The use of clays materials of the Tyumen region in the treatment of natural and waste water

A Zagorskaya* and L Pimneva

1Tyumen Industrial University, Volodarskogo str., 38, Tyumen, 625000, Russia

* Corresponding author: zagorskajaaa@tyuiu.ru

Abstract. An assessment was made of the ecological status of water bodies in the South of the Tyumen Region, which play a significant role in the region’s water use and are sources of drinking and industrial water supply. The hydrochemical characteristics of natural waters and the water use conditions that determine the indicators of water quality in water bodies and streams are considered. Critical levels of pollution have been established for zinc, copper, manganese, iron, cadmium, chromium, nickel and aluminum in all water bodies of the Tyumen region. The reasons for optimizing the purification processes at the existing water supply and wastewater treatment facilities in the region are given. The structure and chemical composition of clay materials of the Tyumen region was studied. The efficiency of extraction of nickel ions of kaolin, montmorillonite and mixed kaolin and montmorillonite clays has been investigated. The quantitative characteristics of the process of nickel ion adsorption on all the presented natural clays are obtained. It is established that the mixed natural clay has higher values of exchange capacity in relation to nickel ions. It is noted that the description of the adsorption equilibrium corresponds to the Langmuir model. The possibility of using kaolinite, montmorillonite and mixed clays as a reagent for purifying natural and waste waters at the existing treatment facilities of the Tyumen region is presented.

1. Introduction
According to the classification of the Federal Service for Hydrometeorology and Environmental Monitoring of the Russian Federation, water bodies of the Tyumen region belong to the 4th class - “dirty”. The unsatisfactory state of water bodies is associated with the transit formation of the main water masses and pollution in the overlying areas (Sverdlovsk, Kurgan, Omsk regions and the Republic of Kazakhstan). Statistics show that industrial growth in the Tyumen region also makes a significant contribution to water pollution. In total, about 130 large industrial and agricultural facilities operate in the region with a total consumption of 315.4 million tons of water per year. Of the effluents entering the rivers and lakes of the Tyumen region, only 69.4% are sufficiently cleaned [1]. The dynamics of pollution in the water bodies of the region is presented in Figure 1 and 2.
Figure 1. Mass of pollution discharged into water bodies over the past 5 years

Figure 2. Kinds of pollutions in ton per year

The specificity of water pollution in the Tyumen region is related to the natural background for a number of pollution: difficult and easily oxidizable organic substances (COC, BOC), compounds of iron, copper, manganese [1, 2]. However, for the last 8 years there has been a steady accumulation of heavy metal ions in natural components of the environment [2-4]. The concentrations of heavy metal ions in the water bodies of the city are presented in Figure 3. Special attention should be paid to pollution first and second hazard classes: cadmium, lead, mercury and nickel. Reducing their concentration, blocking the transfer of the food chain is important for the health of the population of the region as a whole [5].
Figure 3. According to the concentration of heavy metal ions (mg / dm3) MAC of water bodies (mg / dm3)

In this regard, the technologies of purification of natural and waste waters are acquiring particular relevance, which make it possible to extract heavy metal ions as efficiently as possible with minimal economic costs, and a number of research studies are now being carried out [6-13]. The presence in the Tyumen region of clay deposits allows us to consider them as available material, which can easily be integrated into the existing scheme of cleaning any treatment facilities in the area.

2. Subjects and methods
The purpose of this work is to study the adsorption properties of natural clay minerals of the Tyumen region in relation to nickel ions and the possibility of using them for the purification of natural and waste waters.

In the work were used natural clay minerals of the Tyumen region. Analysis of the chemical composition of clays was determined by a scanning electron microscope (SEM).

According to the data obtained, its main components are oxides in the amounts presented in Table 1.

| Clays | SiO₂ | Al₂O₃ | Na₂O | K₂O | CaO | Fe₂O₃ | TiO₂ | MgO | Ni |
|-------|------|-------|------|-----|-----|-------|------|-----|----|
|       |      |       |      |     |     |       |      |     |    |
| Before adsorption | | | | | | | | | |
| MMT   | 50.24| 20.78 | 0.73 | 3.37| 0.60| 8.52  | 0.91 | 1.79| -  |
| K     | 49.22| 46.87 | 0.96 | 0.80| 0.86| 1.12  | 0.94 | -   | -  |
| K + MMT | 53.62| 20.29 | 0.41 | 3.88| 1.53| 13.13 | 1.71 | 1.63| -  |
| After adsorption | | | | | | | | | |
| MMT   | 48.62| 16.59 | 0.39 | 0.37| 0.33| 7.49  | 0.52 | 1.64| 1.52|
| K     | 50.20| 45.77 | 0.06 | 0.44| 0.41| 1.38  | 1.08 | -   | 0.008|
| K + MMT | 52.18| 19.57 | 0.34 | 3.81| 0.52| 16.66 | 1.84 | 1.28| 0.008|

Table 1. - The chemical composition of natural clays, mass. %
The mineralogical and phase composition of natural clays (Fig. 3.) was determined by X-ray phase analysis using a DRON diffractometer with a copper anode (λ = 1.5406 Å).

Figure 4 shows that the particles of natural clays have sizes less than 1 micron in the form of thin leaves with irregular outlines.

The adsorption activity of natural clays is determined by the fact that they contain the mineral montmorillonite [14]. The crystal lattice of montmorillonite is a three-layer packet in which between the layers of silicon-oxygen tetrahedra there is a layer of aluminum-octahedra. The distance between the packages can vary from 0.4 to 2.0 nm, which promote to the ion exchange of such clays.

The objects of study of the adsorption properties of natural clays were model nickel nitrate aqueous solutions. Dilution methods were used to prepare solutions with various concentrations of nickel ions from nickel nitrate solutions. The adsorption process was studied under static conditions. The ion concentration is nickel-plated before and after the adsorption process by the standard method using the trilonometric method [15]. The adsorption capacity of clay minerals was calculated as a function of the concentration of the solutions at a constant temperature. The amount of adsorption is determined by the excess of the substance at the phase boundary compared with the equilibrium amount of this substance. The calculation of adsorption was carried out according to the equation:

$$ A = \frac{(C_0 - C_p) \cdot V}{m} $$

where $C_0$ - the initial concentration of nickel ions in solution, mol/l; $C_p$ - the equilibrium concentration of nickel ions in solutions after the adsorption process, mol/l; $V$ – adsorbent mass, g , $m$ – adsorption, mol/l;
The results of the analyzes were processed with the calculation of the arithmetic average value of the adsorption value for each of the studied concentrations from three experiments performed in parallel.

3. Results

As a result of the experimental studies shown in Figure 6, that with an increase in the concentration of nickel ions the magnitude of adsorption increases.

![Figure 6. Adsorption isotherms of nickel (II) ions depending on the concentration of the initial solution on clays: kaolinite (1), montmorillonite (2) and mixed (3)](image)

According to the BET classification, the isotherms obtained on three types of natural clays are a type I isotherm, which reflects monomolecular adsorption [3]. The lower part of the isotherms is convex (Fig. 6, curves 2 and 3) can be associated with the presence of micro- and macropores in the adsorbent. In the clay adsorbent with a mixed composition (Fig. 6, curve 1), the convex lower part of the isotherm is absent, adsorption does not occur due to micropores.

The type of isotherms shows the degree of affinity of the adsorbed ions to the adsorbent. The adsorption isotherm allows to determine the maximum exchange capacity of the adsorbent. To describe the adsorption process, the Langmuir model was used:

\[
A = A_\infty \frac{K_L \cdot C_p}{1 + K_L \cdot C_p}
\] (2)

or

\[
\frac{C_p}{A} = \frac{C_p}{A_\infty} + \frac{1}{A_\infty \cdot K_L}
\] (3)

where \(A\) - the amount of sorbed copper and \(A_\infty\) - the limiting sorption value (mmol / g),

\(C_p\) - the equilibrium concentration of copper ions in solution (mmol / ml),

\(K_L\) - the concentration constant of sorption equilibrium characterizing the intensity of the sorption process, ml / mmol.

Figure 7 shows the Langmuir adsorption isotherm in linear form.
Figure 7. Isotherm of nickel ion adsorption on clays: kaolinite (1), montmorillonite (2) and mixed (3)

Linear treatment of nickel ion adsorption isotherms from aqueous solutions on natural clays: are presented in Table 2.

| Const. | MMT clay | Kaolin clay | K + MMT |
|--------|-----------|-------------|---------|
| A∞, mmol/g | 83.33 | 12.82 | 125 |
| kL, ml/mmol | 0.002 | 0.032 | 0.002 |
| R² | 0.999 | 0.995 | 1 |

The obtained calculations show that the maximum adsorption increases in the series:

Kaolinite > montmorillonite > mixed (K + MMT) clays

According to the obtained results, it can be concluded that clays containing montmorillonite in their composition have a higher adsorption capacity with respect to nickel ions as compared to kaolin clay.

4. Conclusion

In the course of the research, it was found that the sorption capacity of montmorillonite clays with respect to nickel ions is 122 mg Ni / g (montmorillonite), 18.8 mg Ni / g (kaolinite) and 183.38 mg Ni / g (mixed K + MMT) clay. This confirms the possibility of using this type of clay in the processes of purification of natural and waste waters.

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