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Removal of uranyl ions by p-hexasulfonated calyx[6]arene acid

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ABSTRACT

Radioactive pollution is a significant threat for the people's health. Therefore highly effective radioactive decontamination methods are required. Ion exchange, biotechnologies and phytoremediation in constructed wetlands have been used as radioactive decontamination technologies for uranium contaminated soil and water remediation. Recently, beside those classical methods the calix[n]arenic derivatives' utilization as radioactive decontaminators has jogged attention. The present work aims to present the preliminary research results of uranyl ion sorption studies on the p-hexasulfonated calyx[6]arenic acid. The effect of temperature, contact time, sorbent amount and uranyl concentration variation on sorption efficiency was investigated. Isotherm models revealed that the sorption process fit better Langmuir isotherm.

1. Introduction

The radioactive environmental pollution represents a continuous challenge for the scientific community due to it is carcinogenic action. The literature shows that uranium causes severe ailments of human body, when is accumulated in kidney, liver and bones [1–4]. The mineral resources' exploitation represents a key pollution source due to the generation of huge amounts of wastes contaminating large land surfaces [2]. Under this context uranium mining activity in Romania during the time has generated about 6,000,000 m^3 of low radioactive material contaminating about 1000 ha of land, pilled up in over 150 waste heaps and stored in two tailing ponds [2].

Since 2001 most of the uranium mining sites have been subjected to the ecological reconstruction and closure operations. Ionic exchange has been used for the radioactive contaminated wastewaters treatment [7–9].

The adsorption on different materials, biotechnologies and phytoremediation were studied as environmentally friendly alternatives to the classical radioactive decontamination methods [5,6,10–28]. Another, relatively recent developed remediation method involves reactive iron nanoparticles utilization for uranium immobilization based on system's redox potential manipulation [29–35].

Flotation has also been investigated as a highly effective remediation tool [36–49]. The literature has reported a new class of organic compounds, generically named calix[n]arenes with derivatives, which have highly selective extraction capacity towards different ionic and molecular species [48–50]. Those represent besides the crown ethers and cyclodextrines an important class of "host" type supramolecular systems. Their ability to "host" different inorganic and organic ionic or neutral species from solutions, solids and gases, introduced them among the most investigated versatile organic tools. The sulfonic, hydroxamic and carboxylic functional groups that substitute, either the hydrogen from the phenolic nuclei or the phenolic hydroxyls, determines their selectivity towards uranium increasing [50–55]. The present contribution aims to point out the uranyl sorption efficiency of the p-hexasulfonic calyx[6]arenic acid from a synthetic solution.

2. Material and methods

All the reagents used were analytical grade. Uranyl nitrate (MERCK) was the investigated uranium (VI) source in all experiments. The synthetic solutions were prepared with deionized water. Uranium (VI) concentration range was 40–80 mg U(VI)/L. The solution pH ranged between 2 and 6. Temperature variation domain was 293.15–323.15 K and sorbent amount was varied from 0.01 to 0.05 g. Contact time ranged between 30 and 180 min.

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The p-hexasulfonated calyx[6]arene acid (CS6) has been synthesized by electrophile substitution reaction, that represent the "upper-rim" reactions of alcoholic groups belonging to the simple calyx[n]arenas.

The p-tert-butylcalyx[6]arene sulfonation using sulfuric acid is resumed by the stoichiometric reaction between p-tert-butylcalyx[6]arene ($C_{66}H_{84}O_6$) and the sulfuric acid when the p-hexasulfonated calyx[6]arene acid ($C_{42}H_{36}O_{24}S_6$) and isobutyl acid sulfate ($(CH_3)_3C{-}OSO_3H$) has resulted as follows:

$$C_{66}H_{84}O_6 + 12H_2SO_4 \overset{T\,^{\circ}C}{\rightarrow} C_{42}H_{36}O_{24}S_6 + 6(CH_3)_3C - OSO_3H + 6H_2O \qquad (1)$$

It runs in respect with the aromatic ring electrophile substitution reactions. The sulfonation reaction mechanism was studied by kinetic determinations. The reaction could be intermediated by the following species: $H_3SO_4^+$, SO_3 or HSO_3^+. The kinetic determinations pointed out, that sulfur trioxide is the sulfonation reagent resulted, when the sulfuric acid is used. It results according to the subsequent equation (Eq. (2)):

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^+ + HSO_4^- \qquad (2)$$

Sulfur trioxide is a strong electrophile reagent containing an electron-deficient sulfur atom. When it reacts with the aromatic core, a positively charged intermediary occurs. Unlike other substitution reactions to the aromatic core sulfonation is a reversible reaction. The final proton release is a slow reaction, emphasized by sulfonation of isotopic marked aromatic compounds.

Sulfonation reactions are strongly depending on the sulfuric acid concentration and the working conditions. The hexasulfonated calyx[6]arene acid (CS6) synthesis was conducted by direct sulfonation of p-tert-butil-calyx[6]arene with concentrated sulfuric acid (96–98%). The sulfonic derivative of the calyx[6]arene has been separated following the flowsheet showed by Fig. 1.

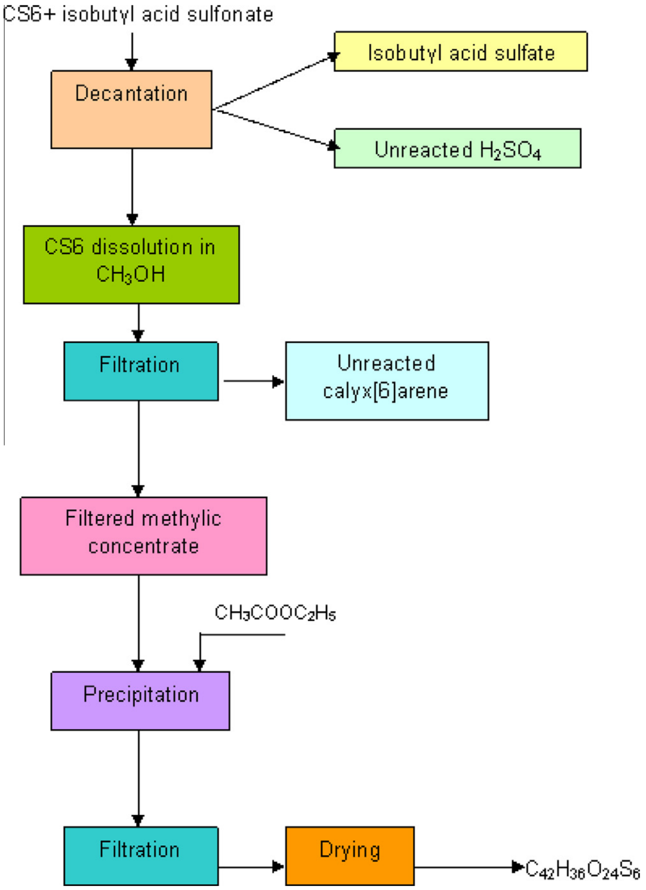

Fig. 1. p-Hexasulfonated calyx[6]arene acid (CS6) separation.

The NMR analysis of the separated product has confirmed its chemical structure as is pointed out in Figs. 2 and 3. The spectral peaks have corresponded to the chemical formulae of p-hexasulfonated calyx[6]arene acid.

Scanning electron microscopy (SEM) analysis was performed using a SEM VEGA II LSH scanning electronic microscope with an EDX QUANTAX QX2 detector.

Sorption was studied in static system. Decontamination efficiency was investigated by determining the specific parameters of the sorption process.

The uptake percentage of uranium (VI) from the solution (%) was calculated according to the following equation:

$$\text{sorption } (\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

where C_0 is the initial concentration of U(VI) (mg L^{-1}) and C_e (mg L^{-1}) is the equilibrium concentration of U(VI) respectively.

The adsorbed amount of uranium (VI) (U) on the adsorbent mass unit (q) has resulted from Eq. (2):

$$q = \frac{(C_0 - C_e) \cdot V}{m}, \ (\text{mg U/g adsorbent}), \qquad (2)$$

where m is the adsorbent mass (g) and V is the volume of solution (L).

The distribution coefficient K_d defined as the ratio between the U(VI) concentration of the uploaded adsorbent and the one in the solution at the equilibrium state was calculated according to the Eq. (3):

$$K_d = \frac{(C_0 - C_e)}{C_e} \cdot \frac{V}{m} \ (\text{mL g}^{-1}) \qquad (3)$$

where C_0 is the initial concentration of U(VI) (mg L^{-1}) and C_e (mg L^{-1}) is the equilibrium concentration of U(VI), V is the volume of solution (mL) and m is the adsorbent mass (g).

The effect of the adsorption parameters (temperature, contact time, adsorbent mass) on the decontamination efficiency was studied by varying one parameter and keeping the others constant. All the experiments were carried out in duplicate with a standard error of 5%.

3. Results and discussion

3.1. Contact time effect on decontamination efficiency

The U(VI) adsorption was studied using a synthetic solution with three different concentration: 40, 60 and 80 mg/L at a pH value of 4.5 and a temperature of 293.15 K. The adsorbent mass was 0.05 g and the contact time ranged between 30 and 180 min. Fig. 4 shows that sorption equilibrium was reached after 120 min.

3.2. Temperature effect on the decontamination efficiency

The temperature is an important parameter that influences the adsorption process. Therefore it was studied and was varied in the field 293.15–323.15 K. The obtained experimental results on equilibrium (Fig. 5) pointed out that the adsorption is an endothermic process enhanced by the high temperatures.

3.3. Adsorbent mass effect on decontamination efficiency

Another important economically influencing factor is the amount of the adsorbent used in the decontamination process. The higher adsorbent amount used, the less effective is the process.