Analysis of the physicochemical and sorption characteristics of composites based on zeolite and chamotte clay

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Abstract. Clays and aluminosilicate materials are known as effective sorbents for purification of wastewater from various types of contaminants. Some properties and sorption activity of materials based on the zeolite of Shankanai deposit and Chamotte clay towards Cd^{2+} ions were analyzed in the present work. The structural characteristics of the studied objects, their qualitative and quantitative composition were determined by the SEM and EDAX methods. It was found that maximum adsorption capacity (q_e) of the initial zeolite for extraction Cd^{2+} ions is (7.3±0.11) mg/g, while for Chamotte clay this value equals to (5.3±0.12) mg/g. After modification with polyvinylpyrrolidone, q_e increased to (10.1±0.08) mg/g for zeolite, and (8.5±0.15) mg/g for Chamotte clay. Developed specific surface of the composite material (sorbent) and complexation with the active centres of the polymer could be a result of Cd^{2+} ions binding.

1 Introduction

In recent years, the use of heavy metals in industrial, agricultural, household areas has increased [1]. Water pollution with heavy metals occurs due to the discharge of wastewater, which is the result of mining and smelting, household and agricultural residues, industrial waste from ferrous and non-ferrous metallurgy, as well as heavy metals contained in insecticides [2-5].

The most common metal ion in industrial wastewater is cadmium. It is identified as a public health problem. Cadmium infects liver, placenta, kidneys, lungs, brain and bones [6]. Chronic exposure to cadmium can lead to anaemia, anosmia (loss of smell), cardiovascular disease, kidney problems, osteoporosis, and hypertension [7]. In addition, with prolonged exposure to low concentrations, it can accumulate in the kidneys, which ultimately leads to severe diseases, as well as to fragility of bones and damage of the lungs [8].That is why close attention is paid to the resource-saving orientation of scientific research, which allows saving materials and natural resources in modern conditions [9].

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Adsorption is progressively used to increase the efficiency of wastewater treatment from various contaminants [10]. This method makes it possible to intensify wastewater treatment processes, to reduce the costs of the used reagents, operating facilities and treatment without deteriorating the quality of purified water [11, 12].

High adsorption properties and low cost of aluminosilicate materials and industrial waste make them promising for use in adsorption purification of water bodies, especially from heavy metal ions [13, 14].

Thus, the authors of Ref. [15] studied the sorption capacity of Chamotte clay. Chamotte Clay is a secondary product obtained during heat treatment of kaolin clay (at 1250-1500^{0}C) [16]. It is characterized by high mechanical strength and chemical resistance. Another one advantage of Chamotte Clay use is utilizing of industrial waste, which could solve another environmental problem.

It is known, that zeolites are exchangeable for heavy metal ions. Due to this property, they are widely used in wastewater treatment technologies in various industries. Thus, Ref. [17] presents the results of studying the properties of zeolite ores of the Shankanai deposit and the efficiency of purifying natural waters from Pb^{2+} ions. The sorption capacity was studied with non-activated zeolite under static conditions. In this case, the degree of water purification from lead ions was quite high (98 ± 2) %, and the maximum adsorption was 14 mg/g. The authors found that the sorption process is described by the Langmuir isotherm.

However, not all raw materials have high sorption activity. There are cases when it is necessary to influence (thermally, chemically, mechanically, etc.) on the object to increase its activity, in other words to make modification.

In this work, the modification of zeolite and Chamotte clay was carried out with a polymer – polyvinylpyrrolidone (PVP).

PVP is a hygroscopic, amorphous, water-soluble linear polymer [18]. PVP contains grafted complexing groups capable of forming strong bonds with ions of various metals dissolved in water. Therefore, PVP could be used in adsorption processes due to the presence of active centers – nitrogen atoms. These atoms can interact with metal ions and form strong insoluble complexes [19].

Thus, this study is devoted to analysis of the properties of composite materials based on the natural zeolite and Chamotte clay.

2 Materials and methods

2.1 Testing Materials

In the course of the study, we used natural zeolite from the Shankanai deposit (Almaty region, Kazakhstan) and Chamotte clay (Teplosvet Inzhiniring LLC, Kiev, Ukraine), that are denoted as Z and C, respectively. Polyvinylpyrrolidone (PVP) (molecular weight - 10,000 g/mol) was used as a modification agent; $CdCl_2$ was used in adsorption experiments. All the chemicals were of analytical grade and purchased from Sigma Aldrich (Germany).

2.2 Equipment

Determination of the surface properties of the materials and elemental analysis by EDAX method was carried out by using a scanning electron microscope Quanta 3D 200i Dual system, FEI (the National Open-Type Nanotechnology Laboratory (NOTNL) at Al-Farabi Kazakh National University (KazNU)). The concentration of cadmium ions in the solutions was determined with a Shimadzu 6200 atomic absorption spectrophotometer. The specific surface area and pore volume were determined with a Quantachrome Nova 4200e device by nitrogen sorption to its relative pressure of 0.2 atm at -196 ◦C.

2.3 Modification procedure

The natural Z and raw C were impregnated with 0.1% PVP solution at a solid-liquid ratio 1:5, and stirred at 200 r.p.m. for 24 hours at room temperature. The experiment was carried out under pH =6. After that the solids were separated from solutions and dried at t ≈ 100 ° C for 1 hour, and then left on air for 24 hours. The samples were denoted as Z + PVP and C + PVP for modified zeolite and clay, respectively.

2.4 Adsorption experiments

1 g of sorbent was added to 100 ml of 10 mg/L Cd^{2+} solution and stirred at 200 r.p.m. at room temperature and pH = 6. At regular time intervals, aliquots were taken for analysis of Cd^{2+} ions content until equilibrium.

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

$$q_e = \frac{C_0 - C_e}{m} * V, \tag{1}$$

where C_0 и C_e represent initial and equilibrium concentrations of Cd(II) (mg/L), V is the volume of Cd(II) solution (L) and m is the mass of adsorbent (g).

3 Results and discussion

3.1 Characterization of raw and modified materials based on zeolite and chamotte clay

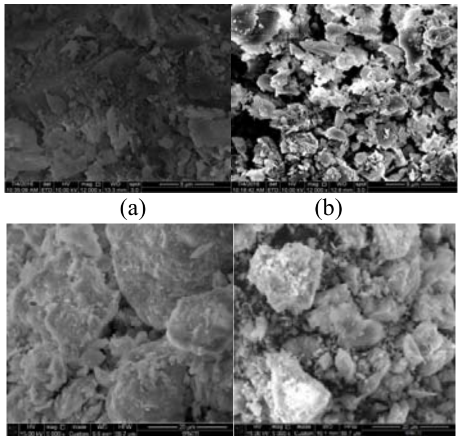
Table 1 shows the values of the specific surface area and specific pore volume of the initial and modified materials based on Z and C.

Table 1. Textural characteristics of the studied materials.

Characteristics	C	C+PVP	Z	Z+PVP
Specific surface, m^2/g	9.49	11.93	3.51	2.93
Specific pore volume, cm^3/g	0.004	0.005	0.016	0.018

Modification of C with a polymer leads to a slight increase from 9.49 to 11.93 m^2/g in the specific surface area and from 0.004 to 0.005 cm^3/g in pore volume. At the same time, the treatment of Z with PVP leads to a decrease in the specific surface area from 3.51 to 2.93 m^2/g. It can be assumed, that in the case of C, the interaction with PVP occurs due to the formation of bonds between the surface functional groups of C and PVP groups. In the case of Z, the interaction occurs due to chemisorption of the polymer (the formation of bonds between functional groups) and physical sorption (clogging of the pores of Z with the polymer). The contribution of physical sorption can lead to a decrease in the values of the specific surface area of the sorbents.

Scanning electron microscopy (SEM) was used to describe the morphology of the original objects and their modified forms. The results are shown in Fig. 1.



(a) (b) (c) (d)

Fig.1. Fragments of SEM images of (a) natural Z, (b) modified Z, (c) raw C and (d)modified C.

Samples of natural Z (Fig. 1 (a)) and raw C (Fig. 1 (c)) are represented by dense formations with strong agglomerates and irregularly shaped particles of various sizes. The average size of the particles equals to (2.44 ± 4.38) μm for Z, and (1.29 ± 1.61) μm for C.

After modification the surface structure of the materials changes. The morphology of Z after modification with PVP (Fig. 1 (b)) is characterized by large intergrown particles of irregular shape, and spherical particles are seen in small quantities. After modifying C with PVP (Fig. 1 (d)), the sample becomes more homogeneous, agglomerate structures become coarse and pores become more developed.

Thus, the modification of the original objects with PVP leads to the production of materials with a more developed surface structure and increased porosity.

After elemental analysis (Table 2) of Z and C, it was found that both objects are aluminosilicate materials. The Si/Al ratio of Z is 3, which is average for natural zeolites. For C the ratio 1.2 that corresponds to the structure of kaolin clay because the framework of the clay is composed of oxides of silicon and aluminum in a ratio of approximately 1:1. In addition, the studied samples contain some amounts of Na, Mg, K, Ca, and Fe that proves the presence of the cation exchange capacity in the corresponding objects.

Table 2. Elemental composition of research samples, %.

Sample	C	O	Na	Mg	Al	Si	K	Ca	Fe
Z	8.95	68.16	0.77	1.61	4.10	12.36	-	0.79	3.25
C	6.71	43.22	0.44	0.50	22.40	26.62	0.86	0.16	33.98

3.2 Sorption characteristics of raw and modified materials based on zeolite and chamotte clay

Fig. 3 shows the adsorption capacities (q_e) of initial and modified Z and C with respect to Cd^{2+} ions. The graph shows that the maximum adsorption capacities were (5.3±0.12) mg/g and (8.5±0.15) mg/g for the initial and modified chamotte clay respectively. For zeolite this value reaches (7.3±0.11) mg/g for initial, and (10.1±0.08) mg/g for modified form.

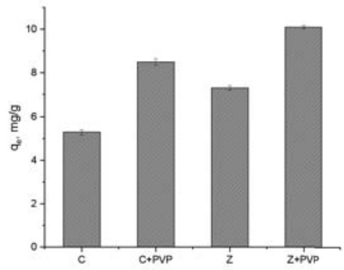


Fig. 3. Adsorption capacities of initial and modifies Z and C with respect to Cd^{2+} ions.

Thus, the inclusion of PVP in composition of the studied materials leads to an increase in the sorption properties. This may be because PVP, dissolving in water, forms a complex compound with aluminosilicate materials ($[Al\,(NO_2)_6] \bullet [SiO_4]$) due to the dissolved lactam cycle [20]. In this case, Al^{3+} acts as a complexing agent, while NO_2^- group acts as a ligand. Due to the NO_2^- group, the negative surface charge increases which leads to a stronger attraction of the positively charged Cd^{2+}- ions.

4 Conclusions

The modification of natural Z and C with PVP leads to the production of composite materials with a more developed surface structure and increased porosity. Based on the analysis of the cadmium ions sorption results by initial and modified objects, it was revealed, that maximum adsorption capacities equal to (7.3±0.11) mg/g for Z and (5.3±0.12) mg/g for C, while for modifies materials this value reaches (10.1±0.08) mg/g and (8.5±0.15) mg/g for Z and C respectively. An increase in the sorption activity of the modified objects could be due to the binding of cadmium ions by the active centers of the polymer. It can be assumed, that in the case of C, the interaction with PVP occurs due to the formation of bonds between the surface functional groups of C and PVP groups. In the case of Z, the interaction occurs due to chemisorption of the polymer (the formation of bonds between functional groups) and physical sorption (clogging of the pores of Z with the polymer).

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