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Sorption of Pb (II) and Cu (II) from Acid Solution by a Natural Sorbent: Kinetic Study, SEM and BET.

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ABSTRACT

The sorption of Pb^{2+} and Cu^{2+} cations from phosphoric acid using a natural zeolite has been studied. The effect of pH =2, initial copper concentration (1–100 mg), sorbent dose (2 g), contact time (5–60 min) and temperature (298 K) was studied.

Keywords: Natural zeolite, phosphoric acid medium, sorption, lead, copper.

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INTRODUCTION

Heavy metals in the environment arise from both natural and industrial emissions. They not only can be non-degradable, but also will be accumulated in animals, plants and human body, causing serious disorders. Therefore, the disposal of heavy metals has been listed as a priority and the standards of emissions have become increasingly strict. In the past few decades, many conventional methods have been developed to remove heavy metals, including oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Nowadays, adsorption has become one of the most promising methods for removing metal ions from wastewater and from acid solution due to their regeneration, high efficiency and economy [1-2]. Toxic heavy metals are derived mainly from lead, mercury, cadmium, chromium, copper, arsenic species constitute a severe health threat [3-5].

Based on the industrial applications and potential pollution impact on the environment, the metals of environmental concern are lead and copper. Lead heads the list of environmental threats because even at extremely low concentrations it causes brain damage in children [6-8].

Phosphoric acid produced by wet process contains a variety of impurities. Among the most typical impurities is toxic lead, copper. Purification of H_3PO_4 is a major problem. Numerous processes exist for removing heavy metals, for example ion exchange, phytoextraction, precipitation, reverse osmosis, electrodialysis and ultrafiltration. Most appropriate are natural aluminosilicate zeolites with microporous structure. Among zeolites that present in Kazakhstan the better is high-silica Shankanay deposit zeolite. the use of such materials in the process of phosphoric acid purification, because it is an acid-resistant sorbent it can be used in the process of purification from the impurities of heavy metals, including lead and copper [9].

Fourier transformer infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM), Brunauer, Emmett and Teller (BET) analysis were carried out to understand the surface and functional group of natural zeolite. The batch method was used. Parameters such as contact time, initial Cu(II) concentration were investigated.

EXPERIMENTAL

Materials

All reagents used were of AR grade. Lead and copper, were prepared using analytical grade $Pb(NO_3)_2$ and $Cu(NO_3)_2$ obtained from Sigma Aldrich and Fluka Chemical Corporations. Analytical grade phosphoric acid was used.

Instruments

Concentrations of the investigated metals were determined atomic absorption spectrophotometer AAS - 400 model PerkinElmer, USA.

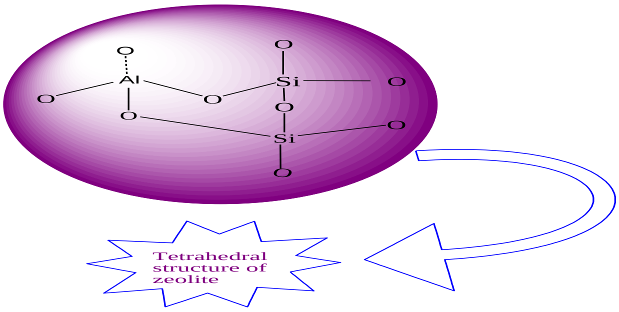
FTIR spectra of the Zeolites were recorded on a Perkin Elmer Spectrum (400–4000 cm^{-1}) 100 with ATR apparatus, USA. Shapes and size of the zeolites were examined by scanning electron microscope (SEM, model QUANTA 250 FEG).

The N_2-adsorption and desorption of the samples were measured by Quadrasorb *SI*-KR/MP specific surface area analytical instrument.

The surface area were calculated by using the Brunauer–Emmett–Teller (BET) isotherm , Heating Microscope with Automatic Image Analysis EM-201-17.

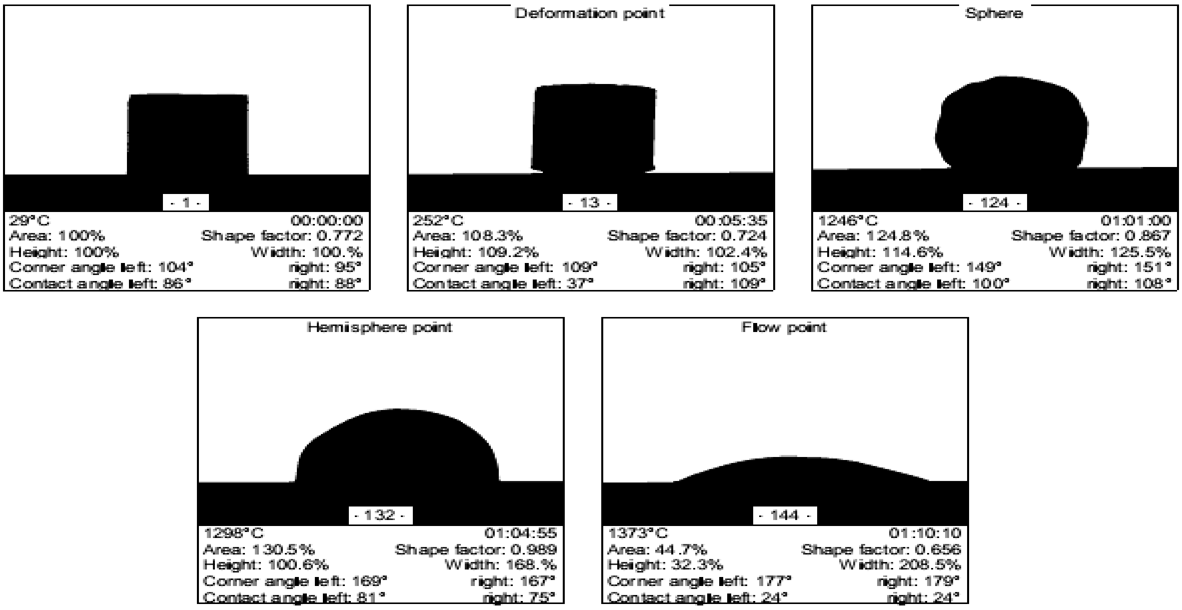
RESULTS AND DISCUSSION

Properties of natural zeolite



Scheme tetrahedral structure of natural zeolite

Figure 1 Picture-Analysis Identification (Picture-Analysis for Identification zeolite)



Characteristic temperatures: deformation temperature: 252 °C, deformation range: 252-1298 °C, sphere temperature: 1246 °C, hemisphere temperature: 1298 °C, flow range: 1298-1373 °C, flow temperature: 1373 °C (Figure 1).

Sorption procedure

Sorption investigated were conducted with the initial copper concentration varied from 1 --100 mg/L (Table 2) at a temperature of 298 K for 5-60 minutes (Table 1), 2 g / L natural zeolite of Shankanay field was used. We used 20% (pH=2) phosphoric acid. After sorption, zeolite particles were filtered, washed with distilled water.

The metal ion removal percentage (% R) can be calculated as:

$$\% R = \frac{C_0 - C_t}{C_0} \times 100$$

where C_t (mg / L) is the metal concentrations at time t (minutes).

Table 1 present the sorption of the metal ions at different of contact time at optimum initial concentrations.

3.3 Effect of contact time

Analysis of the data showed that the dilute phosphoric acid (20% H_3PO_4), increasing process time of 30 minutes to the degree of sorption Cu^{2+} increases and then decreases (Table 1).

Sorption of Pb^{2+} cations to 5-20 minutes decreases, in the range of 30 minute increases, and then decreases.

Table 1: Effect of contact time on the adsorption Pb^{2+} and Cu^{2+} with natural zeolite (metal ions concentration, 50 mg/L; pH 2; T= 298±1 K).

№	time (min)	natural zeolite	
		$Pb(NO_3)_2$	**$Cu(NO_3)_2$**
1	5	50.8	20.45
2	10	44.92	36.7
3	20	22.53	40.4
4	30	85.16	88.07
5	40	22.98	56.43
6	60	19.92	32.66

As for lead and copper optimum time is 30 minutes adsorption process. Appearance of a maximum on the sorption curves of lead and copper desorption due process of zeolite in phosphoric acid, which occurs upon prolonged contact of the sorbent with sorbate. Comparison of the level of sorption of lead and copper showed that in the test conditions more cations Cu , cations than Pb^{2+} were sorbed. For example, if a 30 minute process R_{Pb}=85.16%, and R_{Cu} = 88.07%.

Effect of initial Cu^{2+} ions concentration on the adsorption

Sorption of Pb2+ and Cu2+ on natural zeolite as a function of copper concentrations was studied at 25°C by varying the metal concentration from 1 to 100 mg/l while keeping all other parameters constant. The results are shown in Table 2. Percentage sorption for Pb2+ and Cu2+ decreases with increasing metal concentration in phosphoric acid. The heavy metal uptake is explained to different mechanisms of ion-exchange processes as well as to the sorption process (Table 2).

Table 2: Effect of the amount of Cu^{2+} on zeolite at different initial concentrations.

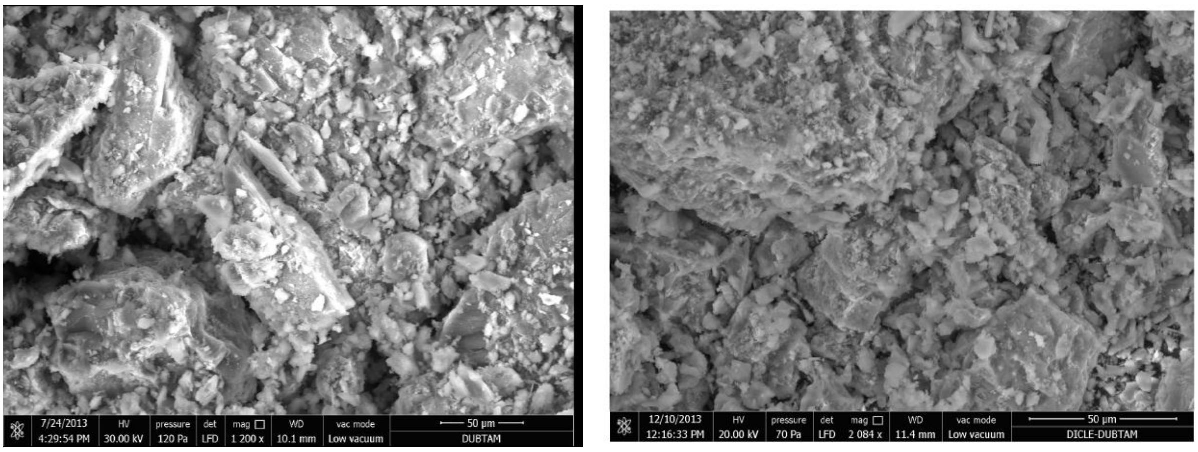
№	C(Cu^{2+}) m / L	natural zeolite	
		$Pb(NO_3)_2$	**$Cu(NO_3)_2$**
1	0,001	79.19	65.75
2	0,0209	71.33	79.52
3	0,0505	85.16	88.07
4	0,0802	51.36	68.46
5	0,1	38.51	73.25

During the ion-exchange process, metals had to move through the pores of the natural zeolite mass, but also through channels of the lattice, and they had to replace exchangeable ions (mainly sodium and calcium) [4]. The maximal exchange levels attained were as follows: Pb^{2+} 85.16 %, Cu^{2+} 88.07%; Thus, knowing the concentration of lead and cadmium cations in the phosphoric acid process conditions can be selected to maximize its purification extirpating impurity metals.

SEM Analysis

Scanning electron microscopy (SEM) analysis technique was used for monitoring the surface physical morphology of the adsorbent. Figures 2a–b show the SEM micrographs of the natural zeolite and zeolite after sorption Pb and Cu , respectively. It shows evidence that the zeolite structure was changed at absorbing the Pb(II) and Cu(II) cations. The adsorbent has irregular structure, in this way allows the adsorption of Pb(II) and

Cu(II) cations on different parts of the adsorbent. After Pb(II) and Cu(II) adsorption, a significant change is observed in structure of the natural zeolite as a result of metal cation adsorption.



(a) (b)

Figure 2: SEM micrographs for: (a) natural zeolite and (b) - Pb, Cu loaded zeolite.

Table 3

Sample Code	BET Specific surface area (m^2/g)	Total Pore volume, cm^3/g	Average pore rādiuss (Å)
natural zeolite	4,113	$1{,}621*10^{-2}$	78,80
acid treated zeolite	4,504	$1{,}466*10^{-2}$	65,07
Pb^{2+}-Cu^{2+} loaded zeolite	1,413	$4{,}154*10^{-3}$	58,81

Brunauer, Emmett and Teller (BET), most common method used to describe specific surface area:
The BET equation

$$\frac{1}{\left[V_a\left(\frac{P_0}{P}-1\right)\right]} = \frac{C-1}{V_m C} \times \frac{P}{P_0} + \frac{1}{V_m C}$$

P = partial vapour pressure of adsorbate gas in equilibrium with the surface at 77.4 K (b.p. of liquid nitrogen), in pascals,

P_0 = saturated pressure of adsorbate gas, in pascals,

V_a = volume of gas adsorbed at standard temperature and pressure (STP) [273.15 K and atmospheric pressure (1.013×10^5 Pa)], in millilitres,

V_m = volume of gas adsorbed at STP to produce an apparent monolayer on the sample surface, in millilitres,

C - dimensionless constant that is related to the enthalpy of adsorption of the adsorbate gas on the powder sample.

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CONCLUSIONS

Using physico-chemical analysis methods (electronic microscopy, BET, Picture-Analysis Identification) shows that natural zeolite activates without breaking the structure and adsorbs cadmium alone or together with lead cations.

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