

Energetic Aspects Related to Heavy Metals Adsorption on the Surface of Volcanic Tuff I. The Influence of Activation Parameters in Cu^{2+} Adsorption

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Abstract: The article develops some physico-chemical aspects presented along of copper ions adsorption in treatment of wastewaters using volcanic tuff. In the experiments volcanic tuff from Stoiana Pâglișa (Romania) has been used. Different concentrations of NaCl and HCl solutions were used for activation of tuff. The increase of activation solutions' concentrations indicates an intensification of specific adsorption of copper as consequence of energetic changes of the active centers spread on the tuff surface.

Key words: Copper adsorption, clinoptilolite, activation process

INTRODUCTION

Volcanic tuffs with their composition of natural zeolites, belong to hydrated aluminosilicates with three dimensional structure characterized by the associated anionic tetrahedric of $(\text{Si}, \text{Al})\text{O}_4$. The inside structure, containing numerous pores connected one to another by 2.2–9 Å diameters channels and occupied with different cations, explains the ionic exchange property of the tuffs. The cations from the solutions which the tuffs are in contact of, can easily replace the cations from inside of the tuffs' pores, without changing their structure and electric charge. This fact recommends the tuffs for treatment of wastewaters polluted with heavy metals like an alternative method to classical methods^[1-7].

From chemical point of view, the zeolites contain alkaline and alkaline-earth metallic ions and are presented under the general formulae $(\text{Me}^+, 1.5\text{M}^{2+})_x(\text{Al}_x\text{Si}_y\text{O}_{2(x+y)})z\text{H}_2\text{O}$, where $x < y$; Me – Na, K, Li; M – Ca, Mg, Ba, Sr.

MATERIALS AND METHODS

Volcanic tuff from Stoiana Pâglișa (Romania) characterized by a high content of clinoptilolite $(\text{Na}_6[\text{Al}_6\text{Si}_{30}\text{O}_{72}]\cdot 24\text{H}_2\text{O})$ was used for experiments (Table 1^[8]).

The physico-chemical aspects related to the copper adsorption on mentioned tuff were analyzed in order to increase the adsorption capacity. In this end, two steps were performed:

Activation of the tuff: Two types of NaCl and HCl solutions (Merk purity) with 0.1, 0.5, 1 and 2 mol L^{-1}

concentrations were used in the stage of activation tuff. For each experiment, an amount of 10 g tuff with the average granulometry of 0.048 ± 0.008 mm was contacted, under the continuous stir, with 250 ml activation solution. After 4 h, the tuff was filtered, rinsed up to completely remove of Cl^- ions (negative reaction in the presence of AgNO_3) and dried about 24 h at 105°C .

Adsorption of the copper ions on the tuff's activated surface: A volume of 300 mL synthetic solution ($\text{pH}=5$) containing $102.61 \text{ mg L}^{-1} \text{ Cu}^{2+}$ was added over activated tuff. At every five min, solution samples were collected and polarographic analyzed (Radelkis OH 110) in order to determine the remained copper contain. Also, the experiments were performed in the same conditions, with only one analysis of copper contain, after 4 h, time enough for the system to reach the equilibrium state.

RESULTS AND DISCUSSION

The obtained results are presented in Table 2. As the values shows, the increase of NaCl concentration from 0.1 to 2 mol L^{-1} induces in the next step of adsorption an increase of copper adsorption capacity. It rise with 8.65%, from $5.5320 \text{ mg Cu}^{2+} \text{ g}^{-1}$ tuff to $6.0108 \text{ mg Cu}^{2+} \text{ g}^{-1}$ tuff. Similar behavior can be noticed in case of activation with HCl solutions, but for the same concentrations a 6.5% increase of copper adsorption capacity can be observed from $5.5128 \text{ mg Cu}^{2+} \text{ g}^{-1}$ tuff to $5.8716 \text{ mg Cu}^{2+} \text{ g}^{-1}$ tuff (Fig. 1). The lower copper adsorption capacity of tuff activated with HCl solutions indicates a higher affinity of tuff for Na^+ rather than H^+ .

Table 1: Mineralogical and chemical composition of Stoiana Paglisa – Romania volcanic tuff

Nr. crt.	Mineral	Contain (%)	Component	Content (%)
1	Zeolite (clinoptilolite)	50-62	Ignition losses	10.14
2	Volcanic glass	36-48	SiO ₂	65.59
3	Feldspat	1-1.5	Al ₂ O ₃	13.70
4	Biotite	1-1.5	Fe ₂ O ₃	1.47
5	Limonite	0.5-1	CaO	4.72
6	Calcite	1-1.5	MgO	0.92
7	Hornblende	<0.5	K ₂ O	1.65
8	Montmorillonite	<0.5	Na ₂ O	1.60
9	-	-	TiO ₂	0.14

Table 2: The influence of activation solutions' concentrations on the activation process of the tuff

Time minutes	Copper ions concentration (mg Cu ²⁺ L ⁻¹)															
	Concentration of NaCl activation solution (mol L ⁻¹)								Concentration of HCl activation solution (mol L ⁻¹)							
	0.1	0.1	0.5	0.5	1	1	2	2	0.1	0.1	0.5	0.5	1	1	2	2
0	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61	102.61
5	88.98	79.75	82.78	71.10	76.95	63.52	72.83	58.42	90.59	82.10	87.39	77.49	84.29	73.16	79.82	67.21
10	76.95	61.47	66.68	48.40	57.08	38.13	50.89	31.86	79.82	65.28	74.18	57.92	68.89	51.38	61.58	42.98
15	66.38	46.97	52.89	32.30	41.86	22.10	34.97	16.53	70.18	51.54	62.75	42.81	56.02	35.50	47.10	26.77
20	57.09	35.55	41.87	21.10	30.31	12.30	23.58	8.08	61.58	40.40	52.89	31.27	45.29	24.08	35.68	16.17
25	48.96	26.63	32.91	13.45	21.65	6.54	15.58	3.68	53.92	31.43	44.42	22.54	36.41	16.02	26.77	9.45
30	41.87	19.74	25.67	8.35	15.23	3.28	10.06	1.54	47.10	24.25	37.15	16.03	29.09	10.42	19.86	5.30
35	35.68	14.45	19.86	5.02	10.54	1.55	6.33	0.57	41.05	18.54	30.95	11.22	23.09	6.62	14.57	2.85
40	30.31	10.45	15.23	2.92	7.17	0.67	3.87	0.18	35.68	14.05	25.67	7.72	18.20	4.08	10.55	1.45
T (°C)	20	50	20	50	20	50	20	50	20	50	20	50	20	50	20	50

Table 3: The thermodynamic parameters obtained in case of tuff activation with NaCl and HCl solutions

Parameter	Concentration of NaCl solutions (mol L ⁻¹)					Concentration of HCl solutions (mol L ⁻¹)				
	0	0.1	0.5	1	2	0	0.1	0.5	1	2
q (mg Cu ²⁺ g ⁻¹) 50°C	5.8470	5.9664	6.1410	6.1494	6.1530	5.8470	5.8890	5.9250	5.9676	6.0816
n 20°C	0.8741	0.8729	0.8718	0.8707	0.8691	0.8741	0.8734	0.8735	0.8728	0.8720
n 50°C	0.8729	0.8712	0.8682	0.8633	0.8548	0.8729	0.8719	0.8708	0.8697	0.8666
k 20°C	0.00945	0.01251	0.01868	0.02482	0.02925	0.00945	0.01097	0.01414	0.01723	0.02186
k 50°C	0.01695	0.02181	0.03113	0.03941	0.04353	0.01695	0.01940	0.02424	0.02899	0.03556
Ea (KJ mol ⁻¹)	15.339	14.593	13.408	12.139	10.437	15.339	14.967	14.150	13.660	12.774
ΔEa (KJ mol ⁻¹)	0	0.746	1.931	3.200	4.902	0	0.372	1.189	1.679	2.565
X _T	0.0033	0.0044	0.0068	0.0109	0.0205	0.0033	0.0038	0.0051	0.0062	0.0086
X _P	0.9502	0.9696	0.9980	0.9994	1	0.9502	0.9570	0.9629	0.9698	0.9883

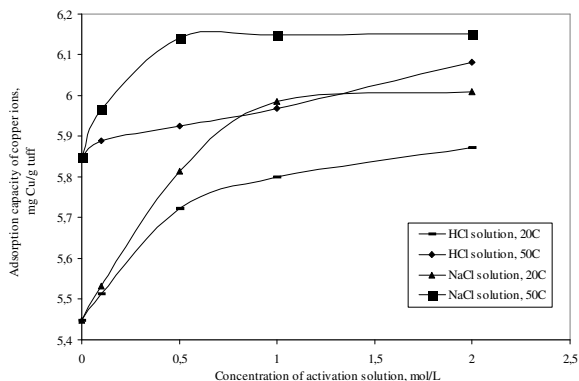


Fig. 1: The influence of activation solutions' concentrations on the adsorption capacity

Temperature is another parameter which influences the copper adsorption. As the Fig. 1 indicates, in case of the tuff activated with 2 mol L⁻¹ NaCl solution the increase of temperature from 20°C to 50°C generated an

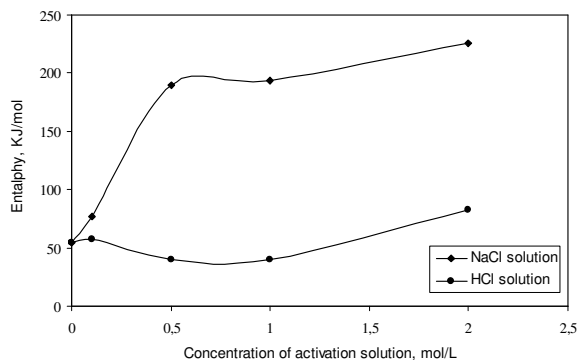


Fig. 2: The enthalpy of the copper adsorption process on volcanic tuff

increase of adsorption capacity with 2.3%, from 6.0108 mg Cu²⁺ g⁻¹ tuff to 6.1530 mg Cu²⁺ g⁻¹ tuff. In case of activation with 2 mol L⁻¹ HCl solution, the increase is about 3.57%, from 5.8716 mg Cu²⁺ g⁻¹ tuff to 6.0816 mg Cu²⁺ g⁻¹ tuff. The intensification of the diffusion

inside of the tuff structure can explain the favorable effect of high temperature on the adsorption capacity. Also, it reflects that the copper adsorption on studied tuff is based on low activated chemisorption process. Starting from the equilibrium constant^[9-11]:

$$k_c = \frac{F_e}{1 - F_e} = \frac{c_0 - c}{c} \quad (1)$$

where:

- k_c the equilibrium constant, [adimensional]
- F_e the adsorbed fraction at equilibrium, [adimensional]
- c_0 the initial copper concentration in solution, [mg Cu²⁺ L⁻¹]
- c the copper concentration at equilibrium state, [mg Cu²⁺ L⁻¹]

The thermodynamic parameters of the copper adsorption on volcanic tuff were calculated as follows:

$$\Delta G = -R \cdot T \cdot \ln k_c \quad (2)$$

$$\Delta H = \frac{2.303 \cdot R \cdot T_1 \cdot T_2}{T_1 - T_2} \ln \frac{k_c T_1}{k_c T_2} \quad (3)$$

where:

- ΔG the variation of free energy, [KJ mol⁻¹]
- ΔH the variation of adsorption enthalpy, [KJ mol⁻¹]
- ΔS variation of adsorption entropy, [KJ mol⁻¹ K⁻¹]
- T temperature, [K]
- R gas constant, [8.31433 J mol⁻¹ K⁻¹]

In Fig. 2 and 3 are presented the influence of the tuff's activation conditions on the enthalpy and free energy of the adsorption process. Based on these, some particularly conclusions can be advanced:

In case of volcanic tuff activated with 0.1-2 mol L⁻¹ increasing concentrations solutions of NaCl the values of free energy decrease in range of -4.97 KJ mol⁻¹ ÷ -9.06 KJ mol⁻¹. It indicates that the adsorption process will occur faster as the concentrations of activation solutions will be higher. Physically point of view, it is equivalent with an advanced replacement of alkaline and alkaline-earth cations from the tuff's native structure. The affinity of volcanic tuff for Na⁺ rather than H⁺ is proved by the higher values of free energy obtained in case of volcanic tuff activated with HCl solutions.

The enthalpy of the adsorption process is higher as the activation solutions' concentrations increase. Also, the more concentrated are the activation solutions the more endothermic is copper adsorption process.

The both variations of enthalpy and free energy of the adsorption process with concentration of activation solutions indicate the energetically non-homogeneity of

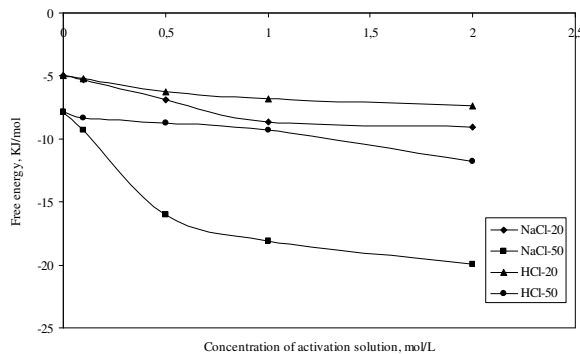


Fig. 3: The free energy of the copper adsorption process on volcanic tuff

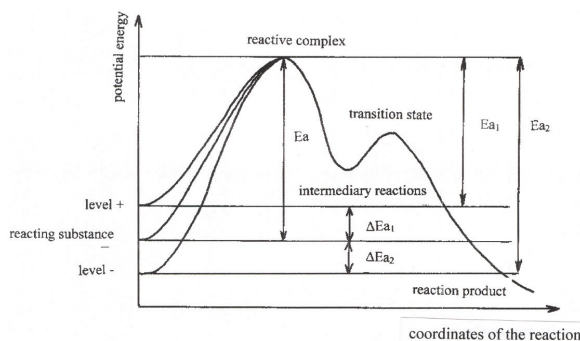
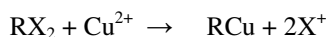


Fig. 4: Potential energy diagram for a two stage process with a slow rate stage

the adsorption active centers located on the surface of the tuff. In confirming of this hypothesis the apparent activation energy of the process was calculated. For this end, the adsorption process was considered to occur like a low activated chemisorption (absorption), represented by the reaction:



and described by the kinetic equation^[12]:

$$v = k \cdot c^n \quad (4)$$

where:

- RX_2 the volcanic tuff before the adsorption of copper ions
- RCu the volcanic tuff after the adsorption of copper ions
- V the reaction rate, [mol Cu²⁺ min⁻¹ L⁻¹]
- C the copper concentration in solution, [mol Cu²⁺ L⁻¹]
- n the partial reaction order reported to copper, [adimensional]
- k the reaction constant which includes the ratio tuff weight/contact solution weight, [adimensional]

Starting from the values calculated at two different temperatures, the apparent activation energy of the process can be determined using the equation^[13]:

$$E_a = \frac{R \cdot T_1 \cdot T_2}{T_1 - T_2} \cdot \ln \frac{k_1}{k_2} \quad (5)$$

where:

E_a apparent activation energy, [KJ mol⁻¹]
 T_1, T_2 work temperature, [K]
 k_1, k_2 the values of reaction constant at T_1 and T_2 ,
 [Lⁿ⁻¹·mol¹⁻ⁿ·min⁻¹]

Using the TURBO-PASCAL computer program, the values for partial reaction orders, reaction constants and apparent activation energy have been calculated.

The values of partial reaction orders in range of 0.8545 – 0.9368 (Table 3) present the kinetic model for the adsorption process as being as pseudo-order 1. Also, a decrease of the apparent activation energy with the increase of the activation solutions' concentrations is observed.

In the Arrhenius expression for the reaction constant:

$$k = k_0 \cdot e^{-\frac{E_a}{R \cdot T}} \quad (6)$$

where:

k_0 pre-exponential term, [Lⁿ⁻¹·mol¹⁻ⁿ·min⁻¹]

the expression:

$$X_T = e^{-\frac{E_a}{R \cdot T}} \quad (7)$$

is named „Boltzmann factor“^[13] and represents, physically speaking, the fraction of molecules with the energy level higher than E_a and more precisely, the active molecules capable to develop the chemical reaction. In case of our adsorption process, the Boltzmann factor represents the fraction of active centers (active sites) on the surface of the tuff, characterized by the E_a potential energy being capable to adsorb the copper ions.

The Fig. 4 presents the potential energy diagram of two stages process, one of these considered slow rate stage. The activation energy is calculated as difference between the energy of activated complex and reactings energy (the complex site-copper ions). As we mentioned before, the high concentrations of activation solutions are reflected in low values of apparent activation energy corresponding to high specific adsorption. The decrease of apparent activation energy is represented in Fig. 4 by the curve corresponding to E_{a1} energy for R+ level of reactings. For this variation, an hypothesis which can be formulated, based on the energetic changes of the sites from the surface of the adsorbant, in parallel with constant maintaining of the activated complex's energy (represented by the pick of

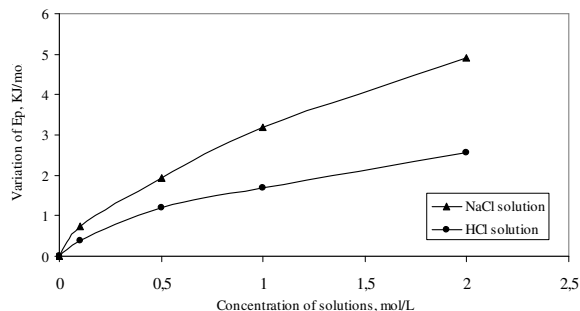


Fig. 5: The influence of activation solutions' concentrations on the potential energy of the adsorption process

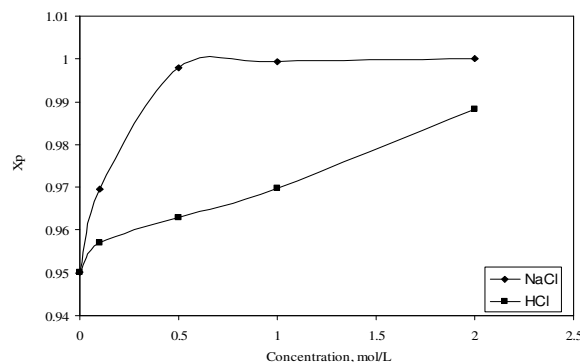


Fig. 6: The influence of activation solutions' concentrations on the active center fraction

the potential energy curve), because of the replacement the ions from the adsorbant surface. As consequence, the idea of increasing the potential energy of the adsorbant surface' sites can be advanced, simultaneously with the increase the number of active centers for adsorption of copper ions.

The difference between the apparent activation energies for cases of copper adsorption on the native tuff and activated tuff with NaCl and HCl solutions, supports the hypothesis above presented. Because of these increase of potential energy, an additional number of active centers will have the energy required to reach the energetic level of activated complex and will be capable to adsorb the copper ions. The fraction of these active centers, can be qualified in two ways:

1. Using Boltzmann factor (equation 7).
2. Starting from experimental adsorption, the fraction of active centers, X_p , can be calculated (in case of maximum specific adsorption - recorded at 2 mol L⁻¹ NaCl solution, pH=5.0 and t=50°C- $X_p=1$ can be considered).

The Table 3 presents the calculated values of energetic parameters (apparent activation energy, X_T , Boltzmann factor, X_p and ΔE_a) for both cases of tuff activated with NaCl and HCl solutions. In Fig. 5 and 6 are presented the variation of potential energy of active centers and the fraction of active centers on the tuff' surface with the concentration of the activation solutions.

CONCLUSION

Based from the aspects presented above, we can conclude the follows:

1. Direct correlation between the activation solution's concentrations and the specific adsorption of copper ions.
2. Adsorption process of copper ions on the analyzed volcanic tuff is developed under a pseudo-order 1, which proves the interaction between an active site located on the adsorbent' surface and a copper ion from the contact solution.
3. The adsorption process is endothermic and occurs spontaneous with negative variation of free energy.
4. An increase of active centers' fraction capable to participate in the adsorption process is recorded as the concentrations of activation solutions are higher.

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