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Adsorption of lead (II) ions from water solutions with natural zeolite and chamotte clay

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ABSTRACT

Natural zeolites and clays are known as effective and low-cost materials to use as adsorbents of different pollutants. The adsorption behavior of the Pb^{2+} ions adsorption on Kazakhstani natural zeolite and Ukrainian Chamotte clay has been studied in this work. The samples are characterized by SEM, EDAX, and XRD methods. The maximum uptake of lead ions (q_{max}) was determined as 14 mg/g for zeolite and 11 mg/g for clay. Langmuir and Freundlich isotherm models were used to describe the adsorption mechanism. It was observed that Langmuir isotherm model best describes the adsorption of Pb^{2+} on natural zeolite and clay. The separation factors (K_R) were calculated from the Langmuir isotherm.
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1. Introduction

Heavy metals (HM) are one of the most dangerous pollutants of the environment. They can accumulate in the human body causing severe disruption of different organs. Lead is among the most toxic HM for people, especially children. Lead poisoning can cause problems with cardiovascular, enzyme and reproductive systems, dysfunction of kidneys and liver, both the peripheral and the central nervous systems are influenced by lead exposure [1].

Lead is present in tap water to some extent as a result of its dissolution from natural sources, but primarily from household plumbing systems in which the pipes, solder, fittings or service connections to homes contain lead. Polyvinyl chloride (PVC) pipes also contain lead compounds that can be leached from them and result in high lead concentrations in drinking-water [2].

Adsorption methods of water treatment from lead ions have proven their efficiency [3]. Natural zeolites and clays are effective and accessible materials to use as adsorbents of different pollutants [4,5,6,7]. The application of natural zeolites as adsorbents of metal cations, particularly lead, has been reported in numerous studies. Thus, Shirzadi et.al. [8] used an Iranian natural clinoptilolite for lead ions adsorption in micronized and nanoparticle forms. Kragovic et.al. [9] have observed the adsorption capacity of natural zeolite as 66 mg/g. J. Peric et.al [10] used the Croatian zeolite clinoptilolite as a natural ion exchanger, and reported the high efficiency of removal for Pb (II) ions.

Clays are widely used as an adsorbent of heavy metal ions. Adsorption activity of bentonite [4], kaolin [11], montmorillonite [12,13] and other types of clay have been reported in recent years. Chamotte clay is white heat-treated kaolin clay with stone properties, resistant to aggressive media, which contains highly dispersed hydroaluminosilicates. The clay does not require additional purification after secondary use. It can be used in industry in large quantities [14]. There is not much information about the study of the application of chamotte clay as adsorbent. In [15] Chamotte clay has been used as an adsorbent for biodiesel purification from glycerol. Moreover, chamotte clay was used for purifying ethyl biodiesel samples from palm kernel oil by chemical and biochemical catalysis. The adsorption properties of Chamotte clay modified with polyvynylpirrolidone with respect to Cd(II) and Pb(II) ions has been reported in our previous work [16].

The current work is dedicated to the study of the adsorption capacity of natural zeolite and Chamotte clay for Pb^{2+} - ions removal.

2. Materials and methods

2.1. Samples characterization

High-resolution scanning electron microscope FEI 400 Magellan, USA was used to study the morphology of obtained materials.

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Elemental analysis was performed using the same equipment by Energy Dispersive X-Ray Spectroscopy (EDAX).

XRD patterns of the samples were investigated in the two-theta range 10–80° at a step size of 0.05 using a Bruker D8 Advance diffractometer with Cu-Ka source at 40 kV and 40 mA.

2.2. Materials and chemicals

The natural zeolite used in this work comes from the Shankanai deposit of Almaty region, Republic of Kazakhstan. The chamotte clay comes from Ukrainian deposit and provided by Teplosvet Inzhiniring, LLC, Kiev. $Pb(NO_3)_2$ of analytical grade and provided by Sigma Aldrich Chemistry (Germany) was used to prepare the model solutions for adsorption process. Experiments were carried out with demineralized water.

2.3. Adsorption experiments

Adsorption experiments were performed in static mode at room temperature and pH = 6. 1 g of sorbent was mixed with 100 mL of $Pb(NO)_3$ solutions of different concentrations (5, 10, 20, 50, 100, 200, 500 mg/L) and mixed for 24 h using magnetic stirrers at 200 r.p.m. Then the suspensions were centrifuged at 6000 r.p.m and 10 mL of supernatant was separated for analysis. Initial and equilibrium concentrations of Pb^{2+} were determined using Atomic Absorption Spectrometer Shimadzu 6200, Japan.

The amount of adsorbed Pb(II) (q_e) was calculated using the following Eq.1:

$$q_e = \frac{C_0 - C}{m} * V, \quad (1)$$

where C_0 and C represent initial and equilibrium concentrations of Pb(II), mg/L; V is the volume of Pb(II) solution, L;

m is the mass of adsorbent (zeolite or clay), g.

3. Results and discussions

3.1. Characterization of samples

SEM images of the natural zeolite and Chamotte clay are presented in the Fig. 1. The morphology of natural zeolite is represented by dense agglomerates of various shapes and sizes. As it is known, zeolites have a three-dimensional crystal lattice [17], which accounts for their porosity. The presence of pores can also be seen in the SEM image of the zeolite. Particles of Chamotte clay are represented by layers of flocculent formations of irregular shape and various sizes. Clays have a layered structure, and as a result they are also porous [6].

Table 1 and Fig. 2 provide data on the particle size distribution of the studied materials. Thus, the average area of zeolite particles is (2.438 ± 4.383) μm^2, and clay is (1.285 ± 1.611) μm^2. Large values of standard deviation are due to large variations in particle sizes and shapes, which is typical for materials of natural origin.

The results of elemental analysis of the samples are presented in the Table 2. The frameworks of both zeolite and clay are composed of SiO_2 and Al_2O_3 oxides [6,18]; therefore, the content of such elements as silicon, aluminum, and oxygen prevails in their composition. There are also metals such as Na, K, Mg, as well as Ca and Fe in the zeolite, which act as exchange cations to compensate for the excess negative charge of the surface of minerals [19].

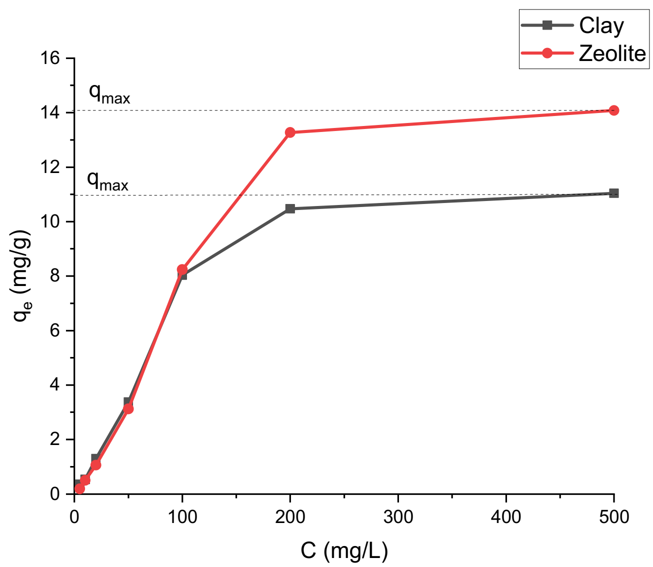

Fig. 2. Pb^{2+} ions adsorption isotherm on the natural zeolite and Chamotte clay.

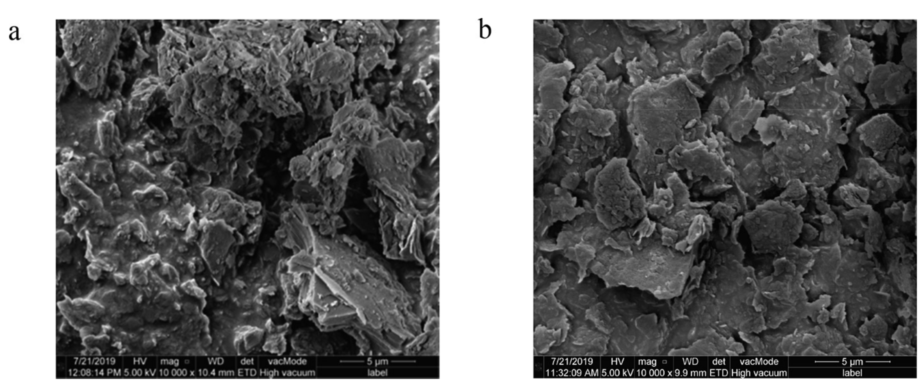

Fig. 1. SEM-image of (a) natural zeolite; (b) chamotte clay.

Table 1
Particle size distribution of zeolite and chamotte clay.

No	Sample	Area, μm^2	St dev	Min	Max
1	Zeolite	2.438	4.383	0.005	24.851
2	Chamotte clay	1.286	1.611	0.005	9.386

Table 2
Elemental analysis of zeolite and clay.

No	Sample	C, Wt%	O, Wt%	Al, Wt%	Si, Wt%	Na, Wt%	K, Wt%	Mg, Wt%	Ca, Wt%	Fe, Wt%
1	Zeolite	8.21	40.73	6.39	29.38	0.51	1.15	1.78	5.53	6.31
2	Chamotte clay	6,71	43,22	22,40	26,62	0,44	0,86	0,50		

Table 3
Parameters obtained when fitting the experimental data to the Langmuir and Freundlich isotherms.

Theory	Parameters	Zeolite	Clay
Langmuir	R^2	0,999	0,999
	K_L, L/mg	(0,4297 ± 0,0496)	(0,8502 ±0,0491)
	q_m, mg/g	(14,2027 ± 0,0372)	(11,056 ± 0,0282)
Freundlich	R^2	0,886	0,819
	β	(0,4463 ± 0,0715)	(0,3377 ± 0,0710)
	K_F	(22,4739 ± 2,9483)	(28,7010 ± 2,9483)

It should also be noted that the Si/Al ratio is 4.6 for zeolite, and 1.2 for clay. Thus, the content of silicon oxides in the zeolite framework is almost 5 times higher than that of aluminum. While the clay framework is composed of silicon and aluminum oxides in a ratio of approximately 1 : 1, which corresponds to the structure of kaolin clay [6].

The XRD patterns suggest that the crystalline structure of natural zeolites consists of clinoptilolite, quartz and anorthite; and the structure of clay consists of kaolinite, mullite and quartz.

3.2. Adsorption results

A study of the adsorption properties of natural zeolite and chamotte clay was carried out with respect to Pb^{2+} ions, one of the most toxic heavy metals. The results of studying the process of sorption of metal ions from solutions with an adsorbate concentration of 5, 10, 20, 50, 100, 200, 500 mg/l of the studied materials are presented in Fig. 2.

According to the IUPAC classification, the adsorption isotherms of lead (II) ions by the studied zeolite and clay are of type I isotherm, which 'approaches a limiting value' and usually is used to describe adsorption on microporous solid adsorbents having relatively small external surfaces (e.g. activated carbons, molecular sieve zeolites and certain porous oxides), the limiting uptake being governed by the accessible micropore volume rather than by the internal surface area [20]. Also, such isotherms are called Langmuir isotherms. The adsorption capacity q_{max} was 14 mg/g for zeolite and 11 mg/g for clay.

When describing the sorption process, adsorption models of sorption isotherms are of great importance. They show how metal ions are distributed between the adsorbent and the liquid phase when they are equilibrium depending on the concentration (adsorbent/adsorbate). In the present work, sorption isotherms were calculated according to the theories of Langmuir and Freundlich. Parameters obtained by fitting the experimental data to the Langmuir and Freundlich isotherms are shown in the Table 3.

As can be seen from the Table 3, the Langmuir isotherm better describes the process of adsorption of lead ions by the studied materials, since the correlation coefficients were $R^2 = 0.999$ for zeolite and clay. Also, the values of adsorption capacity q_{max} obtained graphically almost coincide with the values obtained from the graph $q_e = f(C)$ (Fig. 3), which also proves the relevance of this model.

It was reported in the work [21], that according to [22] it is possible to calculate from the Langmuir isotherms the separation factor (K_R), (Eq. 3) which is useful to determine whether the separation is or not favorable in batch systems.

$$K_R = \frac{1}{1 + K_L C_0} \tag{3}$$

where K_L is the Langmuir constant (L/mg), C_0 is the initial concentration of Pb^{2+} (mg/L). If $K_R > 1$ the adsorption is not favorable; if $K_R = 1$ the adsorption is linear; if $0 < K_R < 1$ the adsorption is favorable; and if $K_R = 0$ it is irreversible. The separation factors for both zeolite and clay are within $0 < K_R < 1$, i.e. adsorption is favorable. It can also be assumed that adsorption is more favorable on zeolite because the K_R values for zeolite are greater than for clay. It also corresponds to the fact, that the values of q_{max} are bigger for zeolite as well. With an increase in the concentration of metal ions, the separation factor $K_R \to 0$, i.e., tends to be irreversible.

4. Conclusions

In the present study, adsorption ability of the natural zeolite and Chamotte clay towards Pb(II) ions has been studied. The maximum uptake of lead ions (q_{max}) was determined as 14 mg/g for zeolite and 11 mg/g for clay. Langmuir and Freundlich isotherm models were used to describe the adsorption mechanism. It was observed that Langmuir isotherm model best describes the adsorption of Pb^{2+} on natural zeolite and clay, the correlation coefficients R^2 were 0.999 for both adsorbents. It means that a monolayer of adsorbate is formed on a heterogeneous surface. The separation factors (K_R) were calculated from the Langmuir isotherm: $0 < K_R < 1$for both zeolite and clay, i.e. adsorption is favorable. It may be concluded that both natural zeolite and Chamotte clay can be used as low-cost adsorbents for wastewater treatment from lead (II) ions.

CRediT authorship contribution statement

A.B. Rakhym: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft. **G.A. Seilkhanova:** Supervision, Project administration, Writing - review & editing. **T.S. Kurmanbayeva:** Investigation, Methodology, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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