Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2016.1183230

57 (2016) 27843–27850
December

Taylor & Francis
Taylor & Francis Group

Modification of natural zeolite for Cu removal from waste waters

Sajjad Aghazadeh[a,*], Eshagh Safarzadeh[b], Mahdi Gharabaghi[a], Mehdi Irannajad[b]

[a]*School of Mining Engineering, College of Engineering, University of Tehran, Tehran, Iran, emails: sajadaghazadeh@yahoo.com (S. Aghazadeh), gharabaghi@ut.ac.ir (M. Gharabaghi)*
[b]*Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, Tehran, Iran, emails: eshagh.safarzadeh@gmail.com (E. Safarzadeh), irannjad@ut.ac.ir (M. Irannajad)*

Received 6 September 2015; Accepted 10 April 2016

ABSTRACT

In the current research work, the ability of a Fe-modified clinoptilolite for Cu^{2+} adsorption from aqueous solution was investigated. Mineral characteristics were examined by optical microscope, X-ray diffraction, SEM, and chemical analysis using XRF spectroscopy. Results showed that clinoptilolite, quartz, and gypsum are the main minerals and natural clinoptilolite contained high amounts of SiO_2 (61.0%) and Al_2O_3 (9.3%) in the representative sample. The effects of important parameters including chemical conditioning, initial metal concentration, initial pH, and environmental temperature on Cu^{2+} adsorption were investigated. The results showed that the Cu^{2+} adsorption mechanism was strongly dependent on metal concentration and pH. In addition, adsorption data have been interpreted in terms of Langmuir and Freundlich equations. Basing on observation, Fe-modified clinoptilolite has a particularly high potential for Cu^{2+} removal.

Keywords: Clinoptilolite; Iron nitrate; Copper; Adsorption; Waste water

---

1. Introduction

Nowadays, polluting industries are dealing with the issue of heavy metal removal from aqueous media due to their hazardous repercussions for the water quality and their toxicity for living organisms.

Heavy metals in wastewaters are not biodegradable and hence tend to gather in living organisms, causing various illnesses and problems [1,2]. Main methods to remove heavy metals from wastewaters include coagulation, carbon adsorption, ion exchange, precipitation, reverse osmosis, etc. [3]. Adsorption process is usual for the removal of heavy metals from the waste water and has advantages when compare to other removal techniques because it is more economical and readily available [4,5].

Zeolite usage for environmental remediation is an established method. The unique physical and chemical properties (crystallinity, thermal stability, well-defined cage structure of molecular size, ion exchange, etc.) combined with their abundance have made them useful in many industrial and research applications [6–9].

The prominence of zeolite use in environmental application is due to its high ion exchange capacity, molecular sieve properties, which can be easily modified to make them selective of certain ion sizes, nontoxic nature, wide availability in natural forms, the low cost of its synthetic fabricating, its disposal after use, and its simple use [1,2,7,10]. Their main

---

*Corresponding author.

applications are as chemical sieves, water softeners, and adsorbents that all of these refer to their structural characteristics and adsorbent properties [11]. Different complexes of alkaline and alkaline-earth cations and water molecules can be held in structural cavities and channels of zeolite [12,13]. The main process for removal of heavy metals from drinking water and wastewaters using zeolites is ion-exchange, wherein Na^+, K^+, Ca^{2+}, etc. ions that are present in the pores of zeolite are replaced by toxic metal ions from solution [14,15]. Ion exchange process depends mainly on the nature and concentration of cations and anions, temperature, pH, and crystal structure of the zeolite [16–18].

Clinoptilolite is the most well known and abundant natural zeolite that has partly high purity large minable sedimentary deposits in many parts of the world [19,20]. The negative charge of the clinoptilolite framework is counterbalanced with cations such as (Na^+, K^+, Ca^{2+}, Mg^{2+}) which come from tetrahedral-coordinated aluminum [21].

Chemical conditioning of zeolite surface with certain surfactants makes it a potential adsorbent for cationic species. Fe-modified zeolites were reported to be capable of adsorbing high concentrations of heavy metals in solutions, which mainly depend on the pH, temperature, and metal concentration [22–28].

In this study, an economical, readily available, and successful adsorbent material, clinoptilolite, was identified as an attractive alternative adsorbent for Cu^{2+} removal from polluted aqueous solutions after coating with iron oxides. The main aim of this study was to survey the capability of using Fe-modified clinoptilolite for the maximum removal of Cu^{2+} ions from aqueous solutions.

2. Material and methods

2.1. Materials

Representative samples of natural zeolite were taken from Abegarm mine (Semnan, Iran) with a particle size range of 0.5–0.7 mm. A solution of metal was prepared in a concentration of 1,000 mg/L using metal salt dissolved in deionized water. The artificial Cu solution for batch study was made using $CuSO_4{\cdot}6H_2O$ while pH values were adjusted by adding NaOH and HCl solutions. Mineralogical characteristics of sample was examined by X-ray diffraction (XRD), chemical analysis (XRF), optical microscopy, and scanning electron microscopy (SEM) after and before the experiment.

2.2. Sample preparation

The Fe-modified sample was made by following the method of pure goethite preparation [29]. The sample was prepared by mixing 30.0 g of clinoptilolite, 100 ml of freshly prepared 1 M Fe $(NO_3)_3$ solution, and 180 ml of 5 M KOH solution in a 2 L polyethylene flask. The suspension was diluted to 2 L with twice distilled water and was held in a closed polyethylene flask at 70°C for 60 h. Then, the precipitate was washed (until free of NO^{3-} ions) and finally dried for one day.

3. Mineralogical results

In order to identify the mineralogy of the sample and determine interlocking minerals, several thin and polished sections were prepared from different parts of sample and then studied by optical microscope. According to Fig. 1, the main minerals were found to be clinoptilolite, quartz, and gypsum. In addition, iron oxide (Hematite), calcite, and plagioclase were determined as minor minerals inside the representative sample.

Mineralogical study including XRD test was performed. The results showed that clinoptilolite, quartz, and gypsum were the main minerals with high peak representation in Fig. 2. XRF also was carried out which the result is shown in Table 1. As can be seen, natural clinoptilolite contained high amounts of SiO_2 (61.0%) and Al_2O_3 (9.3%) while the contents of other metal oxides were insignificant. Clinoptilolite ($(Na, K)_6(Al_6Si_{30}O_{72}){\cdot}20H_2O$) has a density 2.16 g/cm^3, hardness of 3–4 with white color and monocline crystals. $CaCO_3$ was distributed in the clinoptilolite because pH of adsorption in the clinoptilolite/water ratio of 1:1 was higher than 7 which implies that alkaline agent ($CaCO_3$) should be presented in the clinoptilolite sample.

For further sample characterization, scanning electron microscope (SEM) was used before and after experiment. Results are given in Fig. 3. It is observed that the particles have a rather spherical morphology. In addition, cation exchange capacity of clinoptilolite was found to be about 1.73 mequiv g^{-1} and the main exchange cations were Ca^{2+}, Mg^{2+}, Na^+, and K^+ with prevalence of the latter.

As it appears from SEM images in Fig. 3, microporous structures (i.e. 3-D structures) of modified clinoptilolite have been remarkably increased comparing to its natural form. This feature could be attributed to washing out some impurities from the surface of natural clinoptilolite and forming new porous structures instead.

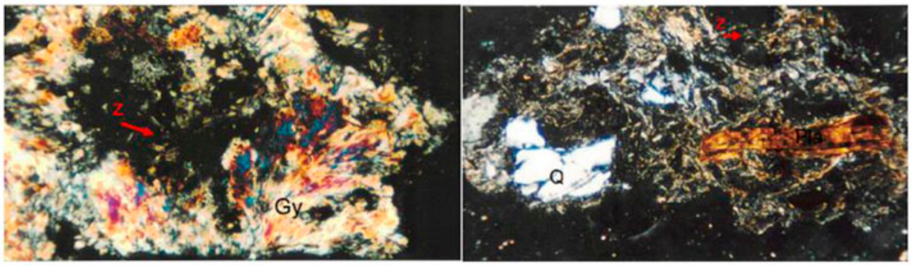

Fig. 1. Zeolite sample polish sections, Gy = Gypsum, Z = Zeolite, Q = quartz.

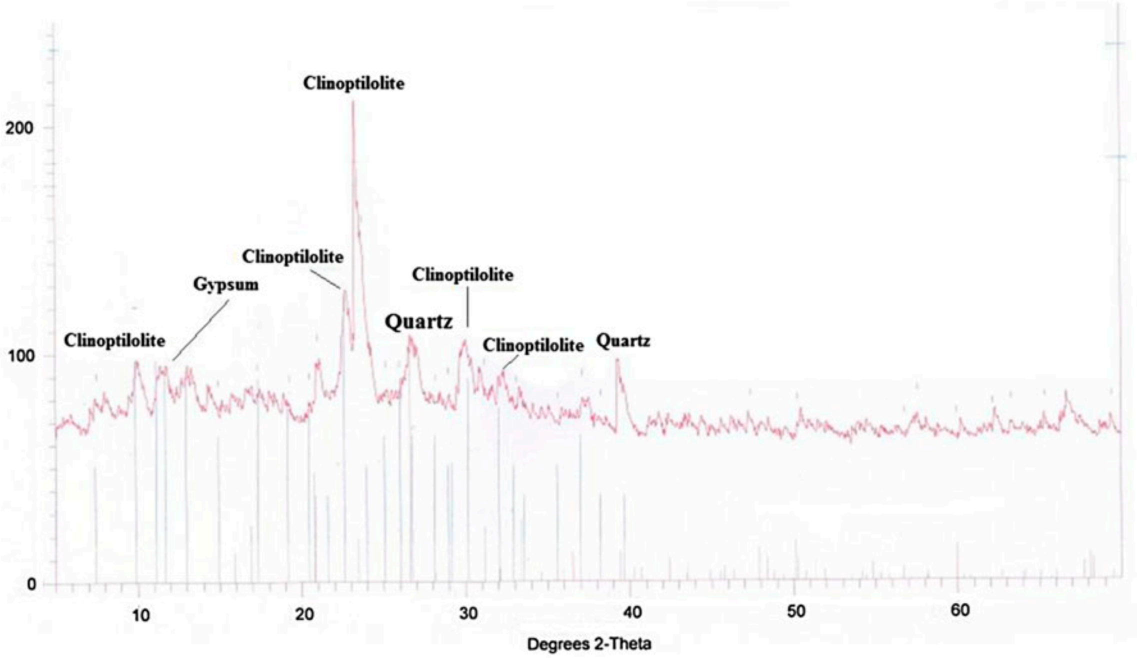

Fig. 2. XRD spectra of head sample.

Table 1
Chemical composition of clinoptilolite sample using XRF (wt. %)

Components	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI	Si/Al
%	61.3	0.33	9.55	1.40	3.68	0.78	3.68	2.68	2.80	13.90	6.42

4. Results and discussion

4.1. Batch adsorption studies

Batch adsorption studies were conducted by mixing 2 g of natural or Fe-modified clinoptilolite with 40 ml of synthetic solutions containing different concentration of heavy metal ions, at 23 ± 2˚C. The mixture was equilibrated for 24 h and then filtered. The final concentration of the heavy metal ions in the aqueous phase was then determined using atomic absorption spectrophotometer (AAS). The error in analyzing the cations was approximately ±5.61% for Cu^{2+}.

The following parameters were used in order to survey the system at equilibrium: adsorption capacity of the substrate (q_e) expressed in terms of metal amount absorbed on the unitary natural adsorbent mass (mg g^{-1}) and adsorption efficiency of the system ($\%S_{eff}$) indicated from the percentage of removed

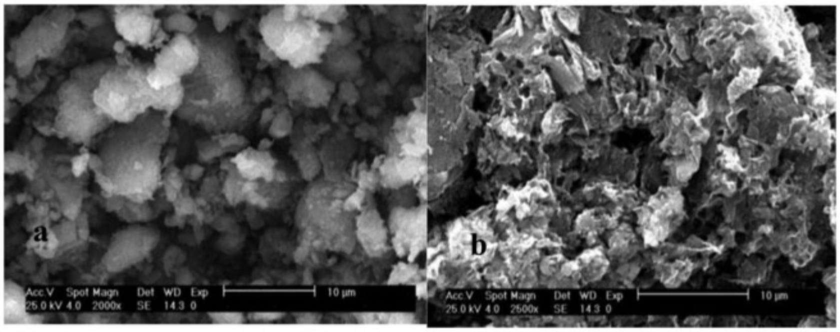

Fig. 3. SEM images of clinoptilolite before and after modification by $Fe(NO)_3$ (a) natural clinoptilolite and (b) modified clinoptilolite by $Fe(NO)_3$.

metal ion relative to the initial amount. These parameters have been calculated as indicated below:

$$q_e = \frac{(C_i - C_f) \times V}{m} \quad (1)$$

$$S_{eff} = \frac{(C_i - C_f)}{C_i} \times 100 \quad (2)$$

where C_i (mg L^{-1}) and C_f (mg L^{-1}) are the initial and final concentration of metal ion in the solution, respectively. V (L) is the volume of solution and m (g) is the mass of adsorbent.

4.2. Effect of solution pH

The effect of solution pH was investigated in four different values from 2.5 to 5.5. Then, 40 ml of solution with initial concentration of 500 mg/L was contacted with 2 g of Fe-modified clinoptilolite for 24 h. The amount of copper ions adsorbed from solution increases with an increase in initial solution pH as shown in Fig. 4. Natural zeolite preferentially adsorbs H^+ ions from solution to heavy-metal ions [30,31], and thus in more acidic conditions more H^+ ions are adsorbed from solution. As pH value increases from 2.5 to 5.5, the H^+ ions concentration tends to decrease, giving way to more heavy-metal ions being adsorbed from solution as indicated by the increase in q_e [32].

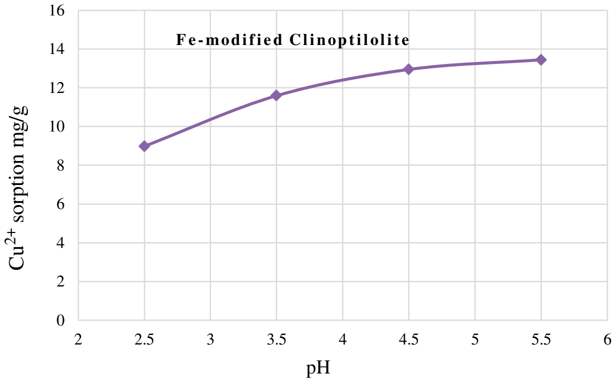

Fig. 4. Effect of initial pH on metal adsorption for (T = 20°C, pH 2.5–5.5, S/L = 1/20).

In addition, natural zeolites are generally weakly acidic in nature and are selective for hydrogen, which leads to more alkaline solution when the exchanger is equilibrated with relatively dilute electrolyte solutions making metal hydroxide precipitation feasible [33]. Thus, the solution pH increases as the reaction proceeds.

A slight precipitation was observed in some of the adsorption reactions which indicate that removal of heavy-metal ions from solution by natural zeolite was not only due to ion exchange reactions and also metal ions could be adsorbed on the surface of natural zeolite by precipitation.

4.3. Effect of metal concentration on Cu^{2+} adsorption

Copper adsorption was examined using extent range of Cu initial concentrations. Fig. 5 represents the adsorbed Cu amounts in relation to the solution Cu^{2+} concentrations. It seems that the Fe-modified clinoptilolite tends to improve Cu adsorption on its surface as Cu initial concentration of the solution increases from 200 to 1,000 mg/L. Owing to the presence of non-crystalline Fe formations located in cationic positions in the zeolite channels, as well as of amorphous iron oxides (goethite) located at the surface of the zeolite crystal, the new sample has higher adsorption capacity than untreated clinoptilolite [34]. The higher adsorption detected for the Fe-modified clinoptilolite,

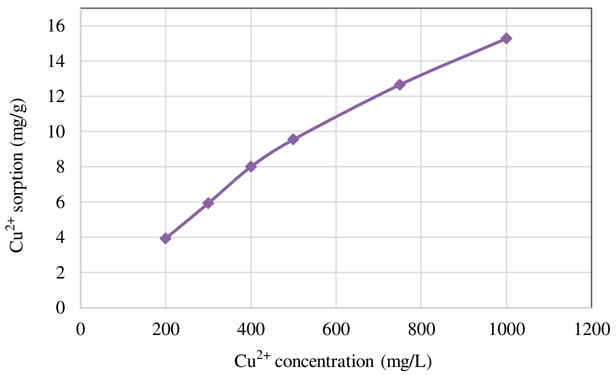

Fig. 5. Effects of metal concentration on metal adsorption ($T = 20$°C, pH 4.5–5.5, $S/L = 1/20$).

is also due to its high negative surface charge [23]. The experimental adsorption capacity of Cu^{2+} for the conditioned clinoptilolite was 15.26 mg of Cu^{2+} per one gram of zeolite, indicating that this adsorbent was appropriate for copper removal from aqueous media.

4.4. Effect of temperature on Cu^{2+} removal

The influence of temperatures (20, 40, and 60°C) on the metal removal efficiency was examined while keeping all other parameters constant (Fig. 6). Forty milliliters of solution with initial concentration of 500 mg/L was contacted with 2 g of Fe-modified clinoptilolite for 24 h in different temperatures in an oven. Obviously, since the temperature of the conditioning was being raised, the reaction kinetics has been increased. Because temperature increases the kinetic energy of reacting molecules by causing frequent collisions; therefore, this increases the successful exchange of cations in Fe-modified clinoptilolite, such as K^+ and Ca^{2+} facilitating the exchange of heavy-metal ions in aqueous solutions [35,36]. As can be seen from Fig. 6, temperature did not affect the Cu^{2+} adsorption for low Cu^{2+} concentrations including 200, 300, 400, and 500 mg/l. However, increasing Cu^{2+} concentration up to 1,000 mg/l tends to slightly improve Cu^{2+} adsorption on the surface of Fe-modified clinoptilolite.

4.5. Adsorption isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships; the two main isotherm models used in this work are the Langmuir and Freundlich models.

Langmuir isotherm is used for describing monolayer homogeneous adsorption processes with the following equation [37]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L\, q_m} \tag{3}$$

where C_e is equilibrium concentration of Cu^{2+} ions (mg/L) and q_e is the amount of the Cu^{2+} ions adsorbed (mg) by per unit of clinoptilolite (g). q_m and K_L are the Langmuir constants related to the monolayer capacity (mg/g) and the equilibrium constant (mg/L), respectively.

Freundlich isotherm is used for explaining the adsorption on heterogeneous surfaces as follows [38]:

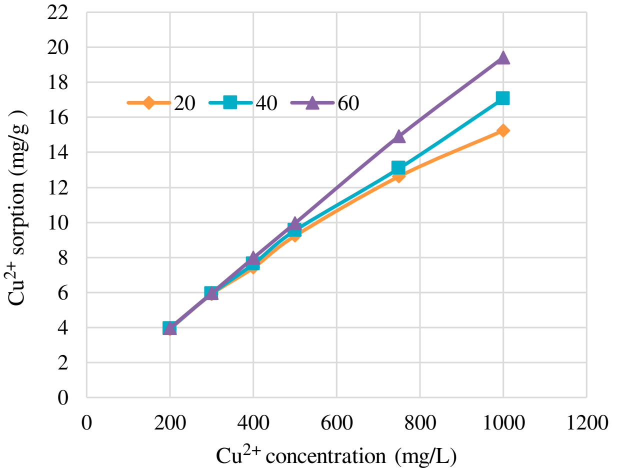

Fig. 6. Effect of temperature on Cu^{2+} adsorption ($T = 20$, 40, 60°C, pH 3.5–5.5, $S/L = 1/20$).

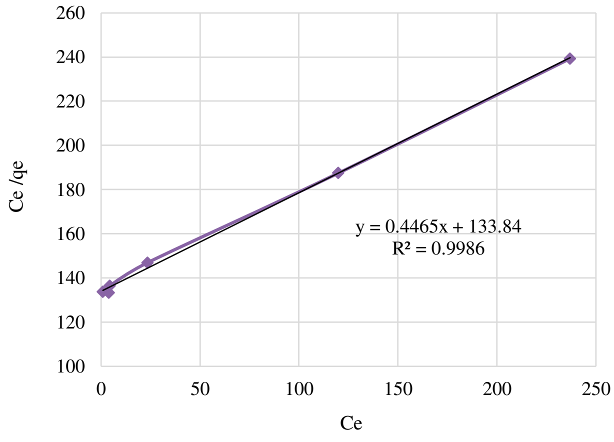

Fig. 7. Linearized Langmuir isotherms for Cu^{2+} adsorption by Fe-clinoptilolite.

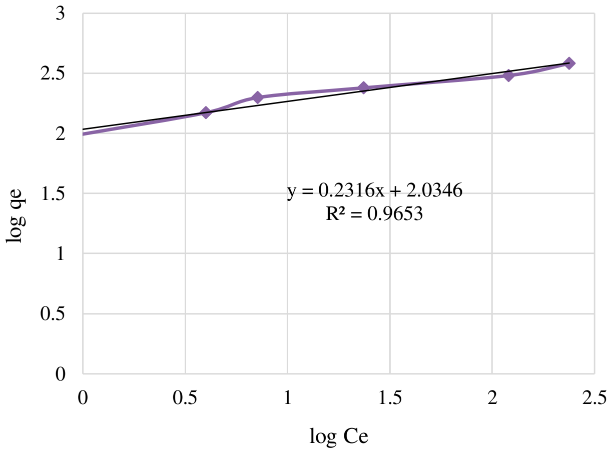

Fig. 8. Linearized Freundlich isotherms for Cu^{2+} adsorption by Fe-clinoptilolite.

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{4}$$

where K_F (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

As shown in Figs. 7 and 8, the experimental data fits well with the linearized Langmuir and Freundlich isotherms. Generally, the Langmuir isotherm provided the best correlation for Fe-modified clinoptilolite with a regression coefficient of 0.99 (Fig. 7).

Freundlich parameters (K_F and n) specify whether the nature of adsorption is either favorable or unfavorable [39]. The intercept and the slope refer to adsorption capacity and adsorption intensity, respectively. A partly slight slope of $n < 1$ indicates that adsorption intensity is favorable to the entire range of concentrations studied, while a steep slope ($n > 1$) means that adsorption intensity is good (or favorable) at high concentrations but much less at lower concentrations [39,40]. A high value of the intercepts, K_F, is indicative of a high adsorption capacity [40]. In the present adsorption study, n value is more than unity which indicates that adsorption intensity is favorable at high concentrations.

The usage of two isotherm models for Cu^{2+} adsorption suggests that monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions. The adsorption of Cu^{2+} ions on the clinoptilolite is complex which suggests that there is more than one mechanism in the adsorption process.

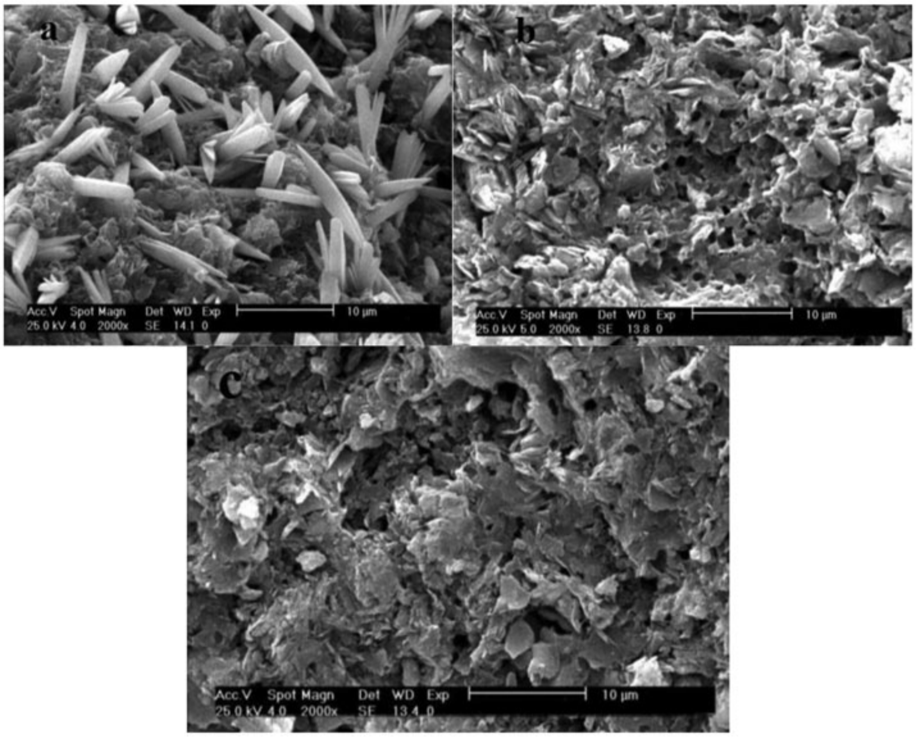

Fig. 9. SEM images after Cu^{2+} adsorption (a) Cu^{2+} adsorption on the surface of Clin-Fe; Temperature: 40°C, pH 4, Cu^{2+} con.: 1,210 ppm, time: 12.5 h, (b) Cu^{2+} adsorption inside porous structures of Clin-Fe; Temperature: 40°C, pH 4, Cu^{2+} con.: 650 ppm, time: 12.5 h, (c) Cu^{2+} adsorption decrease because of pH decrease; Temperature: 40°C, pH 2.5, Cu^{2+} con.: 650 ppm, time: 12.5 h.

4.6. SEM images after adsorption mechanism

In order to examine zeolite surface before and after adsorption mechanism and control this mechanism, initial samples of zeolite before the experiment (Fig. 3) and residues of Cu^{2+} after adsorption (Fig. 9) were investigated. Based on drawn conclusions from Fig. 3, Fe-modified zeolite surfaces were abundant in microporous structures. As adsorption time increases, Cu^{2+} in aqueous solution interacts with surface structures and causes zeolite surface to be altered (Fig. 9). As pH and temperature increase in the solution, Cu^{2+} precipitation (i.e. in the form of copper hydroxide) on the zeolite surface tends to increase which implies that precipitation along with ion exchange and adsorption could affect the mechanism. In general, as soon as adsorption time, temperature, and pH increase in the solution, precipitation on the surface of zeolite improves. However, pH decrease in the solution will inhibit Cu^{2+} precipitation on the zeolite surface (Fig. 9(c)). This shows that pH strongly affects the porous structure of Fe-modified zeolite by precipitation in the pH values less than 4.

5. Conclusion

Adsorption study of Cu^{2+} using Fe-modified clinoptilolite was investigated in the present research work. The main minerals were clinoptilolite, quartz, and gypsum, and iron oxide (hematite), calcite, and plagioclase were determined as minor minerals inside the representative sample. Clinoptilolite contained high amounts of SiO_2 (61.0%) and Al_2O_3 (9.3%). Adsorption was significantly dependent on the pH and initial metal concentration while temperature slightly improved the Cu^{2+} adsorption only for Cu^{2+} concentrations higher than 500 mg/l. Results showed that the highest q_e values were obtained using solutions adjusted at pH values between 4.5 and 5.5. Furthermore, Cu^{2+} adsorption was improved by increasing Cu^{2+} initial concentration from 200 to 1,000 mg/L and temperature from 20 to 60˚C. In this study, the fitting of Langmuir and Freundlich equations used to describe the metal adsorption process showed that the Langmuir isotherm gives the best agreement over the whole adsorption range. Adsorption isotherms also revealed that monolayer adsorption and heterogeneous surface conditions exist under the experimental conditions. SEM images proved that precipitation along with ion exchange and adsorption controls the Cu^{2+} adsorption mechanism, especially for higher pH and temperature values. Moreover, it was found that Fe-clinoptilolite is an effective and inexpensive adsorbent for Cu^{2+} removal from aqueous solutions.

References

[1] M.A. Stylianou, M.P. Hadjiconstantinou, V.J. Inglezakis, K.G. Moustakas, M.D. Loizidou, Use of natural clinoptilolite for the removal of lead, copper and zinc in fixed bed column, J. Hazard. Mater. 143 (2007) 575–581.
[2] M. Sprynskyy, B. Buszewski, A.P. Terzyk, J. Namieśnik, Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+}, and Cd^{2+}) adsorption on clinoptilolite, J. Colloid Interface Sci. 304 (2006) 21–28.
[3] W.W. Eckenfelder, Industrial Water Pollution Control, McGraw-Hill, New York, NY, 1989.
[4] Ö. Yavuz, Y. Altunkaynak, F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite, Water Res. 37 (2003) 948–952.
[5] H. Cui, L.Y. Li, J.R. Grace, Exploration of remediation of acid rock drainage with clinoptilolite as sorbent in a slurry bubble column for both heavy metal capture and regeneration, Water Res. 40 (2006) 3359–3366.
[6] K.B. Payne, T.M. Abdel-Fattah, Adsorption of divalent lead ions by zeolite and activated carbon: Effect of pH, temperature, and ionic strength, J. Environ. Sci. Health Part A 39(9) (2004) 2275–2291.
[7] K.B. Payne, T.M. Abdel-Fattah, Adsorption of arsenate and arsenite by iron treated activated carbon and zeolite; effects of pH, temperature, J. Environ. Sci. Health 40(4) (2005) 723–749.
[8] T.M. Abdel-Fattah, L.K. Isaacs, K.B. Payne, Small arms range lead management issues: Activated carbon, molecular sieves (5A and 13X), and naturally occurring zeolites as lead adsorbents, Fed. Facil. Environ. J. 14(2) (2003) 113–126.
[9] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: A review, J. Hazard. Mater. 97 (2003) 219–243.
[10] J. Perić, M. Trgo, N.V. Medvidovic, Removal of zinc, copper and lead by natural zeolite—A comparison of adsorption isotherms, Water Res. 38 (2004) 1893–1899.
[11] H. Ghobarkar, O. Schäf, U. Guth, Zeolites—From kitchen to space, Prog. Solid State Chem. 27 (1999) 29–73.
[12] M. Wark, W. Lutz, G. Schulz-Ekloff, A. Dyer, Quantitative monitoring of side products during high loading of zeolites by heavy metals, J. Zeolites 13 (1994) 658.
[13] S.C. Stefanovic, L. Curkovic, T. Filipan, Metal ion exchange by natural zeolites, Croat. Chem. Acta 69 (1996) 281–290.
[14] C. Colella, Ion exchange equilibria in zeolite minerals, Miner. Deposita 31 (1996) 554–562.
[15] M. Rožić, Š. Cerjan-Stefanović, S. Kurajica, M.R. Maěefat, K. Margeta, A. Farkaš, Decationization and dealumination of clinoptilolite tuff and ammonium exchange on acid-modified tuff, J. Colloid Interface Sci. 284(1) (2005) 48–56.
[16] I. Rodríguez-Iznaga, G. Rodriguez-Fuentes, A. Benítez-Aguilar, Role of carbonat ions on the ion exchane $Ni^{2+} = 2NH^{4+}$ in natural clinoptilolite Microporous and Mesoporous Materials 41 (2000) 129–136.
[17] A. Maes, A. Cremers, Ion exchange of synthetic zeolite X and Y with Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ions, J. Chem. Soc., Faraday Trans. 1: Phys. Chem. Condensed Phases 71 (1975) 265–277.

[18] I. Rodríguez-Iznaga, A. Gómez, G. Rodríguez-Fuentes, A. Benítez-Aguilar, Natural clinoptilolite as an exchanger of Ni^{2+} and NH^{4+} ions under hydrothermal conditions and high ammonia concentration, Microporous Mesoporous Mater. 53(1–3) (2002) 71–80.

[19] G. Gottardi, E. Galli, Natural Zeolites, Springer-Verlag, Berlin, 1985.

[20] F.A. Mumpton, Natural Zeolites Occurrence Properties and Use, Pergamon, New York, NY, 1976.

[21] Y. Takéuchi, K. Koyama, Clinoptilolite: The distribution of potassium atoms and its role in thermal stability, J. Crystallogr. 145 (1977) 216–239.

[22] A. Dimirkou, Uptake of Zn^{2+} ions by a fully iron-exchanged clinoptilolite. Case study of heavily contaminated drinking water samples, Water Res. 41 (2007) 2763–2773.

[23] M. Doula, Removal of Mn^{2+} ions from drinking water by using clinoptilolite and a clinoptilolite–Fe oxide system, Water Res. 40 (2006) 3167–3176.

[24] M. Doula, Synthesis of a clinoptilolite–Fe system with high Cu sorption capacity, Chemosphere 67 (2007) 731–740.

[25] M. Doula, A. Dimirkou, Use of an iron-overexchanged clinoptilolite for the removal of Cu^{2+} ions from heavily contaminated water samples, J. Hazard. Mater. 151 (2008) 738–745.

[26] A. Dimirkou, A. Ioannou, M. Doula, Preparation, characterization and sorption properties for phosphates of hematite, bentonite and bentonite hematite systems, Adv. Colloid Interface Sci. 97 (2002) 37–61.

[27] L. Zhaohui, J. Jiin-Shuh, J. Wei-Teh, C. Po-Hsiang, C. Chun-Jung, L. Libing, Removal of arsenic from water using Fe-exchanged natural zeolite, J. Hazard. Mater. 187 (2011) 318–323.

[28] E. Eren, Removal of lead ions by Unye (Turkey) bentonite in iron and magnesium oxide-coated forms, J. Hazard. Mater. 165 (2009) 63–70.

[29] U. Schwertmann, R.M. Cornell, Iron Oxides in the Laboratory, Preparation and Characterization, VCH Verlags-gesellschaft mbH, Weinheim, New York, 1991.

[30] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Ion exchange of Pb^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+} on natural clinoptilolite: Selectivity determination and influence of acidity on metal uptake, J. Colloid Interface Sci. 261 (2003) 49–54.

[31] S. Myroslav, B. Buszewski, A.P. Terzyk, J. Namiesnik, Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+}) adsorption on clinoptilolite, J. Colloid Interface Sci. 304 (2006) 21–28.

[32] N. Moreno, X. Querol, C. Ayora, Utilization of zeolites synthesized from coal fly ash for the purification of acid mine waters, Environ. Sci. Technol. 35 (2001) 3526–3534.

[33] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.

[34] J. Pérez-Ramírez, G. Mul, F. Kapteijn, J.A. Moulijn, A.R. Overweg, A. Doménech, A. Ribera, I.W.C.E. Arends, Physicochemical characterization of isomorphously substituted FeZSM-5 during activation, J. Catal. 207 (2002) 113–126.

[35] L. Ćurković, Š. Cerjan-Stefanović, T. Filipan, Metal ion exchange by natural and modified zeolites, Water Res. 31 (1997) 1379–1382.

[36] U. Wingenfelder, B. Nowack, G. Furrer, R. Schulin, Adsorption of Pb and Cd by amine-modified zeolite, Water Res. 39 (2005) 3287–3297.

[37] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.

[38] H. Freundlich, Concerning adsorption in solutions, Z. Phys. Chem. 57 (1906) 385–470.

[39] M.A. Zenasni, S. Benfarhi, A. Merlin, S. Molina, B. George, B. Meroufel, Adsorption of nickel in aqueous solution onto natural maghnite, Mater. Sci. Appl. 4(2) (2013) 153–161.

[40] E. Worch, Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling, Walter de Gruyter, Technical University Dresden, Germany, 2012.