Removal of Heavy Metal Ions with Clay-Based Sorbent

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Abstract. The paper presents research results of heavy metals ions removal from a model multicomponent solution applying a new sorbent obtained on the basis of modified clay and peat of the Samara region. The modification was carried out in a thermal way. The researchers study the new material properties in the range of low concentrations typical for the biologically treated sewage water and wastewater of industrial enterprises. The paper also presents kinetic curves and sorption isotherms for five ions of heavy metals – copper, zinc, manganese, iron and lead.

1. Introduction

The most promising direction in the field of water purification are resource-saving technologies, which allow to effectively remove water contaminants at minimal cost. Purified municipal and industrial wastewater contain ions of heavy metals. Their concentrations vary from thousandths to tenths of mg/l and often exceed the normative values established in the Russian Federation and equal to maximum allowable concentration (MAC) for fishery water bodies. Sorbents based clay demonstrate high capacity relative to ions of heavy metals [1, 2]. Clay, the main sorbent component, is widespread and inexpensive in comparison with activated coals. When clays are modified, their sorption capacity considerably increases.

As the basis for the new sorbent the researchers chose clay deposits of the Samara region. Peat and dolomite were taken as additives and polyvinyl acetate was used as a binder. To change the chemical structure and morphology of the surface and to obtain porosity, the authors applied thermal modification.

This article presents new data obtained in static and kinetic conditions. This data supplement previously published results. The sample under analysis was chosen as the best of ten sorbents on the basis of clay with the fastest kinetics and the greatest sorption capacity [3, 4]. The sample consisted of 10 pieces of yellow clay, 10 pieces of white clay, 10 parts of annealed peat and 1 part of dolomite. Polyvinyl acetate was used as a binder in the volume of 2 mass parts.

2. Methodology of the material preparation

Clay and dolomite pre-soaked for 30 minutes in distilled water for the purpose of separating heavy mineral inclusions. Then they were centrifuged and dried in the oven to a constant weight at a
temperature of 105 °C. Peat was dried, and then subjected to pyrolytic annealing without oxygen access at 600 °C for 15 minutes in SNOL 8.2/1100 muffle furnace. All dry components were carefully stirred. Polyvinyl acetate was added as a binder. The received mass was sent for annealing in a muffle furnace in oxygen environment. The furnace was programmed for gradual heating for 2 hours to 800 °C. The mass was kept there for 4 hours and then it was cooled in the furnace with a gradual decrease in temperature for another 2 hours.

3. Research Process
To determine chemical composition of the original components the researchers used energy-dispersive X-ray fluorescence spectrometry (table 1). The yellow clay composition includes aluminum oxide. Other components contain the same substances, but in different concentrations. Varying ratio of components in the sorbent, it is possible to change concentration of oxides of silicon, iron, calcium, aluminium and other substances.

| Oxide   | White Clay | Yellow Clay | Dolomite |
|---------|------------|-------------|----------|
| SiO₂    | 68.72      | 59.86       | 17.16    |
| CaO     | 13.57      | 0.55        | 70.20    |
| Fe₂O₃   | 8.61       | 1.58        | 8.28     |
| K₂O     | 3.73       | 1.30        | 1.79     |
| SO₃     | 3.64       | n/a         | 1.12     |
| TiO₂    | 1.32       | 1.37        | n/a      |
| Al₂O₃   | n/a        | 35.18       | n/a      |
| ZnO     | n/a        | n/a         | n/a      |
| Other oxides | 0.41 | 0.16 | 1.45 |

The statics and kinetics of the sorption sample were studied on the basis of ions of copper, iron, manganese, zinc and lead. The model multicomponent solution was prepared by dissolving weighed portion of salts CuSO₄∙5H₂O, FeCl₃∙6H₂O, KMnO₄, ZnSO₄∙7H₂O and Pb(NO₃)₂ of "Chemically pure" and "Pure for analysis" grades in distilled water. 5 minutes before the end of contact time mixing machines were switched off, the sample was clarified from clay particles and filtered through the paper filter "Blue Ribbon". The concentration of metals in the solution was determined by the method of atomic-absorption spectrometry with graphite atomization using the Shimadzu AA 7000 device. Static Exchange Capacity (SEC) was figured out for decrease of concentration, mg/g:

\[
COE = \frac{C_{in} - C_f}{m} \cdot V,
\]

where \(C_{in}\) is the initial concentration of metal ions in the solution, mg/l; \(C_f\) is the concentration of metal ions after interaction with sorbent, mg/l; \(m\) is the sorbent weight, g; \(V\) is the volume of solution, l.

Kinetic researches were carried out with the sample of sorbent of 1 g weight and a multicomponent solution of 200 ml volume at duration of contact \(T\) from 5 to 150 minutes. The purpose of this series was to determine the time sufficient for equilibrium, and to compare the concentrations of metal ions in purified water \(C_f\) with regulatory requirements, that is with maximum acceptable concentration (MAC) in the water of water bodies of commercial fishing importance. Table 2 and Figure 1 show the results of kinetic researches. They demonstrate that the time of reaching MAC of ions of metals was 10 minutes for iron and lead, 60 minutes for zinc and manganese, 90 minutes for copper.
Table 2. Kinetics of ions of heavy metals sorption by modified clay sorbent.

| T, Min | Fe^{3+}, C_{in}=1.14 mg/l | Zn^{2+}, C_{in}=1.61 mg/l | Pb^{2+}, C_{in}=0.90 mg/l | Cu^{2+}, C_{in}=0.66 mg/l | Mn^{2+}, C_{in}=0.82 mg/l |
|--------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
|        | MAC = 0.1 mg/l           | MAC = 0.01 mg/l           | MAC = 0.006 mg/l          | MAC = 0.001 mg/l          | MAC = 0.01 mg/l           |
| C_{f}, mg/l | SEC, mg/g | C_{f}, mg/l | SEC, mg/g | C_{f}, mg/l | SEC, mg/g | C_{f}, mg/l | SEC, mg/g | C_{f}, mg/l | SEC, mg/g |
| 5      | 0.009                     | 0.227                     | 0.045                     | 0.313                     | 0.001                     | 0.313                     | 0.005                     | 0.131                     | 0.241                     | 0.116                     |
| 10     | 0.006                     | 0.227                     | 0.019                     | 0.318                     | 0.000                     | 0.318                     | 0.005                     | 0.131                     | 0.199                     | 0.125                     |
| 20     | 0.006                     | 0.227                     | 0.008                     | 0.320                     | 0.000                     | 0.320                     | 0.002                     | 0.132                     | 0.017                     | 0.161                     |
| 40     | 0.006                     | 0.227                     | 0.007                     | 0.320                     | 0.000                     | 0.320                     | 0.002                     | 0.132                     | 0.013                     | 0.162                     |
| 60     | 0.006                     | 0.227                     | 0.003                     | 0.321                     | 0.000                     | 0.321                     | 0.002                     | 0.132                     | 0.005                     | 0.163                     |
| 90     | 0.006                     | 0.227                     | 0.003                     | 0.321                     | 0.000                     | 0.321                     | 0.001                     | 0.132                     | 0.003                     | 0.164                     |
| 150    | 0.006                     | 0.227                     | 0.002                     | 0.321                     | 0.000                     | 0.321                     | 0.001                     | 0.132                     | 0.004                     | 0.164                     |

Figure 1. Kinetics of ions of heavy metals sorption by modified clay sorbent.

To build sorption isotherms the researchers used the method of constant weighed portions and variable concentrations of heavy metal ions (from 27 to 0.05 mg/l). The volume of the solution was 200 ml, the weight of the sorbent – 1 g. Each experiment was conducted twice. The initial solutions were prepared in the volume enough for two parallel samples. Their concentrations were tested analytically. The duration of stirring was taken as 150 minutes sufficient to achieve equilibrium concentration of $C_f$. Table 3 summarizes the experiment results.

PH change after interaction of a sorbent with a solution is explained by the ion character of ions of heavy metals sorption with release of alkaline metals into the processed solution.

4. The static capacity was determined by the formula (1). Sorption isotherms are built while taking average concentrations, defined from two parallel experiments (see Fig. 2). The values of the exchange capacity corresponding to MAC for metal ions are, mg/g: for iron – more than 1.95; for copper – more than 0.75; for zinc – more than 0.464; for manganese – more than 0.011, for lead – more than 0.77. Figure 2 testifies that achieved equilibrium concentration for the ions of iron and manganese corresponded to the maximum capacity of the sorbent, that is 3.17 and 1.14 mg/g. For the ions of copper, zinc, manganese saturation at the given concentrations was not reached and the greatest values of capacity were 2.33, 1.75 and 1.14 mg/g respectively. The ions of iron, copper and zinc sorption flowed at a high speed during the first 5-20 minutes, then the speed decreased and the curves smoothed out.
Figure 2. Statics of ions of heavy metals sorption by modified clay sorbent.

Figure 3 demonstrates the dependence of removal efficiency of heavy metal ions from their initial concentration. They are built on the basis of Table 3 data. It is determined that the purification efficiency was higher at low initial concentrations. Higher equilibrium concentration of metal ions at low initial concentration of the solution can be explained by the transition of iron ions from sorbent to solution in the amount of no more than 0.01 mg/l, which however did not prevent form achieving MAC for commercial fishing importance to the fifth minute of interaction.

Figure 3. Removal of heavy metal ions efficiency depending on the initial concentration.

4. Conclusions
The research yielded the following conclusions:

1. The sorbent, made on the basis of clay of the Samara region, can be used for purification of biologically purified municipal and industrial wastewater from copper, iron, manganese, zinc up to MAC for fishery water bodies.

2. Kinetic researches demonstrated that the time of reaching MAC of ions of metals for the sorbent was 10 minutes for iron and lead, 60 minutes for zinc and manganese, 90 minutes for copper.
3. The values of the sorbent exchange capacity corresponding to MAC for metal ions are, mg/g: for iron – more than 1.95; for copper – more than 0.75; for zinc – more than 0.464; for manganese – more than 0.011, for lead – more than 0.77.

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