



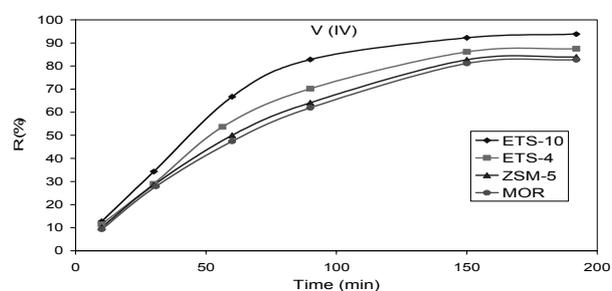
ADSORPTION OF Co(II) AND V(IV) SPECIES ON ZEOLITES

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This paper describes a kinetic study on the uptake on ETS-10, ETS-4, ZSM-5 and MOR zeolites of the Co(II) and V(IV) chemical species contained in the sludge resulted after alkaline leaching of UO_2^{2+} ions from uranium ores. The increase in time of retaining degree of these chemical species on solid zeolites and the characteristic parameters resulted from Langmuir and Freundlich adsorption isotherms are established. A new easier method to determine the kinetics of adsorption process of Co(II) and V(IV) species on these zeolites is proposed. Based on the accounted parameters from these adsorption isotherms, it was concluded that the retaining process of Co^{2+} cations is more intense than that of vanadyl ions for a weak acid pH. The adsorption processes are followed a pseudo-first order kinetics depending on the nature of zeolites and ionic species.



INTRODUCTION

Purification of the environment contaminated with heavy metals, radionuclides or various chemical compounds has attracted many researchers. Different approaches to remove these chemical species from the environment, such as ion exchange, precipitation, phytoextraction, ultra filtration, reverse osmosis, electrodialysis, adsorption on various porous materials were previously developed to remove these polluting agents from environment. Thus, for the remediation of contaminated wastewaters with heavy metal ions resulting from different industrial technologies, some low cost natural absorbent materials provided from agricultural wastes as activated carbon such as: char carbons, coconut husk carbons, coconut shell charcoal, or various minerals and chemical

compounds embedded in silica gel, as chelating substances have been used.¹⁻⁵

Some microbiological collectors and hydrophytic plants which were tested for purification of wastewaters contaminated with heavy metals or radioisotopes resulting from nuclear facilities have been exhaustively described in a series of monographs and papers.⁶⁻¹³

Meanwhile, one of the most remarkable approaches for the decontamination of wastewaters containing heavy metals or other chemical pollutants and petrochemicals, was based on the use of natural and synthetic zeolites.¹⁴⁻¹⁸ Thus, in order to remove a lot of cations or different inorganic anions from wastewaters, clinoptilolite, mordenite and montmorillonite, or ZSM-5, MCM-41, H_4Y , etc, were tested, when a high level cleaning degree by ion exchange between chemical species and solid zeolite was achieved.

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In this paper an original method to determine the kinetics of adsorption process of Co(II) and V(IV) species on ETS-10, ETS-4, ZSM-5 and MOR zeolites is proposed. The data derived from the adsorption isotherms show that under acidic conditions, the retaining processes of Co^{2+} and VO^{2+} ions are something different.

RESULTS AND DISCUSSION

In order to determine the adsorption degree (R) of the metal ions on zeolite, the following equation was used:

$$R = \frac{C_0 - C}{C_0} \times 100 \text{ (%),} \quad (1)$$

where C_0 and C refer to the ion concentration (mmol/L) of the initial solution and that after a given contact time with the sorbent.

In Fig. 1 the variations of cobalt and vanadium ions adsorption on the 0.117 g from four proposed zeolites, at different time intervals are plotted. The initial concentrations of solutions were: 0.140 mmol/L for Co^{2+} and 0.144 mmol/L for VO^{2+} , at room temperature and 6.0 - 6.5 pH values.

Considering Langmuir equation:

$$\frac{1}{q} = \frac{1}{q_0 \cdot K_L \cdot C} + \frac{1}{q_0}, \quad (2)$$

the plotting of the experimental results in $\frac{1}{q} = f\left(\frac{1}{C}\right)$ coordinates, adsorption isotherms result as straight lines that intersect the ordinate axis.

The term “ q ” from the previous relation describes the amount of metal ion retained on the solid mass (mmol/g zeolite), which is calculated with the equation:

$$q = \frac{C_0 - C}{m} \cdot V, \quad (3)$$

where V represents the initial volume of the solution that is in contact with m grams of zeolite.

By intercept of each curve with the ordinate axis (corresponding to a reactant system) can be calculated the equilibrium saturation capacity (q_0) and the slope means the value of the bond energy or interactions strength (K_L) between the zeolite and retained ions.

On the other hand, between the saturation capacity at equilibrium, q_0 (which corresponds to the formation of ions monolayers on the zeolite surface), and the maximum adsorption capacity, q_m , there is a similar relationship as the previous one (2):

$$q_m = q_0 \frac{K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \quad (4)$$

where C_{eq} represents the ion concentrations at equilibrium for 180 min and q becomes q_m .

Taking into consideration the experimental data plotted in the $\ln q = f(\ln C)$ coordinates and based on the relation:

$$\ln q = \ln K_F + \frac{1}{n} \ln C, \quad (5)$$

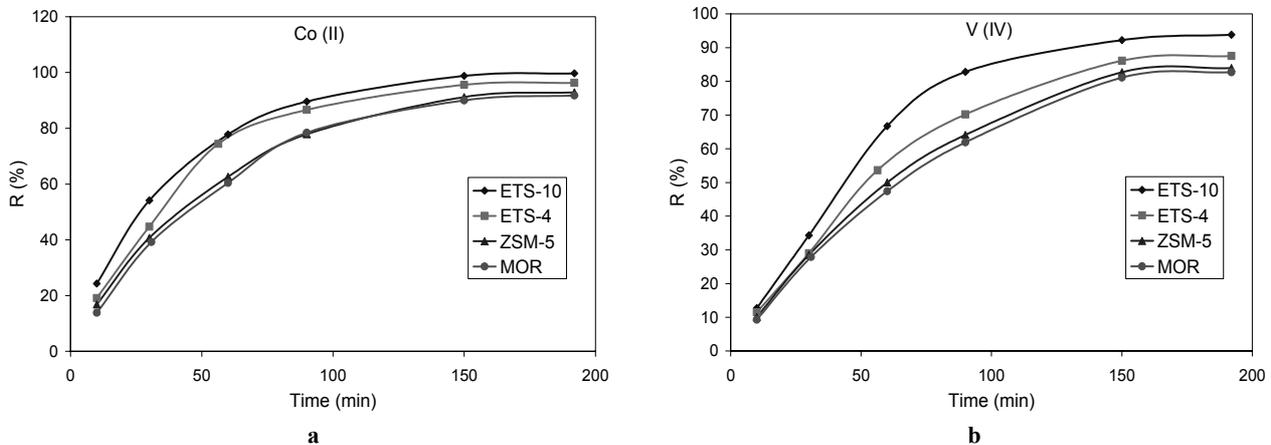


Fig. 1 – The time depending adsorption of cobalt (a) and vanadium (b) species on ETS-10, ETS-4, ZSM-5 and MOR zeolites.

Freundlich adsorption isotherms are determined. The adsorption capacity, K_F , for a given adsorbent system, is obtained by intercept of the straight line with the ordinate, and the slope gives the retaining intensity ($tg\alpha = \frac{1}{n}$) of the chemical species on

zeolite surface, which depends on the heterogeneity degree of the solid surfaces exposed to these interactions.

The experimental data obtained from the Langmuir and Freundlich adsorption isotherms are rendered in Tables 1 and 2.

Table 1

The Langmuir and Freundlich parameters of Co(II) species extracted on the ETS-10, ETS-4, ZSM-5 and MOR zeolites for 3h contact time

Zeolite	C_0 (mmol/L)	m (g) zeolite	C (mmol/L)	q (mmol/g zeolite)	Langmuir		Freundlich	
					q_m (mmol/g)	K_L (L/mmol)	K_F (mmol/g)	n
ETS-10	0.140	0.052	0.064	8.411	28.61	0.05	1.32	0.74
		0.117	0.043	5.094				
		0.208	0.031	3.101				
		0.306	0.023	2.248				
		0.516	0.020	3.130				
ETS-4	0.140	0.052	0.070	7.942	10.47	0.14	1.23	0.79
		0.117	0.049	4.589				
		0.208	0.036	2.951				
		0.306	0.031	2.094				
		0.516	0.022	1.348				
ZSM-5	0.140	0.052	0.073	7.557	7.01	0.17	1.14	0.92
		0.117	0.061	4.010				
		0.208	0.052	2.485				
		0.306	0.040	1.856				
		0.516	0.024	1.336				
MOR	0.140	0.052	0.080	6.826	3.40	0.29	0.12	0.97
		0.117	0.070	3.538				
		0.208	0.056	2.394				
		0.306	0.049	1.751				
		0.516	0.031	1.246				

Table 2

The values of characteristic parameters resulted from Langmuir and Freundlich isotherms for adsorption of V(IV) on the solid zeolites for 3h contact time

Zeolite	C_0 (mmol/L)	m (g) zeolite	C (mmol/L)	q (mmol/g zeolite)	Langmuir		Freundlich	
					q_m (mmol/g)	K_L (L/mmol)	K_F (mmol/g)	n
ETS-10	0.144	0.052	0.101	4.211	15.38	0.06	1.38	1.76
		0.117	0.075	3.025				
		0.208	0.048	2.357				
		0.306	0.041	1.732				
		0.516	0.026	1.164				
ETS-4	0.144	0.052	0.104	3.942	8.64	0.10	1.34	2.04
		0.117	0.087	2.487				
		0.208	0.075	1.766				
		0.306	0.048	1.607				
		0.516	0.029	1.137				
ZSM-5	0.144	0.052	0.109	3.461	3.84	0.19	1.21	2.37
		0.117	0.095	2.170				
		0.208	0.079	1.610				
		0.306	0.067	1.244				
		0.516	0.035	1.083				
MOR	0.144	0.052	0.119	2.480	3.17	0.20	1.13	2.83
		0.117	0.100	1.965				
		0.208	0.080	1.423				
		0.306	0.065	1.314				
		0.516	0.0402	1.027				

Based on the previous quoted papers and considering the resulted parameters accounted from Langmuir and Freundlich adsorption isotherms, it could be assumed that the uptake of Co^{2+} ions (with ionic radius = 0.74 Å) is more intense due to the higher values of q_m and K_F than for the vanadyl cations ($r_{\text{VO}^{2+}} = 1.56$ Å) in weak acid conditions. Moreover the smaller values of K_L for Co^{2+} ions means that less free sorption energy is necessary for their retain on the zeolite mass than for adsorption of VO^{2+} species. For the values of $n \geq 0.8$ is much probable a physical adsorption on solid masses of these simple or hydrated $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{VO}(\text{H}_2\text{O})_4]^{2+}$ species.

Therefore the values shown in Tables 1 and 2 point out a higher adsorption on zeolites of Co(II) species than for V(IV) ones. Furthermore a higher adsorption degree of studied species on ETS-10 than for the other sorbents taken into consideration can be explain rather due to a difference between ionic radii of retained species than the pores size and the values of cationic exchange capacities of zeolites.¹⁹ It seems the principal retaining process on these sorbents is rather connected to Co(II) and V(IV) adsorption on the surface of zeolites than other less possible interactions inside of solid masses as their diffusion or cations exchange.

The characterization of the adsorption process of Co(II) and V(IV) species on zeolites from a kinetic point of view was achieved by use an easier method, instead of previously described²⁰ one, which was based on the fit between the q_0^{exp} and q_0^{theor} values.

As is known the fact that the q_0^{exp} values are established from Langmuir isotherms, meanwhile the q_0^{theor} parameters are deduced by plotting of first or second-order kinetics relations in the coordinates: $\ln(q_0 - q_t) = f(t)$ or $t/q_t = f(t)$.

To determine by means of this new proposed approach, how followed the studied adsorption processes the pseudo-first-, or pseudo-second order of kinetics, the corresponding integrated equations are taken into consideration:

$$k_1 = \frac{1}{t_2 - t_1} \ln \frac{C_1}{C_2}, \quad (6);$$

and

$$k_2 = \frac{1}{t_2 - t_1} \left[\frac{1}{C_2} - \frac{1}{C_1} \right], \quad (7)$$

From these kinetics relations the rate constants (k_1 and k_2) for the more experimental pairs of values: $(C_1 - C_2)$ and $(t_1 - t_2)$, or $(C_2 - C_3)$ and $(t_2 - t_3)$, etc., are accounted.²¹

If the values of the rate constant k_1 : $k_1^{(1)}$, $k_1^{(2)}$, $k_1^{(3)}$... or k_2 : $k_2^{(1)}$, $k_2^{(2)}$, $k_2^{(3)}$... are closer to an average value for k_1 or k_2 , respectively that the determining step of the reaction rate corresponds to the first or second order kinetics. The results of kinetic study are presented in Tables 3 and 4.

Table 3
The values of k_1 and k_2 rate constants for adsorption reactions of Co(II) on 0.117 g zeolites

Zeolite	Time (min)	0	10	30	60	90	150
		C [mmol/L]	0.140	0.106	0.064	0.031	0.014
ETS-10	k_1 [min^{-1}]	0.027	0.025	0.024	0.026	0.028	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0039	0.0052	0.0094	0.021	0.0915	
	C [mmol/L]	0.140	0.113	0.077	0.036	0.019	0.006
ETS-4	k_1 [min^{-1}]	0.021	0.019	0.024	0.021	0.021	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0028	0.0035	0.0084	0.0145	0.031	
	C [mmol/L]	0.140	0.116	0.083	0.052	0.031	0.012
ZSM-5	k_1 [min^{-1}]	0.018	0.016	0.015	0.017	0.015	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0024	0.0029	0.0040	0.0075	0.013	
	C [mmol/L]	0.140	0.121	0.085	0.056	0.030	0.014
MOR	k_1 [min^{-1}]	0.014	0.017	0.014	0.020	0.012	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0019	0.0029	0.0035	0.0085	0.010	

Table 4
The values of rate constants k_1 or k_2 for retaining process of V(IV) on 0.117 g zeolites

Zeolite	Time (min)	0	10	30	60	90	150
		C [mmol/L]	0.144	0.126	0.095	0.048	0.025
ETS-10	k_1 [min^{-1}]	0.013	0.015	0.021	0.021	0.013	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0020	0.0026	0.0067	0.012	0.016	
	C [mmol/L]	0.144	0.128	0.103	0.075	0.043	0.020
ETS-4	k_1 [min^{-1}]	0.012	0.011	0.010	0.018	0.012	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0015	0.0019	0.0023	0.0064	0.0087	
	C [mmol/L]	0.144	0.130	0.103	0.079	0.052	0.025
ZSM-5	k_1 [min^{-1}]	0.011	0.011	0.009	0.013	0.012	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0016	0.0019	0.0019	0.0043	0.084	
	C [mmol/L]	0.144	0.131	0.104	0.082	0.055	0.027
MOR	k_1 [min^{-1}]	0.010	0.011	0.008	0.013	0.011	
	k_2 [$\text{L mol}^{-1} \text{min}^{-1}$]	0.0014	0.0019	0.0017	0.0039	0.0060	

From the experimental data it can be observed that the uptake of Co(II) and V(IV) species on ETS-10, ETS-4, ZSM-5 and MOR zeolites undergoes a pseudo-first order kinetic reaction. Based on these results, the retaining of Co(II) and V(IV) chemical species is mainly achieved rather by a physical adsorption on the external surface or inside of zeolitic pores than through an ionic exchange.

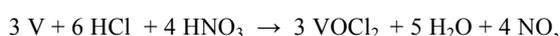
EXPERIMENTAL

The zeolites were supplied by several chemical companies and their values of pores size and CEC taken from literature mentioned above are rendered in Table 5.

After alkaline leaching of uranyl ions from uranium ores, the resulted sludge as a slime pulp dark colored effluent solution was left for a week for settling down of brown-black solid mass. The water was drawing off from the rest of sludges which was used afterwards for experiments.

An amount of 0.5 kg of solid uranium slurry was placed in a 4 L covered porcelain capsule and then the solid mass was totally covered with aqua regia (3 vol HCl_{conc} + 1 vol $\text{HNO}_{3\text{conc}}$). The obtained mixture, stirred continuously, was left for maceration for one week at room temperature. Then, over the reactant system about 10 volumes of distilled water were added to facilitate the metallic ions transfer into solution, removed from sludges as soluble compounds.

In the case of cobalt and vanadium microelements, the aqua regia reacts as follows:



bringing them in ionic form. Much more the two ions Co^{2+} and VO^{2+} can be found as hydrated species: $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and $[\text{VO}(\text{H}_2\text{O})_4]^{2+}$ in weak acid solutions.²²

This reaction mixture was vacuum filtered through a G-3 glass crucible. Then, the solid mass, deposited on the filter, was washed several times with distilled water and for subsequent experiments the resulting solution containing microelements leached from the uranium sludges was used. The volume of the filtered solution was adjusted by evaporation to 2 L. Finally, the pH of the resulted solution was adjusted slowly by means of a ammonium hydroxides (25%), till 5.5- 6.0 to carrying out the Fe^{3+} , Al^{3+} , Cr^{3+} , and Ti^{4+} as solid hydroxides or hydrated oxides. From the remaining in solution of metallic ions, this study is focused to the adsorption of Co (II) and V(IV) species on ETS-10, ETS-4, ZSM-5 and MOR zeolites only in different experimental conditions. For all experiments the concentrations of cobalt and vanadium species were determined by atomic absorption spectrometry using a Continuum Source Atomic Absorption Spectrometer – contrAA® 300.

Afterwards 50 mL capacity cylindrical glass vials were filled with different amounts of solid adsorbents and 10 mL from this new prepared solution containing Co(II) and V(IV) species together with other leached microelements. At given time intervals, from glass vials, amounts of 3 mL solution were taken out in order to determine the cobalt and vanadium concentrations by atomic absorption spectrometry.

In fact, all experiments took into account two aspects:

a) to follow the variation of concentration Co(II) and V(IV) species depending on the zeolite-solution contact time: 10, 30, 60, 90 and 150 min for the same amount of adsorbent (0.117 g); and

b) to study for the same contact time (180 min) the decrease of Co(II) and V(IV) concentrations after their uptake from solutions on different amounts of zeolites: 0.052, 0.117, 0.206, 0.308 and 0.516 g.

Table 5

The characteristic parameters of used zeolites

Zeolite type	MOR	ZSM-5	ETS-4	ETS-10
Pores size (Å)	7.0	5,5	3.7	8.0
Cation exchange capacity (meq/g zeolite)	2.9	1.75	5.17	4.5

CONCLUSIONS

Present paper studied the possibility to remove the Co(II) and V(IV) microelements from uranium sludges by means of ETS-10, ETS-4, ZSM-5 and MOR zeolites as solid sorbents. This adsorption process was investigated plotting the Langmuir and Freundlich isotherms. In addition, the values of the q_m , K_L , K_F , and n parameters which describe quantitatively the uptake on zeolites of cobalt and vanadium ions, were accounted. The retaining degree of Co(II) and V(IV) chemical species increases when the contact time between studied solutions and zeolites is higher, varying as: ETS-10 > ETS-4 > ZSM-5 > MOR.

On the other hand, this paper proposes a new and easier approach for establishing the kinetics reaction order regarding the dynamic adsorption of the Co(II) and V(IV) species on the solid zeolites. For the studied systems the adsorption process follows pseudo-first order kinetics.

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