PROBLEMS OF ENVIRONMENTAL PROTECTION AND BALANCED NATURE MANAGEMENT

UDC 66.021.2.081.3:546.39 **DOI: 10.31652/2786-6033-2023-1(3)-33-38**

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Usage of spent clay sorption materials in leather and fur production technologies

The work is devoted to solving the current problem of increasing the level of environmental safety of treatment industrial wastewater of leather production from chromium ions (III) through the use of natural and modified bentonite. The most promising way of wastewater purification is the sorption technology, which is widely used in many countries to prevent pollution of the environment by wastewater from industrial enterprises. Studies of the use of natural and modified bentonite in the adsorption of Cr^{3+} ions have been carried out. The purpose of the research was to study the use of clay sorbents previously applied for the purification of wastewater from heavy metal ions in technological processes of leather and fur production. The possibility and modes of application of spent bentonite dispersions for the processing of leather semi-finished products to increase resource conservation and environmental friendliness of leather production were also established. The influence of the process duration on the sorption efficiency of chromium ions has been studied. Studies have been conducted to use spent bentonite in tanning and filling processes. The efficiency of modification of montmorillonite has been proved and the expediency of using mineral dispersion for qualitative formation of the structure and properties of the leather during tanning has been established.

The efficiency of adsorption of anionic dyes on spent montmorillonite is investigated. Was identified a high level of adsorption of anionic dyes at pH 5-6.5. The role of the dye structure, the level of the critical concentration of micelle formation on the dye adsorption on the surface of montmorillonite is provided. Utilization of spent bentonite by using it as part of multifunctional materials for the processing of leather semi-finished products contributes to a considerable increase in resource conservation and environmental friendliness of leather production.

Keywords: *ecological safety, natural clay sorbents, adsorption, bentonite, ions of heavy metals, modification, semi-finished item*

Introduction. Wastewater and surface water contamination with chromium ions remains a dramatic environmental problem that currently has no sufficiently effective solution. In spite of a great number of scientific studies, the technologies developed on their basis have not been widely used, since they are not flawless enough and provide no opportunity to achieve the necessary depth of clearance. The issue of wastewater filtering is also of great importance in leather technology, since chromium (III) salts are used for leather tanning, while the maximum degree of tanning is 90%, and the rest goes down the drain.

The most promising way of wastewater purification is the sorption technology, which is widely used in many countries to prevent pollution of the environment by wastewater from industrial enterprises. At present, considerable experience has been accumulated in the use of natural clays and their modified forms for the purification of wastewater from heavy metal ions. The foremost advantages of using adsorption materials are the following ones:

1. Deposits of natural sorbents are widespread in Ukraine;
2. Natural sorbents are a cheap and available material;
3. The spent natural adsorbent can be regenerated by the desorption method, although it is possible to use the spent sorbent in subsequent sorption;

4. Adsorption technologies provide a high degree of purification.

A thorough analysis of the latest publications revealed that an important direction of scientific research nowadays is also the determination of effective methods of regeneration and ways of utilization of sorbents, which were hitherto used as sorbents in the treatment of wastewater and communal drains. Ultimately, the utilization of sorption materials helps not only reduce the man-made burden on the environment, but also improve the technologies of creating alternative materials due to the use of high-quality clay material.

At present, highly dispersed spent minerals are extensively used in many sectors of the national economy, including the production of various consumer goods. However, the limitation of scientific research determines the low level of use of spent clay sorbents in leather production processes. Their use is based on specific colloidal chemical properties, which are caused by the crystalline structure of minerals.

The chemical composition and peculiarities of the crystalline structure of highly dispersed minerals in terms of the ratio of alumino- and silica layers determine the complex of their sorption, exchange, coagulation properties as well as their ability to disperse. The relevance of this research for leather production is also due to the need to dispose of sorbents used for wastewater filtering, in particular for chromium-containing wastewater from tanning and decor shops.

The purpose of the research was to study the use of clay sorbents previously applied for the purification of wastewater from heavy metal ions in technological processes of leather and fur production. The possibility and modes of application of spent bentonite dispersions for the processing of leather semi-finished products to increase resource conservation and environmental friendliness of leather production were also established.

Materials and methods, Wastewater after tanning is regarded the most concentrated in leather production since it makes up 1% of the total water consumption. It has an acidic reaction, its pH is from 3 to 6.5. Such wastewater contains a maximum of: 170 g/dm^3 of dense sediment, 15 chlorides, 22 sulfates, and 5 chromium oxide.

Heavily polluted wastewater includes spent solutions after re-dosing, which also contain a considerable amount of chromium salts (in terms of Cr_2O_3, a maximum of 3g/dm^3). The amount of such waste is approximately the same as after tanning.

Foregoing studies allow stating [2] that the use of sorption methods is most effective at an initial content of chromium ions of 1-1.5 g/dm^3. That is, preliminary wastewater treatment is advisable, which includes the stage of sedimentation, filtration and reagent sedimentation with lime followed by the subsequent removal of the formed sediment [4]. The resulting filtrate contains about 1 g/dm^3 of chromium ions and 5 g/dm^3 of chloride ions.

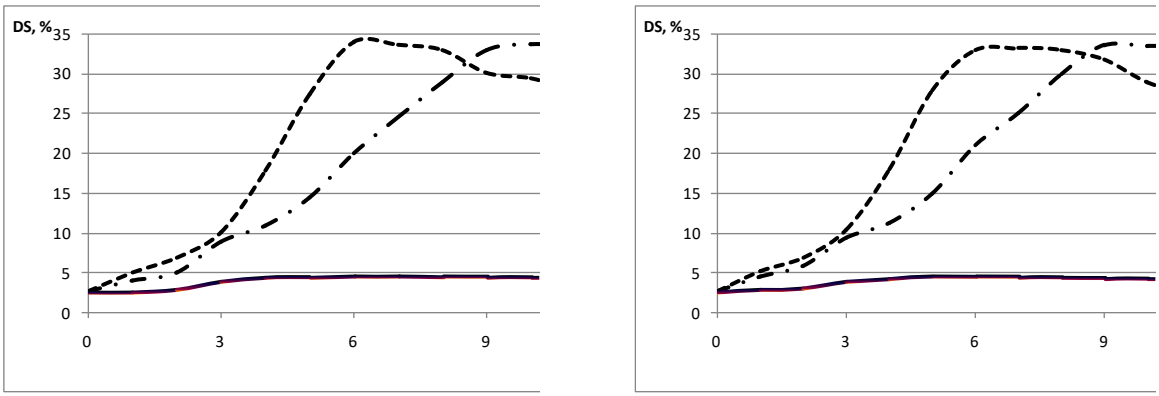
We obtained the results of determining the content of chromium ions in the spent dry sorbent according to the known method [5]. The practical content of metal ions in the clay sample is 95-97% of the calculated value of Cr^{3+}.

Research results. Taking into consideration the structural features and colloidal chemical properties of highly dispersed minerals, in particular bentonite, it is possible to use them as fillers for chrome semi-finished products and to regulate the formation of the dermis structure during the production of skins depending on their intended purpose [6]. In research papers [7,8], the possibility of effective use of bentonite specially modified with chromium salts in the processes of filling, tanning, and re-tanning of leather semi-finished products was much paid attention to. Given the structural features and colloidal-chemical properties of highly dispersed minerals, we investigated the possibility of using bentonite saturated with chromium ions at the stage of wastewater filtering, as a filler in chrome semi-finished products, a component of pigment pastes or to regulate the formation of the dermis structure during tanning.

Bentonite dispersion is extremely influenced by the following factors: the nature of the salt chosen for dispersion and its concentration (Cs,%). The degree of swelling (Ds,%) of water dispersions of spent bentonite (experiment) and pure bentonite (control) under the influence of sodium carbonate H_2CO_3, sodium formate HCOONa, and sodium hexametaphosphate $Na_6P_6O_{18}$•$6H_2O$ was determined.

The results of the relevant studies are presented in Figure 1, indicating that the best level of dispersion is achieved when using sodium carbonate, but it is also possible to achieve a sufficient degree of swelling when using sodium hexametaphosphate The nature of the dependences for modified and spent bentonite is very similar.

The best influence of sodium carbonate on dispersion structure formation and dispersing determined its use in further research. To establish the optimal consumption of sodium carbonate, the viscosity of dispersions was determined at different salt consumption.



control experiment

Fig. 1. The degree of swelling of aqueous bentonite dispersions under the influence of salts.
---- H_2CO_3; -•-- $Na_6P_6O_{18}•6H_2O$; ── HCOONa.

The results of rheological studies indicate that the highest viscosity of the dispersions is achieved with a sodium carbonate consumption of 5.5-7% and at the same time determines the maximum degree of dispersion of the system both with spent bentonite and in the case of its previous modification.

The viscosity of dispersions with different degrees of saturation with chromium ions was also established. The results of the research are presented in Figure 2.

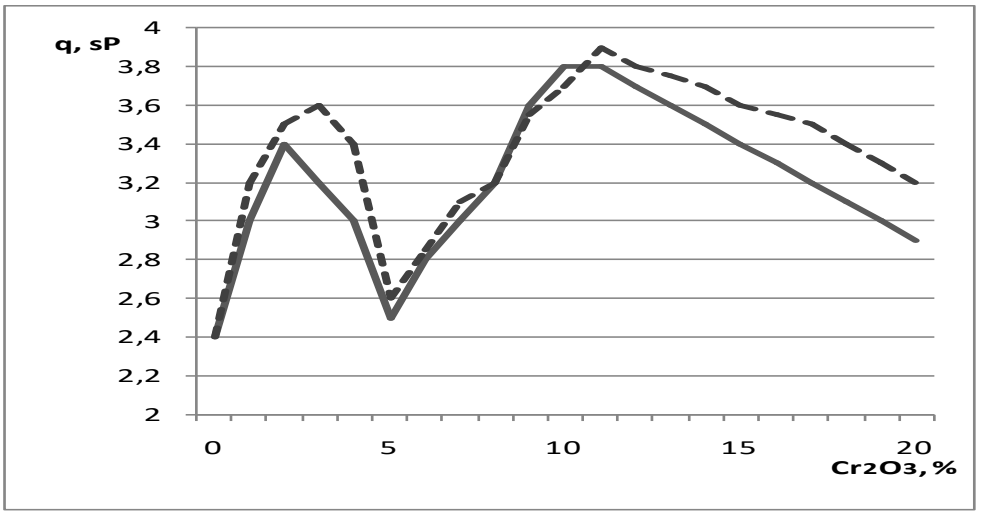


Fig. 2. Dependence of kinematic viscosity on the content of chromium ions in bentonite.
── control — —experiment

In general, the analysis of the dependence of viscosity on the consumption of chromium indicates the obtaining of the most diluted dispersions of spent and natural bentonite with the content of chromium compounds in them of 5–6% Cr_2O_3 by mass of montmorillonite. At the same time, the dispersions are characterized by a stable pH level in the range of 3–4 at the appropriate consumption of chromium compounds. The dilution effect can be explained by the adsorption of sodium ions and mutual repulsion between montmorillonite particles.

The adsorption stability of the dispersions was evaluated by settling them for 30 minutes at different pH values, which were adjusted by mixing appropriate amounts of HCI 0.02 M, NaCl 0.02 M, and NaOH 0.02 M solutions. The obtained results indicate that the dispersions based on spent bentonite show high stability in wide pH ranges. A certain level of delamination is observed at pH 2.5 and at pH 12. In the latter case, hydrolysis of chromium compounds probably occurs, which is confirmed by a change in the color of the dispersion. Therefore, it is feasible to recommend the use of dispersions based on spent bentonite in liquid processes occurring in acidic (pH=3) and slightly acidic (pH=4.5÷5.6) environments.

The degree of adsorption of anionic dyes by dispersions of spent bentonite was determined to study the possibilities of obtaining hybrid pigments, As a result of processing spent bentonite with solutions of anionic dyes of different chemical composition, the efficiency of adsorption of anionic dyes on mineral particles was determined (Table 1).

Table 1. Qualitative analysis of adsorption of dyes on bentonite

Type of dye	Molecular weight	Dye consumption, % of the mass of completely dry mineral			
		25	50	75	100
Anionic dark green	863	-	-	-	+
Anionic black	859	-	-	-	+
Anionic blue	637	-	-	+	+
Anionic yellow	710	+	+	+	+
Barvalan blue-black	794	+	+	+	+
Barvalan bright red	836	+	+	+	+

+ – appearance of a colored ring around a sample of modified montmorillonite
- – absence of paper staining around the sample of modified montmorillonite

A low level of adsorption of such dyes as barvalan bright red, barvalan blue-black and anionic yellow was visually established. This is evidenced by the absence of coloring of bentonite in the color of the dye after its separation from the dispersion medium: only a colored ring around the sample was observed. At any dosage of the aforementioned anionic dyes from the mass of the mineral, the color of the solid phase in the color of the dye did not occur.

However, as a result of the use of anionic dark green and anionic black dyes, the dispersed phase was completely colored in the color of the dye, which indicates the ability of the dye particles to adsorb on the surface of the modified bentonite and interact with each other to a greater extent. Only when the dye was dosed at 100% by weight of the mineral, a slight staining of the diffusion ring occurred during paper chromatography, which indicates the maximum level of absorption of the dye on the surface of the clay mineral.

Qualitative analysis revealed no regularities regarding the influence of the molecular weight of the dye on the intensity of adsorption. Perhaps, the crucial importance is not the molecular weight, but the presence of various reactive dye groups (-OH, -COOH, -NH2, -SO3H), which are capable of interacting with montmorillonite particles.

The research results testify to the fact that the dyes anionic dark green, anionic black and anionic blue are able to precipitate and adsorb on the bentonite surface when their consumption is 100% of the mass of the completely dry mineral, that is, when the ratio of montmorillonite: dye is 1:1, which is taken into account in further research. The obtained results also demonstrate that the adsorption level of the selected dyes (anionic black, anionic blue, and anionic dark green) was determined and adsorption isotherms of these dyes on chromium-containing bentonite particles were obtained, which is shown in Figure 3.

Given that adsorption is a function of dye concentration, pH, concentration electrolyte, solid phase concentration, and temperature, during the tests temperature, pH, electrolyte and solid phase concentration were constant. It should be noted that the nature of adsorption for all dyes corresponds to the Langmuir isotherm. At the beginning, all curves were characterized by rapid growth, i.e., in this area, dye molecules are adsorbed on the surface of montmorillonite particles due to the electrostatic interaction of the chromium cation with the dye anion. Further, the peak of each isotherm shows the saturation of the bentonite surface with dye molecules and the neutralization of the surface charge of the mineral. The interaction with montmorillonite is completed by polymolecular dye adsorption due to Vander-Waals forces [6].

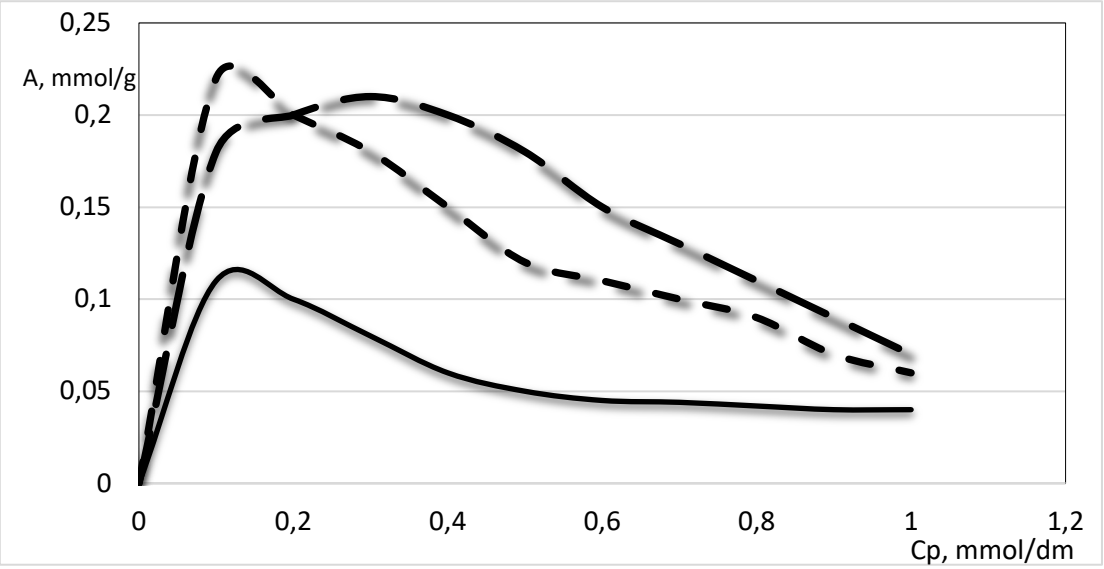


Fig. 3. Adsorption isotherms on montmorillonite of dyes: anionic black (──), anionic dark green (- - -) and anionic blue (— —).

Comparison of the adsorption isotherms of different dyes (fig. 1) demonstrates that the maximum adsorption is observed in the case of anionic dark green use. Despite the fact that the adsorption of all the dyes chosen for the study increases, the lowest adsorption maximum is observed for the anionic black dye. This phenomenon can be explained by the rapid formation of micelles in solutions of anionic black. The manifestation of the steric factor during the adsorption of its associates in the micropores of the cationic form of chromium-containing bentonite is so significant that the amount of its adsorption reaches minimum values. The lower level of adsorption of dyes from micellar solutions, compared to molecular solutions, is explained by steric complications. Increasing the concentration of the anionic black dye above 0.4 mmol/g causes rapid, irreversible polymolecular adsorption, which is positive for obtaining a high-quality pigment. An increase in the concentration of anionic blue and anionic dark green dyes causes a further decrease in the level of adsorption of dyes, which is probably due to the predominant formation of micelles. It is worth noting that for all the selected anionic dyes, it was visually established that a pigment of a saturated, intense color was obtained, especially in the case of using an anionic black dye.

Conclusion. The chance of using dispersions of spent bentonite containing chromium ions for tanning, re-tanning and filling of leather semi-finished products with partial replacement of chromium compounds was established. The use of dispersions based on spent bentonite with a residual content of chromium ions dispersed by sodium carbonate will definitely contribute to the effective formation of the chrome tanning hides, structure and quality indicators.

The ideal composition of dispersions with specified rheological properties and sufficient stability was also determined: the content of chromium ions in spent bentonite is 5÷6%. in terms of Cr_2O_3, consumption of sodium carbonate 5.5-7%, the pH is ranges from 3 to 4.

The combination of chromium compounds and chromium-containing montmorillonite dispersions for tanning will allow reducing the consumption of chromium tanner, improve the degree of absorption of chromium compounds and reduce their concentration in spent tanning liquids.

A high level of adsorption of anionic black, anionic dark green and anionic blue dyes, which are widely used in industry, was revealed. The role of the dye structure, its functional groups and the level of the critical concentration of micelle formation on the level of adsorption of the dye on the surface of montmorillonite is demonstrated.

Utilization of spent bentonite by using it as part of multifunctional materials for the processing of leather semi-finished products contributes to a considerable increase in resource conservation and environmental friendliness of leather production.

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Review received 26.02.2023