problematic. In the case of entropic accidents or natural disasters, the hazard and harmful degree of radioactive polluted waters augments.

Experimental

The study of the ionic exchange kinetics was performed using montmorillonitic pillared clays with a granulometry of 0.02–0.2 mm. As pollutant we used synthetic solutions obtained from radioactive cation salt dissolved in distilled water; the radioactive salt that we used was the uranyl chloride. Concentration of synthetic pollutant was constant ($4\cdot10^{-4}$ M) for all tests. The evolution of the process was recorded by surveying the cation concentration in solution with spectrophotometric methods. As control method we used the atomic sorption method. Spectrophotometric determination of concentration was realised using the Cecil 1011 UV-Vis Spectrophotometer. Uranium ion concentration was determined at 670 nm wavelength, as a function of the specific colour of the complex formed by uranium and Arsenazo III. Concentration determination by absorption realised by a Varian-AA 880 atomic absorption spectrophotometer.

Choosing the pillared clays samples

The depollution capacity of pillared clays was tested on some samples selected upon their acid-base properties [1], determined by thermoprogramated desorption method [2] (TPD). Figures 1 and 2 present the diagrams that characterise the surface properties of some medium samples of montmorillonite clays pillared with polyhydroxycations of aluminium and copper [3, 4].

If we compare the acidity surfaces [5] (Figs 1 and 2) we obtain a diagram of pillared montmorillonite acidity variation in two cases: the clay was pillared with aluminium or copper polyhydroxycations.

From the comparative diagram of acidity presented in Fig. 3, for the case of uranyl infested waters depollution we selected the clay pillared with copper polyhydroxycations due to their higher acidity. This is why, the clay pillared with copper is more adequate for the depollution process [6], comparing to those pillared with aluminium.

For this study we selected a lot of clays pillared with copper polyhydroxycations and tested its acid-

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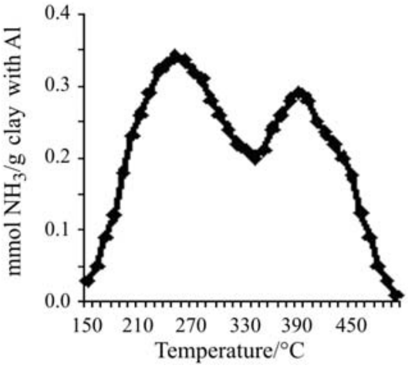

Fig. 1 TPD diagram for acid properties determination. The space acidity variation function on temperature for montmorillonite pillared with aluminium polyhydroxycations

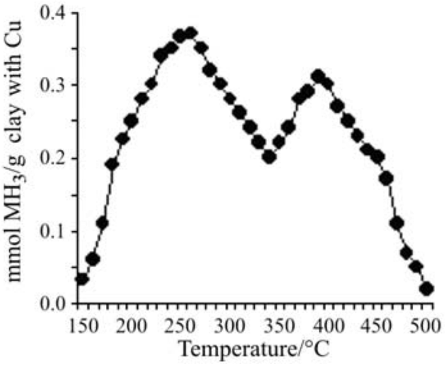

Fig. 2 TPD diagram for acid properties determination. The space acidity variation function on temperature for montmorillonite pillared with copper polyhydroxycations

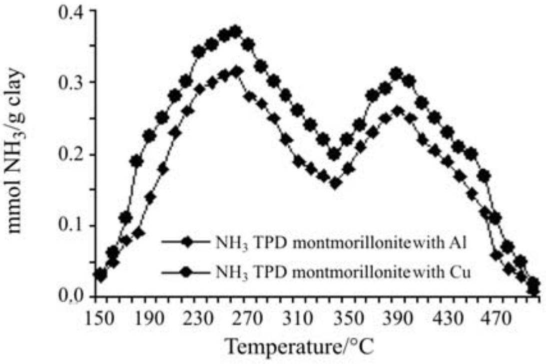

Fig. 3 TPD diagram for acid properties determination. The space acidity variation with temperature for montmorillonite pillared with aluminium and copper polyhydroxycations

base properties [7]. Figures 4 and 5 present the acidity and basicity variation function on temperature for montmorillonitic pillared clay.

The diagrams from Figs 4 and 5 show that this clay presents pronounced acidity and extremely low basicity. That means that pillared clay presents an active surface formed by active centres which can block pollutant cations.

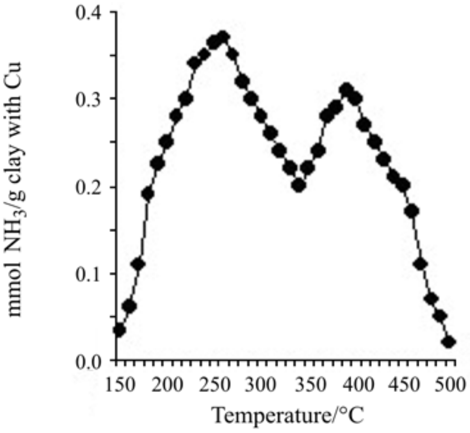

Fig. 4 TPD diagram for acid properties determination. The space acidity variation function on temperature for montmorillonite pillared with copper polyhydroxycations

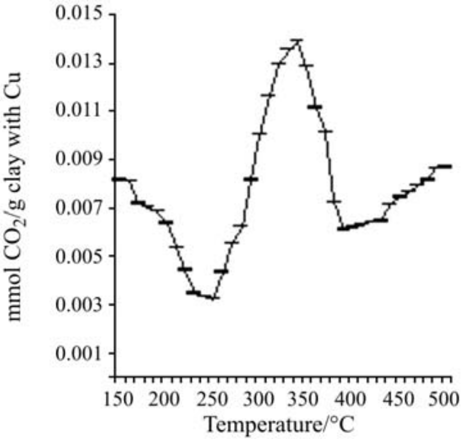

Fig. 5 TPD diagram for basic properties determination. The space basicity variation function on temperature for montmorillonite pillared with copper polyhydroxycations

After preliminary determinations (determination of acid and basic centres [8]), we continued with the study of the depollution kinetics for uranyl cations in dynamic system. We studied the kinetics of the cationic depollution at different isotherms in order to determine the optimum for the depollution process. Synthetic solutions of uranyl chloride in distilled water with $4\cdot10^{-2}$ M concentration were used.

Kinetics of uranyl retention on clay pillared with copper polyhydroxycations, on different isotherms

The method consists in depollution of the synthetic radioactive solutions by mixing them with montmorillonitic pillared clays. The depollution process was studied in dynamic system, under stirring in a discontinuous reactor.

A 10 g sample (clay pillared with copper polyhydroxycations) weighted with precision (four decimals) was introduced in a thermostated reactor [8] that contains 250 mL uranyl synthetic solution of 10^{-4} M. Homogenization was obtained by stirring (200 rot min^{-1}). On pre-established time intervals (10 min) the uranyl concentration was determined using a Genius 20 spectrophotometer. As measure of process time evolution we used the ion exchange degree:

$$G=\frac{\text{IEC}}{\text{IEM}}\cdot 100 \qquad (1)$$

where G – degree of polluants retention (%), IEC – clay ion exchange capacity (meq g^{-1}) calculated with relation:

$$\text{IEC}=\frac{e}{m_\text{p}} \qquad (2)$$

where e – number of equivalents changed (meq); m_p – clay sample mass, (g).

The number of equivalents changed has been determined based on solution analyse, respectively:

$$e=\frac{V(c_\text{i}-c_\text{f})}{E_{\text{g}_\text{M}^{Z+}}} \qquad (3)$$

where V – solution volume (mL); c_i, c_f – initial and final solution concentration (mg mL^{-1}); $E_{\text{g}_\text{M}^{Z+}}$ – gram-equivalent value for the U^{4+} cation, IEM – montmorillonite ion exchange capacity (meq g^{-1}).

Temperature influence on time evolution of the pollutant retention degree. Study on the UO^{2+} cation fixation process in dynamic system on different isotherms

The experiment was realised at isotherm conditions (298, 303, 313 and 353 K). The results obtained at different temperatures are illustrated in curves G–time in Figs 6–9. In order to highlight the origin of the points from the kinetics curves we also presented the raw data (Table 1).

The radioactive elements found in effluents, especially in uranium industrial areas, present a serious risk to generate incurable diseases. This is why the study for establishing efficient methods in radioactive infested waters depollution has flourished. In this paper we illustrated the study of the depollution process through ion exchange involving the fixation of the uranyl cation in the clay matrix.

The diagram showed in Fig. 6 presents the variation of the uranyl fixation degree (G) on the 298 K isotherm, in Fig. 7 for the 303 K isotherm, in Fig. 8 for the 313 K isotherm and in Fig. 9 for the 353 K isotherm. Those diagrams were generated from tables with experimental data (as Table 1) in which we determined the ion exchange capacities (IEC) and then the cation retention degree.

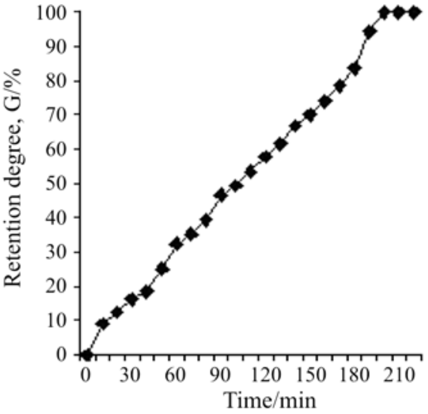

Fig. 6 Variation of the degree of UO^{2+} cation fixation on clay, function on time on the 298 K isotherm

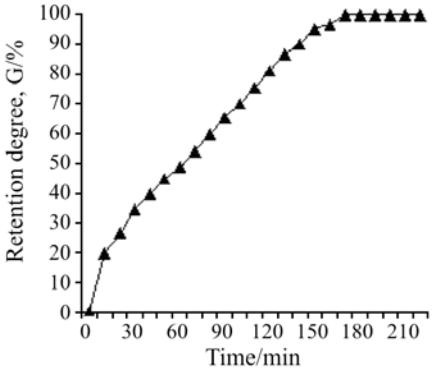

Fig. 7 Variation of the degree of UO^{2+} cation fixation on clay, function on time on the 303 K isotherm

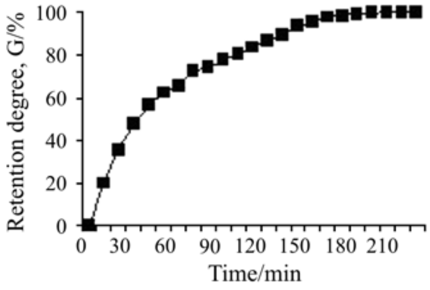

Fig. 8 Variation of the degree of UO^{2+} cation fixation on clay, function on time on the 313 K isotherm

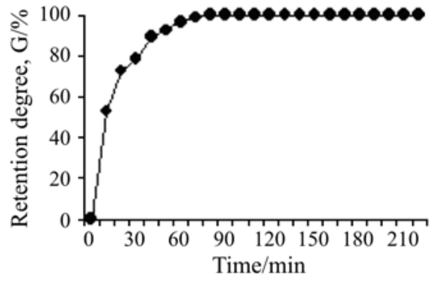

Fig. 9 Variation of the degree of UO^{2+} cation fixation on clay, function on time on the 353 K isotherm

Table 1 UO^{2+} fixation capacity in clay matrix of montmorillonite pillared with copper polyhydroxycation, on the 293 K isotherm

Experiment	Time/ min	IEM/ meq g^{-1}	IEC/ meq g^{-1}	*G*/ %
1	0	5.3	0	0
2	10	5.3	0.580504	9.13
3	20	5.3	0.421975	12.56
4	30	5.3	0.324357	16.34
5	40	5.3	0.285868	18.54
6	50	5.3	0.209984	25.24
7	60	5.3	0.162876	32.54
8	70	5.3	0.149633	35.42
9	80	5.3	0.134347	39.45
10	90	5.3	0.113783	46.58
11	100	5.3	0.107614	49.25
12	110	5.3	0.099121	53.47
13	120	5.3	0.091600	57.86
14	130	5.3	0.086123	61.54
15	140	5.3	0.079365	66.78
16	150	5.3	0.075703	70.01
17	160	5.3	0.071738	73.88
18	170	5.3	0.067456	78.57
19	180	5.3	0.063420	83.57
20	190	5.3	0.056216	94.28
21	200	5.3	0.053021	99.96
22	210	5.3	0.053011	99.98
23	220	5.3	0.053005	99.99
24	230	5.3	0.053005	99.99
25	240	5.3	0.053005	99.99
26	250	5.3	0.053005	99.99
27	260	5.3	0.053005	99.99
28	270	5.3	0.053005	99.99
29	280	5.3	0.053005	99.99
30	290	5.3	0.053005	99.99
31	300	5.3	0.053005	99.99
32	310	5.3	0.053005	99.99
33	320	5.3	0.053005	99.99
34	330	5.3	0.053005	99.99
35	340	5.3	0.053016	99.97
36	350	5.3	0.053170	99.68
37	360	5.3	0.053341	99.36

The direct experimental results (concentration evolution in time) processed by relations (1)–(3) gave the necessary data (Table 1) for drawing the kinetics curves (mmol NH_3 adsorbed/g clay) – (time of contact).

From Figs 6–9 result the temperature influence on the degree of radioactive decontamination of polluted water.

From the diagram result that, an increment of temperature leads to an increment in pollutant radioactive cations retention velocity. The highest depollution degree is obtained at 353 K temperature.

In Fig. 10 are presented all the curves for all the isotherms on which we carried out the experiments. In Fig. 11 we made a comparison between the radioactive pollutant retention kinetics on the clay pillared with aluminium and on natural clay, unpillared, at 353 K.

Analysing the curves presented in Fig. 10 we can see that in all cases they tend to the value corresponding to the total exchange. The increment of the temperature places the curves near the abscissa, which denotes an increasing of the exchange velocity and, in conclusion, the increasing of the radioactive decontamination degree.

As shown in Fig. 10, the optimum value for the temperature in decontamination process of waters pollutes with uranyl, using montmorillonite pillared clay, is 353 K. For the 298 K isotherm retention equilibrium of the uranyl cations, is established after 3 h. For the 303 K isotherm, retention equilibrium of the radioactive uranyl cations is established after 2 h and a half. For the 313 K isotherm, thermodynamic equilibrium for the retention of uranyl is realised after 2 h and for the 353 K isotherm after 1 h.

We also performed a comparative analysis by measuring the depollution capacity of in the case of two materials: montmorillonite unpillared clay and the montmorillonite clay pillared with copper poly-

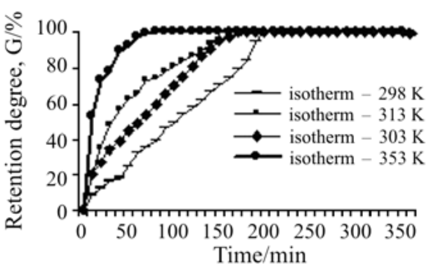

Fig. 10 The variation of the degree of UO^{2+} cation fixation on clay, function on time on different isotherms

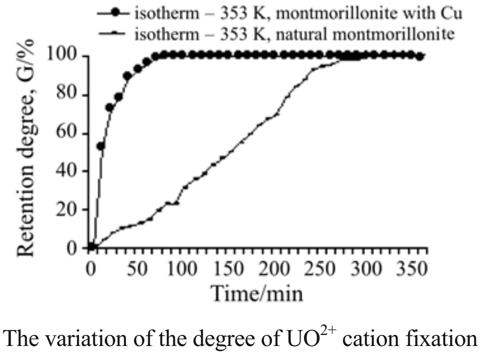

Fig. 11 The variation of the degree of UO^{2+} cation fixation with pillared clay and natural clay on the 353 K isotherm

hydroxycations. The results are presented in Fig. 11; the tests were performed at the optimum temperature determined a priori (353 K).

Analysing the curves from Fig. 11 it can be easily observed that all reach the same floor, but at different time intervals. This means that using montmorillonite pillared clays as decontamination material the adequate value for total exchange is reached after 60 min (at 353 K isotherm). Using as decontamination material montmorillonite clays untreated chemically and unpillared, a total exchange is made after 240 min for the same temperature.

Conclusions

In this paper are presented researches made in the field of decontamination capacity of at waters polluted with radioactive elements, using modified montmorillonite clays with Romanian origin (Valea Chioarului). The researches were carried out in order to obtain some types of clays with good surface properties which make them readily to use in depollutions processes. Several types of chemically modified clays were synthesised. The best surface properties were obtained using clays pillared with copper polyhydroxycations. In order to highlight their surface properties we made measurements with a programmed thermodesorption installation. The best surface properties for the retention of UO^{2+} cations were determined at clays modified by ion exchange and pillared with copper polyhydroxycations. The kinetics tests show the influence of temperature on time evolution of ion exchange degree of UO^{2+} cation, in the case that we use a discontinuous reactor with stirring – dynamic regime.

Description of installations and testing methods is known [8].

The results obtained were presented as kinetics curves *G*–time (Figs 6–11). The highest efficiency of the depollution process is obtained for the clays samples pillared with copper polyhydroxycation on the 353 K isotherm. On this isotherm, the equilibrium of the UO^{2+} retention process with copper pillared clays was obtained after 60 min; utilising other isotherms the equilibrium was obtained after 120 min. When using unpillared clays, the equilibrium of the retention process was obtained after 240 min.

By pillaring method is developed a higher surface, a better porosity and a better accessibility for the pollutant cation at the retaining surface. These improved properties lead to a better diffusion of the pollutant cations at the pillared clay surface and a higher efficiency of the depollution process.

Using this type of microporous materials we realized a depollution process with a 99.99% efficiency, which eliminates the risks of lower quantities of radioactive elements present in waters purified by classical methods.

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