Adsorption method of purification of stocks from chromium(III) ions by bentonite clays

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Abstract

The process of sorption of chromium(III) ions with a stationary sorbent layer of bentonite clays was investigated. The main advantages of using bentonites in water purification technologies are described: powerful geological reserves, cheap process of rock extraction, easy preparation for transportation and use, possibility of using waste sorbents in other technologies that is why there is no need in costly regeneration.

The influence of various factors (process duration, an adsorbent layer) on the degree of wastewater purification from chromium ions, the effect of pumping speed on the dynamic capacity of the sorbent was studied and the effective volume was determined. The adsorption efficacy increases with the increase of the adsorbent layer, what can be explained by the development of the active sorption surface. As the initial concentration of chromium ions increases, the time of appearance of the first traces of the contaminant at the exit of the column increases, as well as the total time to channeling. The results of the studies indicate a higher adsorption capacity of modified bentonite with respect to Cr³⁺ ions compared to its natural formula. The cleaning efficacy of the solution with a concentration of chromium ions of 0.5 g∙dm⁻³ is increased by 5% when using 15 g of modified bentonite and 6,5% in the case one uses 20 g compared to the natural form.

Key words: adsorption, bentonite, chromium ions, environmental safety, natural clay sorbents, wastewater purification

INTRODUCTION

The problem of environmental protection is extremely important to modern communities although it has been known for a long time. Modern conditions of human life are increasingly demanding and lead to the possible consequences of its activities, not only because the violation of environmental principles forms a circle of irreparable costs in nature, but also because by changing the environment in one direction or another, people directly and indirectly affect the genetic fund, reduce the possibility of a full life.

The objective reality of the modern world indicates that the environmental consequences of human activity are becoming a major factor in the development of a society. It is important to understand and adopt modern value orientations, semantic attitudes, to form a new image of a human being, that would be friendly towards both himself and the natural environment. Without such global psychological
restructuring of the human-natural environment, all eco-
omic, environmental and scientific-technical measures will be of limited nature and will not be an important basis for overcoming an environmental disaster.

Modern industrial wastewater purification technologies have to meet three requirements which are the following:

1) socio-psychological, aimed at meeting the society’s expectations as for environmental situation improve-
ment;
2) economic: price optimization and quality criteria;
3) technological, aimed at reducing material and labour coefficient.

Sorption methods of water purification take the lead-
ing place according to the integrated criteria. Some sci-
entists have dedicated their studies over the last few years to heavy metal adsorption with the help of dewatered iron-containing waste sludge [YILDIZ et al. 2018]. Considerate attention is also being paid to studying on the use of ferruginous sludge from water treatment plants [WOLOWIEC et al. 2017].

It should be noted that heavy metals form a group of the most dangerous pollutants in the environment. In sur-
face natural reservoirs (seas, lakes, rivers, reservoirs) with industrial wastewater, a considerable amount of heavy metal ions enters, which has become a significant obstacle in the life of macrobiota. The wastewater of the electro-
plating, paint and leather industries contain a large number of soluble and insoluble heavy metal compounds that have an unpleasant odour, dark colour, foam and are toxic. The content of chromium(III) ions, for example, in sewage production of leather can reach 3000 or more mg·dm⁻³ [PETRUS, WARCHOL 2005]. Given the toxicity of this metal, wastewater containing its compounds is subject to mandary purification prior to their discharge into natural res-
ervoirs.

The compounds of tri- and hexavalent chromium ex-
hibit the opposite physiological effect. If micro amounts of Cr(III) compounds play an important role in mammalian metabolism, then Cr(VI) compounds have toxic effects on biological systems and carcinogenic effects on humans. Compared to Cr(III) compounds, chromium(VI) com-
 pounds are soluble in a wide pH range, have greater mobility and are therefore more dangerous to living organisms. In addition, the harmful effects of hexavalent chromium are exacerbated due to the fact that the negatively charged ions HCrO₄⁻, CrO₄²⁻, Cr₂O₇²⁻ limited undergo sorption by clays, which increases their mobility and enhances the haz-
ardous effect [SAKALOVA et al. 2017]. Ranges from a few tenths of a microgram in a dm⁻³ to a few micrograms in a dm⁻³ in polluted ponds it reaches several tens and hundreds of micrograms in a dm⁻³. The average concentration in seawater is 0.05 mg·dm⁻³, and in groundwater it is usually within n·10⁻¹ n·10⁻³ mg·dm⁻³ [MALOVANYY et al. 2019]. The chromium content of reservoirs for drinking purposes shall not exceed the maximum permissible concentration (MPC) for Cr(VI) of 0.05 mg·dm⁻³. The MPC in the water of the reservoir used for fishery purposes for Cr(VI) is 0.001 mg·dm⁻³.

One of the promising ways of manifestation of green-
ing is the study of sorption separation as a method of ex-
traction of radioactive, toxic and valuable impurities from aqueous solutions. Ion-exchange methods have particular advantages in cases where the initial concentration of unwanted impurities is relatively small and the degree of their extraction should be high.

In terms of prospects for the application of innovative methods of treatment of chromium-containing wastewater in the leather and fur industry, in comparison with existing (reagent electrochemical, membrane, ion exchange methods) the most effective today are sorption methods. The use of active sorbents allows to thoroughly treat efflu-
ents that contain even small concentrations of these metals, and it is known that the content of Cr₂O₃ in wastewater after tanning and before duplication is relatively small, and ranges from 0.5–2.2 mg·dm⁻³. Sorbents of natural origin are increasingly used for water purification: clay rocks, apatites, zeolites. The use of such sorbents is due to their relatively high sorption capacity, cation exchange properties of some of them, relatively low cost and availability.

Analysis of recent publications (WARCHOL et al. [2006]; KOLODNYNSKA et al. [2017]) indicates the feasibil-
ity of using adsorption methods for the purification of wastewater from heavy metal ions using natural dispersed minerals as adsorbents [KONEFAL et al. 2015], as modifi-
cation objects [ILANGO, NATRAYASAMY 2018; REPO et al. 2017], or carriers for mycelium fungi Aspergillus immobi-
лизation [SATIVKA et al. 2015]. Modified natural sorbents have improved properties concerning heavy metals [REPO et al. 2013], and immobilized on sorbents fungi Aspergillus are used for purifying effluents from hexavalent chro-
mium. Quite often, silica gels [REPO et al. 2011], clay ma-
terials [ANNAN et al. 2018; QIN et al. 2016], humic com-
plexes [MENG et al. 2017] are used to purify wastewater from heavy metal ions. Purification of aqueous solutions with the help of dispersed sorbents is in accordance with the principle of environmental life of modern man, that is, indicates compliance with the requirements of environ-
mentally friendly and energy-saving production [PALA-
MARCHUK 2011]. Powerful geological reserves, cheap rock extraction, easy preparation for transportation and use, the ability to use waste sorbents in other technologies are the main advantages of using natural minerals. One of the types of promising natural sorbents, which have been used as an object of research, is bentonite – a natural clay sorbent with a layered structure. The main mineral that provides the adsorption properties of bentonite is montmo-
rillonite.

The main advantages of using bentonites for the treat-
ment of chromium-containing effluents include:

- natural bentonites are widespread in Ukraine;
- natural sorbents are an affordable, inexpensive materials;
- adsorption technologies using bentonites provide a high degree of wastewater treatment from heavy metal ions;
- spent natural adsorbent can be disposed within the tech-
nologies of leather and fur production;
- bentonite saturated with chromium ions can be reused for wastewater treatment of preparatory processes and spent nickel plating fluids.
MATERIALS AND METHODS

The purpose of the work is to study wastewater treatment of chromium (III) ions by adsorption on natural sorbents. Studies of the adsorption process, as a manifestation of environmentally oriented activity, have been carried out in an adsorption column with a fixed layer of adsorbent. The proposed technical solutions make it possible to significantly simplify and reduce the cost of sewage treatment in various industries, including galvanic and leather industries.

Bentonite (type 2:1) from the Cherkasy deposit of bentonite and Paligorskite clays was used for the research. The preparation process for bentonite consists of several steps. The raw material was crushed and dried in a drying chamber at a temperature of 120°C for 45 min. Then the clay was ground and separated into appropriate fractions. Water was purified on a laboratory adsorption column having a diameter of 35 mm and a height of 300 mm using bentonite clay. The prepared clay was poured into a column.

The total weight of the sorbent in the adsorption column was 15–25 g. The volume of the sorbent in the column was 21.6 cm³ and 29 cm³, respectively, by the weight of the sorbent 15 and 20 g (usually to make it more clear it has been used OK unit “column volume” – standard volume of column for the same weight of sorbent). In fact, this is a dimensionless quantity, which is denoted by the indicator \( V_{\text{eff}} \). The solutions containing the content of Cr³⁺ ions in the solution was determined by the titrimetric method. To establish the range of mode parameters which require a detailed study of adsorption processes, a series of preliminary experiments was performed which made it possible to draw the following preliminary conclusions:

- fluctuations in temperature from +10 to +30°C have no significant effect on the degree of adsorption of Cr³⁺ bentonite ions;
- the optimal average pumping rate of the model solution through the adsorption column of the given height is 0.3–0.5 cm³·min⁻¹, at higher speed the amount of adsorbed Cr³⁺ is reduced and the lower speed increases the probability of a strong thickening of the pulp which complicates the processes of further filtration;
- the interval of investigated concentrations (0.5–2.0 g·dm⁻³) of chromium ions was chosen based on practical considerations in accordance with the possible content of Cr³⁺ cation by real effluents;
- it is preliminary established that the complete saturation of bentonite clay with Cr³⁺ ions is achieved at a layer of sorbent 15–20 g, for 1–3 days depending on the concentration of the model solution.

To determine the dependence of the sorption efficiency on the concentration of chromium(III) ions, model solutions with an initial concentration of pollutant from 0.5 to 2 g·dm⁻³ were passed through an adsorption column at 15 g absorbent layers; 20 g; the temperature of the model solution was 20°C. The solutions were analysed through each column volume, the average passage time was 3–4 min·cm⁻³, the control points were determined every 40 cm³ of the solution.

RESULTS AND DISCUSSION

As shown by the saturation curves of bentonite (Fig. 1) by chromium ions, presented in the form of the concentration of heavy metal ion at the outlet of the column \( C_{\text{out}} \) on the volume of pumped model solutions \( V_{\text{eff}} \), the adsorbent consumption has a significant influence on the course of the saturation process. With the same concentrations of chromium ions, the volume of the solution and the adsorption time before the full saturation of the adsorbent are much higher. The highest effective volume when pumping a model solution through a 15 g sorbent layer is 30.3, and when passing a solution through 20 g sorbent it is 41.4 cm³. These values in both cases are observed for model solutions with the highest concentration of heavy metal ion and this suggests that the use of a fixed-bed adsorption method to remove low concentrations of pollutants (less than 0.5 g·dm⁻³) is possible at lower bentonite costs. Also, with an increase in the initial concentration of chromium ions within the experimental values, the time of appearance of the first trace of the pollutant at the exit of the column increases, and the time to slip in all cases quickly occurs at the concentration of the pollutant at the

![Saturation curves of bentonite with a model solution](image.png)

Source: own study
exit from the column 70% of the initial one. The exceptions are the dependence on the concentration of chromium ions (Cr_{3+}) of 0.5 g dm^{-3} – in this case, the increase in the concentration at the outlet of the column is linear.

According to the results of the experiment, the maximum absorption of chromium(III) ions is 70.2–83.2% for the consumption of sorbent weighing 20 g and 63.5–82.2% in the case of mass of sorbent 15 g (Tab. 1). The adsorption efficiency increases with the increase of the adsorbent layer, which can be explained by the development of the active sorption surface.

**Table 1.** Indicators of sorption efficiency at different initial concentrations of chromium(III) ions in solution

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Weight of bentonite 15 g</th>
<th>Weight of bentonite 20 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial concentration $C_0$ of Cr^{3+} (g dm^{-3})</td>
<td>The first traces Cr^{3+} in the purified solution (OK)</td>
<td>Effective volume $V_{at}$ (OK)</td>
</tr>
<tr>
<td>1080</td>
<td>0.5</td>
<td>1.39</td>
</tr>
<tr>
<td>1230</td>
<td>1.0</td>
<td>1.39</td>
</tr>
<tr>
<td>2480</td>
<td>1.5</td>
<td>0.92</td>
</tr>
<tr>
<td>3205</td>
<td>2.0</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Source: own study.

The results of the studies indicate a higher adsorption capacity of modified bentonite with respect to chromium ions compared to its natural formula. The cleaning efficacy of the solution with a concentration of chromium ions of 0.5 g dm^{-3} is increased by 5% when using 15 g of modified bentonite and 6.5% in the case one uses 20 g compared to the natural form. It is important to mention that the modification of bentonite can be carried out by pre-soaking it in the spent acid solution [SABADASH et al. 2017], for example, in a solution after nickel plating that has undergone mechanical cleaning.

The proposed wastewater treatment method from chromium(III) ions may find implementations for wastewater treatment in various industries. We have considered the application of the method in the leather industry. In our opinion, one of the ways of using the method can be carried out in the following scheme (Fig. 2).

**Table 2.** Efficacy indicators of sorption of chromium(III) ions with the concentration of 0.5 g dm^{-3} on modified bentonite

<table>
<thead>
<tr>
<th>No.</th>
<th>Time (min)</th>
<th>Weight of bentonite 15 g</th>
<th>Weight of bentonite 20 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>1.86</td>
<td>11.00</td>
</tr>
<tr>
<td>2</td>
<td>1220</td>
<td>1.30</td>
<td>12.47</td>
</tr>
</tbody>
</table>

Source: own study.

The water with chromium(III) ions from collector 1 are fed to the adsorption columns 2 and 3. The columns work by shift: one of the columns operates in adsorption mode, the other in adsorbent overload mode. Purified effluents emanating from the adsorption column are used as industrial water in the leather production process. The column in adsorption mode works to saturate the adsorbent with chromium ions, which leads to a breakthrough at the exit of the column. After locking of the breakthrough, the columns are switched with the help of valves 4, 5, 6 and 7. The sewage for purification is fed to another column, and the column, which worked in the adsorption mode, is unloading the spent adsorbent and loading a fresh portion of bentonite. The spent adsorbent (saturated with chromium(III) ions bentonite) can be used in leather production.
CONCLUSIONS

The effectiveness of the use of natural mineral sorbents, in particular bentonite clays, for wastewater treatment is confirmed by their advantages over other sorbents, namely: they benefit in accessibility, cost, regeneration and reusability. They have confirmed the importance of modern human environmental activity, which is implemented in the system of target ecological installations, value ecological relationships and environmental orientations, which determines the prospect of using bentonite clays for wastewater treatment of chromium(III) ions by adsorption.

According to the results of the experiment, the efficiency of adsorption increases with increasing layer of adsorbent. Thus, the maximum absorption of chromium(III) ions occurs at a layer of sorbent 20 g and low concentrations of pollutant and is 83.2%.

The degree of wastewater purification during adsorption with a fixed sorbent layer at different concentrations of chromium(III) ions and quantities of the sorbent was determined. The bentonite consumption was found to be 20–22 g dm⁻³ of contaminated water to purify the solution containing Cr³⁺ ions at a concentration of 1–2 g dm⁻³.

The basic technological scheme of sewage treatment of leather production from chromium(III) ions is offered. Processed adsorbent saturated with chromium ions can be used in leather production for tanning, filling and finishing of natural leather.

REFERENCES


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