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Uranium (VI) adsorption equilibrium on purolite resin SGA 600 U/3472+

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Abstract: This paper characterizes uranium (VI) sorption from synthetic solutions using a fixed bed Purolite resin SGA 600 U/3472 system. The effect of the sulphate anion presence in the liquid phase on sorbtion dynamics and equilibrium is analysed. In the industrial processing of solutions obtained from leaching of uranium ore (alkaline/acid), in a continuous system, there are several compounds which strongly compete with uranium for ion exchange sites and consequently these substances depress the uranium adsorption. The influence of vanadate, molybdate, chloride, and nitrate is known, therefore, in this paper, the adsorption equilibrium isotherms for uranium (VI) are obtained for different sulphate ion concentrations in solution. The adsorption capacity variation of the Purolite resin SGA 600U/3472 with the number of adsorption/desorption cycles is also studied. The experimental results reveal the negative impact of high sulphate ion content in solution on the adsorption capacity of the resin Purolite SG 600 U / 3472 with uranium (VI) and therefore it is considered one of the compounds which strongly affect the uranium adsorption.

Keywords: *Uranium • Sulphate • Adsorption • Ion exchange resin • Loading capacity*

1. Introduction

The industrial application of ion exchange is widespread in areas that range from water softeners, wastewater treatment and analytical chemistry to purify pharmaceuticals, precious and radioactive metals [1-4]. Nowadays, ion exchange process is widely used in many industrial applications or research areas. Fixed bed columns are commonly used because of their advantages: high endurance at mechanical degradation in both stirred or moving beds, easy to work with, the system can be fully automated, easy regeneration with high recovery of the species of interest [5,6]. There are several methods of phase contacting depending on significant factors (the chemical content of used solutions, operational costs, etc.) such as stage wise or differential contacting, with single or multiple contact, in fixed, fluidized, stirred or moving bed [7,8,9].

The efficacy of ion exchange process is influenced by various parameters: the chemical composition and flow rate of feed solution, total capacity of ion exchanger, fixed bed height, operating temperature. Among these parameters an important role is held by the ion exchanger selectivity which is used in ion substitution, ion separation or ion removal. The affinity of ion exchangers have been the subject of many papers and simple rules were mapped. It has been developed for the situations where toxic ion substituion or column ion exchange separation occur [8-12].

Important areas of use of granular ion exchangers are chemistry (analytic, organic and inorganic), medicine, food industry, wastewater treatment, uranium hydrometallurgy [11-13]. Due to the wide range of use and various industries applications ion exchange process was the subject of many research papers [8-12].

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The purpose of the research presented in this paper was to determine how sulphate ion concentration affects adsorption capacity of uranium (VI) with a Purolite SGA- 600U/3472 ion exchange resin. The influence of sulfate ions on uranium adsorption capacity of this resin was investigated in dynamic conditions using various solutions with different compositions. The resin was also tested for several cycles of adsorption/desorption to estimate its lifetime and maximum adsorption capacity. These results can be used to a certain extent in industrial application and to establish optimal parameters in ion exchange operation.

2. Experimental procedure

2.1. Materials and methods

The Purolite SGA- 600U/3472 ion exchange resin, used in this research, was supplied by PUROLITE. It is a strongly basic anionite, with gel structure, special type for soluble anionic complexes for uranium recovery from acidic or alkaline medium. Structurally, this anionite is a polystyrene polymerized with divinylbenzene, with excellent integrity of the granules and mechanical strength at applications with the features showed in Table 1.

The activation of the resin for uranium adsorption was done by repeated treatment with sodium hydroxide (NaOH) 4%, (HCl) 4% and water (H_2O) as follows: the resin was soaked in a 4% NaOH solution and washed until a pH = 7 is reached. After that, the resin was contacted with a 4% HCl solution and the resin was washed with distilled water near neutral and it was ready for experiment.

2.2. Chemical reagents

In order to determine the influence of SO_4^{2-} ion over the resin loading capacity with U(VI), adsorption trials were performed on three clear synthetic solutions similar to the industrial solutions obtained from leaching of uranium ore, with different ionic composition of the sulphate ion namely: U - 0.66 g L^{-1}; CO_3^{2-} - 8.97 g L^{-1}; HCO_3^{-} - 8.85 g L^{-1} ; SO_4^{2-} - 10.03 g L^{-1}; (SO_4^{2-} - 23.83 g L^{-1}; SO_4^{2-} - 32.13 g L^{-1}). The synthetic uranium solution was prepared from uranyl sulphate (UO_2SO_4) and sodium carbonate (Na_2CO_3) by dissolving the uranyl sulfate in distilled water and adding sodium carbonate to obtain the alkaline medium. For the solutions with various sulfate ion composition a specific volume of sulphuric acid (97% - Merck) was added to the synthetic solution. All used chemicals had analytical grade (Merck - Germany).

Table 1. Properties of the Purolite SGA- 600U/3472 ion exchange resin.

Appearance:	spherical beads
Functional group:	type 1 quaternary ammonium ionic
Ionic form:	chloride, Cl^-
Total capacity (min.):	1.4 eq L^{-1} (30.6 Kg ft^{-3}) (Cl^- form)
Moisture retention:	40 - 50% (Cl^- Form)
Particle size range:	800 - 1300 μm
Reversible swelling, $Cl^- \rightarrow OH^-$	(max.) 20%
Shipping weight:	675 - 700 kg m^{-3}
Temperature limit, Cl^- Form:	100°C
Temperature limit, OH^- Form:	60°C

2.3. Experimental methodology

For testing fixed-bed adsorption, in dynamic conditions with a flow rate of 5 BEV h^{-1} (BEV, Bed Equivalent Volume resin), a 10 mm diameter glass column was used. The column was fitted at the ends with frits in order to prevent resin loss by entrainment in the effluent. For analytical control 50 mL volumes of effluent were collected.

The concentration of uranium ions for the initial and final solution was established by colorimetric method according to romanian standard (STAS 12849/1-90), using a spectrophotometer UV-VIS CECIL 1011. Reagents used were of chemical or analytical purity (for analyzes) and were used without further treatment.

2.4. Calculation

The mean momentary resin adsorption capacity with U(VI), q_i, was determined by the difference between the amount of uranium in the initial and final solution, per volume of resin (Eq. 1).

$$q = \frac{\sum_{j=1}^{i} G_v (c_{uin} - c_{ufj}) \tau_j}{V_r} \quad (1)$$

where c_{uin} is the uranium concentration of initial solution, g L^{-1}, c_{ufi} is the momentary uranium concentration at bed exit solution, g L^{-1}, V_r is the volume of resin, L, and G_v represent the volumetric flow rate of solution which traverse the resin bed (G_v = 5 BEV h^{-1} × 5×10^{-3} L BEV^{-1}). The effect of the number of cycles of adsorption/desorption on sorption dynamics and equilibrium in respect to the Purolite resin SG 600 U / 3472 was obtained by using of a synthetic solution containing 10 g L^{-1} SO_4^{2-}. In this case for uranium desorption from the resin a chlorine solution (100 g L^{-1} NaCl with

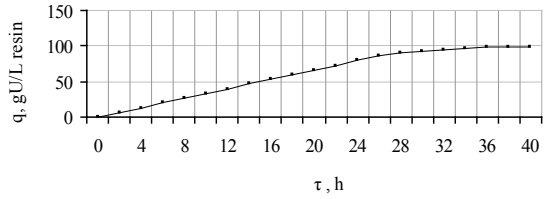

Figure 1. The dynamics of isothermal saturation with uranium (VI) of Purolite resin SG 600 U / 3472 Conditions: i) anions solution composition: U (VI) -0.66 g L^{-1}; CO_3^{2-} -8.97 g L^{-1}; HCO_3^- -8.85 g L^{-1}; ii) t=20°C.

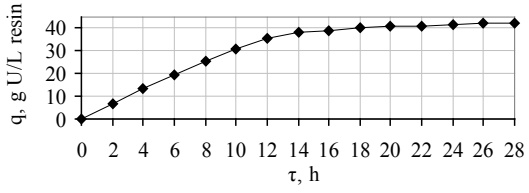

Figure 2. The dynamics of sothermal saturation with uranium (VI) of Purolite resin SG 600 U / 3472. i) anions solution composition: U (VI)-0.66 g L^{-1}, CO_3^{2-} -8.97 g L^{-1}, HCO_3^- -8.85 g L^{-1}, SO_4^{2-} -10 g L^{-1}; ii) t=20°C.

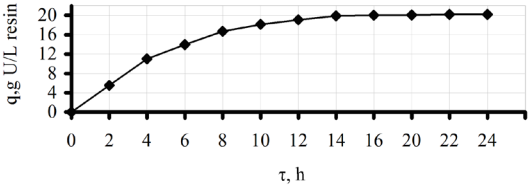

Figure 3. The dynamics of isothermal saturation with uranium (VI) of Purolite resin SG 600 U / 3472. i) anions solution composition: (i) U - 0.66 g L^{-1}, CO_3^{2-} -8.97 g L^{-1}, HCO_3^- -8.85 g L^{-1}, SO_4^{2-} - 23 g L^{-1}, ii) t=20°C.

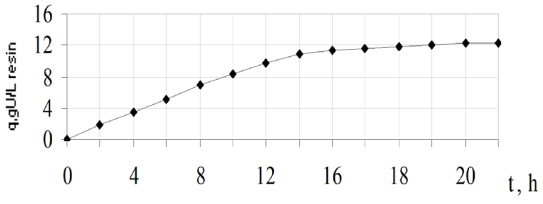

Figure 4. The dynamics of isothermal saturation with uranium (VI) of Purolite resin SG 600 U / 3472. i) anions solution composition: (i) U (VI) -0.66 g L^{-1}, CO_3^{2-} -8.97 g L^{-1}, HCO_3^- -8.85 g L^{-1}, SO_4^{2-} -32 g L^{-1}; ii) t=20°C.

10 g L^{-1} Na_2CO_3) at a flow rate of 1 BEV h^{-1} with a sampling interval of 1 hour was used. All reported data correspond to 20°C working temperature.

3. Results and discussions

The adsorption-desorption of uranium from carbonate solutions occurs according to the Reaction 2:

$$4\left(R^+ - Cl^-\right) + \left\{4Na^+ + \left[UO_2\left(CO_3\right)_3\right]^{4-}\right\} \Leftrightarrow \Leftrightarrow \left\{4R^+ - \left[UO_2\left(CO_3\right)_3\right]^{4-}\right\} + 4\left(Na^+ - Cl^-\right) \quad (2)$$

The experimental results given by Figs. 1-5 shows the dynamics of uranium (VI) concentration retained in Purolite resin. The difference between Fig. 1 and Figs. 2-4 is given by SO_4^{2-} concentration of U (VI) in working solution.

The adsorption capacity of uranium (VI) in Purolite resin SGA 600 U/3472 from solutions without sulfate anions according to the data presented is 98.85 g U(VI) L^{-1}. Also it is easy to observe that in this case the U(VI) distribution constant is very high ($k_d = c_{s\infty} / c_{l\infty}$ = 98.85/0.66 = 147 (g U/L_{rs}) (g U/L_{sol})$^{-1}$. From slope of dependency q *vs.* τ it establish that the resin U(VI) retention rate is very close to 4.16 g U(VI) (L_{rs} h)$^{-1}$.

The experimental results obtained for a solution containing 10 g L^{-1} SO_4^{2-} are shown in Fig. 2.

As can be seen from the data presented, the uranium adsorption capacity of Purolite resin SGA 600 U/3472 from solutions containing 10.03 g L^{-1} SO_4^{2-} is 42.31 gU L^{-1}, is lower than the adsorption capacity of the non sulfate solution. The participation of SO_4^{2-} to sorption process strongly affect the U(VI) distribution constant, which is now k_d = 63.7 (gU L_{rs}^{-1}) (gU L_{sol}^{-1})$^{-1}$. Due to competition of the CO_3^{2-}, HCO_3^- , SO_4^{2-} anions, which are present in solution in much larger quantities, the resin U(VI) retention rate decreases and the uranium retention rate decreases to 2.66 g U(VI) (L_{rs} h)$^{-1}$.

The experimental data obtained for a solution containing 23 g L^{-1} SO_4^{2-}, presented in Fig. 3, revealed an increasing sulfate concentration accelerating the diminishing of U(VI) distribution constant and of resin U(VI) retention rate.

According to the results presented, the adsorption capacity with uranium of Purolite resin SGA 600 U/3472 for this solution is 20.18 gU L^{-1} resin; this value of the resin adsorption capacity is five times smaller than the ideal solution and twice lower than in the solutions from preceding cases.

The experimental results obtained for a solution containing high sulfate concentration (32 g L^{-1} SO_4^{2-}), shown in Fig. 4, lead to the conclusion that the negative effect of the high concentration of sulfate on retention of U(VI) in the resin is more powerful than linear. Now k_d down to 18.46 (gU L_{rs}^{-1}) (gU L_{sol}^{-1})$^{-1}$ whereas the resin U(VI) retention rate decreases to below 0.75 g U(VI) (L_{rs} h)$^{-1}$.

Figs. 1-4 show that with increasing of concentration of SO_4^{2-} in solution, the sorption equilibrium and the sorption dynamics relative to uranium (VI) are strongly affected.

The increase of sulfate ions drastically affects the rate of uranium adsorption and, consequently, the operating capacity of the resin. When a decision is taken regarding the installation of an alkaline treatment circuit, it should be kept in mind that uranium capacity loss attributed to an increased sulfate ions can be overcome by removal of SO_4^{2-} anions contained in the solution in increasing amounts.

The results shown agree with similar data from literature [16,17] particularly with the increase in sulfate ion concentration values, and the decreased ion exchange resin adsorption capacity. This decrease is explained by the competition of sulfate ions with uranium for adsorption on the resin. This mechanism should be understood as it is only a decrease of the uranium adsorption capacity of the resin, with its nominal capacity remaining the same, constant, as a function on the number of active groups placed inside the resin by synthesis.

The repetitive reuse of Purolite resin SGA 600 U/3472 resin is another process factor with important effect on sorption equilibrium and the sorption dynamics relative to uranium (VI). Fig. 5 reflects the experimental results for the adsorption capacity depending on the number of cycle of adsorption/desorption.

The results shown in Fig. 5, show that the adsorption capacity of the resin drops to 71.42% of its initial capacity after 50 cycles and after 100 cycles the capacity drops to 42.86%, for more cycles, the capacity doesn't change much.

4. Conclusions

The experimental results revealed the negative impact caused by the increasing sulphate ion content in solution, on the adsorption capacity of the resin Purolite SG 600 U / 3472 for uranium (VI). For a solution with 10 g L^{-1} SO_4^{2-} the adsorption capacity with uranium (VI) is 42.31 gU L^{-1} resin, for a solution containing 23 g L^{-1} SO_4^{2-} is 20.18 gU L^{-1} resin and for a solution with a 32 g L^{-1} SO_4^{2-} content is 12,19 gU L^{-1}, compared with adsorption for ideal solutions where the resin loading was 98.85 gU L^{-1}. The study of the adsorption capacity of uranium (VI) on the resin Purolite SG 600 U / 3472 showed that uranium (VI) adsorption decreased with an increasing number of cycles, after 150 cycles of adsorption the capacity was 39.68% of the initial capacity of the resin.

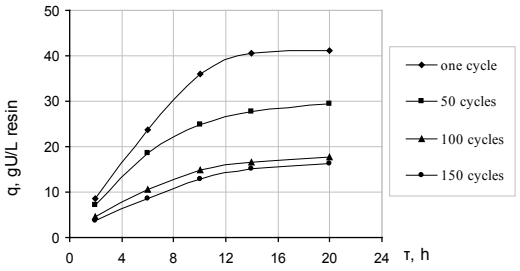

Figure 5. Effect of cycles sorption number on dynamics of isothermal saturation with uranium (VI) of Purolite resin SG 600 U / 3472. i) anions solution composition:U (VI) -0.66 g L^{-1}, CO_3^{2-} -8.97 g L^{-1}, HCO_3^- -8.85 g L^{-1}, SO_4^{2-} -10 g L^{-1}; ii) t=20°C.

The resin adsorption capacity of uranium is diminished because of the competition with CO_3^{2}, HCO_3^-, SO_4^{2-} anions contained in the solution in increasing amounts. The effect of sulphate ion on adsorption capacity of Purolite resin SG 600 U/3472 is due to the equilibrium changes from the liquid phase. Without sulphate ions (effective SO_4^{-2} is present from UO_2SO_4) in the alkaline media the complexation of the U (VI) as $UO_2(CO_3)_3^{4-}$ is very strong. By adding sulphate ions (sulphuric acid supplementation) in the liquid phase other complexation such as carbonato-complexes as well as carbonato- hydroxo-complexes [18]:

$$\sum_{\alpha,\beta}\alpha[(UO_2)_\alpha(CO_3)_\beta]^{2\alpha-2\beta}, \sum_{i,j,k} i[(UO_2)_i(CO_3)_j(OH)_k]^{2i-2j-k},$$

$$[(UO_2)_3O(OH)_2HCO_3^+]$$

appear. These complexes are no longer active in the ion exchange process. The reported data from Figs. 1–4 seem to show a formal kinetic of pseudo second order type when both adsorbate ($UO_2(CO_3)_3^{4-}$) and adsorbent (functional sites of Purolite resin) are involved in the rate determining step of the sorption process. The decreasing of active $UO_2(CO_3)_3^{4-}$ concentration in liquid determines the decrease of resin sorption capacity.

The knowledge of the changes in Purolite resin loading capacity SG 600 U / 3472 depending of sulphate ion content in solutions and the adsorption / desorption number of cycles is required to establish further optimal parameters in ion exchange operation. When choosing this type of resin the operating capacity of the resin, durability and resistance to fouling of the resin in presence of a high content of sulfate ions should be considered.

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