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ORIGINAL RESEARCH ARTICLE

Synthesis of Linde F zeolite by alkaline treatment with caustic potash from volcanic rock from sillar, Peru: Its application in the adsorption of copper (II)

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ABSTRACT

This paper reports the results of the synthesis of zeolitic material with adsorbent capacity from a rock of volcanic origin from sillar, Arequipa, Peru. The experimentation was carried out in a stainless steel reactor using solutions with different concentrations of KOH (2.0, 2.5 and 3.0 M), at a constant temperature of 150 ℃ and with a contact time between the volcanic material and the solution of 24, 48 and 72 h. The product obtained was characterized by means of scanning microscopic analysis (SEM) and cation exchange capacity (CIC).

The results showed that synthetic zeolite was produced as a function of KOH concentration as the most influential independent variable. The highest cation exchange capacity (CEC) observed was 27.91 meq/100 g and corresponded to the formation of Linde F zeolite obtained with a 3.0 M KOH solution and for a time of 72 hours using a material whose particle size was 4 mm. Adsorption tests were performed using solutions containing Cu^{2+} cations in order to evaluate their adsorption capacity and kinetics.

Keywords: Cation Exchange Capacity; Volcanic Material; Zeolite Linde F; Kinetics; Alkaline Treatment

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1. Introduction

Southern Peru has important deposits of non-metallic minerals, one of the best known is sillar (Arequipa, Peru) with reserves of volcanic rock or ignimbrite mineral. Industries such as mining, agriculture, animal feeding, water purification, pharmaceuticals, etc.[1], require low-cost adsorbent materials with the capacity to be used in environmental remediation. A viable alternative is the use of natural or synthetic zeolites that exhibit high cation exchange capacities. It is possible to synthesize zeolites from pure chemical reagents and precursors of natural origin (natural zeolite, perlite, bentonite, kaolin, pozzolan, fly ash, etc.), since they are abundant in nature and contain a high content of silica and alumina[2]. Zeolites find their application due to their efficient ability to act as cation exchangers, catalysts, filters, and biofilters, in various chemical and environmental treatment processes.

Methods such as hydrothermal conversion, alkaline fusion and hydrothermal conversion, microwave-assisted conversion[3,4] have been developed using especially fly ash from thermoelectric power plants as cheap precursors[5]. The types of synthetic zeolites that are formed present diverse physical, chemical, mineralogical and morphological properties according to the different obtaining conditions such as temperature, alkalinity, crystallization and liquid/solid ratio. Consequently, a control of all these variables in the synthesis process can result in obtaining a zeolitic product suitable for industrial application[6].

According to this background, it is considered appropriate to carry out the present research work in order to give added value to the sillar mineral that exists in the Arequipa region, Peru, by applying an alkaline conversion treatment in order to obtain zeolitic materials with the capacity to exchange cations. It also seeks to evaluate its possible applications in the field of environmental remediation for the treatment of mining or industrial effluents.

The present study was divided into two stages. In the first, the ashlar was characterized by chemical and physical analysis. Then, an alkaline treatment with KOH solutions was applied, varying the particle size, concentration and contact time. The zeolitic product obtained was analyzed by electron microscopic chemical-morphological analysis (SEM) and cation exchange capacity (CIC). In the second stage, adsorption tests were carried out using Cu^{2+} containing solutions. The results obtained, which are consistent with those reported in the literature, allow us to positively foresee the possibility of deepening the technical-economic considerations related to the zeolitization of the ignimbritic mineral ashlar to obtain synthetic zeolite.

2. Materials and methods

2.1 Material preparation

Crushing and screening operations were performed on the volcanic material (ashlar) to obtain particle sizes of 2, 3 and 4 mm; which have been used for the synthesis tests with alkaline treatment. These particle size classes were chosen with the purpose of exploring the possibility of their potential use in the production of filters for the treatment of contaminated water.

2.2 Characterization and analysis equipment

The chemical composition and morphological analysis of the volcanic material and the zeolitic product were analyzed using a FEI Quanta 200 high and low vacuum electron microscope (SEM) with SED and BSED microanalysis detectors[7]. For the evaluation of cation exchange capacity (CEC), double cation exchange tests were performed using 1.0 N sodium acetate and 1.0 N ammonium acetate solutions. Maximum adsorption analysis of Na^{+} and Cu^{2+} was possible using a Perkin Elmer OPTIMA-2100-DV ICP adsorption equipment in Laboratorios del Sur.

2.3 Reagents

The solutions used were prepared with the following salts: KOH (99.5%), $NaC_2H_3O_2{\cdot}3H_2O$, $NH_4C_2H_3O_2{\cdot}3H_2O$ (99.0%), $CuCl_2{\cdot}2H_2O$ (99.09%), isopropyl alcohol (99.0%), purchased from Diproquim.

2.4 Tests for the production of Linde F zeolite

Tests to obtain synthetic zeolite were carried out using an AISI 304 stainless steel container that was placed inside the oven at a temperature of 150 °C. In the container were placed 10 g of volcanic material with particle sizes of 2, 3 and 4 mm and KOH solutions with concentrations of 2, 2.5 and 3 M, maintaining a solid/liquid ratio of 12:5. The contact time between the liquid and solid was 24, 48 and 72 hours. Singh *et al.*[8] reports using 150 °C and 48 hours to synthesize zeolite by alkaline activation using KOH solutions. The obtained product was washed with distilled water and filtered to finally take it to oven drying at 60 °C for a time of 6 hours, conditions defined according to the reviewed literature[9].

2.5 Analysis of cation exchange capacity (CEC)

Analytical Method 9081 was used to determine the cation exchange capacity[10]:

Weigh 4 g of fine particle size material, and transfer the sample into the circular base centrifuge container with a capacity of 50 mL.

(1) Add 33 mL of 1.0 N sodium acetate solution, cap the tube, subject to mechanical shaker for 5 min, and centrifuge the solution until the liquid is clear.

(2) Decant the liquid and repeat step (1), 3

more times.

(3) Add 33 mL of isopropyl alcohol (99%), cap the tube, subject to mechanical shaker for 5 min, and centrifuge until the liquid is clear.

(4) Repeat the procedure instep (3), 2 more times.

(5) Add 33 mL of the ammonium acetate solution, cap the tube, subject to mechanical shaker for 5 min, and centrifuge until the supernatant liquid is clear. Decant the solution into a bottle with a capacity of 100 mL.

(6) Repeat the procedure described in step (5), 2 more times.

(7) Make up a volume of 100 mL ammonium acetate solution and determine the Na^+ concentration by atomic absorption, emission spectroscopy, or an equivalent method.

2.6 Cu^{2+} adsorption tests

In order to evaluate the adsorption capacity as a function of time, tests were carried out with the zeolitic product that presented the highest cation exchange capacity. In glass bottles containing 1 g of zeolite, 150 mL of Cu^{2+} solution with a concentration of 1,000 mg/L were poured. After 24, 48 and 72 hours, 100 mL of solution were taken for Cu^{2+} analysis.

The determination of the adsorption capacity at different Cu^{2+} concentrations was carried out using glass containers of 200 mL capacity, where 150 mL of Cu^{2+} solution with concentrations of 1,092, 871, 764, 327, 109 and 55 mg/L and 1 g of zeolitic product were placed. During the tests the containers were shaken to improve the contact between the solution and the zeolitic material. The contact time will be determined by time-varying tests. After the contact time between the solid and liquid had elapsed, the solutions were filtered and 100 mL of solution was taken to analyze Cu^{2+} by atomic adsorption.

3. Results and discussion

3.1 Characterization of volcanic material (ashlar)

3.1.1 Chemical composition

Table 1 presents the analysis of volcanic material (ashlar) in its natural state.

Table 1. Chemical composition—Sillar in its natural state

Element	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
Composition	4.92%	0.27%	14.43%	74.99%	3.02%	1.11%	1.11%

A high content of SiO_2 and Al_2O_3 essential for the zeolite synthesis process by alkaline treatment can be clearly seen. Thus, ashlar has a SiO_2 + Al_2O_3 content equal to 89.42%. Ferrarini *et al.*[11] indicated that this ratio should be higher than 89%, in addition to the fact that these elements are present in minerals such as quartz (SiO_2) and mullite ($3Al_2O_3 \cdot 2SiO_2$) and compounds containing Ca, Fe are impurities that can limit their application in the synthesis of zeolites.

3.1.2 Morphological characterization

Figure 1 shows pyroclastic formations of glassy appearance containing SiO_2 and Al_2O_3 (cristobalite, quartz, anorthoclase and orthoclase) in addition to porosity of varying size.

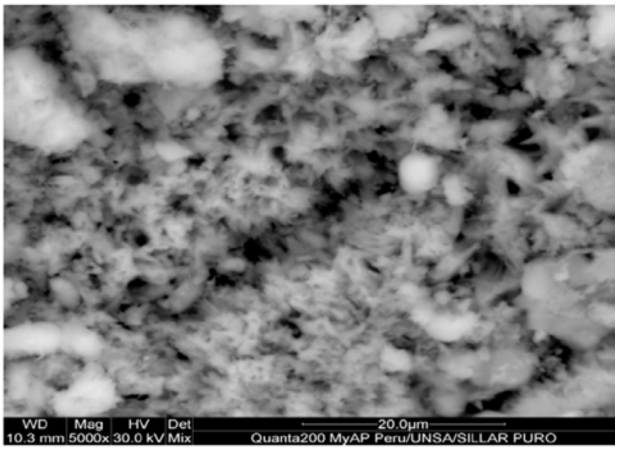

Figure 1. SEM micrograph showing pyroclastic formations.

3.1.3 Synthesis of zeolite Linde F

Table 2 shows the values of cation exchange capacity (CEC) determined in samples of zeolitic products obtained under different test conditions, and that presented by the untreated material.

Table2. Cation exchange capacity (CEC)

Test	Test conditions	(CIC) meq/100 g
1	2 mm/2 M/24 h	10.96
2	4 mm/2 M/24 h	14.26
3	2 mm/3 M/24 h	27.13
4	4 mm/3 M/24 h	16.00
5	2 mm/2 M/72 h	11.91
6	4 mm/2 M/72 h	11.39
7	2 mm/3 M/72 h	27.04
8	4 mm/3 M/72 h	27.91
9	3 mm/2.5 M/48 h	11.65
10	3 mm/2.5 M/48 h	12.26
11	3 mm/2.5 M/48 h	11.13

Table 3 presents the zeolitic content compared to a Linde F zeolite obtained by synthesis from fly ash with a cation exchange capacity equal to 140 meq/100 g[12]. It is shown that the product obtained in this research presents a maximum Linde F zeolite content of 19.93%.

The results obtained manifest high values of cation exchange capacity, in the order of 27.91 and 27.13 meq/100 g. It is possible to conclude that at a KOH concentration of 3 M there is a high dissolution of silica and alumina during the conversion process by alkaline treatment.

Table 3. Linde F zeolite content for different test conditions

Sample	Particle size (mm)	Concentration KOH (M)	Time (Hours)	CIC (meq/100g)	Zeolite Linde F (%)
1	2	2	24	11.0	7.86
2	4	2	24	14.3	10.21
3	2	3	24	27.1	19.36
4	4	3	24	16.0	11.43
5	2	2	72	11.9	8.50
6	4	2	72	11.4	8.14
7	2	3	72	27.0	19.29
8	4	3	72	27.9	19.93
9	3	2.5	48	11.7	8.36
10	3	2.5	48	12.3	8.79
11	3	2.5	48	11.1	7.93
Linde F zeolite	140.00	100.00			

Table 4. Chemical composition—Synthetic zeolite

Element	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
Composition	6.33%	20.34%	61.52%	7.28%	1.75%	0.54%	2.23%

3.2 Characterization of the zeolitic product

The synthetic zeolite that showed the highest cation exchange capacity (4 mm/3 M/72 hours) was characterized physically, chemically and morphologically to define its type and identify it.

3.2.1 Chemical composition

Table 4 shows the result of the chemical analysis expressed in oxides present.

3.2.2 Morphological characterization

Figure 2 show tetragonal and prismatic crystal formations of Linde F zeolite from the dissolution of ashlar matrix. Miyaji *et. al.*[12] mention obtaining regular prism-shaped crystals in the synthesis of Linde F zeolite employing fly-ash.

Figure 2. Linde F zeolite formation in ashlar pyroclastic matrix. Test 4 mm/3 M/72 h.

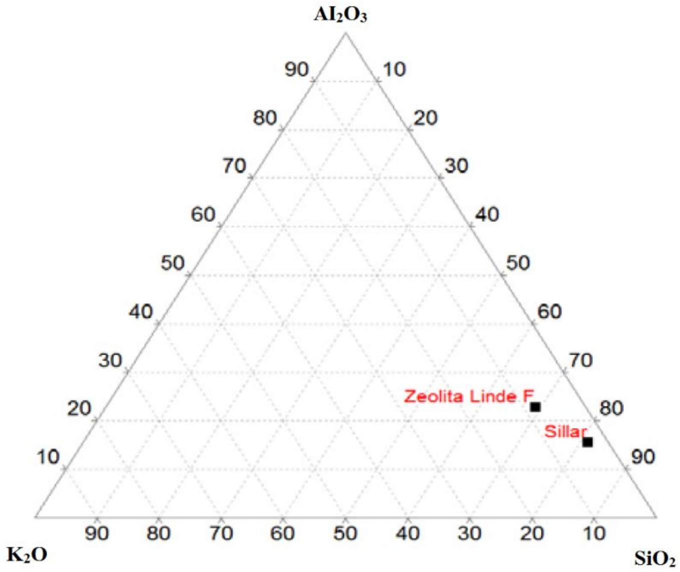

Figure 3. Ternary diagram for SiO_2, Al_2O_3 and K_2O_2 components.

Comparing the chemical analysis of the natural ashlar and the one corresponding to the synthetic zeolite Linde F by means of the TRIPLOT Version 4.1.2 software, it is possible to appreciate the movement of the zeolite composition as a function of its main chemical components SiO_2, Al_2O_3 and K_2O. **Figure 3** shows the ternary diagram containing the compositions of the ashlar and the zeolitic material Linde F. The enrichment of K_2O and Al_2O_3 from 3.02 to 7.28% and from 14.43 to 20.34%, respectively, is notable.

3.3 Adsorption of Cu^{2+} cation

The amount of adsorbed cation was calculated as the difference between the initial and final concentration in the solutions[13,14]. **Table 5** shows the adsorption capacity of Cu^{2+} as a function of contact time.

Table 5. Adsorption of Cu^{2+} cations with Linde F zeolite

Time (hours)	**Initial conc. (mg/L)**	**Final conc. (mg/L)**	**Initial Cu^{2+} (mg)**	**Final Cu^{2+} (mg)**	**Cu^{2+} adsorbed (mg)**	**Cu^{2+} adsorbed (mg/g)**	**Cu^{2+} adsorbed (%)**
Feeding	1,000						
4		916.00	150.0	91.6	58.4	58.4	38.9
8		916.00	150.0	91.6	58.4	58.4	38.9
12		916.00	150.0	91.6	58.4	58.4	38.9
16		896.00	150.0	89.6	60.4	60.4	40.3

From **Table 5**, it is clear that after 8 hours, for these test conditions, the amount, in mg of Cu^{2+} per gram of zeolite, of the exchanged cations remains constant.

3.4 Adsorption kinetic model

The model proposed by Blanchard[15], called pseudo-second order turns out to be the most suitable to explain the adsorption procedure of Cu^{2+} cation on synthetic zeolite. Pseudo-second order kinetic model (1):

$$\frac{t}{q} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (1)$$

Where, q_e is the amount of Cu^{2+} adsorbed at equilibrium by the zeolite expressed in (mg/g), q is the amount of Cu^{2+} at a time t in (mg/g), k_2 is the constant of the pseudo-second order model and t is the contact time. **Figure 4** presents the adsorption kinetics for the linearized pseudo-second order model.

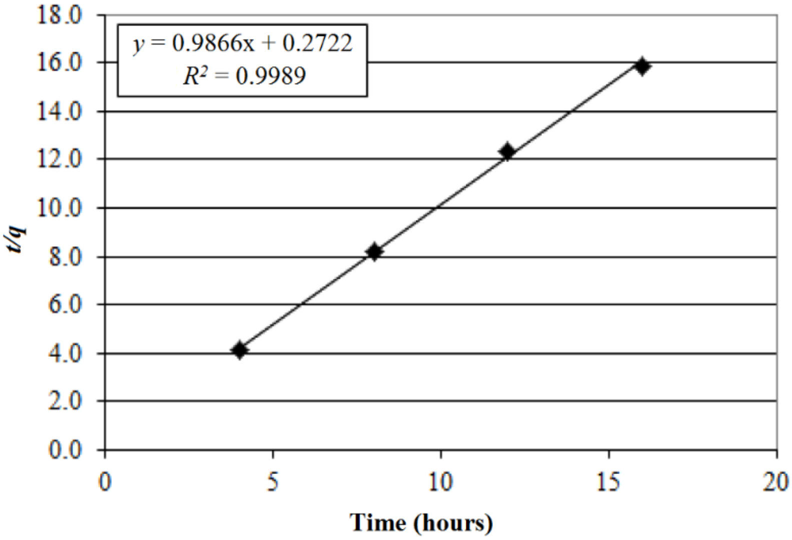

Figure 4. Cu2+ kinetics for the pseudo-second order model.

Table 6. Adsorption of Cu^{2+} at different concentrations

Test	Initial conc. (mg/L)	Analysis (mg/L)	Initial Cu^{2+} (mg)	Final Cu^{2+} (mg)	Cu^{2+} adsorbed (mg)	Cu^{2+} adsorbed (mg/g)	Cu^{2+} adsorbed (%)
1	1,092.00	896.00	163.80	134.40	29.40	29.40	17.95
2	870.99	720.00	131.04	108.32	22.72	22.72	17.34
3	764.40	624.00	114.66	93.60	21.06	21.06	18.37
4	326.58	266.40	49.14	40.09	9.05	9.05	18.43
5	108.97	78.10	16.38	11.74	4.64	4.64	28.33
6	54.57	42.10	8.19	6.32	1.87	1.87	22.85

Table 6 shows the results of the Cu^{2+} adsorption tests at varying concentration and a constant contact time of 8 hours.

3.5 Freundlich, Langmuir and Temkin Adsorption isotherms

The experimental data were correlated using the adsorption models proposed by Freundlich, Lagmuir and Temkin[16,17].

The linearized Freundlich equation is as the following (2):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{2}$$

Where C_e is the equilibrium concentration of the solution to be adsorbed (mg/L), q_e is the adsorption capacity of the adsorbate, in (mg/g), K_f is the Freundlich constant related to the adsorption capacity, n is the Freundlich constant related to the adsorption intensity or degree of adsorption favorability.

The linearized Langmuir equation is as the following (3):

$$\frac{1}{q_e} = \left(\frac{1}{K_l \times q_{max}}\right)\frac{1}{C_e} + \frac{1}{q_{max}} \tag{3}$$

Where, q_{max}. is the maximum adsorption capacity of the dye under the given conditions (mg/g), K_l is the Langmuir constant indicating the affinity of the adsorbate for the adsorbent, q_e is the adsorption capacity of the adsorbate, in (mg/g), C_e is the concentration of the solution at equilibrium (mg/L).

The linearized Tenkim equation is expressed as the following (4):

$$q_e = Bt \times \ln(At) + Bt \times \ln\times (C_e) \tag{4}$$

Where, q_e is the adsorption capacity of the adsorbate, in (mg/g), *Bt* is the constant relating the heat of adsorption (J/mol), *At* is the equilibrium binding constant (maximum binding energy) (L/mg), C_e is the equilibrium concentration of the solution to adsorb (mg/L).

Figures 5, **6** and **7** show the adsorption isotherms of Freundlich, Langmuir and Tenkim.

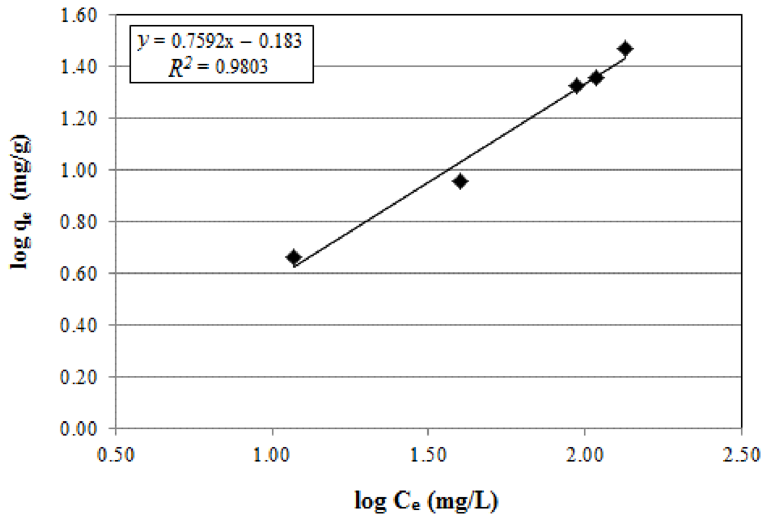

Figure 5. Freundlich adsorption isotherm.

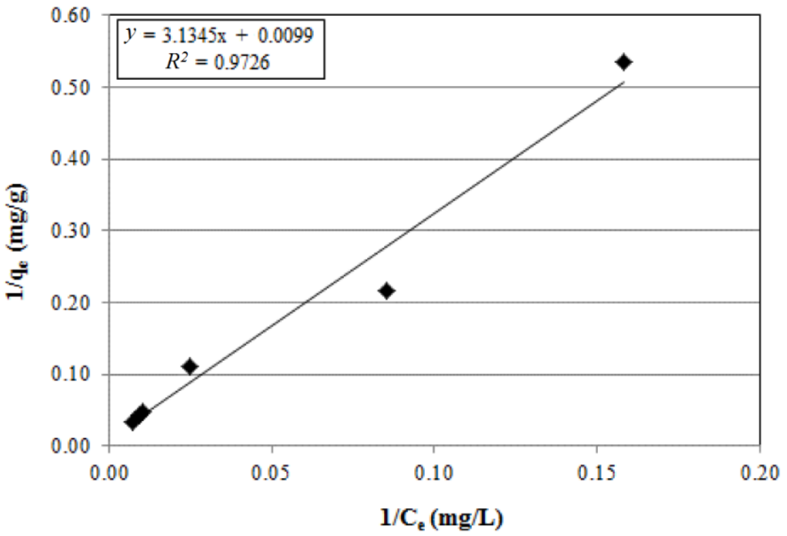

Figure 6. Langmuir adsorption algorithm.

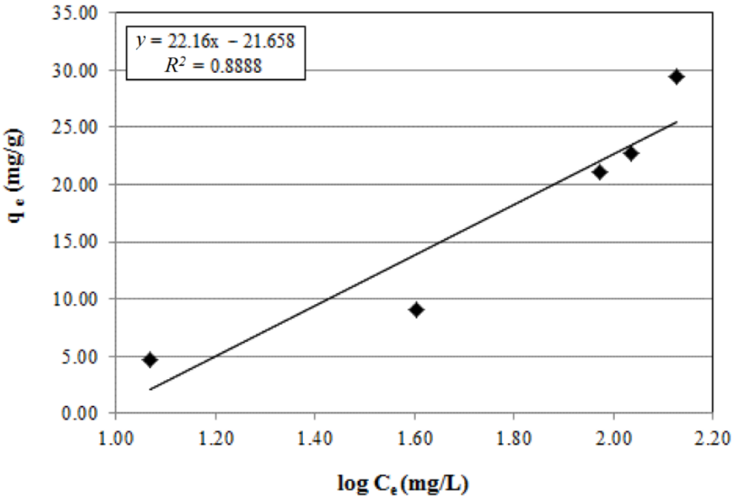

Figure 7. Tenkim adsorption isotherm.

Table 7 shows the values of the constants relative to the Freundlich, Langmuir and Tenkim isotherms with their corresponding correlation coefficients (*R*) relative to the experimental values at equilibrium.

Table 7. Parameter values of Langmuir, Freundlich and Temkin isotherms and their corresponding correlation coefficient (*R*)

Isotherm	**Constant**	**Value**	R^2
Langmuir	K_L (L/mg)	0.00316	0.972
	q_{max} (mg/g)	101.01	
Freundlich	K_f (L/g)	1.524	0.980
	n	1.3172	
Temkin	Bt (J/mol)	22.160	0.888
	At (L/mg)	0.376	

The analysis of the results obtained in the synthesis tests to obtain Linde F zeolite from ashlar and the Cu^{2+} adsorption tests by the zeolitic product revealed that: at the temperature of 150 °C, and with a test condition 4 mm/3 M/72 hours, the glassy part contained in the ashlar dissolves and goes on to form Linde F zeolite crystals on it. At this temperature, the dissolution of the constituents of the initial material and the formation of zeolite crystals is ensured.

3.6 Effect of particle size

For particle sizes of 2 and 4 mm, with high concentration and with prolonged contact times between the solution and the solid, the cation exchange capacity reaches between 27.04 and 27.91 meq/100 g. Due to the large particle size, the conversion process is performed only at the surface level.

3.7 Effect of KOH concentration

With respect to the concentration of the KOH solution, the best CIC results are obtained when 3 M concentrations are used (27.04, 27.13 and 27.91 meq/100 g). At higher concentrations, the pH increases, which ensures good dissolution of the silicon- and aluminum-containing mineralogical phases to form a gel that will later crystallize into zeolitic products. Hu *et al.*[18] states that the alkalinity in the mixture is an important factor to consider in determining the crystallinity and composition of the zeolitic product.

3.8 Effect of contact time

The best results are obtained in tests with longer conversion times. In particular, for conversion times of 72 hours and particle sizes of 2 and 4 mm, the best CIC values were obtained when high concentrations of KOH were used. Chen and Cheng[19], argue that it is important to consider a dependence between the time and the reaction temperature, so that at a high temperature and at a prolonged time, the presence of silicon and free aluminum from the dissolution of the glassy phase of the precursor is ensured.

3.9 Adsorption of Cu^{2+} cation

The adsorption of the zeolitic material in milligram per gram for the Cu^{2+} cation is of the order of 29.40 mg/g (17.95%) for an initial concentration of 1,092.00 mg/L, and 4.64 mg/g (28.33%) for an initial concentration of 108.97. This behavior depends on the fact that the adsorption phenomenon is influenced by the charge density, as well as by the hydration energy and the atomic radius of the Cu^{2+} cations. The fit of the pseudo-second-order kinetic model (R^2 = 0.999) allows us to state that the adsorption of Cu^{2+} ions occurs on the active sites of the zeolite and involves chemisorption mechanisms between the adsorbate and the adsorbent[20,21].

The analysis of the Langmuir, Freundlich and Temkin isotherms shows that there is a linearity and closer fit with the Freundlich isotherm (R^2 = 0.980). Therefore, it can be considered that this isotherm is the one that governs the adsorption process of Cu^{2+} ions on Linde F zeolite. The active centers of the adsorbent are energetically heterogeneous, which indicates that they present different affinities so that initially the adsorption phenomenon originates because the active sites with higher affinity are occupied by the Cu^{2+} cation and the formation of a layer is generated, however, the remaining free sites interact with the adsorbate by means of Van der Waals forces giving rise to the formation of other layers (multilayers)[22,23]. The value of the $1/n$ constant of 0.759, evidence that the adsorption phenomenon of Cu^{2+} on Linde F zeolite is favorable.

4. Conclusions

The alkaline treatment under different conditions of volcanic ashlar ore from quarries in the city of Arequipa, Peru, produces Linde F zeolite with its own textural characteristics and cation exchange capacity. The zeolitic product obtained under test conditions using particle sizes of 4 mm, 3 M KOH solution and a synthesis treatment for 72 hours at a constant temperature of 150 ºC, presents a cation exchange capacity CIC = 27.91 meq/100 g. Under these experimental conditions, Linde F synthetic zeolite is formed at a content of 19.9%. Using the zeolitic material obtained at the test condition 4 mm/3 M/72 hours; an adsorption of 29.40 mg of Cu^{2+}/g of synthetic zeolite is obtained after a contact time of 8 hours. The adsorption process of Cu^{2+} on Linde type F zeolite was according to the Freundlich isotherm and is best described by Blanchard's pseudo-second order kinetic model.

Considering that there are considerable reserves of volcanic rock (ashlar) available, the relatively moderate temperature to produce Linde F zeolite (150 ºC), as well as the possibility of using particle sizes 2 and 4 mm, make its conversion very viable with great potential for application in different productive sectors.

Conflict of interest

The authors declared no conflict of interest.

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