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Peculiar properties of LTA/FAU synthetic composite zeolite and its effect on Cu^{2+} adsorption: factorial experimental design

Leila S. Silva[a], Giselle S.C. Raulino[b], Carla B. Vidal[c,*], Marçal José Rodrigues Pires[d], Ronaldo F. Nascimento[c]

[a]*Departament of Physics, Federal University of Ceará, Campus do Pici, 6030, 60440-554, Fortaleza, CE, Brazil, email: leilinhasds@hotmail.com (L.S. Silva)*
[b]*Department of Chemistry, Federal Institute of Education and Science of Ceará, Campus Aracoiaba, Ceará, Brazil, email: gisellescr@yahoo.com.br (G.S.C. Raulino)*
[c]*Department of Analytical Chemistry and Physico-Chemistry, Federal University of Ceará, Campus do Pici, Bl. 940, 60451-970, Fortaleza, CE, Brazil, Tel. +55 85 3366 9042, email: carlab.vidal@gmail.com (C.B. Vidal), ronaldo@ufc.br (R.F. do Nascimento)*
[d]*Faculty of Chemistry, Pontifical Catholic University of Rio Grande do Sul, Ipiranga Avenue, 6681, 90619-900 Porto Alegre, RS, Brazil, email: mpires@pucrs.br (M.J.R. Pires)*

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ABSTRACT

Synthetic zeolites have been widely studied as metal ion adsorbents from aqueous solutions due to their physical and chemical properties, such as their cationic exchange capacity, which gives them a high adsorption capacity. Copper is a toxic metal that is of particular concern due to its toxicity, and it is introduced into the environment mainly through the disposal of industrial effluents. It has a tendency to accumulate in groundwater, but it can contaminate the soil and air as well. In this work, a FAU/LTA (Faujasite and Linde type A) composite zeolite was investigated for its efficiency in removing copper metal ions from aqueous solutions. A material characterization was performed in order to determine its morphology and chemical composition. Using an experimental design, the main variables that affect the adsorption process were studied. The optimal values that were determined from the experimental design studies were 200 mg L^{-1} for initial concentration and 100 mg for the mass of adsorbent. Kinetics studies indicated that the adsorption equilibrium was reached within 5 min. A maximum adsorption capacity of 120 mg g^{-1} was found through isothermal studies. The results showed that the mix of synthetic zeolite (FAU/LTA) is very efficient in the removal of copper from aqueous solutions.

Keywords: Synthetic zeolite; Adsorption; Metal ion

1. Introduction

The use of natural water resources by man as a way of transforming the natural environment for his own benefit did not always account for its finitude, vulnerability and resilience. Because it is an indispensable resource for life and because of the emergence of environmental problems, a growing awareness regarding the rational use of water resources has occurred in recent decades [1–4].

Many substances, such as toxic metal ions, have increased in effluents and consequently in natural waters, mainly from industrial activities. Such chemical species can be found in high concentrations in the air due to the incineration of urban and industrial waste, which causes their volatilization and forms ashes that are rich in metals, or due to laboratories that do not properly treat the effluent, and in water bodies by means of the emission of industrial effluents, mainly those of metallurgical industries. Metals are non-degradable and can accumulate in environmental

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*Corresponding author.

compartments, where they manifest their toxicity and are highly mobile, making it very difficult to track the fate of metal species once introduced into the ecosystem [5–7].

Although small amounts of copper are essential to the proper functioning of organs and metabolic processes, larger amounts are toxic to the human body. The main sources of anthropogenic contamination for copper are the municipal wastewater and effluent from the manufacturing processes of copper parts [8,9].

The removal of these chemical species is a subject of great interest due to increasingly strict environmental legislation for the disposal of these substances in addition to the negative effects on the human body. Brazil's environmental legislation limits the disposal of toxic metal ions in concentration to a range of 0.1 to 5.0 mg L^{-1}, depending on the ion. For copper, the limit is 1.0 mg L^{-1}. However, the potentially toxic metals are a valuable resource for different industrial applications. Therefore, recovery and recycling of these metal ions are particularly interesting, especially from the perspective of protecting natural resources [10,11].

Technologies for the treatment of metal ions in wastewater, such as chemical precipitation, electrolysis, ion exchange, reverse osmosis and adsorption using various porous solid materials, have been employed in the removal of these pollutants. However, operating costs and final effluent quality can be a hindrance to the use of these techniques [12,13].

Adsorption is a solid-fluid mass transfer process in which certain solids are chemically or physically accumulated on their surface in the presence of liquid or gaseous solutions, which allows separating them from the other components of the solutions [14,15].

The adsorption of metal ions using zeolites prepared from coal ash as low-cost adsorbents is an effective alternative for the removal of metal ions in environmental samples. This is in addition to reducing industrial solid waste disposal, because thermoelectric plants that use coal as fuel to generate electricity are considered to be a major source of pollution and are responsible for generating a substantial amount of pollutants, including coal ash. Coal ash is used largely in the production of cement and concrete as well as for adsorbents, catalysts and in the manufacturing of ceramic materials.

Synthetic zeolites have a wide range of properties and differentiated pore sizes that allow excellent efficiency in their applications as molecular sieves. Their production and industrial application began in the 1950s, and more than 150 types of synthetic zeolites are known today. The large adsorption capacity of zeolites depends on their pore volume and pore diameters. This allows them to be used as adsorbents in both purification processes and separation processes [16–19].

Zeolites can be synthesized from charcoal ashes, which are rich in silicon and aluminum. They are abundant and available all over the globe because wherever there is energy production through the burning of coal, there are considerable amounts of ash.

The zeolites faujasite (FAU) and Linde type A (LTA) are two of the most important zeolites because of their extensive commercial applications. From the perspective of framework structure, both FAU and LTA zeolites are composed of stacked sodalite cages. For FAU zeolites, sodalite cages are linked together by double six-membered rings to form large cavities called super cages [20]. For LTA zeolites, sodalite cages are linked together by double four-membered rings to form a cage. These two types of zeolites, with their respective properties, can improve the adsorption properties of metal ions from aqueous solutions. Among the existing zeolites, we highlight the LTA/FAU synthetic composite zeolite,which is normally produced by hydrothermal treatment. This zeolite has been synthesized in pressurized reactors at high temperatures.

Based on the above, the objective of this paper is to study copper adsorption using a mixture of the FAU and LTA zeolites as an adsorbent. They were synthesized under mild conditions using Brazilian coal fly ash for use in the treatment of aqueous effluents contaminated with the Cu^{2+}. Here, we study the variables that interfere in the adsorption process using a factorial experimental design as a tool.

2. Experimental section

2.1. Materials

Fly ash samples were collected from the electrostatic precipitators of the Presidente Médici Thermoelectric Power Plant (UTPM, Candiota, Brazil)

NaOH (99.5%) and $CaCl_2 \cdot 2H_2O$ (100%) Merck reagents were used to prepare solutions of these compounds in different concentrations. Alkaline solutions of $NaAlO_2$ (95%) (from Sigma-Aldrich), as an additional source of Al, were used for the zeolite synthesis tests. All solutions were prepared with ultra-pure deionized water (Milli-Q, Millipore,> 18 MΩ cm^{-1}).

To prepare the copper solutions for the adsorption tests, the analytical grade salts ($Cu(NO_3)_2 \cdot 3H_2O$) and $CaCl_2 \cdot 2H_2O$ from VETEC were used; sodium acetate (CH_3COONa) (DYNAMIC), glacial acetic acid (CH_3COOH) (SYNTH) and nitric acid (HNO_3) (VETEC) were used as reagents.

2.1.1. Zeolite synthesis

The zeolite synthesis tests were performed at the Environmental Analytical Chemistry Laboratory of Pontifica Universidade Católica do Rio Grande do Sul (PUC-RS). The zeolite mixture was synthesized according to the methodology adapted from Cardoso et al. [19]. The sequential flowchart of the material synthesis process is illustrated in Fig. 1.

The fly ash samples (30.0 g) were activated using 300.0 mL NaOH solution (2.0 mol L^{-1}) in a water bath under agitation for two h at 100ºC in order to extract the silicon from the fly ash. The solution was filtered, the filtrate (250 mL) was collected, and an extra source of aluminum was added to the filtered solution. Afterwards, the solution was held in a borosilicate glass reactor (Schott) for 1.5 h at 90ºC, and then the temperature of the solution was increased to 95ºC for 2.5 h (hydrothermal process).

After completion of the hydrothermal process, the zeolitic material was removed from the stove, and upon reaching the ambient temperature, it was filtered (glass fiber membrane, Millipore). The filter that contained the resulting zeolite was oven dried (105°C, 2 h) and then calcined (550°C, 5 h).

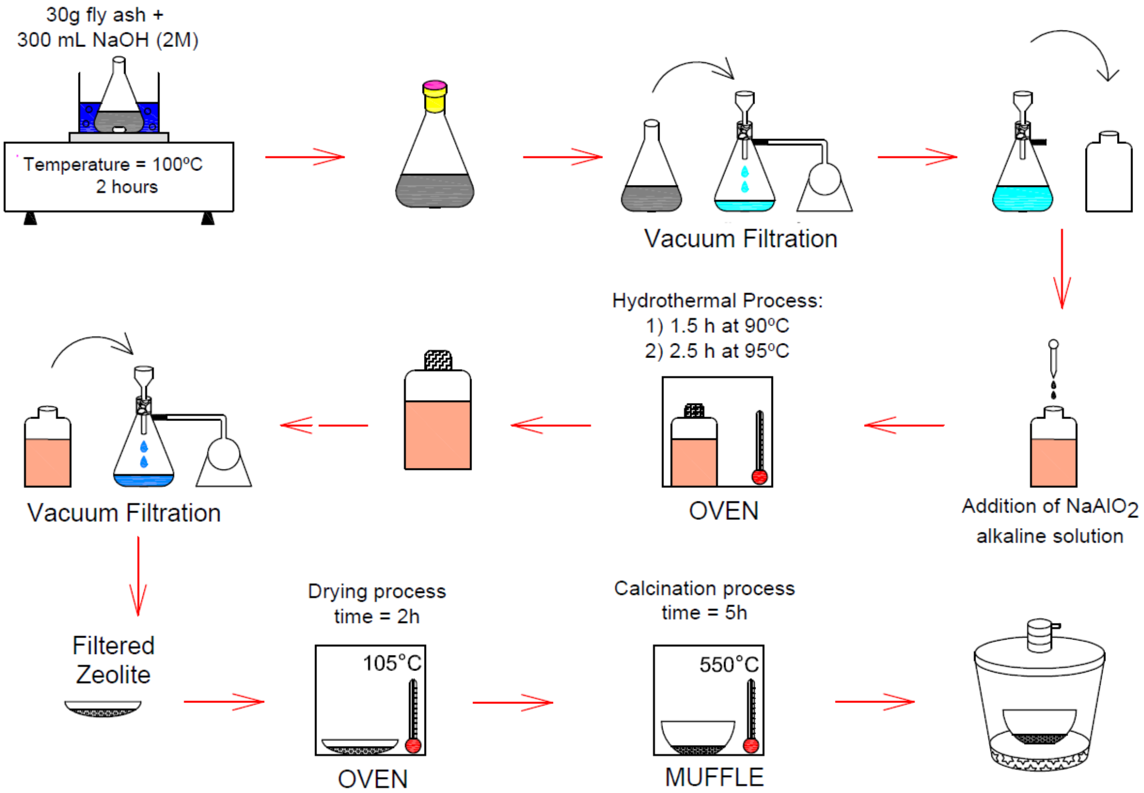


Fig. 1. Flowchart of zeolite synthesis from coal fly ash.

2.2. Characterization of the synthesized zeolite

The following characterization is an important process to obtain information about zeolite properties, such as crystallinity, specific area, morphology and chemical composition. These techniques complement each other for a better understanding of zeolite characteristics.

Among the various solid characterization techniques, X-ray diffraction is the most widely used in determining the crystalline phases that are present in clay minerals. This is possible because in these materials, the atoms are arranged in crystalline planes separated from each other by distances that are of the same order of magnitude as the X-ray wavelengths.

X-ray powder diffraction (XRD) patterns were recorded using an XRD diffractometer (DMAXB Rigaku X-ray diffractometer) with a CuKα radiation for crystalline phase with a routine power of 2000 W.

Elementary analysis was performed using energy-dispersive X-ray spectrometry (EDX) utilizing EDAX software.

Scanning electron microscopy (SEM) was performed on a JEOL JSM 6060 instrument with a resolution of 5 nm at 30 kV. Analyses were performed on a powdered sample that had previously been dried. A thin layer of gold sputter coating was added to avoid specimen charging [15].

FTIR spectroscopy was performed on a Prestige spectrometer from Shimadzu, Japan using the attenuated total reflectance method (ATR). The spectrum was generated and collected 32 times and corrected for the background noise. The experiments were performed on the powdered samples, without KBr addition.

2.3. Batch adsorption tests

2.3.1. Experimental design

A two-level factorial design (2^3) (screening design - STAT GRAPHICS Centurion, Stat Point technologies, Inc, VA 20186, USA) [21] consisting of 16 + 4 (central points) experimental trials was developed in duplicate. To determine the factors that influence the removal of metal ions by zeolite phases and to investigate the interaction effects of various parameters, three factors,including pH, adsorbent mass and initial metal concentration,were varied at two levels, as shown in Table 1.

Batch adsorption tests were conducted as follows: 25 mL Cu^{2+} solution was added to Erlenmeyer flasks in order to investigate the effects of pH, adsorbent mass and initial concentration according to the experimental design. The experiments were maintained under 200 rpm agitation for 48 h.

The equilibrium adsorption capacity (q) of the adsorbent for each test was calculated according to Eq. (1):

$$q = \frac{\left(C_i - C_f\right) * V}{m} \qquad (1)$$

where q is the equilibrium adsorption capacity (mg g^{-1}), C_i and C_f are the initial and final concentrations of the metal

Table 1
Factors used in the 2^3 fractional factorial design for studying the adsorption of Cu^{2+} on zeolite

Factors	Symbols	Levels		
		–1	0	+1
pH	A	2.0	3.5	5.0
Adsorbent mass (mg)	B	10	55	100
Initial metal concentration (mg L^{-1})	C	10	105	200

ion (mg L^{-1}), respectively, V is the volume of the solution in liters (L) and m is the mass of the adsorbent in grams (g).

2.3.2. Adsorption kinetics

After the experimental design tests, the best conditions were selected and used in the adsorption kinetics studies. For this experiment, 10 and 100 mg of the adsorbent were added to the Erlenmeyer flasks, and then 25 mL of 200 mg L^{-1} copper solution was added at pH 2.0 under a constant stirring rate of 200 rpm. The time intervals chosen were 1, 5, 10, 30, 60, 180, 360, 1440 and 2880 min. The experiments were performed in duplicate.

2.3.3. Adsorption Isotherms

100 mg of zeolite was added to the mono-element solution in the 25-mL Erlenmeyer flasks, with metal ion concentrations in the range of 10–1500 mg L^{-1} at pH 2.0. The experiments were performed in duplicate at 200 rpm for 24 h.

2.3.4. Copper quantitation

The concentration of Cu^{2+} was measured with an atomic absorption spectrophotometer (Varian AA240FS) using a hollow cathode lamp with a detection wavelength of 327 nm. Prior to analysis, samples were filtered and properly diluted with ultra pure water. The Cu^{2+} concentration should fit the linear range of the calibration curves, which ranged from 0.5 to 24 mg L^{-1} using the external standard method.

The software Hydra/Medusa Chemical Equilibrium Database and Plotting [22] was used to predict the polycations that were present in the solution according to the species-pH diagram.

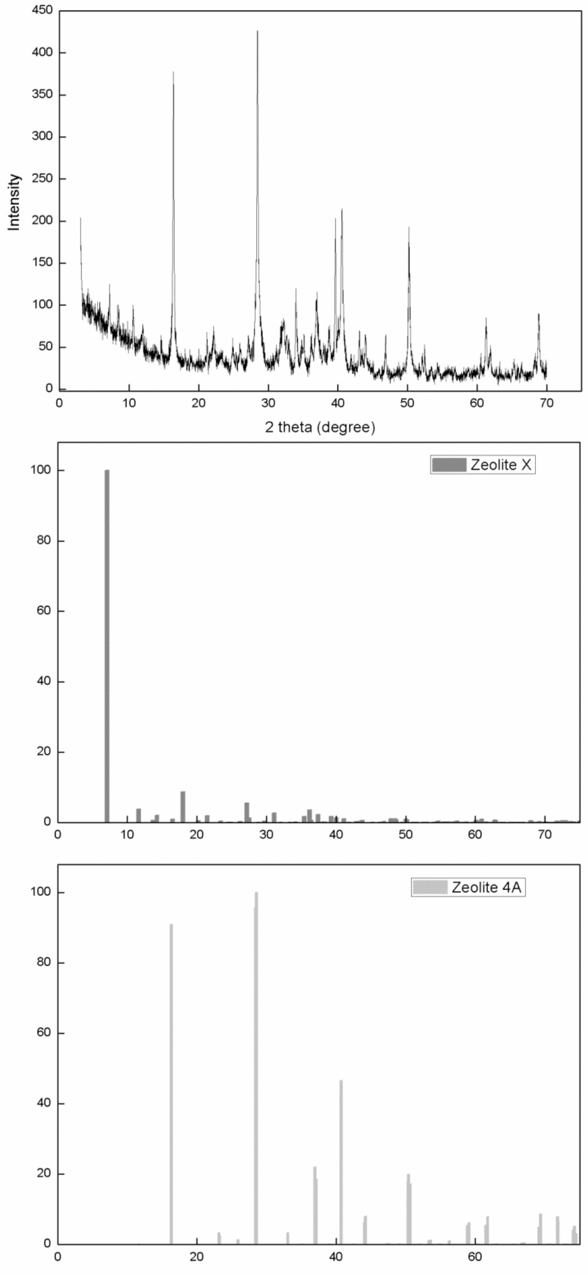


Fig. 2. XRD patterns of zeolite, Reference codes: 01-072-2422 (zeolite X); 01-072-2329 (Zeolite A.).

3. Results and discussion

3.1. Characterization of synthesized zeolites

X-ray diffraction (XRD) analysis was performed to identify the crystalline phases present in the material in order to identify the synthesized zeolite type. According to the XRD results (Fig. 2), there were two crystallographic phases, including FAU (zeolite X) and LTA (zeolite 4A) zeolites, indicating the formation of a material composed of a mixture of both zeolites.

LTA and FAU zeolites have different characteristics. The first presents low stability in an acid medium due to zeolite dealumination. The second presents good stability, which is an important factor for the adsorption tests of Cu^{2+} in acidic solutions.

It is well-known that the FAU/LTA composite zeolite is easily obtained from $Na_2O–Al_2O_3–SiO_2–H_2O$ systems using the tetramethyl ammonium cation (TMA+) as a structure-directing agent [20]. However, according to Queroel et al. [23], depending on the experimental conditions and the chemical composition of the ashes used in the synthesis, different types of zeolites are obtained by whatever method of synthesis was applied. More recent research has focused on processes that generate pure zeolites rather than a mixture

Table 2
Elemental analysis data, mass fraction (% m/m)

Element	%
O	32.20
Si	26.30
Al	24.00
Na	16.00
K	0.80
Cl	0.70

of materials. However, pure zeolites do not always obtain good results in toxic metals adsorption and the process of hydrothermal zeolite synthesis can often lead to the formation of LTA/ FAU composite zeolites.

The energy-dispersive X-ray (EDX) analysis was performed with the purpose of identifying and determining the elements present in the adsorbent. According to the percentage data (Table 2), it is apparent that the Si/Al ratio was equal to 1.11. Values of Si/Al > 1 are not common in type A zeolites, which proves the presence of a mixture of zeolitic phases. The literature reports Si/Al ratios of 1, 1.24 and 2.66 for zeolite types A, X and Y, respectively [24].

The morphology of the zeolite was evaluated by scanning electron microscopy, which can reveal the details of the surface morphology and aggregation of the adsorbent particles.

The morphology of the synthesized sample (Fig. 3) was similar to that reported in [24], in which a faujasite-type zeolite is identified by octahedral (bipyramidal) forms. It is noted in the micro graph that the crystal is well-defined, indicating good crystallinity for the synthesized phase. Crystals with cubic forms (typical morphology of zeolite 4A) [18,19] and spherical forms (relative to the presence of fly coal ash) [23] were also found, demonstrating the predominance of a mixture of zeolites (FAU and LTA) in the synthesized sample.

To identify the functional groups that contitute the zeolites, the zeolite absorption spectra in the infrared region were obtained. Fig. 4 shows the infrared spectra of the zeolites. The large band appears in the range from 500 to 1300 cm^{-1}. These bands are linked to Si-O-Si and Si-O-Al stretching vibrations [2,16].

3.2. Experimental design

To select the best conditions for the adsorption process of copper ions in the zeolite, a combination of the factor levels that were studied was performed. These include the initial concentration of the metal ions in solution, the adsorbent mass and pH. The experiments were conducted in duplicate. Table 3 presents the factorial design matrix and the average adsorption capacities for Cu^{2+} in the mixture of zeolites for each experiment.

It is apparent that the adsorption capacities vary widely depending on the experiment; that is, depending on the conditions to which the adsorbent and the adsorbate were subjected. It is also apparent that the highest adsorption capacity was found under the conditions of Experiment 9.

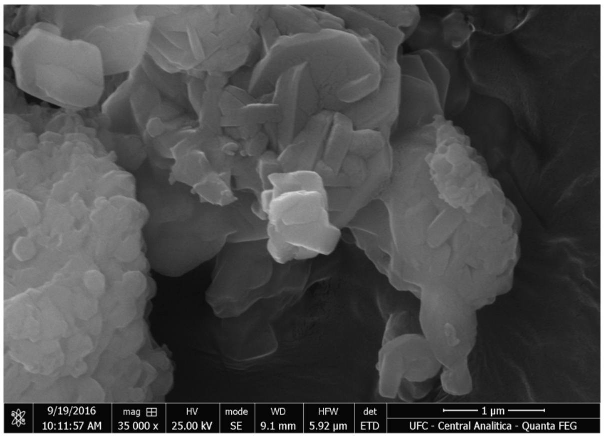


Fig. 3. SEM micrograph of synthetic zeolite.

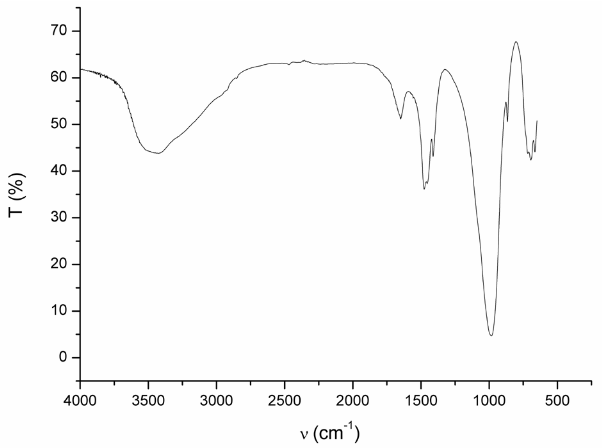


Fig. 4. Infrared spectrum of zeolite mixture.

Table 3
2^3 experimental range and levels of independent variables and average adsorption capacities for Cu^{2+}

Tests	pH	Adsorbent Mass (mg)	C_{in} (mg L^{-1})	q (mg g^{-1})
1	3.5	55	105	16.08
2	5.0	100	10	2.42
3	5.0	10	10	15.58
4	5.0	100	200	41.25
5	2.0	10	10	3.54
6	5.0	10	200	22.14
7	2.0	10	200	11.24
8	2.0	100	10	2.98
9	2.0	100	200	53.04
10	3.5	55	105	17.36

The analysis of variance (ANOVA) was performed for the data that are reported in Table 3 in order to evaluate the effects and significant coefficients. From the ANOVA, the coefficients were plotted on a Pareto chart (Fig. 5), where the effect was standardized, and the significant

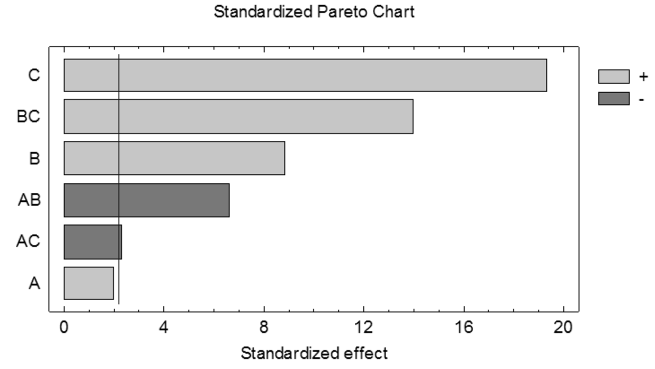


Fig. 5. Standardized Pareto chart of factorial design experiment, where: A - pH, B - adsorbent mass and C - initial metal concentration.

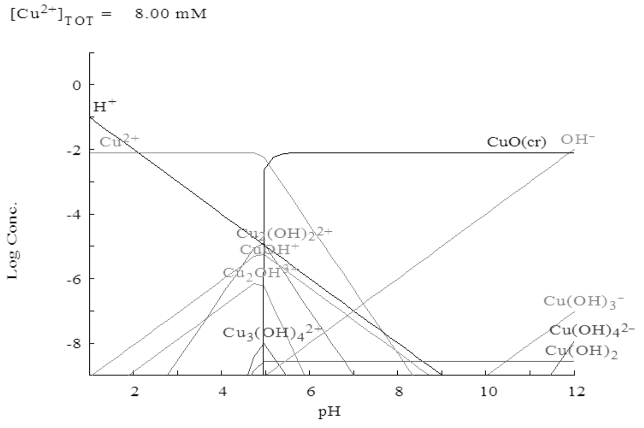


Fig. 6. Cu^{2+} complexes with OH- (Hydra/Medusa Chemical Equilibrium Database and Plotting Software).

variables were shown with a 95% confidence interval (p-value).

In the Pareto chart, it is apparent that the pH individually did not have a significant influence. However, the effects of interactions between the pH and the adsorbent mass and/or initial concentration showed significant and negative effects. The efficiency in the ion exchange process between the metallic ions and the adsorbent material depends on the size and the charge of the cation as well as the structure of the zeolite [26]. The pH affects the adsorption to the extent that it determines the degree of distribution of the chemical species. Since the surface charge of the zeolite is negative throughout its length, cation adsorption is favored [27,28]. An increase in pH leads copper to form complexes with OH^- (Fig. 6), and these complexes may not have as much affinity to the zeolites or even a steric hindrance due to the size of the complex. Thus, the best adsorption capacity occurred with the lowest pH. Similar results were found by Abreu and co-workers [29] in the study of cation removal from produced water using the synthetic zeolite 4A. The authors found better percentages of removal at pH 1.0, which agrees with results of the present study.

It is important to note that although it was not significant, the pH variable had a positive effect and was thus contrary to the interactions with the other variables. If the experiments had been conducted in a traditional manner, the pH variable would have been fixed at the highest level studied, leading to lower adsorption capacities. This shows the usefulness of factorial design in considering these interactions and leading to more consistent results and the overall analysis of the data.

The initial concentration and adsorbent mass variables had significant and positive effects on the adsorption tests. This means that the increase in the initial concentration of the ion studied and the increase of the mass of the adsorbent used resulted in an increase in the adsorption capacities of Cu^{2+} by the zeolite mixture. The interaction between the mass and initial concentration factors also resulted in a positive effect.

At pH 2, different cationic complex species are present in the solution (e.g., $Cu(OH)^+$ and$Cu_2(OH)^{n+}$), which might participate in the adsorption process.

The results obtained through factorial design suggest that an increase in the adsorbent mass provides a greater number of adsorptive sites on the zeolite, favoring an increase in the percentage of removal of the pollutant. That is, the larger the mass of the adsorbent, the more sites will be available for the coupling of the metal. Therefore, the best adsorption capacity was observed in the experiment with the largest zeolite mass. Sousa and co-workers [8] studied the removal of metal ions using treated green coconut shell and found an optimal dosage of adsorbent to be 30 g L^{-1} for Pb^{2+} and Cu^{2+} and 40 g L^{-1} for Cd^{2+}, Zn^{2+} and Ni^{2+}, varying the dosages from 10 to 50 g L^{-1}.

The initial concentration variable was the variable that presented the greatest significant and positive effect. By increasing the initial concentration, there is an increase in the concentration gradient; that is, the diffusion occurs so that the molecules of the more concentrated medium pass into the less concentrated medium until equilibrium is established. In addition, there is a liquid film around the particle that must be overcome by the ions in solution [30]. Thus, the increase in the initial concentration resulted in increased migration of the ions through the film, resulting in higher adsorption capacities.

Fig. 7 shows the main effects of the variables in the Cu^{2+} adsorption process associated with the synthetic zeolite.

It is apparent that the initial concentration and adorbent mass variables had positive effects. The adsorption capacity increased from approximately 5 to 30 mg g^{-1} when the initial concentration was increased from 10 to 200 mg L^{-1} and from 12 to 25 mg g^{-1} when the adsorbent mass was increased from 10 to 100 mg. This increase in adsorption capacity due to the increase in the initial concentration suggests that at higher initial concentrations, it is possible that a higher adsorption capacity could be found.

The effect of the pH variable, although positive, was not significant, as previously mentioned. It is apparent that the capacity increased from approximately 19 mg to 20 mg g^{-1} as pH increased. A linear mathematical model was obtained from the results, which is presented in equation 2. This model describes the behavior of the system within the experimental range studied, and it is possible to predict the copper adsorption capacity of the zeolite mixture. These equations are important because they summarize all

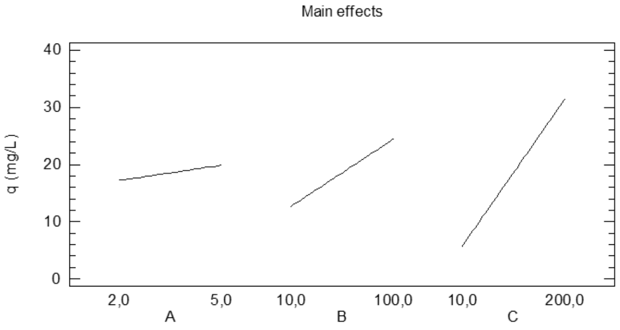


Fig. 7. Main effects of the variables on the Cu^{2+} adsorption process by the synthetic zeolite, where: A - pH, B - adsorbent mass and C - initial metal concentration.

the planning information carried out in a compact way and through we can calculate all the results.

$$q_{(Cu)^{2+}} = -9{,}95 + 5{,}61A + 0{,}13B + 0{,}053C - 0{,}065AB \\ -0{,}011AC + 0{,}0022BC \quad (2)$$

The linear coefficients and their interactions, in addition to being used in the generation of models as explained above, define or approximate the most adequate conditions to maximize the ion removal efficiency based on the synergies and impacts of the evaluated effects on the adsorption capacity [31]. Thus, a response optimization study helps to identify the operating conditions that will result in a desirable maximum response [32]. From the obtained data, an optimization function was used in order to determine the optimal conditions for maximum removal of the copper ion using the zeolite. The following conditions were found to obtain the higher adsorption capacities: pH of 2.0; adsorbent mass of 100 mg, and initial copper concentration of 200 mg L^{-1}.

Table 4 shows the predicted and experimental values of zeolite adsorption capacity under the optimized conditions. The calculated t value obtained using Student's t-test is also presented to statistically verify if there is a difference between the predicted and experimental values (H_0: exp. = pred.). It can be observed that the experimental value was lower than that predicted value that was obtained using Eq. (2). However, the t-test showed that the experimental value is statistically equal to the predicted value, showing that the model is predictive for the studied range.

3.3. Adsorption kinetics

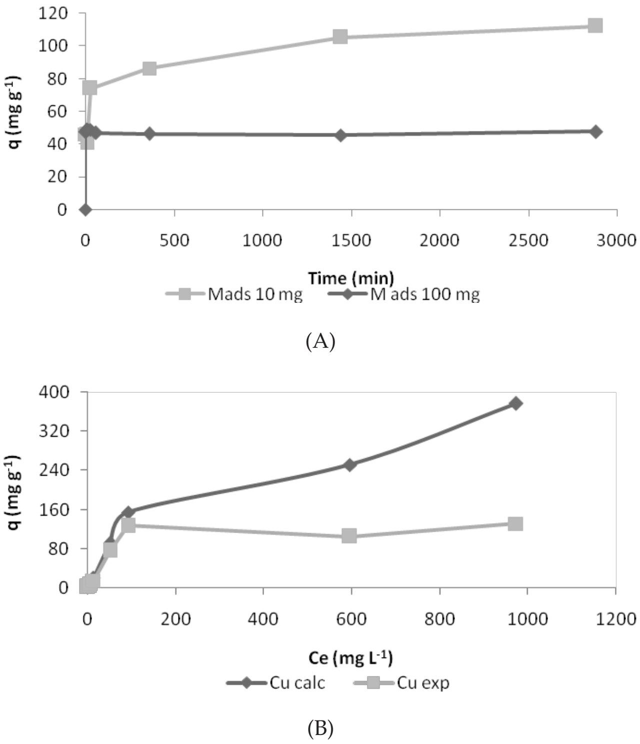
Adsorption kinetics studies express the solute removal rates that control the residence time of the adsorbate in the solid–solution interface. In practice, the concentration of the adsorbate remaining in solution decreases with time, and at a certain point, it reaches a constant value. From that moment onward, there is no further removal of the pollutant (metal) from the solution. The time required to reach this state is called the equilibrium time [1].

Fig. 8A shows time versus zeolite adsorption capacity using 10 and 100 mg of adsorbent. When the system was run using 10 mg of zeolite, the equilibrium time was reached in 24 h, whereas using 100 mg, a faster equilibrium time of 5 min was observed. It is apparent that for the kinetic test using 100 mg of adsorbent, the efficiency removal of 95% was achieved in the initial time, whereas using 10 mg of adsorbent, the maximum removal efficiency was reached at 24 h (1440 min).

Table 4
Predicted and experimental adsorption capacities values obtained by the optimization function for zeolite

Ion	*q* (mmol g^{-1})		*t* calculated
	Predicted	Experimental	
Cu^{2+}	51.32	44.23	–3.75

Critical *t* = 12.7 (degrees of freedom = 1; α = 0.05).



(A)

(B)

Fig. 8. Adsorption kinetics (A) and Adsorption isotherms of Cu^{2+} using zeolite as an adsorbent from experiment and calculated from experimental design (Eq. (2)) (B).

Antunes and co-workers [33] performed adsorption kinetics tests using zeolite 4A for removing metal ions in a batch system. They found that the adsorption process occurred in two steps. In the first 30 min, they observed fast adsorption, after which the equilibrium time was reached slowly.

According to Vidal and co-workers [16], the adsorption kinetics are initially fast because adsorption occurs predominantly on the outer surface, followed by a slow adsorption step onto the inner surface of the adsorbent. The zeolite microporous volume is considered to be large [16], which might explain the slow adsorption process obtained in the present work. As the first step of adsorption might be affected by the metal ion initial concentration and stirring rate, an increase in the metal ion concentration turned the diffusion process onto the zeolite outer surface more rapidly [34].

3.4. Adsorption Isotherms

The adsorption isotherms were determined for the metal-zeolite system, setting the equilibrium time as 24 h and the solution pH as 2.0. Adsorption isotherms of the Cu^{2+} onto the zeolite phases were obtained by plotting the concentration of Cu^{2+}adsorbed on the solid phase (q) vs. its concentration in the liquid phase (C_e). As shown in Fig. 8B, the value of maximum adsorption found was 120 mg g^{-1} for the isotherm experimental test. Analyzing the shape of the isotherm, more information about the adsorption process can be obtained. It can be observed that, until reach saturation, the experimental isotherm obtained is linear. This tells us that the adsorbate mass retained (per unit mass of the adsorbent) is proportional to the equilibrium concentration of the adsorbate in the liquid phase. It may be seen that a high concentration of solute in the liquid phase is required for a high concentration of adsorbate in the solid phase. Although, the adsorption capacity of Cu^{2+} increased with increasing equilibrium concentration and attained a saturated value, presenting a plateau.

To verify the behavior of the mathematical models obtained from the experimental design study, values of q were calculated using Eq. (2) for the same experimental conditions that were used in the adsorption isotherm,which were compared to the experimental data (Fig. 8B).

It is apparent that the calculated data fit the experimental data, especially at low concentrations. The isotherms overlap until the point where the equilibrium concentration is reached. Thus, these results show the importance and usefulness of experimental planning as a tool in the modeling and prediction of data in adsorption systems. There are no data in the literature that have performed the same study for comparison purposes.

Table 5 shows the results obtained from the Cu^{2+} adsorption tests using the LTA/FAU synthetic zeolite phases as adsorbents in the present work compared to other studies that only used pure phase zeolite as an adsorbent. It is clear that the mixture of phases in the synthesized zeolite that was used in this work showed better Cu^{2+} adsorption capacity than pure zeolites.

Table 5
Comparison of adsorption capacity of different zeolites in adsorption of Cu^{2+}

Method	Zeolite	Adsorption capacity (meq g^{-1})	Reference
Fixed-bed column	Na-clinoptilolite	0.68–0.84	[35]
Fixed-bed column	Natural clinoptilolite	0.16–0.55	[35]
Fixed-bed column	Natural clinoptilolite	0.08–0.55	[35]
Equilibrium isotherms	Natural clinoptilolite	1.00	[36]
Fixed-bed column	Na-clinoptilolite	1.39	[37]
Batch System	Na-clinoptilolite	1.76	[38]
Fixed-bed column	Natural clinoptilolite	0.37	[28]
Batch System	FAU/LTA composite zeolite	3.80	This work

4. Conclusions

An experimental design is fundamental for finding the best adsorption conditions. The present work showed that the initial concentration and adsorbent mass variables had significant effects on the adsorption of copper in a mixture of synthetic zeolites as well as their respective interactions. The pH variable individually had no significant effect. However, its interactions with the other two variables had significant negative effects. The adsorption kinetics showed that the equilibrium time was reached after 24 h. The adsorption isotherm study indicated a maximum zeolite capacity for copper ion removal of approximately 120 mg g^{-1}. The mixture of LTA and FAU types of zeolites proved efficient in copper removal, and as such,the mixture can be evaluated for use in environmental treatments that involve copper in aqueous solutions.

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