

## THE EFFICIENCY OF WASTEWATER PURIFICATION FROM CHROMIUM (III) IONS BY NATURAL CLAY SORBENTS

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**Abstract.** The study confirmed the promising application of clays mineral sorbents for wastewater purification from Chromium (III) ions. The process of chromium ions absorption from drain water by means of natural mineral sorbent glauconite in static conditions was investigated.

The adsorption processes were adapted to the known technological schemes of sewage and polluted surface water purification from heavy metal ions. There were measured the technological aspects of water purification by using adsorption on natural dispersed sorbents.

**Key words:** natures dispersed sorbents, sewage, ions of heavy metals, bentonite and glauconite clays.

### 1. Introduction

Pollution of natural reservoirs as a result of human activity is one of the most important problems nowadays. Its solution requires the united efforts of the world scientific community. The current pace of the world population growth will lead to further increase in the volumes of industrial production, power industry, the increase in the areas used in agriculture, and building of urban infrastructure. The development of all these industries requires intensive use of water resources. It is inevitably connected with rapid increase in the pollution of wastewater. Negligent attitude to this problem provokes enormous catastrophic consequences.

Heavy metals form a group of the most dangerous environment pollutants. A huge amount of heavy metal ions gets into natural surface waters (seas, lakes, rivers, reservoirs) along with industrial wastewater. They become a substantial obstacle to the livelihood of hydrobionts. Heavy metals get into sewage from non-ferrous metallurgy enterprises, electronic radio engineering and leather industry, as well as from all industries where electrotyping is used. Sewage water can contain one component, however usually this number is bigger.

Among the causes of surface and groundwater pollution in Ukraine there is an increasing number of sludge storages, slagheaps and dumps, which accumulate 1500 tons of solid waste annually. Potentially dangerous are storage facilities and storage sites used for galvanic sludge production. Heavy metals that are stored in these sludge storages get into groundwater, being washed off with sewage and fall into natural water. Vital functions of hydrobionts are negatively affected by accumulation of these compounds in an organism. Moreover, high content of such metals as chrome and zinc makes water use impossible in a number of technological processes [1].

The existing chemical and physical-chemical methods of contaminated water purification (chemical precipitation, coagulation, chlorination, ozonation, reverse osmosis, etc.) which involve active chemical action or physical influence on water, allow removing

certain contaminants from it, often worsening physical and chemical properties of the water and breaking the natural balance of salts dissolved in the water. At the same time, in nature, there are safe possibilities of water purification with equalization of salt balance in it when water passes through the terrestrial and underground aquifers of minerals (clays, aluminosilicates, zeolites, etc.) [2] which have huge adsorptive properties towards anthropogenic toxic substances. The sorption on natural clay sorbents can be used along with the methods that have been successfully used for the solution of this problem and proved to be quite effective. Natural sorbents are unique materials that allow cleaning different environments (airspace, reservoirs, waste water) from toxic substances, including heavy metals, radionuclides, etc.

### Setting the task and its solution

Purification of aqueous solutions using dispersed sorbents meets a lot of requirements of ecologically clean and energy-saving production based on the principle of zero-waste.

The efficiency of adsorption purification reaches 80–95 %, depending on the chemical nature of the adsorbent, the size of the adsorption surface and its availability, the chemical structure of the substances and their state in the aqueous solution. Activated carbon, synthetic sorbents and some waste products (ash, mud, etc.) are used as adsorbents. Non-carbon sorbents of natural and artificial origin – clay rocks, zeolites and some other materials are used for purification of water more and more often [2].

Huge geological reserves, cheap mining rocks, simple preparation for transportation and use, the possibility of using waste sorbents in other technologies eliminating the need for expensive cost of regeneration are the main advantages of using natural minerals.

Glaucanite is a mineral of silicates group (mica group) (K, Na, Ca) (Fe<sup>3+</sup>, Al, Fe<sup>2+</sup>, Mg)<sub>2</sub> [Al<sub>x</sub>Si<sub>4-x</sub>O<sub>10</sub>](OH) • nH<sub>2</sub>O, x ≤ 1, n = 1 – 2. The content of the components varies widely: SiO<sub>2</sub> – 44–56 %; Al<sub>2</sub>O<sub>3</sub> – 3–22 %; Fe<sub>2</sub>O<sub>3</sub> – 0–27 %; FeO – 0–8 %; MgO – 0–10 %; K<sub>2</sub>O – to 10 %; H<sub>2</sub>O – 4–10 %. Also, impurities of lithium (Li) and Bor (B) are also present. It has a layer structure and is present in the form of finely crystalline, sometimes soil-like aggregates of various shades of green. Its hardness is 2–3 and the density is 2200–2900 kg/m<sup>3</sup>. It possesses high cation exchange properties (up to 1500 mg per 100 g).

Bentonites are minerals, which are finely dispersed high-plastic rocks of the smectic composition (mostly montmorillonite and beidellite). Approximate component content is: SiO<sub>2</sub> – 48–58 %; CaO – 1–9 %;

Al<sub>2</sub>O<sub>3</sub> – 11–14.8 %; Fe<sub>2</sub>O<sub>3</sub> – 6–7.5 %; FeO – 0.1–0.5 %; MgO – 1.3–5 %; K<sub>2</sub>O – 0.2–1.5 %; H<sub>2</sub>O – 8.3–11 %. It also contains such impurities as MnO, TiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, SO<sub>3</sub> i P<sub>2</sub>O<sub>5</sub>. A structure of 2:1 type is characteristic for bentonite in which the montmorillonite crystals consist of layers which, in turn, are composed of two layers of silicon-oxygen tetrahedral, connected by a layer of alumino-hydroxyl-silicate tetrahedral. The tetrahedron positions are filled with cations of silicon. Its hardness is 2–4 and the density is 1800–2400 kg/m<sup>3</sup>. The capacity of absorption of heavy metal cations of natural montmorillonite bentonite is 1821 mg/100 g.

Comparison of these two minerals shows their similarity in hardness and density. However, dispersion level of glauconite and bentonite is different. Glaucanite is characterized by a larger particle size, which positively influences its further deposition after the adsorption process. Still, a significant difference in the values of effective natural surface (112 mg/g for glauconite and 260 mg/g for bentonite) and capacity of monolayer (1.73 mol/g in glauconite and 3.12 mol/g in bentonite) should determine significantly lower adsorption capacity of glauconite, but we observe similar absorption level values of heavy metal cations. Most likely, this can be explained by the different chemical composition and structure of clay minerals, however more detailed explanation can be obtained as a result of experimental studies.

**The purpose of the work** is to investigate the efficiency of purifying wastewater from chromium ions (III) by natural clay sorbents.

### 2. Materials and methods

The work is dedicated to experimental research on the sorption of chromium ions (III) from salt solutions by bentonite and glauconite clays. For research, the mineral sorbent glauconite of the Adamiv group of deposits of the Khmelnytsky region was used, natural sands containing 50–70 % minerals glauconite and bentonite (type 2: 1) from the Cherkasy deposit of bentonite and palygorskite clays.

Investigation of chromium sorption process in static conditions was carried out by the method of individual portions. Initially model solutions of salts of the investigated metal were prepared with the concentration of 0.5 to 2.5 g/l. During experiments, parameters such as the layer of adsorbent (5–25 g for 50 cm<sup>3</sup> of model water), concentration of the initial solution (0.5–2.5 g/l), the duration of the process (20 min – 24 h) and the temperature of the solution (20 °C – 60 °C) were investigated. The residual concentrations of chromium ions (III) in the solution were determined by the titrimetric method.

The residual concentration of trivalent chromium ions was experimentally investigated in case different water absorbent layers absorb wastewater with the same concentration of chromium (III) ions at room temperature. For determination the optimum layer of adsorbent is up to 50 ml of the test solution with a concentration of  $C_0$  ( $Cr^{3+}$ ) = 2.5 g/l added from 5 to 25 g of adsorbent. Solutions were analyzed after 1 hour, 2 hours, 24 hours [3, 4].

### 3. Results and discussion

The values of residual concentrations are given in Table. 1. The degree of removal of chromium ions from an aqueous solution increases with an increasing of the adsorbent layer, that can be explained by the improvement of an active sorption surface [5]. In this case, the increment of specific adsorption is somewhat lagging behind the growth of the mass of the adsorbent, we can conclude that sorption has mainly the superficial nature.

Table 1

**Influence of the adsorbent layer on the change of initial concentration of chromium ions (III)( $C_0(Cr^{3+}) = 2,5 \text{ g/l}$ ;  $t = 20 \text{ }^\circ\text{C}$ )**

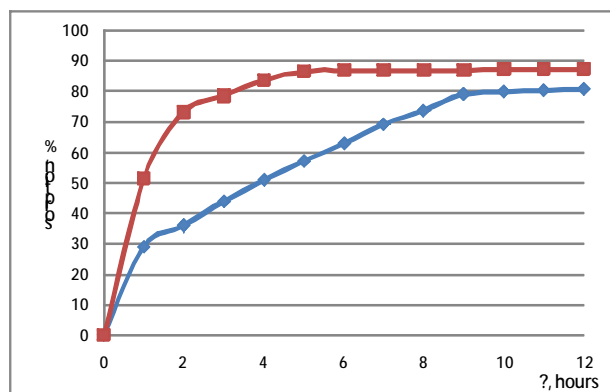
$\tau$ , hours	Adsorbent layer, g				
	5	10	15	20	25
$C_\tau(Cr^{3+})$ , g/l					
Bentonite clay of the second productive layer, layer II - 3					
1	2.445	2.095	1.793	1.524	1.424
2	2.228	1.878	1.605	1.498	1.398
20	0.605	0.535	0.480	0.340	0.218
Glaucanite clay of the second productive layer					
1	2.458	2.286	1.895	1.782	1.688
2	2.422	2.040	1.775	1.680	1.525
20	0.712	0.680	0.625	0.458	0.448

The next step was to determine the dependence of the amount of adsorption extract of the pollutant from the model solutions from the contact time of bentonite and glaucanite with contaminated water and from process conditions: static or periodic mixing. The results of these researches are presented in Fig. 1.

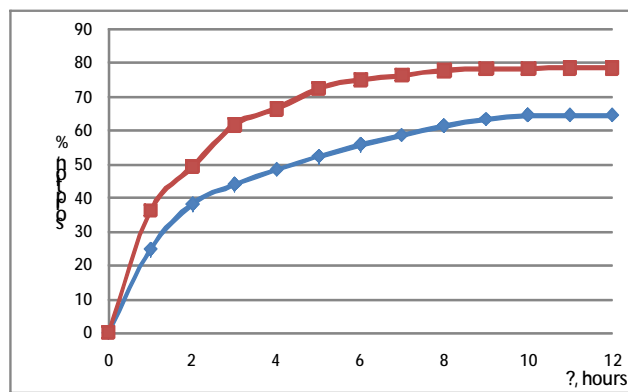
As we can see from the results obtained, the process of sorption passes through two mechanisms, separated in time. In the first 20– 30 minutes, ions occupy free active centres on the surface of the adsorbent, after that the rate of the process is significantly reduced and adsorption begins in pores of the mineral, where it has a

moderate development to the establishment of sorption equilibrium with time about ~ 1–2 hours . A similar dependence is observed with the use of glaucanite clay, however, while the process is somewhat slowed down. With an increase of the concentration of metal ions the degree of adsorption decreases, as the saturation of the surface of the mineral occurs by adsorbate, which again confirms the surface sorption nature.

As we can see from Fig. 1, the sewage purification by bentonite is more intense. Thus, the full saturation of its absorption capacity can be achieved in 6 hours, and maximum purification for 10 hours.



(a)



(b)

**Fig. 1.** Kinetic of adsorption of chromium ions (III) by bentonite (a), and glaucanite (b)

We observe that total adsorption capacity in the case of bentonite usage can be achieved in 8 hours under conditions of periodic mixing of it, whereas when using glauconite the maximum level of chromium ions extraction is reached in 10 hours.

Adsorption of chrome ions by glauconitic occurs with less intensity, therefore, glauconite is characterized by a lower reactivity.

Isotherms of adsorption of chromium ions (III) were based on experimental data (Fig. 2).

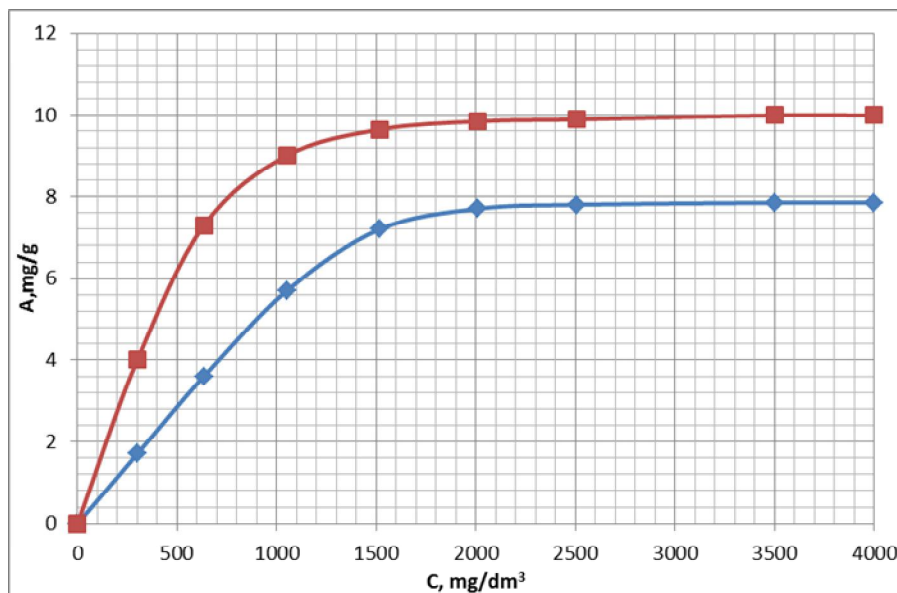


Fig. 2. Isotherms of adsorption of chromium ions (III) on the bentonite (—■—) and the glauconite (—◆—)

We can see from the graphic dependencies when using bentonite and glauconite adsorbents, the isotherms constructed are deviated from the linearity. In both cases, the most suitable way of adsorption is to describe the Langmuir model [6, 7]. In the coordinates of Langmuir, the equations have the form:

$$Y = 630 \cdot \frac{0.0001c}{1 + 0.0001c}; \text{ bentonite} \quad (1)$$

$$Y = 494 \cdot \frac{0.000078c}{1 + 0.000078c}; \text{ glauconite} \quad (2)$$

Thus, the correspondence of the experimental data to the Langmuir isotherms indicates that sorption of chromium ions (III) occurs with the formation of molecular layers with the highest activity of the upper layer.

The value of the coefficient  $A_{\infty}$  (603 and 494) indicates the higher absorption capacity of bentonite compared to glauconite. Therefore, we determine that adsorption capacity of chromium ions of bentonite is 22 % higher than glauconite.

## Conclusions

The conducted research confirmed the promising use of bentonite and glauconite clay for wastewater purification.

According to the results of the experiment, the maximum absorption of chromium ions (III) occurs

within 1–2 hours, and practically complete absorption takes 12 hours.

The efficiency of adsorption increases with the increase in the adsorbent layer, which can be explained by the development of an active sorption surface.

It has been experimentally proved that bentonite, with its ion exchange ability, is superior to glauconite in relation to chromium ions (III). With adsorption duration of 8–12 hours and concentration of 2.5 g/l, the degree of chromium ion extraction by bentonite and glauconite is – 75,8–91 %, and 70–82 % respectively,

It has been established that experimental data are best described by the Langmuir isotherm when using both adsorbents. Constants of isotherms as well as the value of adsorption capacity for bentonite and glauconite have been calculated.

The prospect and efficiency of the use of natural mineral sorbents, in particular, bentonite and palygorskite clays, for the purification of sewage are confirmed by their advantages over other sorbents, namely: they win in affordability, cost, the possibility of regeneration and multiple use.

## References

- [1] Kombinovani protsesy intehrovanykh tekhnolohii ochyshchennia stichnykh vod iz vykorystanniam

- sorbentiv mineralno– syrovynnoi bazy Ukrainy / M. S. Malovanyi, I. M. Petrushka, H. V. Sakalova, T. M. Vasylynych // Rozvytok i vidtvorennia resursnoho potentsialu subiektiv ekoloho-ekonomichnykh, turystychnykh ta ekoinformatsiynykh system. Lviv: V–vo NU “Lvivska politehnika”, 2015. 340 s. S. 208–239.
- [2] Petrus R., Malovanyj M., Varchol J., Odnorig Z., Petrushka I., Leskiv G. *Texnologiyi ochyshhennya stokiv iz zastosuvanniam pryrodnyx dyspersnyx sorbentiv // Ximichna promyslovist` Ukrainy*. No. 2 (55), 2003. S. 20–22, (in Ukrainian).
- [3] Petrushka I. M., Jatzyshyn J. J., Petrushka K. I. (2014). Cesium sorption intensification by complex natural sorbents from liquid radioactive media. *Eastern-European Journal of Enterprise Technologies*. V.5. 10(71),47.
- [4] Sabadash V. Concurrent sorption of copper and chromium cations by natural zeolite. / V. Sabadash, J. Gumnitsky, O. Mylanyk, L. Romaniuk// *Environmental problems*. 2017. Vol. 2, number 1. P. 159–162.
- [5] Lyudmila Melnyk, Oleksandr Bessarab, Svitlana Matko, Myroslav Malovanyy (2015). Adsorption of Heavy Metals Ions from Liquid Media by Palygorskite. *Chemistry & Chemical Technology*. 9 ( 4). P. 467–470. doi: 10.23939/chcht 09.04.467.
- [6] Y. M. Gumnyckyj, O. V. Sydorochuk. Sorbcija ioniv xromu iz vodnyx rozchyniv pryrodnym klynoptylolitom // *Visn. NU “Lvivska politehnika”*: Ximiya, texnologiya rehovyn ta yix zastosuvannya. L`viv, 2013. No. 761. S. 303–305, (in Ukrainian).
- [7] Malovanyj M. S., Yarema O. R., Sakalova G. V., Vasylynych T. M. Ochyshhennya stichnyx vod shkiryanogo vyrobnyctva vid ioniv xromu na pryrodny`x ceolitam // *Visnyk KNUTD*. № 6. 2011. S. 81–85, (in Ukrainian).
- [8] T. M. Vasylynych, G. V. Sakalova. Doslidzhennya efektyvnosti ochyshhennya stichnyx vod vid ioniv kuprumu (III) na pryrodnyx adsorbentax.- *Visnyk XNU*. – 2012. № 4. S. 233–235, (in Ukrainian).
- [9] G. V. Sakalova, T. M. Vasylynych et al. Investigation of the metod of chemical desorption for extraction of nikel ions (II) from bentonite clays // *Enviromental problems–2017*. Vol. 2, No. 4. P. 187–190.