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Adsorption of Pb(II) and Cd(II) from aqueous solutions on Kyzylsok natural clay modified by polyvinylpyrrolidone

Abstract. Present work considers the production of a cheap and effective sorbent based on natural clay originated from the Kyzylsok deposit (Almaty region, Kazakhstan) to purify wastewater from heavy metal ions (Cd^{2+}, Pb^{2+}). It was found that the starting clay sample is applicable for the extraction of Cd^{2+} ions (the degree of extraction is (97.40 ± 1.99) %), while for the extraction of Pb^{2+} ions the initial clay must be modified by impregnation with 0.1 % polyvinylpyrrolidone (PVP) aqueous solution. The degree of extraction of Pb2+ ions with modified clay increased from (70.01 ± 1.77)% to (98.03 ± 1.13)%. The desorption of metal ions which was also investigated in the work did not exceed 2% confirming the usability of untreated and modified clay as sorbents for a long time. It was found that the sorption process is described by the monomolecular Langmuir isotherm model and the kinetic model of the pseudo-second-order.

Key words: natural clay, polyvinylpyrrolidone, modification, sorption, desorption, cadmium (II) ions, lead (II) ions.

Introduction

Water is an essential resource for maintaining human life (food, blood circulation, respiration, reproduction, etc.). More than two-thirds of the earth's surface is covered with water, but only a small part of it is suitable for drinking, cooking or irrigation [1]. Serious problems arise from the uneven regional distribution of water resources, due to the increase in its use due to the growing population and rising living standards, which contribute to water pollution. This leads to a reduction in the available water supply [2].

Industrial wastewater and agricultural waste are major environmental pollutants. Most industries dump waste water containing toxic substances into rivers without high-quality treatment [3]. Environmental pollution, especially with heavy metals and minerals in wastewater, is the most serious problem in Kazakhstan. Heavy metals are one of the main pollutants in marine, land, industrial and even treated wastewater [4].

The main sources of heavy metal emissions are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, timber and wood products [5]. Heavy metals are transported by wastewater and pollute water sources downstream of the industrial site [6]. Most of the heavy metal ions discharged into wastewater are toxic and carcinogenic and pose a serious threat to human health [7].

The release of a large amount of hazardous materials into the natural environment leads to many environmental problems and, due to their biodegradability and persistence, can accumulate in the elements of the environment, and, thus, can pose a significant hazard to all living things [8].

The accumulation of such elements in the human body can lead to irreparable consequences. For example, acute exposure to lead can cause headaches, loss of appetite, abdominal pain, fatigue, insomnia, hallucinations, dizziness, renal dysfunction, hypertension and arthritis, while chronic exposure can lead to birth defects, mental retardation, autism, psychosis, allergies, paralysis, weight loss, dyslexia, hyperactivity, muscle weakness, kidney damage, brain damage, coma, and even death [9]. In addition, exposure to lead can disrupt the functioning of intracellular "secondary messengers" and alter the functioning of the central nervous system [10].

In turn, exposure to cadmium can cause damage to bones and lungs, impaired function and kidney

disease. In addition, under the influence of cadmium, calcium metabolism disorders, the formation of kidney stones and hypercalciuria occur [11]. The International Agency for Research on Cancer classifies cadmium as the first group of carcinogens leading to oncological diseases [12].

The solution to this urgent problem requires the widespread use of modern technologies for the purification of water resources, which include adsorption methods.

In recent years, the possibility of using natural and modified clays as adsorbents for the removal of various toxic heavy metal ions from aqueous solutions has been thoroughly studied. For example, in [13], the sorption activity of natural zeolite and chamotte clay concerning Pb^{2+} ions was studied. As a result, it was determined that the objects of study have a sufficiently high sorption capacity (14 mg/g for zeolite and 11 mg/g for clay), and the process itself is described by the Langmuir model.

In another work, the adsorption of Cd^{2+}, Pb^{2+}, Cr^{6+} ions from wastewater using natural clay was investigated [14]. This study confirms that clay is a good adsorbent for removing these metals from wastewater. Also, the value of the Langmuir and Freundlich constants indicates a good adsorption capacity.

The high sorption capacity of clays is due to a number of important properties: a large specific surface area, porosity, surface charge, surface functional groups, etc. [15]. Therefore, clays and clay minerals can be used as sorbents for cleaning various toxic contaminants, including heavy metals.

However, since clays are formed as a result of natural transformations and weathering of soils, not all of them have the necessary structure that provides the above properties. And thus, not all natural clays have a high sorption capacity.

It is possible to increase the sorption capacity of clay by modification, as evidenced by many studies [16]. For example, in [17] the adsorption of lead (II), zinc (II) and cadmium (II) in single-element and multi-element systems on untreated, acid-activated and aluminum-coated Tunisian smectite was investigated. The chosen order of adsorption Pb (II)> Zn (II)> Cd (II) showed the importance of the phenomenon of competition in the adsorption of the pores of the clay material.

Thus, there is a need to develop new composite materials with high sorption characteristics. However, many sorbents have a high cost, an insufficient degree of purification of water bodies from various toxic substances. In this regard, the purpose of this study is to obtain an effective composite material

based on natural clay from the Kyzylsok deposit. The modification of natural clay was carried out with polyvinylpyrrolidone (PVP).

PVP is an amorphous linear polymer. It is hygroscopic, soluble in water, non-toxic, has an affinity for organic polymers. Its aqueous solutions have a slightly acidic reaction (pH 5). It is reasonable to associate the high sorption capacity of the pyrrolidone fragment with its structure (Fig. 1) [18]:
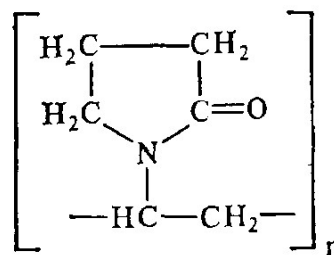

Figure 1 – The structure of PVP

This class of reagents represents compounds with grafted complexing groups that form strong bonds with metal ions dissolved in water [19]. Therefore, a probable sorption mechanism can be considered as complexation associated with the presence in the PVP structure of functional groups with donor nitrogen atoms, which, in turn, can bind metal ions into strong complexes.

Materials and methods

The following were used in the work: clay from the Kyzylsok deposit (Almaty region, Kazakhstan), polyvinylpyrrolidone (PVP) with a molecular weight of 10,000 g/mol, $Pb(NO_3)_2$, $CdCl_2$. All chemicals were of analytical grade and purchased from Sigma Aldrich (Germany).

Equipment. To determine the surface properties of the clay, we used a Quanta 3D 200i Dual system (FEI, USA) scanning electron microscope. Elemental analysis of the natural clay was carried out using energy dispersive spectrometry (EDAX). The initial and residual metal concentrations were determined by a Shimadzu 6200 atomic absorption spectrophotometer. The results were processed using the ORIGIN 9.5.1 software.

Modification of clay. Original clay was previously ground and sifted through a sieve to remove mechanical impurities. A 0.1% PVP solution is mixed with the clay in a 1:10 ratio, stirred at 200 rpm for 24 h, filtered and dried at t ≈ 100 ° C for 1 hour, and then in the air for 24 hours. The obtained

composite was stored in a properly closed plastic container.

Study of Pb^{2+} and Cd^{2+} adsorption-desorption processes. 1 g of the adsorbent was mixed with 100 ml of 5 – 500 mg/L Pb^{2+} or Cd^{2+} solution, stirred at 200 rpm until reached equilibrium. Aliquots were taken at regular intervals for analysis for the content of Cd^{2+} и Pb^{2+} ions to study the kinetics of the process. The desorption process was carried out in the following way: 1 g of dried sediments obtained after sorption was mixed with 100 ml of distilled water, stirred at 200 rpm until reached equilibrium. The liquid was separated from the solid and analyzed for the content of Cd^{2+} и Pb^{2+} ions.

The extraction degree (E) was calculated using equation 1:

$$E = \frac{C_0 - C_e}{C_0} \cdot 100\% \qquad (1)$$

where C_0, C_e are initial and equilibrium concentrations of metal ions, mg/L.

The adsorption capacity was calculated using equation 2:

$$q_e = \frac{C_0 - C_e}{m} \cdot V \qquad (2)$$

where q_e is adsorption capacity, mg/g; m is the mass of adsorbent; V is the volume of metal solution.

The desorption degree (D%) was calculated using equation 3:

$$D = \frac{m_2}{m_1} \cdot 100\% \qquad (3)$$

where m_1 is content of metal in clay after the sorption, mg/g; m_2 is the content of metal after desorption, mg/g.

Results and discussion

Characterization of samples. The studied clay belongs to sedimentary rocks and is a product of rock weathering. Dry clay itself is a lumpy mass of grey-brown color and earthy smell. The color of the clay indicates that it contains iron, potassium and calcium [20], which was confirmed by elemental analysis. Clay has a low swelling capacity. When mixed with water, it forms a plastic and viscous clay dough, which, after kneading and mixing, acquires the ability to take any shape and keep them after drying. Also, clay has a low hardness and can be easily pulverized by hand.

The primary task of the study was to identify the composition and structural features of the initial samples.

Using the SEM and EDAX methods, the qualitative and quantitative composition of the original natural clay was determined (Table 1, Figures 2 and 3).

Table 1 – Elemental analysis of natural clay by EDAX method

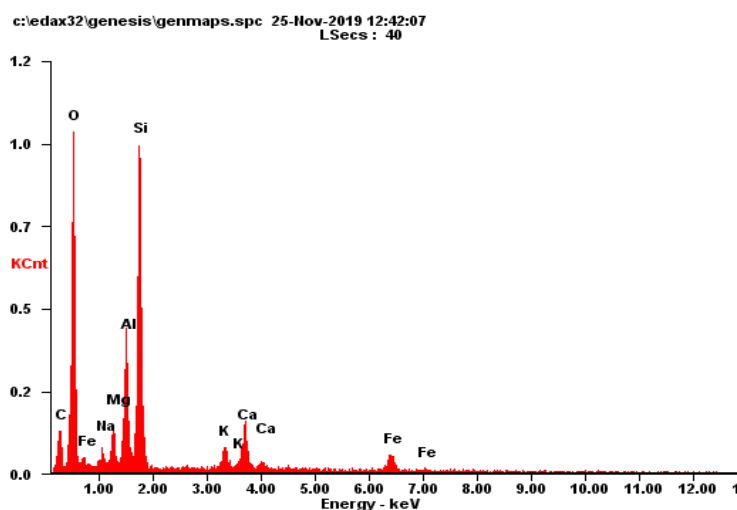| Element	C	O	Na	Mg	Al	Si	K	Ca	Fe
Weigh, %	17.02	39.26	0.89	2.24	6.70	18.57	2.77	5.59	6.97
Atomic, %	27.01	46.77	0.74	1.76	4.73	12.60	1.35	2.66	2.38

Figure 2 – Plot of the intensity of X-ray radiation over energy

The data show that the particles of the studied clay have a predominantly aluminosilicate chemical composition. Along with this, an insignificant content of Mg, Ca, Fe, Na, and K atoms is noted, which can serve as a confirmation of the presence of an exchange layer of these cations in the composition of the clay.

The study of morphological and microstructural features with a scanning electron microscope (Figure 3), showed that the particles of the studied clay are characterized by an anisometric shape. At the same time, clay is an association of particles with size of (15.51 ± 10.61) μm.

Results on equilibrium adsorption. The sorption capacity of the selected sorbents was tested concerning Pb^{2+} and Cd^{2+} ions. The results of Pb^{2+} and Cd^{2+} ions adsorption onto original and modified clay from 10 mg/L solutions are presented in Table 2. The equilibrium was reached in 30 minutes, which indicates that the adsorption is fast.

It was observed that the degree of extraction of Cd^{2+} ions by the original clay reaches 98-99%, while about 70% for Pb^{2+} ions. This suggests that the original clay can be used for the sorption of Cd^{2+} ions without any treatment, and it requires modification for Pb^{2+} ions extraction. Apparently, the surface of the initial clay has reaction centers that are more selective to Cd^{2+} ions.
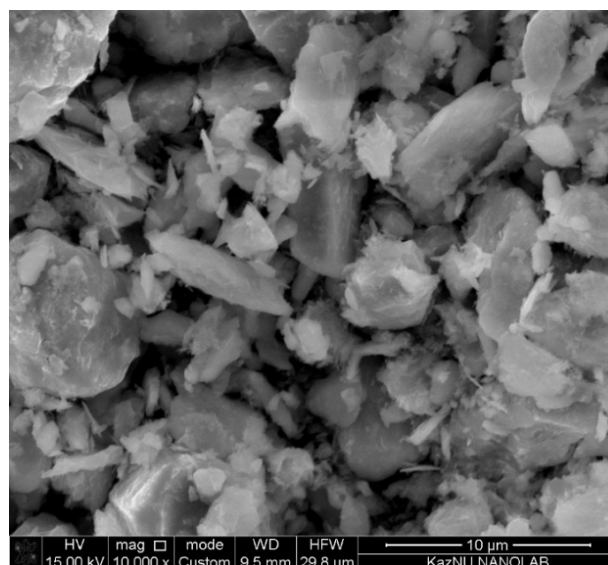

Figure 3 – SEM image of the original natural clay

Table 2 – The degree of extraction (E, %) and adsorption capacity (q_e) of Pb^{2+} and Cd^{2+} ions by the original and modified clay (T = 298 K, pH = 6, C_0 = 10 mg/L, contact time = 24 h)

Sorbent	E, %		q_e, mg/g	
	Pb^{2+}	Cd^{2+}	Pb^{2+}	Cd^{2+}
clay	70.01±1.77	97.40±1,99	0.49±0.01	0.78±0.02
clay + 0,1% PVP	98.08±0.99	-	0.67±0.01	-
clay + 0,5% PVP	98.11±1.64	-	0.67±0.01	-
clay + 1% PVP	98.03±1.13	-	0.67±0.01	-

As can be seen from the Table 2, the extraction degree of lead ions increased from 70% to 99% after modification with 1% PVP solution.

The larger values of Cd^{2+} ions adsorption by the initial clay are probably related to the difference in the ions sizes and hydration shells. The radius of the cadmium ion is 0.95 Å, and the radius of lead is 1.20 Å. The configuration of both hydrated metal ions in an aqueous solution is an octahedron [21], i.e. cadmium ions are smaller than lead, so they are better retained in the pores of the clay due to the physisorption. Therefore, further modification of clay with PVP increases the lead ions adsorption due to the contribution of chemical sorption.

The effect of the concentration of PVP in the obtained composite materials was investigated, the results of which are also presented in Table 2. Based on the data obtained, it can be concluded that the change in the concentration of PVP does not particularly affect its sorption properties. Therefore, because of economic feasibility, the most suitable concentration of the modifier is the lowest, that is, 0.1% PVP.

To assess the applicability of the adsorbent for a long time, the ability of metal ions to desorption is of great importance. The degree of desorption of the said metal ions over time is presented on Figure 4.
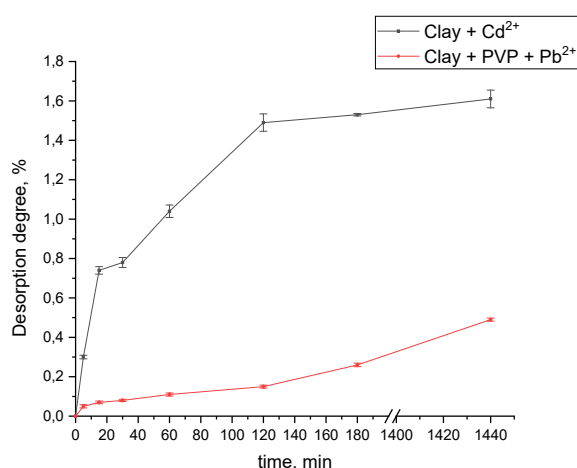
Figure 4 – Plot of the degree of desorption (%) of Pb^{2+} and Cd^{2+} ions by the original and modified clay over time

As can be seen from Figure 4, the desorption of metals is very slow and does not exceed 2%. Consequently, metal ions are tightly bound to sorbents, which makes it possible to use such sorbents for a long time.

Adsorption isotherms. The experimental adsorption isotherm of Cd^{2+} ions adsorption on clay and Pb^{2+} ions adsorption on modified clay are shown on Figure 5.

Adsorption capacity of clay minerals towards Pb^{2+} varies between 0.45 and 239 mg/g and between 3.87 and 981 mg/g for Cd^{2+} [22]. The maximum adsorption capacity of clay was found to be 11.2 mg/g for Cd^{2+}, and in the case of modified clay 7.6 mg/g for Pb^{2+}, which are average results for natural clays.
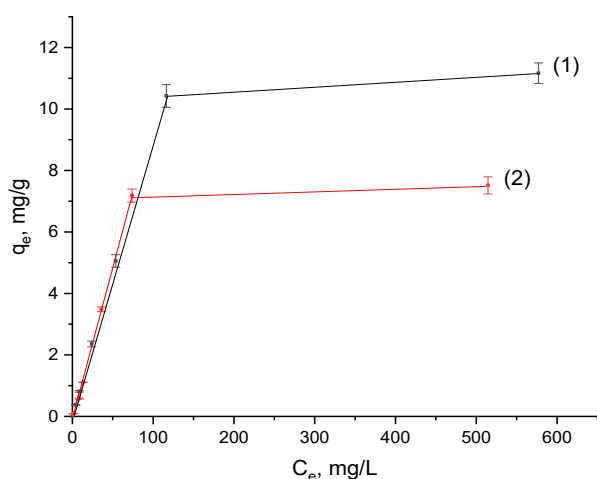

Figure 5 – Adsorption isotherm of (1) Cd^{2+} ions on clay; (2) Pb^{2+} ions on clay + 0.1% PVP

The equilibrium experimental results of Pb^{2+} and Cd^{2+} ions have been fitted by linear equations of the Langmuir [23] and Freundlich [24] adsorption models.

A linear form of Langmuir equation (4) can be written as:

$$\frac{C_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{1}{q_m} C_e \qquad (4)$$

where q_e is the amount adsorbed on solid at equilibrium (mg/kg), C_e is the equilibrium liquid concentration (mg/L), q_m is the adsorption capacity or maximum adsorption (mg/g), K_L is the adsorption intensity or Langmuir coefficient (L/mg).

Freundlich isotherm is the earliest known experimental equation describing the sorption of material onto animal charcoal. This isotherm could be applied to non-ideal sorption on heterogeneous surfaces as well as multi-layer sorption. It is expressed by the following equation (5):

$$lnC_s = lnK_F + \frac{1}{n_f} lnC_e \qquad (5)$$

where C_s is the solute adsorbed (mg/g), C_e is the solute concentration at equilibrium (mg/L); K_F is the Freundlich constant, n_f is the equilibrium constant.

The Brunauer, Emmett and Teller (BET) model [25] is based on the concept of the polymolecular theory of adsorption. As applied to adsorption from solutions, the linear BET equation (6) is written as follows:

$$\frac{C_e}{q_e \cdot (C_s - C_e)} = \frac{1}{q_m \cdot K_{BET}} + \frac{(K_{BET} - 1) \cdot C_e}{q_m \cdot K_{BET} \cdot C_s} \qquad (6)$$

where K_{BET} is a constant of the BET equation; C_s is the limiting concentration of an ion in a solution (the solubility of salt at a given temperature).

The BET model provides for a multilayer filling of the surface with an adsorbate, and the active centres have the same energy values. Polylayers can be formed in different parts of the surface, both before and after filling the monolayer. The equilibrium constant K_{BET} characterizes the energy of interaction of the adsorbate with the surface of the adsorbent. Its sign (positive or negative) indicates the applicability or inapplicability of this model for describing adsorption in this system.

Comparing the approximation coefficients (R^2) of the Langmuir, Freundlich and BET models, we can conclude that the Langmuir model is more reliable ($R^2 > 0.99$). The Freundlich model makes it possible

to calculate sorption parameters with lower reliability ($R^2 > 0.90$). The BET model, which describes the multilayer binding of sorbates by homogeneous active centres of the sorbent, is not applicable to the description of this process.

Adsorption kinetics. To study the adsorption kinetics of Cd (II) and Pb (II) ions, the pseudo-first order (proposed by Lagergren) [26] and pseudo-second order (proposed by Ho and McKay [27]) models were applied.

Table 3 – Comparative characteristics of adsorption isotherms models fitting to Pb^{2+} and Cd^{2+} ions adsorption

Parameters of model	clay + Cd^{2+}	clay + 0.1% PVP + Pb^{2+}
Experimental isotherm		
q_{max}, mg/g	11.195	7.558
Langmuir model		
K_L	0.009	0.016
q_{max}, mg/g	10.989	4.934
R^2	0.998	1.000
Freundlich model		
K_F	0.288	0.095
n	1.371	1.395
R^2	0.906	0.944
BET model		
K_{BET}	4.307	6.086
q_{max}, mg/g	5.528	5.476
R^2	0.484	0.684

The most commonly used forms of equations for these models are linear (equations (7) and (8) for pseudo-first and pseudo-second orders, respectively):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (7)$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \qquad (8)$$

where k_1 and k_2 are pseudo-first and pseudo-second order rate constants; q_t is the equilibrium amount of adsorbed cations.

Table 4 – Kinetic parameters of the sorption process of Pb^{2+} and Cd^{2+} ions

System	Pseudo-first order		Pseudo-second order	
	k_1, min^{-1}	R^2	k_2, L*min/mg	R^2
clay + Cd^{2+}	0.0247	0.3110	0.0002	0.9440
clay + 0,1% PVP + Pb^{2+}	0.0159	0.4760	0.0161	0.9760

Comparison of the results in Table 4 shows that the pseudo-second order equation most closely matches the obtained experimental data with high correlation coefficients ($R^2 \approx 1$). This indicates that the sorption process is described by the pseudo-second order reaction model.

Conclusions

- It was found that the natural clay can be used to extract Cd^{2+} ions without modification, the extraction degree reaches (97.40 ± 1.99)% from 10 mg/L solution;

- Modification of natural clay with polyvinylpyrrolidone increases its sorption capacity with respect to Pb^{2+} ions from (70.01 ± 1.77) % to (98.03 ± 1.13) %;

- The adsorption process is quite fast for both original and modified clay. The equilibrium time was 30 min with initial metal concentration $C_0 = 10$ mg/L and a sorbent mass of 1 g per 100 mL of solution;

- The optimal concentration of the modifier in the composite material was 0.1% PVP solution;

- The bonding between adsorbents and metal ions are very strong. The amount of desorbed metal ions does not exceed 2% of the adsorbed amount;

- The adsorption of Cd^{2+} onto natural clay and Pb^{2+} onto modified clay is most clearly described by the monomolecular theory of Langmuir;

- The kinetics of studied metals adsorption on clay and modified clay is described by the pseudo-second order model.

Acknowledgements

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