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The Effect of Preparation Conditions on the Removal Efficiency of Water Pollutants Using LTA Zeolite

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Abstract

In this study LTA zeolite was prepared from kaolin. The effect of ultrasonic irradiation on the crystal structure and ability to ion exchange of some heavy metals were studied. Many techniques were used to characterize the prepared zeolite includes X-ray diffraction analysis (XRD) with crystal lattice analysis, Electron paramagnetic resonance (EPR) and finally ion exchange isotherm of some heavy metal ions. The results showed that the ultrasonicated zeolite exhibits different behavior towards ion exchange with increasing its capacity. The ultrasonicated zeolite showed little increase in the lattice parameters with increasing in the crystal size. Fitting adsorption isotherms on the metal adsorbed showed an observable change in the behavior of ultrasonicated zeolite towards the metals exchanged.

Keywords

Zeolite, XRD, Lattice Parameters, Ultra Sonication, Ion Exchange, Silica

1. Introduction

The preparation of zeolites from clays and raw materials was a subject of many researches in the past decades [1] [2] [3] [4]. The zeolites were considered to be three dimensional alumino silicate structures consists of tetrahedral of TO_4 (T, Si or Al). The resulting combination of these tetrahedra resulted in excess negative charge which balanced by a mobile cation [5]. These distinct proprieties of zeolite enable it form perfect performance in ion exchange. In addition to that, the three dimensional arrangements inside the zeolite structure add a variety of porous structures within the range of micropores [6] [7]. Many synthetic zeolites require what is called template, acts as a directing agent to the required pores [8]

[9]. Most of these templates are organic compounds; however water could also be considered as a template for some kinds of zeolites like LTA, FAU, ANA [10] [11] [12]. Many syntheses today include the ultrasonic as a helping and new parameters in preparation of many inorganic and organic compounds [13] [14] [15] [16] [17]. The effect of ultrasonic in such preparation is subject of many studies in that area [15] [16]. Our systems include the preparation of LTA for white Saudi silica. To our knowledge this is the first time to study the effect of ultrasonic in such system. We aim to shed some light on the effect of ultrasonic on the crystal structure and its effect on ion exchange behavior towards some heavy metals.

2. Experimental

2.1. Materials Used

Saudi Arabia white silica is utilized for additional source of silica, Sodium hydroxide (Merck), copper nitrate (Merck), nickel Nitrate (Merck), Lead (II) Nitrate (Merck). Local kaolin.

2.2. Synthesis

Synthesis of materials was carried out by first hydrothermal treatment of white silica with sodium hydroxide for 24 hours at 150˚C under autogenous pressure.

The role of silica solution is to absorb the ultrasonic irradiation by increasing the viscosity of the gel synthesizing mixture.

After that a gel mixture was prepared from kaolin and silicate solution prepared from the previous step and hydrothermally treated at 95˚C for 5 hours (0 time of ultrasonic irradiation). This step is repeated but the gel mixture is subjected first to ultrasonic irradiation for different time intervals at 70˚C at power of 430 W, then complete the time of 5 hours in normal hydrothermal treatment.

The composition of the mixture is adjusted to prepare LTA zeolite

2.3. Characterization Techniques

2.3.1. Adsorption Experiment

A 0.5 g of zeolite sample is mixed with 100 ml of solutions of Cu^{2+}, Ni^{2+} and Pb^{2+} with diverse concentrations. Continuous stirring at room temperature for 1 hour is utilized.

2.3.2. X-Ray Diffraction Analysis (XRD)

X-Ray diffractograms of different solids are collected using a Bruker D8 advance instrument with CuKα1 target with secondly monochromator 40 kV, 40 mA. Crystal lattice and space group analysis are done using PhilpsX'Pert Plus V. 1.0 23.04. 1999.

2.3.3. Scanning Electron Microscope (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX) Analysis

Scanning electron microscope (SEM) images of different solids and EDX data is collected using instrument "JXA-840 an Electron probe Micro Analyzer-Japan".

2.3.4. Electron Paramagnetic Resonance (EPR)

The EPR spectra are measured on EMX Bruker instrument operated at X-band frequency. The following conditions are global to all solids unless specified in the manuscript. Microwave frequency: 9.79 GHz. Receiver gain: 60. Sweep width: 6000 center at 3480 Gs. Microwave power: 0.202637 W.

2.3.5. Elemental Analysis

Elemental analysis is measured by the use of ICP (Inductively Coupled Plasma) Optical emission Spectrometer, Model Optima 4100 DV, Perkin Elmer, U.S.A.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis (XRD)

The XRD analysis showed that the diffraction pattern of ultrasonic irradiated and non-irradiated samples of zeolites (Figure 1) showed a very well crystalline form of pure phase of LTA zeolite. The crystal lattice analysis of all samples (Table 1) showed a small difference in lattice parameters. The little increase in lattice parameters of ultrasonic irradiated sample suggests that the crystal size is

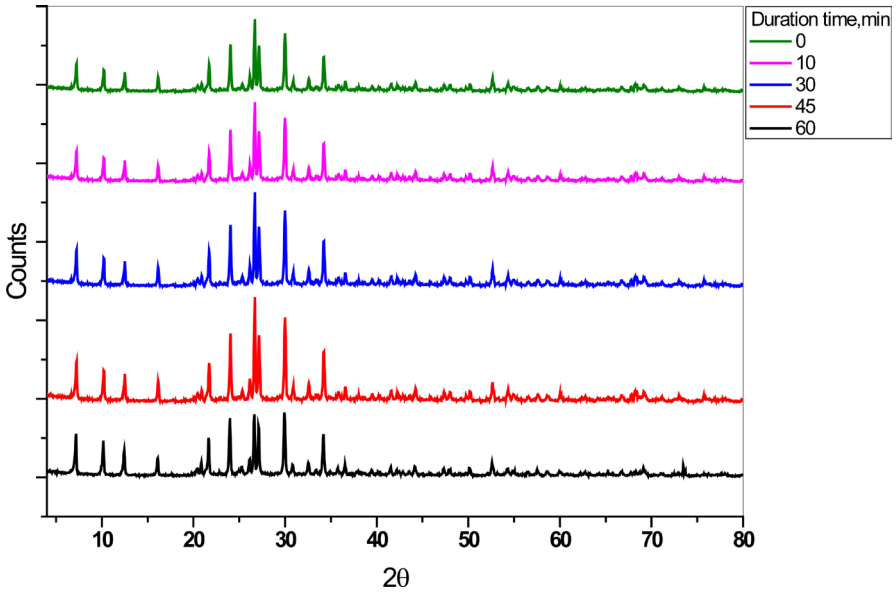

Figure 1. Effect of ultrasonic irradiation time on the XRD patterns of LTA zeolite.

Table 1. Lattice parameters of zeolite samples.

	Lattice parameters	a	b	c	α	β	γ	Space group
Duration of ultrasonic irradiation, min	60	12.296	12.296	12.296	90	90	90	Pm-3
	45	12.290	12.290	12.290	90	90	90	Pm-3
	30	12.288	12.288	12.288	90	90	90	Pm-3
	10	12.282	12.282	12.282	90	90	90	Pm-3
	0	12.280	12.280	12.280	90	90	90	Pm-3

increasing slightly by increasing the time of irradiation. This slight increase will be a subject of investigation on ion exchange behavior.

3.2. Scanning Electron Microscope (SEM) and Energy-Dispersive X-Ray Spectroscopy (EDX) Analysis

SEM images of 60 min ultrasonic irradiated sample and non-irradiated one are given in (Figure 2 & Figure 3). These images showed a very famous cubic structure of LTA zeolites. The image analysis of these images showed that the crystal diameter of irradiated sample has a value of 1.08 μm which is little increase than that of non-irradiated sample which has a value of 0.99 μm. This indicates that the ultrasonic irradiation during the preparation process enhances that crystallization and growth process as confirmed before from the XRD patterns.

The EDX elemental analysis showed that the atomic ratio of Si/Al at the surface for irradiated sample is 1.15 which is less than that of non-irradiated sample (1.2). This means that the Al in irradiated sample is much concentrated to the surface. Hence the presence of Al in tetrahedron of any zeolite structure is responsible for the existence of excess negative charge and consequently of labile cation, then it is supposed that the irradiated sample could be more accessible for ion exchange than that of non-irradiated one. Although the value of Si/Al ratio of LTA zeolite is supposed to be only 1, the effect of surface excess concentration of Al may affect the mode of adsorption of zeolite as will be seen later from correlation of different adsorption isotherms.

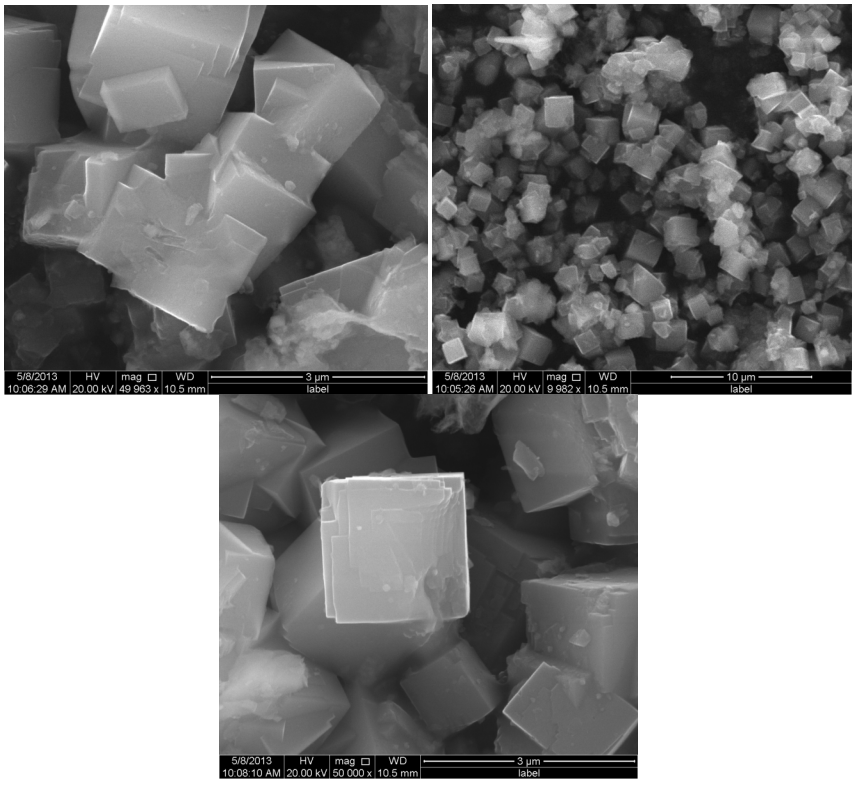

Figure 2. SEM of non-irradiated zeolite sample at different magnifications.

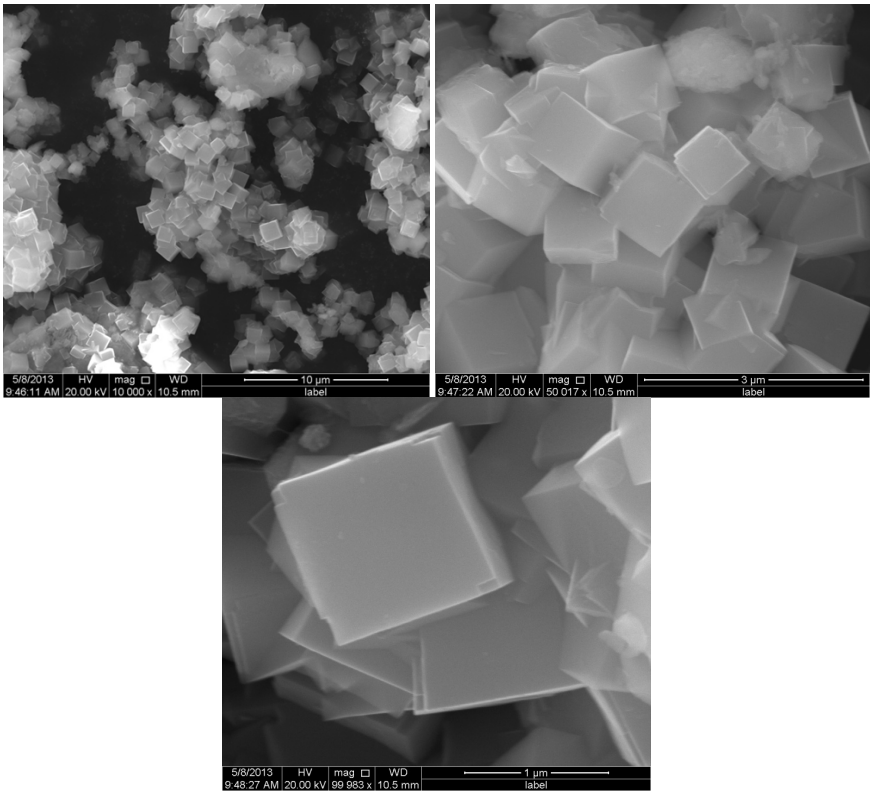

Figure 3. SEM of 60 min irradiated zeolite sample at different magnifications.

3.3. Electron Paramagnetic Resonance (EPR)

The EPR technique is usually used for the detection of paramagnetic centers. The bare zeolite matrix showed a two groups of signals, one centered at g = 4.3 and other at g = 2 which is due to the presence of iron impurities in the raw materials from which zeolite is prepared (**Figure 4**).

The EPR of copper exchanged zeolites (**Figure 5**) showed a sharp signal of Cu^{2+} species which characterize the presence of highly paramagnetic species of copper in zeolite matrix. Although this signal is ordinary for Cu^{2+} species in such matrix, a trial is done for correlate it to the amount of copper species inside the zeolite (**Figure 6**). This correlation was attained linearly with R^2 value near 96 means that it is possible to correlate the peak to peak signal to the amount of copper exchanged on the zeolite matrix. Although the relation is not pass through the origin as could be expected but this may be due to the overlap of signal of iron impurities exist in the bare zeolite matrix with those of copper species.

3.4. Ion Exchange Isotherms

The ion exchange isotherms of copper, nickel and lead ions of both zeolite samples (60 min time ultrasonic irradiated and non-irradiated) are shown in (**Figure 7** & **Figure 8**). Form these figures; it could be observed that for both irradiated and non-irradiated samples the preference of Cu^{2+} and Pb^{2+} ions is much higher than that of Ni^{2+}. Also, the ultrasonic irradiation affects slightly the preference

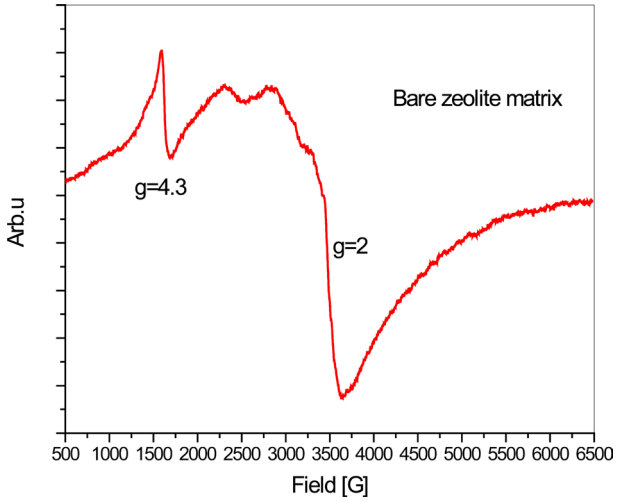

Figure 4. EPR spectrum of bare zeolite matrix.

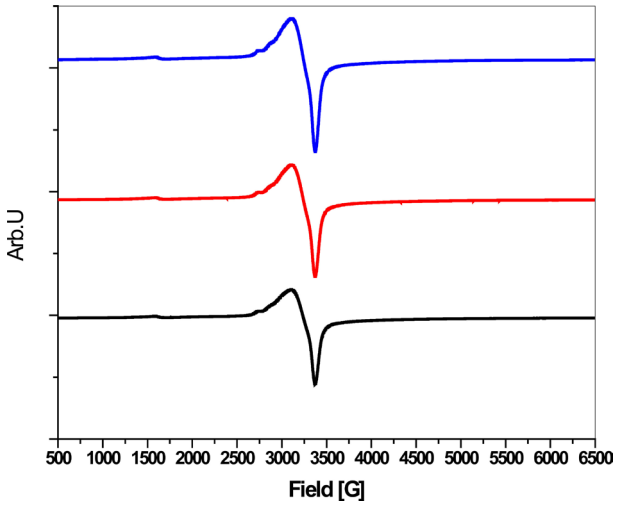

Figure 5. EPR spectra of different samples of ion exchanged copper zeolites at different concentrations.

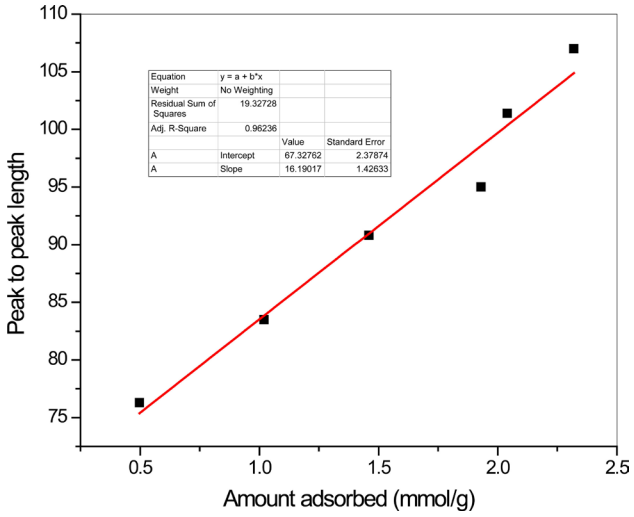

Figure 6. Correlation between peak to peak lengths of EPR signal with the amount adsorbed per gram of copper.

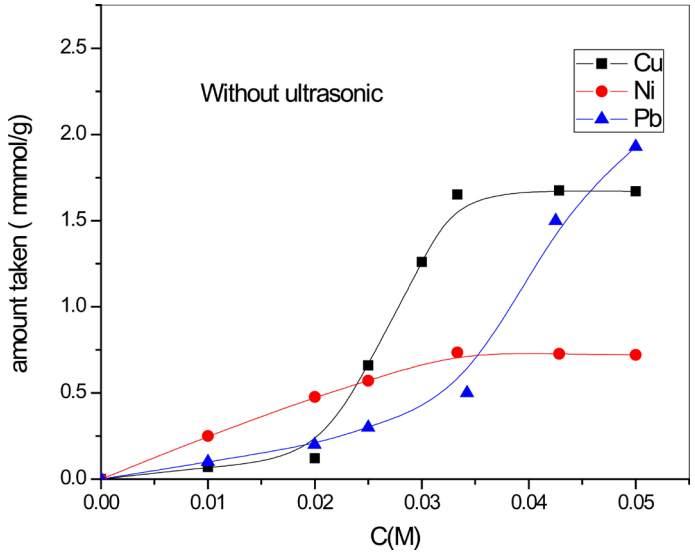

Figure 7. Ion exchange isotherms of copper, nickel and lead ions over non-irradiated sample of zeolite with ultrasonic.

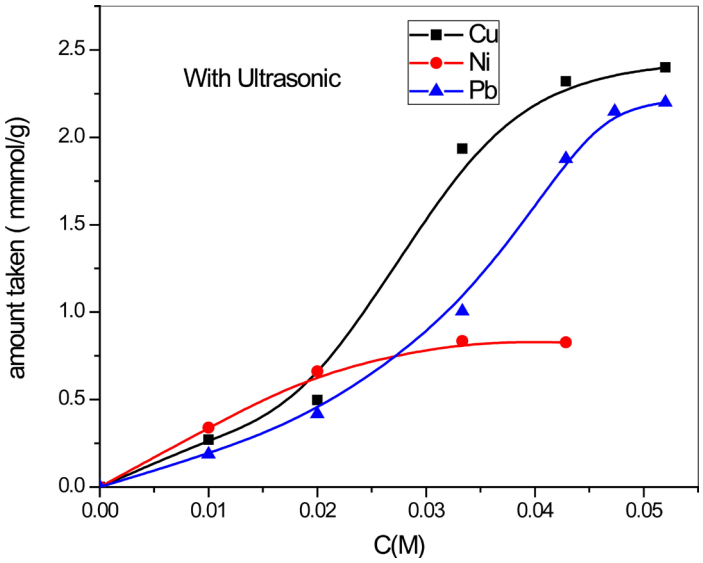

Figure 8. Ion exchange isotherms of copper, nickel and lead ions over 60 min ultrasonic irradiated sample of zeolite.

between Cu^{2+} and Pb^{2+}. (Figures 9-11) showed the different behavior of ultrasonic irradiation time on different ions separately. From these figures, it is clearly observed that there is a progressive increase in the amount adsorbed as the time of ultrasonic irradiation increases.

In order to deeply understand the ion exchange behavior of these samples Langmuir and Freundlish isotherms of different samples are fitted. The correlation factor of both sample are summarized in (Table 2). From this table, it could be recognized that the value of correlation of both isotherms are similar. In other words, the mechanism of ion exchange of these ions should be mixed between two isotherms.

Taking into consideration that the Feundlish isotherm could better represent

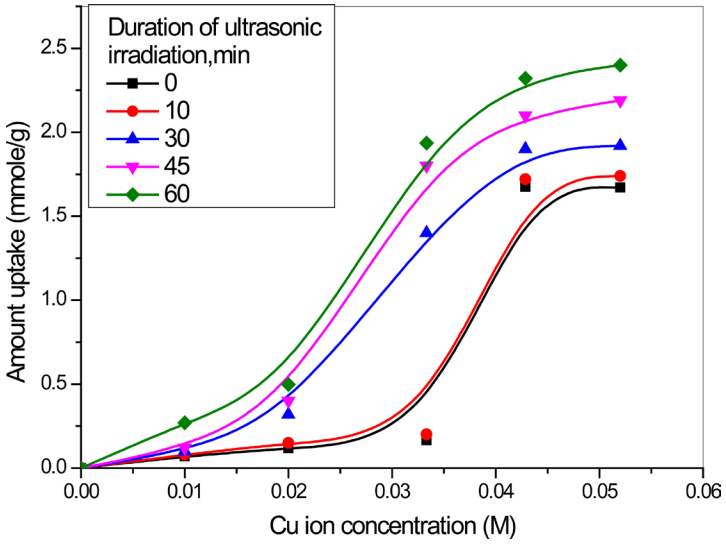

Figure 9. Effect of ultrasonic irradiation on the adsorption isotherm curve of Cu^{2+} ions.

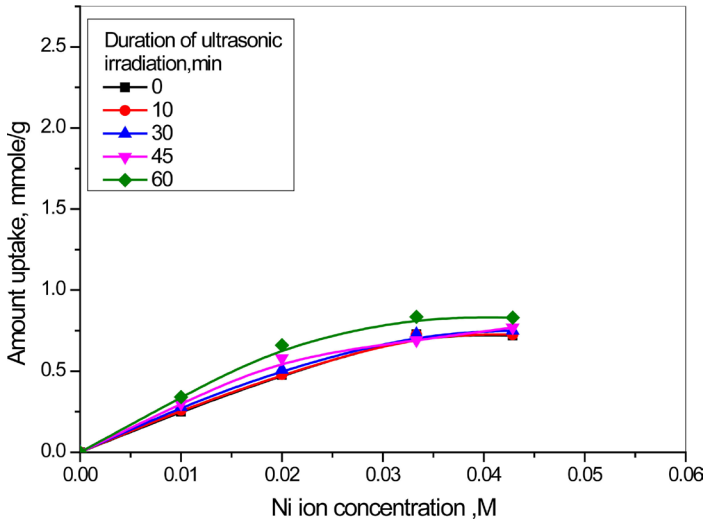

Figure 10. Effect of ultrasonic irradiation on the adsorption isotherm curve of Ni^{2+} ions.

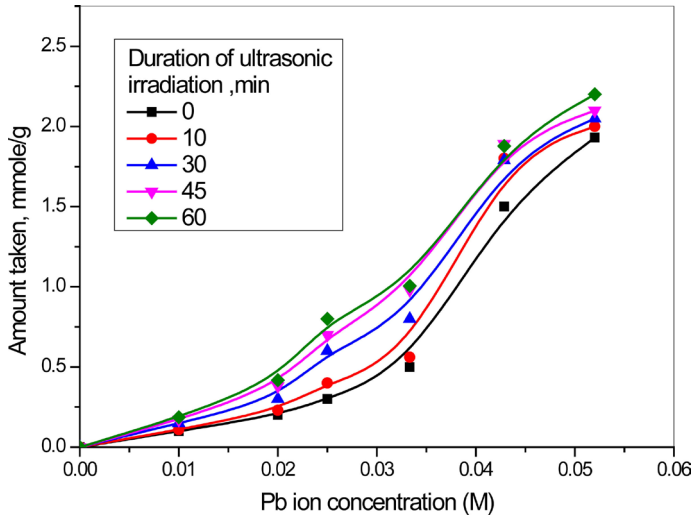

Figure 11. Effect of ultrasonic irradiation on the adsorption isotherm curve of Pb^{2+} ions.

Table 2. Ion exchange capacity of different prepared samples with correlation factors of both Freundlsih and Langmuir isotherms over different samples examined.

	Ion exchanged capacity (mmol/g)	Cu^{2+}	R^2 Freundlisch isotherm	R^2 Langmuir isotherm	Ni^{2+}	R^2 Freundlisch isotherm	R^2 Langmuir isotherm	Pb^{2+}	R^2 Freundlisch isotherm	R^2 Langmuir isotherm
Duration of ultrasonic irradiation, min	60	2.4	0.82	0.81	0.80	0.93	0.88	2.20	0.98	0.95
	45	2.19	0.84	0.82	0.77	0.94	0.90	2.1	0.97	0.96
	30	1.92	0.83	0.9	0.75	0.92	0.88	2.05	0.97	0.94
	10	1.74	0.81	0.86	0.73	0.99	0.98	2.00	0.89	0.93
	0	1.66	0.80	0.88	0.71	0.99	0.99	1.92	0.89	0.98

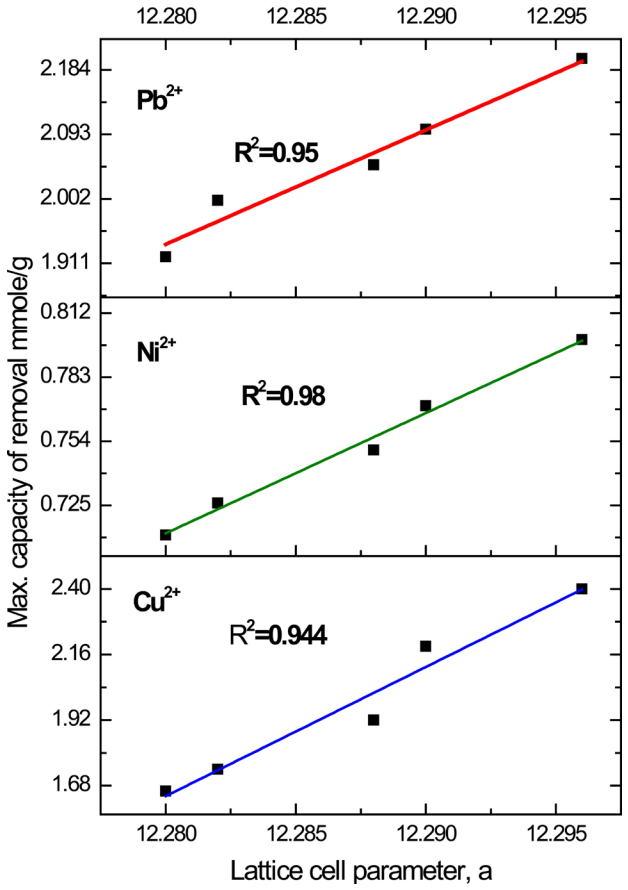

Figure 12. Effect of lattice parameter (a) variation on the maximum capacity of removal of different ions.

the multilayer adsorption, however, Langmuir isotherm could better represent the monolayer one.

The last observation means that the adsorption in zeolite matrix occurs in non-stoichiometric behavior (*i.e.* not ion by ion), however the multilayer adsorption could be contributed. The multilayer adsorption could be understood by assuming that the metal ions could be precipitated due to the excess alkalinity inside the pores [18]. And hence as proven before from XRD, SEM and EDX

analysis that the ultrasonically irradiated samples showed larger size of both pores and crystals this may explain their ability to ion exchange by higher amount more than that of ultrasonic non-irradiated.

In order to declare the role of ultrasonic irradiation on the crystal lattice of zeolite and also with the ion exchange capacity, a relation between the lattice cell parameter of different ultrasonic irradiated and non-irradiated samples with the capacity of each ion exchanged under investigation in this study (**Figure 12**). From this figure it is clear observed that, there is a direct correlation between the crystal lattice parameter (a) with the capacity removed. And hence the crystal lattice was also directly correlated to the time of ultrasonic irradiation (**Table 1**). Hence we can conclude that as the time of ultrasonic irradiation increases the capacity to be removed increases as a consequence of lattice parameter change.

4. Conclusions

From the above study the following conclusions could be drawn:

1) Saudi white silica was used as an absorbing media of ultrasonic in the starting gel of the preparation of LTA zeolite.
2) The irradiation of ultrasonic rays while the preparation process of LTA zeolite affects mainly its crystal and width of its pore.
3) The EPR technique could be used as an alternative technique to measure the amount of copper exchanged on the surface of zeolite.
4) The different in the structure of zeolite during preparation (ultrasonic) appears mainly in its ion exchange behavior towards heavy metals.

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