Wastewater Treatment from Heavy Metal Ions

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Abstract. The article is devoted to the sorption treatment of industrial effluents, which contain heavy metal ions (HMI) by the natural clay mineral kaolinite - an activated adsorbent. The main sources of HMI receipts are revealed - industrial and agricultural production. The influence of heavy metals on human health is considered. The results of studies of wastewater treatment using filtration through an activated adsorbent of Ni²⁺, Cu²⁺, Zn²⁺, Cr⁶⁺, ions, mixed waste are presented. Dolomite and magnetite were chosen as activators. The optimal composition of activators has been determined. When using the proposed method of wastewater treatment, separation into streams of chromium-containing and acid-base wastewater is excluded. The high quality of purified water with an activated adsorbent makes it possible to use it in closed water use systems. The cheapness and availability of natural clay adsorbents, high performance properties, allow us to offer it as an industrial sorbent.

1. Introduction
The main sources of environmental pollution with heavy metals (HM) are industry, vehicles, boiler houses, waste incineration plants, and agricultural production [1].

Particularly dangerous are metal ions entering natural water bodies, where they come not only from industrial enterprises, but also with runoff from agricultural land [1]. Thus, fertilizers and pesticides are potential sources of HM contamination. HMs have a detrimental effect on human health, accumulating in the body. The danger to humans also lies in the fact that HMs are capable of accumulating in food chains, which increases their danger to humans. They cause poisoning, mutation, allergies, lead to cancer and other incurable diseases and even death [1].

The deterioration of the ecological situation and the sanitary state of water bodies has been going on for more than a decade: enterprises dumped wastewater into water bodies with insufficient quality of treatment or even without it. Perhaps this was due to the fact that the existing cleaning methods are complex and not efficient enough. Getting into water bodies, drains with an insufficient degree of purification become ecologically dangerous both for the inhabitants of water bodies and for the water supply of people [2]. Therefore, high-quality wastewater treatment is necessary for the disposal of any industrial enterprise [3].

Wastewater treatment methods should be simple, reliable, with high quality of treatment, capable of completely eliminating the possibility of pollution of water bodies with toxic production wastes [2]. First of all, this concerns the development of new methods and technologies that exclude the discharge of effluents into water bodies and city sewers.

The existing technologies and methods of purification, for the most part, do not provide the high quality of purification, which is required for closed water use systems. Such an opportunity is provided by sorption methods of purification using an activated aluminosilicate adsorbent [2]. Cheap natural
sorbents capable of providing a high degree of purification make the problem of developing new technologies and methods for treating wastewater containing HMI for closed water use systems of enterprises urgent.

The bulk of the proposed adsorbents [4–12] are practically not regenerated, and together with the adsorbed contaminants they are disposed of. The authors have developed an adsorbent for long-term use, the sorption activity of which can be restored by regeneration in a filtration unit. The adsorbent is made from a clay mineral. It is distinguished by high sorption activity and high absorption capacity of HMI.

2. Materials and methods

The object of the study was a natural clay mineral – aluminosilicate adsorbent. It is made from kaolinite with various activating additives. Kaolinite is mixed with an activator, the resulting suspension is granulated and fired. The structure of the crystal lattice of the clay mineral allows the introduction of activating additives into it. In our case, these are calcium and magnesium compounds.

The optimal composition of the adsorbent was selected experimentally. Activation with the addition of dolomite and magnetite in the amount of 15% of the clay mass (three-component adsorbent) turned out to be the most effective for the extraction of HMI. As studies have shown, the activation of the adsorbent with dolomite and magnetite makes it possible to exclude the operation of reducing Cr$_6^+$ to Cr$_3^+$, in contrast to the adsorbent with one of these additives.

The resulting new aluminosilicate adsorbent has high sorption properties and high mechanical strength. Its abrasion does not exceed 15%, which allows it to be used for a long time.

The adsorbent is activated in the filter by circulating a 3% solution of soda ash for 30–35 minutes.

The studies of the sorption activity of the aluminosilicate adsorbent were carried out on model solutions and real industrial effluents.

During the experiments, static, thermodynamic and kinetic methods of studying sorption processes were used, as well as physicochemical methods: rigidity and oxidizability were determined by titrimetric method; turbidity – photocolorimetric method; pH – potentiometric. The concentration of heavy metal ions was measured by electrochemical method (analysis of current-voltage characteristics).

3. Results and discussion

3.1. Physicochemical essence of the process of wastewater treatment with HMI on activated aluminosilicate adsorbent

Numerous studies have established that activated aluminosilicate adsorbent (AAA) has the property of creating a weakly alkaline medium with a positive electrokinetic potential.

After reaction with the OH- group, HMI form hydroxides, which subsequently form micelles with a negative charge. As a result, they are attracted to the granules of the aluminosilicate adsorbent, since the latter have a positive potential. The resulting complex forms a gel-like structure inside the filtering medium.

Based on theoretical and experimental studies, it can be argued that the extraction of HMI from effluents occurs due to internal diffusion of exchangeable alkali metal ions and external diffusion to the grain surface.

3.2. Study of the dynamics of wastewater treatment by filtration through an activated aluminosilicate adsorbent

Investigations of the dynamics of cleaning were carried out on a short layer of activated adsorbent in laboratory and experimental production conditions.

Laboratory installation for filtration: Mariotte bottle with a capacity of 10 liters; filter column with a diameter of 28 mm, a length of 500 mm; the thickness of the adsorbent loading layer is 300 mm, the grain size is 0.5 ... 1.0 mm. Conducted 2 series of tests. The first series: wastes containing one contaminant component were filtered. Second series: mixed flow was filtered.
The filtration rate was 3–5 m/h. The efficiency and dynamics of the wastewater treatment process were determined for three-component AAA. The research was carried out according to the method proposed by E.V. Venitsianov [13]. Model solutions and real waste waters were investigated. Three series of experiments were carried out. To exclude measurement errors, average values were taken. The filtration results of the investigated effluents are presented in tables 1–5. Here, U is the breakthrough concentration of HMI in the filtrate, mg/l (formula 1):

$$U = \frac{C_f}{C_i}$$  (1)

Where $C_f$ is the concentration of HMI in the filtrate, mg/l; $C_i$ is the concentration of HMI in source water, mg/l.

**Table 1.** Test results for the removal of Cr$^{6+}$ from the drain.

| Time, min | 8.7 | 17.3 | 29.7 |
|-----------|-----|------|------|
| 3         |     |      |      |
| 4         |     |      |      |
| 5         |     |      |      |
| 3         |     |      |      |
| 4         |     |      |      |
| 5         |     |      |      |
| The level of the copper ion overshoot concentration $U = C_f/C_i$ |
| Experience number |
| 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
| 30  | 0.00 | 0.01 | 0.02 | 0.04 | 0.05 | 0.03 | 0.05 | 0.02 | 0.04 |
| 60  | 0.00 | 0.00 | 0.06 | 0.07 | 0.09 | 0.06 | 0.09 | 0.05 | 0.10 |
| 90  | 0.05 | 0.05 | 0.10 | 0.11 | 0.14 | 0.12 | 0.13 | 0.12 | 0.17 |
| 120 | 0.08 | 0.09 | 0.15 | 0.16 | 0.20 | 0.19 | 0.20 | 0.19 | 0.22 |
| 150 | 0.12 | 0.12 | 0.21 | 0.22 | 0.23 | 0.22 | 0.24 | 0.25 | 0.26 |
| 180 | 0.17 | 0.17 | 0.26 | 0.26 | 0.28 | 0.27 | 0.29 | 0.30 | 0.31 |
| 210 | 0.21 | 0.22 | 0.30 | 0.31 | 0.33 | 0.34 | 0.36 | 0.36 | 0.37 |
| 240 | 0.25 | 0.26 | 0.36 | 0.34 | 0.36 | 0.38 | 0.41 | 0.42 | 0.43 |

**Table 2.** Test results for the removal of Zn$^{2+}$ from the drain.

| Time, min | 12.4 | 19.5 | 27.9 |
|-----------|------|------|------|
| 3         |     |      |      |
| 4         |     |      |      |
| 5         |     |      |      |
| 3         |     |      |      |
| 4         |     |      |      |
| 5         |     |      |      |
| The level of the overshoot concentration of the zinc ion $U = C_f/C_i$ |
| Experience number |
| 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   |
| 30  | 0.06 | 0.05 | 0.07 | 0.06 | 0.07 | 0.07 | 0.09 | 0.09 | 0.10 |
| 60  | 0.11 | 0.12 | 0.12 | 0.13 | 0.13 | 0.14 | 0.14 | 0.12 | 0.15 |
| 90  | 0.16 | 0.17 | 0.18 | 0.19 | 0.20 | 0.24 | 0.21 | 0.21 | 0.22 |
| 120 | 0.18 | 0.20 | 0.24 | 0.21 | 0.25 | 0.27 | 0.21 | 0.24 | 0.25 |
| 150 | 0.28 | 0.31 | 0.32 | 0.34 | 0.39 | 0.43 | 0.34 | 0.38 | 0.37 |
| 180 | 0.44 | 0.48 | 0.51 | 0.42 | 0.48 | 0.52 | 0.53 | 0.49 | 0.49 |
| 210 | 0.55 | 0.58 | 0.63 | 0.61 | 0.59 | 0.61 | 0.66 | 0.67 | 0.67 |
| 240 | 0.66 | 0.63 | 0.71 | 0.72 | 0.68 | 0.69 | 0.69 | 0.72 | 0.71 |
Table 3. Test results for the removal of $\text{Ni}^{2+}$ from the drain.

| Time, min | 11.3 | 18.5 | 27.9 |
|-----------|------|------|------|
|           | Filtration rate, m/h | 3 | 4 | 5 | 3 | 4 | 5 | 3 | 4 | 5 |
| Experience number U = $C_f / C_i$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 30 | 0.06 | 0.05 | 0.07 | 0.06 | 0.07 | 0.08 | 0.08 | 0.09 | 0.10 |
| 60 | 0.10 | 0.12 | 0.13 | 0.13 | 0.14 | 0.14 | 0.15 | 0.12 | 0.14 |
| 90 | 0.16 | 0.16 | 0.18 | 0.19 | 0.21 | 0.24 | 0.21 | 0.20 | 0.22 |
| 120 | 0.18 | 0.21 | 0.24 | 0.22 | 0.25 | 0.28 | 0.21 | 0.25 | 0.25 |
| 150 | 0.29 | 0.33 | 0.34 | 0.34 | 0.40 | 0.43 | 0.34 | 0.38 | 0.37 |
| 180 | 0.45 | 0.49 | 0.51 | 0.41 | 0.48 | 0.52 | 0.55 | 0.49 | 0.49 |
| 210 | 0.56 | 0.58 | 0.63 | 0.61 | 0.59 | 0.62 | 0.66 | 0.66 | 0.67 |
| 240 | 0.68 | 0.63 | 0.72 | 0.71 | 0.69 | 0.68 | 0.69 | 0.72 | 0.72 |

Table 4. Test results for the removal of $\text{Cu}^{2+}$ from the drain.

| Time, min | 9.6 | 19.3 | 31.7 |
|-----------|------|------|------|
|           | Filtration rate, m/h | 3 | 4 | 5 | 3 | 4 | 5 | 3 | 4 | 5 |
| Experience number U = $C_f / C_i$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| 30 | 0.04 | 0.04 | 0.05 | 0.06 | 0.07 | 0.06 | 0.07 | 0.07 | 0.08 |
| 60 | 0.09 | 0.10 | 0.11 | 0.11 | 0.12 | 0.13 | 0.12 | 0.12 | 0.13 |
| 90 | 0.13 | 0.15 | 0.16 | 0.18 | 0.20 | 0.23 | 0.21 | 0.21 | 0.22 |
| 120 | 0.18 | 0.19 | 0.19 | 0.20 | 0.22 | 0.24 | 0.26 | 0.27 | 0.28 |
| 150 | 0.22 | 0.23 | 0.24 | 0.28 | 0.30 | 0.29 | 0.34 | 0.29 | 0.34 |
| 180 | 0.33 | 0.34 | 0.36 | 0.36 | 0.38 | 0.32 | 0.39 | 0.39 | 0.39 |
| 210 | 0.41 | 0.42 | 0.43 | 0.46 | 0.43 | 0.47 | 0.46 | 0.46 | 0.47 |
| 240 | 0.58 | 0.60 | 0.62 | 0.64 | 0.66 | 0.68 | 0.66 | 0.66 | 0.68 |

Table 5. Mixed runoff removal test results.

| Mixed runoff | Time from the start of filtering, h | Dirt concentration, mg/l In the source drain | After cleaning |
|--------------|-------------------------------------|---------------------------------------------|---------------|
| $\text{Cr}^{3+}$ | 5 | 32.2 | - |
| $\text{Ni}^{2+}$ | 18 | 38.3 | - |
| $\text{Zn}^{2+}$ | 28.1 | 34.5 | - |
| $\text{Cu}^{2+}$ | 32.2 | 38.3 | - |
| $\text{Ni}^{2+}$ | 28.1 | 34.5 | - |
| $\text{Zn}^{2+}$ | 34.5 | - | - |
| $\text{Cu}^{2+}$ | - | - | - |
Purification of chromium-containing wastewater (table 1) occurs without preliminary reduction of Cr$^{6+}$ to Cr$^{3+}$. The data presented (tables 1–5) testify to the effective extraction of HMI by the adsorbent from the drain. The relatively high absorption capacity of contamination by the adsorbent is evidenced by the low rate of advance of the front of their concentrations. When filtering the mixed drain after 18 hours, heavy metal ions were not detected.

3.3. Technological tests of the wastewater treatment process at a pilot plant

Technological tests were carried out at a pilot industrial plant of a car repair plant (St. Petersburg), at the treatment facilities of the electroplating section.

The installation consisted of a tank with waste water with a capacity of 4000 l, from which through a water tap the drain was fed to a filter with a loading from AAA. The filter is made of plexiglass. Its diameter is 100 mm, height – 3000 mm. The height of the filtering load is 150 cm, the size of the granules is 0.8 ... 1 mm, the filtration rate is 3 m/h. During the tests, the concentration of heavy metal ions and pH were determined.

Waste water taken from the reservoir-homogenizer was filtered, where it comes from the galvanic section and contains ITM and acid-alkaline waters. The effluents were not subjected to preliminary reagent treatment. Waste composition, mg/l: Cr$^{3+} = 10.1$, Ni$^{2+} = 8.3$, Zn$^{2+} = 11.6$, Cu$^{2+} = 8.3$ mg/l, Fe$^{3+} = 13.2$ mg/l, pH = 5.5. After 70 hours of filtration, HMIIs were not detected, pH = 7.5. After another 70 hours of filtration, their concentration in the filtrate was significantly lower than the MPC standards for discharge into the city sewage system. The quality of the treated water allows it to be used for technological needs in the closed water use systems of the enterprise.

The proposed cleaning method allows you to purify chromium-containing and acid-base wastewater together. The results of tests for the purification of waste water from HMI, carried out at a pilot plant, showed a high degree of purification for a long time, which indicates its reliability and high quality.

4. Conclusion

A reagent-free method has been developed for purifying waste from ions of heavy metals by filtration through an activated aluminosilicate adsorbent in order to reuse water for technological needs in closed water use systems.

It has been established that the best sorption capacity is possessed by an aluminosilicate adsorbent activated by the addition of dolomite and magnetite in an amount of 15% of the clay weight.

The results of production tests showed a high degree of wastewater treatment. The advantage of the proposed technology is that chromium-containing and acid-base wastewater can be treated together.

The cheapness and availability of natural clay adsorbents make it possible to offer it as an industrial sorbent.

The creation of a closed cycle of water use at industrial enterprises without the release of effluents into water bodies is the most rational solution to the environmental problem.

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