RESEARCH OF CHROMIUM (VI) ION ADSORPTION BY MONTMORILLONITE MODIFIED BY CATIIONIC SURFACTANTS

Vivishit structural and adsorptive properties of montmorillonite, modified with cationic surfactants, have been studied. Chromium in aquatic systems may be mainly in the form of Cr (III) and Cr (VI). Compounds of Cr (VI) have expressed toxic properties. Their removal from aquatic environments is complicated by the fact that chromium is soluble at all pH values, and they are not adsorbed by the minerals of aquifers due to a negative charge. The main aim of this study was to investigate the adsorption of chromium ions on modified montmorillonite.

1. Introduction

Chromium in aquatic systems may be mainly in the form of Cr (III) and Cr (VI) [1]. Compounds of Cr (VI) have expressed toxic properties. Their removal from aquatic environments is complicated by the fact that chromium is soluble at all pH values, and they are not adsorbed by the minerals of aquifers due to a negative charge.

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charge of ions. They are highly mobile in soil underground aquifers [2].

Chemical precipitation, membrane filtration, ion exchange chromatography, dialysis/electrodialysis, reverse osmosis and adsorption are usually used for removal of Cr(VI) from aquatic environment. These methods have many disadvantages, such as incomplete removal of metal, high cost of the reagents, a necessity for large amounts of energy, creation of the toxic sludge and other wastes that require further purification.

One of the most effective ways to remove heavy metals from aquatic environments is sorption method. Taking into account that the use of ion exchange resins is costly, natural silicate materials and silicate-based materials are used for environmental purposes [3]. Thus, the relevance of the article is due to the need to improve modern highly efficient sorbents and technology solutions for their application for the removal of heavy metals and radionuclides from aquatic environments.

2. The object of research and its technological audit

The object of research is the natural layered silicate — montmorillonite of Cherkasy deposit having a cation exchange capacity (CEC) 1.0 mmol/g [4]. Cationic surfactant — hexadecyltrimethylammonium bromide (C_{16}H_{33}N(CH_{3})_{3}Br, Merck) is used for surface modification of montmorillonite.

Natural silicate-based sorbents have sufficiently high cation exchange capacity and can be used as a sorbent for the removal of metal cations. Adsorption of anions on the surface of montmorillonite is very limited.

Given that in aquatic environments chromium compounds are in anionic form [5], it is actual the study of the sorbent synthesis that can effectively remove them. The main direction of increasing sorption properties in relation to anions are targeted regulation of hydrophobic and hydrophilic surface properties by surfactants.

3. The aim and objectives of research

The aim is to determine the optimal ratio of CEC/surfactant (CEC/S) to montmorillonite modification by the cationic surfactants for obtaining sorbents that can remove anionic form of chromium compounds and investigate the impact of the sorbent structure on the absorption properties.

Considering that sorption of various Cr(VI) forms on the surface of layered silicates of varying degrees of modification is poorly understood, to achieve this aim it is necessary to solve the following problems:

1. Investigate the physical and chemical characteristics of the synthesis of composite materials based on layered silicates and cationic surfactants.
2. Investigate the peculiarities of removal of Cr(VI) ions from aquatic environment using obtained sorbents.
3. Investigate an influence of organo-montmorillonite microstructure on removal of Cr(VI) ions and to determine the optimal S/CEC value.

4. Literature review

One of the most common methods to improve sorption properties of natural silicates is its modifying by surfactants [6]. The essence of this method is in cationic exchange reactions. Interlayer cations of clay minerals are displaced by quaternary ammonium cations that can displace Na\(^+\) ions from the ion-exchange positions in montmorillonite, thus increase of the number of hydrocarbon atoms in nonpolar aliphatic group contributes to a more efficient displacement of interlayer cations. In this regard, cationic surfactants are often used for the modification of clay minerals. The number of carbon atoms in these surfactants is typically ranging from 6 to 20 [4].

Published data show that this type of sorbents allows to remove even small amounts of heavy metals from natural waters, including chromium Cr(VI) [7–9].

To determine the optimal ratio of surfactant to the cation exchange capacity of the mineral (S/CEC) it must be taken into account the structure of clay minerals and surfactant capacity to occupy the ion exchange centers of the mineral. Sorption capacity of organoclay increases with the number of surfactants in the interlayer space of clay [10]. With increasing S/CEC ratio, surfactant accommodation in the interlayer space of clay will vary from separate filled monolayer sections by the followed formation of separate double-layer islands, and with increasing S/CEC ratio is completely filled with ion-exchange centers clay, a continuous surfactant monolayer is formed. Double paraffin layer is formed in the case of surfactant injection in the amount that excess CEC of the mineral. Interlayer space is extended in this case. For the cationic surfactants, ammonium groups attached to a silica surface [11]. The porous structure and surface characteristics of organoclay are closely associated with the surfactant distribution in the interlayer space. This means that the organoclay microstructure has a pronounced effect on its sorption properties [12]. The influence of organoclay microstructure on its absorption characteristics is an important aspect of understanding the mechanism of absorption and the possibility for use of synthesized materials to purify the contaminated soil and groundwater recovery, but the amount of work in this area is limited [13–15].

5. Materials and methods of research

Clay material was purified from impurities by coarse phase sedimentation. The obtained paste is dissolved in 1M NaCl solution to replace the exchange complex of doubly charged cations Ca\(^{2+}\) on single Na\(^+\). This operation was performed twice. Mineral was washed from residue of sodium chloride, dried at 105°C. The material was crushed and used fraction 0.1–0.2 mm for further studies.

Determination of the interlayer space of the original and modified samples was carried out by X-ray method using diffractometer ДРОН-4-07 (CuK\(_{α}\) rays). Scanning step was 2–10 degrees. Monominerality of the prepared samples were studied in a range of angles (2\(θ\)) 5–60°.

A suspension of Na-montmorillonite was treated using a dispersant УЗДИ-2T with an ultrasonic frequency of 22 kHz and intensity of radiation 12 W/cm\(^2\). The duration of treatment was 5 minutes [16]. A suspension of Na-montmorillonite was mixed with appropriate amounts of hexadecyltrimethylammonium bromide (HDTMA) and stirred on a magnetic mixer for 2 hours at 60°C.

Organoclay modification was conducted for S/CEC ration from 0.05 to 2. The obtained material was washed with distilled water and dried at 80°C. Organoclay was...
crushed and fraction between the sieves with openings of 0.1–0.2 mm² was selected. Samples for a more detailed study of sorption properties were selected at S/CEC ratio = 1 (OMMT1), at S/CEC ratio = 2 (OMMT2) and Na-montmorillonite (Na-MMT sample).

Separate part of the sample after modification of surfactant clay mineral was kept for 2 hours, and then the height of the sediment was measured. It was expressed as a percentage of the original suspension height.

Potassium dichromate K₂Cr₂O₇ was used for sorption experiments. Sorption was conducted in static conditions at 25 °C. Ionic strength of the solution (0.01 M) was set by means of NaCl. Ratio of solid and liquid phase was 1/500. After setting adsorption equilibrium (1 hour), the aqueous phase was separated by centrifugation and determined an equilibrium concentration of metal in it by spectrophotometric method (UNICO 2100UV) using diphenylcarbazide reagent at a wavelength of 540 nm. The influence of the CEC/S ratio on Cr(VI) sorption was studied at pH 6 and chromium ion concentration of 10 mg/L.

6. Research results

In diffractograms of original montmorillonite (Fig. 1) there is an intense basal reflex d₀₀₁ = 1.268 nm, corresponding to the presence of water molecules in the interlayer space and characteristic of the air-dry samples of the mineral [17]. At the same time, during the modification process, cationic surfactant molecules are sorbed not only on the outer surface of the particles, but also migrate between aluminosilicate packages of montmorillonite layered structure, exchanging Na⁺ ions in ion exchange positions. This is evidenced by basal reflections shift towards higher interplanar distances on diffractograms of the modified samples [18]. The magnitude of this shift d₀₀₁ for OMMT1 and OMMT2 is 1.824 nm and 2.246 nm, respectively, and points to the possibility of formation of a dense double layer of HDTMA molecules in the interlayer space of the mineral for OMMT1 and paraffin layer for OMMT [11].

Research of the sediment height was shown (Table 1) that V-shaped nature of the curve is observed for HDTMA-modified montmorillonite.

Table 1

<table>
<thead>
<tr>
<th>S/CEC</th>
<th>0</th>
<th>0.05</th>
<th>0.1</th>
<th>0.25</th>
<th>0.5</th>
<th>0.75</th>
<th>1</th>
<th>1.25</th>
<th>1.5</th>
<th>1.75</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>suspension height, %</td>
<td>99</td>
<td>99</td>
<td>99</td>
<td>97</td>
<td>97</td>
<td>87</td>
<td>78</td>
<td>57</td>
<td>39</td>
<td>43</td>
<td>20</td>
</tr>
</tbody>
</table>

Fig. 1. Increase of the basal distance for modification: 1 — Na-MMT; 2 — OMMT1; 3 — OMMT2

The largest sorption values are observed for CEC/S = 1:2.5.

More detailed studies were conducted for samples OMMT1, OMMT2 and compared with Na-MMT.

As can be seen (Fig. 3), sorption of Cr(VI) anionic form on Na-MMT is insignificant. At the same time significant increase of sorption values is observed for modified samples of OMMT1, OMMT2 reaching 11 mg/g and 37 mg/g, respectively.

Fig. 2. Dependence of Cr(VI) removal on CEC/S

Fig. 3. Adsorption isotherms: 1 — Na-MMT; 2 — OMMT1; 3 — OMMT2

Research results of pH effect on Cr(VI) adsorption (Fig. 4) showed that the maximum adsorption values for all samples were obtained in an acidic medium at pH = 1.2. A gradual decrease in adsorption was observed at pH from 2 to 6, and from pH = 6 there is a significant decrease of chromium absorption. This suggests that the mechanism of chromate removal associated with its form in solution. Research using a pure HDTMA was conducted to clarify HDTMA role not associated with silicate surface in the chromium adsorption. Fig. 4 shows the dependence of Cr(VI) adsorption on pH-solution for Na-MMT, OMMT1, OMMT2, HDTMA1 and HDTMA2.
An amount of surfactant for this study for HDTMA1 and HDTMA2 samples was taken the same as an amount of surfactant contained in a 0.1 g of OMMT1 and OMMT2 samples respectively.

Adsorption varied within 4.9-2.2 mg/g for OMMT1, OMMT2 samples with changing pH. Experimental data confirm the high adsorption capacity of synthesized materials to removal of the most of chromate at pH close to neutral.

Organo-montmorillonite suspension layering was observed at CEC/S ratio = 0.5. The process associated with gradual surface hydrophobization of the mineral clay and flocculation of the system due to compensate the charge of the particles, which is the least for S/CEC = 1. An adsorption of the second layer of surfactant begins on the montmorillonite surface with a gradual surface hydrophobilization in the case of increasing content of surfactants in the system. This explanation is consistent with previous studies [19]. This process is accompanied by changes in surface charge from negative to positive, hence the maximum sorption of CrO$_4^{2-}$ anions at neutral and alkaline pH values.

Organoclays modified at CEC/S > 1 showed higher adsorption capacity in relation to Cr(VI) compared with sorbents modified at CEC/S = 1, where the surfactant molecules located in the interlayer space of montmorillonite and probably only partially available for reaction with pollutants [20]. It is also clear that some HDTMA not associated with mineral surface and also involved in the removal of Cr(VI) from solution by alkyl ammonium chromate sedimentation.

Chromate removal mechanism is associated with its form in the solution. At lower pH, dominant types of chromium are mostly singly charged anions, HCrO$_4^-$. Thus, a one center is necessary for the exchange of one molecule of chromium (HCrO$_4^-$). Chromate anion displaces of HDTMA form exchange centers of the silicates that form [21]:

Silicate – HDTMA$^+$ + HCrO$_4^-$ ⇄

In contrast, at a pH above 6, mainly present two-charge form of CrO$_4^{2-}$ chromate and requires two exchange centers of organo-montmorillonite surface:

2Silicate – HDTMA$^+$ + CrO$_4^{2-}$ ⇄
↔ Silicate – (HDTMA)$_2$ – CrO$_4$.

In an alkaline environment there is strong competition between the Cr(VI) anions and OH$^-$ and Br$^-$ ions, so the amount of Cr(VI) that adsorbed on organo-montmorillonite is sharply reduced.

7. SWOT-analysis of research results

Strengths. Among the strengths of this study we should be noted the results of Cr (VI) sorption that is confirmed by the above mentioned results of the analysis of modern scientific periodicals. Modification of the montmorillonite surface by cationic surfactants enables to reach the surface recharge from negative to positive sign that allows to ensure removal of anionic inorganic toxicants from aquatic environment.

Weaknesses. Weaknesses of the study are due to the fact that excess surfactant in the composite can significantly degrade the environment. Therefore, to avoid these shortcomings it should pay special attention to necessity for sorbents with optimal CEC/S value.

Opportunities. This research provides a broader vision for the synthesis of sorbents based on natural silicate anions for extraction of heavy metals, namely, the ability to remove Cr(VI) directly from soil layers.

Threats. There aren’t difficulties with the implementation of the results.

Thus, SWOT-analysis of research results allows to determine the main directions for successful achievement of the aim of research, namely, a necessity for preparation of technologies for the synthesis of sorbents on an industrial scale.

8. Conclusions

1. Sorbents are synthesized by modifying the montmorillonite surface by cationic surfactants. It is proved that purposeful regulation of hydrophobic and hydrophilic surface properties improves the sorption properties in relation to the heavy metal anions.

2. It is proved that Cr(VI) ions adsorption increases with increase of CEC/S in synthesized samples. Removal of chromium compounds depends on pH of a solution. The highest values are obtained at pH from 1 to 6. Adsorption properties of organoclays are decreased at pH 6 to 8. Removal of Cr(VI) is not significant in the alkaline environment.

3. It is found that the optimal CEC/S ratio for montmorillonite modification by the cationic surfactant to obtain sorbents that can remove anionic form of chromium compounds is 1. Such compounds remove up to 11 mg/g ions of Cr(VI), which is four times higher compared to natural montmorillonite. The part of HDTMA is not related to mineral surfaces in organoclays modified at CEC/S ≥ 1 and involved in the removal of Cr(VI) from solution with precipitation in the form of alkyl ammonium chromate.
References


ИССЛЕДОВАНИЕ АДСОРБЦИИ МОНОВ ХРОМА (VI) МОНТОМОРРОЛИНОМ, МОДИФИЦИРОВАННЫМ КАТИОННЫМИ ПОВЕРХНОСТНО-АКТИВНЫМИ ВЕЩЕСТВАМИ

Изучены структурные и адсорбционные свойства монтмориллонаита, модифицированного поверхностно-активным веществом (тексадецилтриметиламмоний бромид). Определены оптимальные ионные соотношения для модифицирования монтмориллонаита поверхностно-активным веществом с целью получения данных сорбентов. Получен сорбент со значительно более высокими ионообменными свойствами, чем исходный материал. Данный сорбент может быть использован для эффективного нивелирования соединений Cr(VI) из водных сред.

Ключевые слова: органоглина, монтмориллонит, адсорбция, хром, тексадецилтриметиламмоний бромид.

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