

## The Ion-Exchange Properties of Kaolinite in the Practice of Natural Water Purification

Lyudmila A. Pimneva<sup>1</sup>, Alla A. Zagorskaya<sup>2\*</sup>

<sup>1</sup> Department of General and Special Chemistry, Tyumen Industrial University, Lunacharskogo St., Tyumen, 625001, Russian Federation

<sup>2</sup> Department of Industrial Safety, Tyumen Industrial University, Lunacharskogo St., Tyumen, 625001, Russian Federation

\* Corresponding author's e-mail: 4examples@mail.ru

### ABSTRACT

The article examines the ability of natural clays to extract heavy metal ions from aqueous solutions by ion exchange. The process of extracting metal ions was considered on the example of the absorption of manganese, nickel and cobalt from natural waters. In order to study the chemical and mineralogical composition of natural kaolin, the following were used in the work: X-ray diffraction and X-ray phase methods, as well as IR spectroscopy. The article presents a comparative analysis of the adsorption of manganese, cobalt and nickel ions on natural kaolin under different temperature conditions. The nature of the interaction of the studied metal ions with kaolin was established. The results obtained on the adsorption of the ions under study show the efficiency of using natural kaolin clay for water purification.

**Keywords:** natural kaolin, manganese, cobalt, nickel ions, adsorption

### INTRODUCTION

The surface waters of the Tyumen region's watercourses are among the most polluted in Russia. The situation is further aggravated by the fact that most of the pollution enters the water sources in transit from the overlying areas. The operation of treatment plants in the region depends very much on the seasonal fluctuations of the water quality in watercourses, from unauthorized discharges of wastewater by industrial enterprises, and so on. As a result, the quality of natural water in the region's water sources is deteriorating year by year, and water treatment systems do not provide the desired water quality for a significant part of the time. Therefore, the introduction of modern technologies for natural water treatment based on environmentally friendly natural materials under the current conditions is the most promising.

The use of clay sorbents will reduce the cost of treatment, expand the barrier capabilities of treatment facilities, which will undoubtedly lead to an improvement in the quality of drinking water and reduce the environmental risks for the population of the Tyumen region.

The topic of sorption properties of natural clay materials is widely presented in Russian sources [Kim and other, 2011, Belenova and other, 2015, Buzaeva and other, 2010]. The affinity of various clay materials with respect to metal ions was studied, and the sorption characteristics of materials from various deposits were compared [Poleshchuk and other, 2019, Pimneva, 2017, Balukova, Iwanski, 2009, Lozinskaya, Mitrakova, 2014, Dudina, 2013]. A special feature of this work is a comparative analysis of the sorption capacity of kaolin from the Kyshtyrinskoye Deposit in the Tyumen region, in relation to manganese, cobalt and nickel.

## MATERIALS AND METHODS

The adsorption of manganese, cobalt and nickel ions was carried out from nitrate solutions under static conditions on natural kaolin at temperatures of 298K, 313K and 333K. X-ray diffraction analysis (XRD) was performed using a JEOLJSM 6510 LV scanning electron microscope. The accuracy of determining the element composition is  $\pm 2\%$ .

X-ray phase analysis was performed on a Bruker Diffractometer D2 Phaser with a Lynxeye linear detector ( $\text{CuK}_\alpha$  – radiation, Ni – filter). Infrared spectroscopy was performed on an IR-Fourier spectrometer FSM 1201. The sample for the study was prepared in the form of a tablet with calcined potassium bromide.

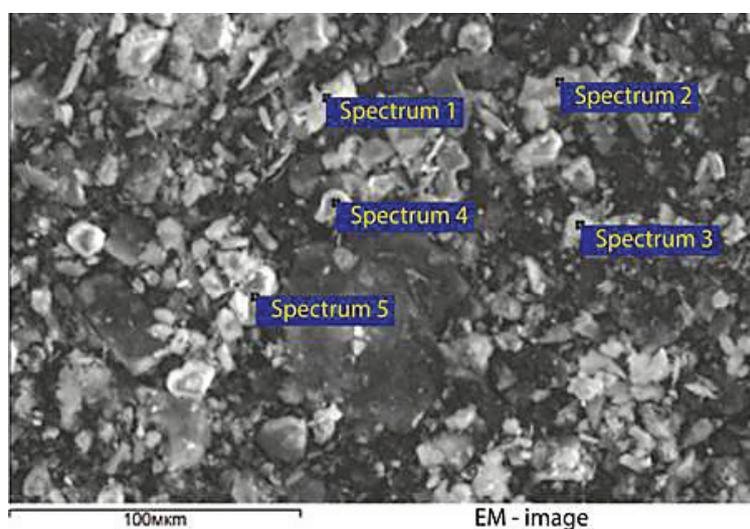
## RESULTS

On the basis of the experimental data obtained, the specific adsorption of manganese, cobalt and nickel ions from nitrate solutions with different initial concentrations on natural kaolin was calculated. Figures 3, 4, and 5 show the effect

of the concentration of metals in the solution and temperature on the process of adsorption by natural kaolin. The specific adsorption increases along the concentration of metal ions in the initial solution. During the adsorption of manganese ions, an inflection is observed, which indicates a change in the adsorption mechanism or the presence of two different energetically or spatially accessible active centers in kaolin [Kotov et al., 2014].

When adsorption occurs at the first stage, kaolin saturation with manganese ions does not occur; at the second stage, with an increase in the concentration of ions in the solution, adsorption occurs simultaneously at various active centers. The mechanism of adsorption at both stages consists in the reaction of ion exchange:

At the second stage, adsorption occurs at less accessible active centers by an ion exchange mechanism. The dependences of adsorption of cobalt and nickel ions are represented by concave curves relative to the concentration axis. As the concentration of ions in the solution increases, the adsorption reaches saturation and leads to the formation of a plateau. Adsorption increases rapidly as saturation is reached.



**Figure 1.** Electron microscopic image of kaolin indicating the point of determination of the elemental composition shown in Table 1

**Table 1.** Elemental composition of natural kaolin

Spectrum	O	Na	Al	Si	K	Ca	Fe	Subtotal
Spectrum 1	66.43	–	15.68	16.88	0.74	0.02	0.25	100
Spectrum 2	63.34	1.19	15.62	16.61	0.98	0.06	2.20	100
Spectrum 3	60.69	–	17.98	20.07	0.80	–	0.46	100
Spectrum 4	65.38	0.96	14.62	18.59	0.12	–	0.32	100
Spectrum 5	25.13	–	28.73	39.82	–	–	6.32	100

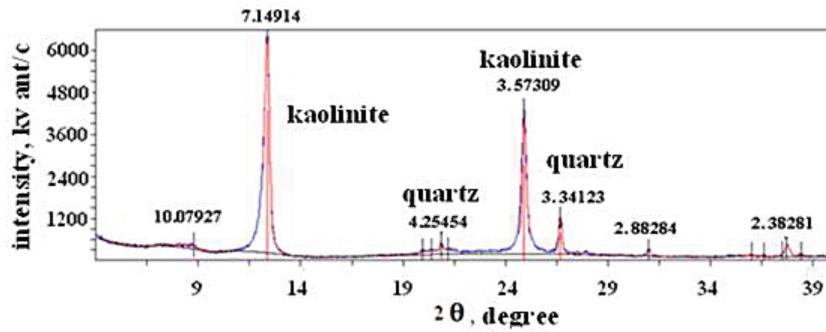


Figure 2. The diffraction pattern of kaolinite

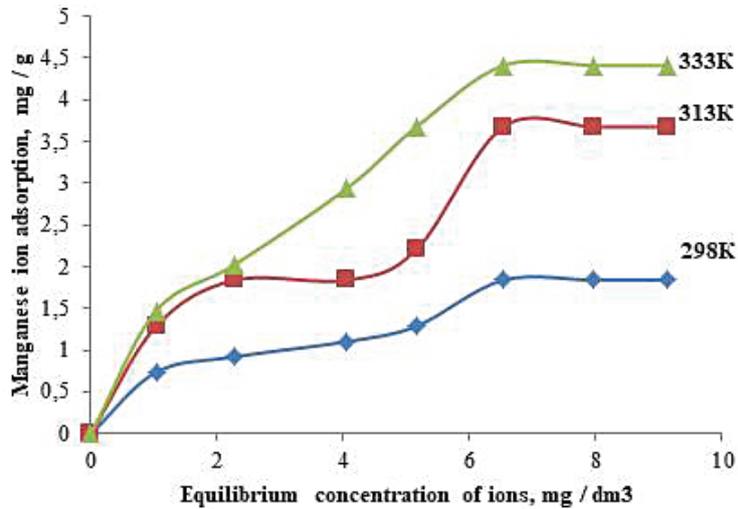


Figure 3. Adsorption capacity of kaolin for manganese ions at temperatures of 298, 313 and 333 K

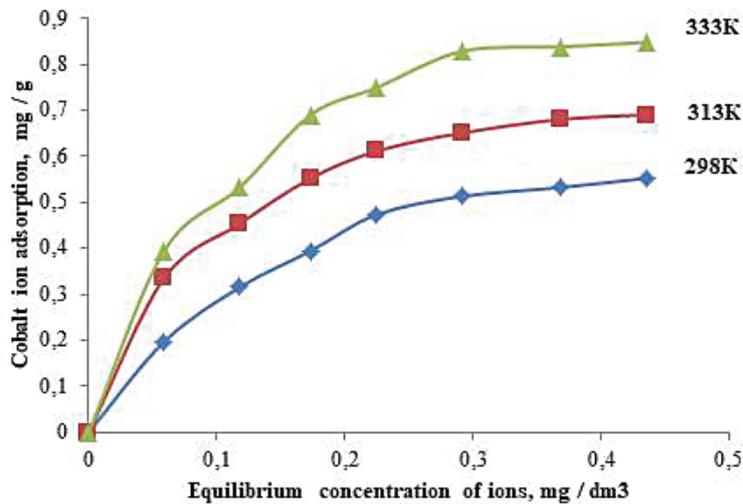


Figure 4. Adsorption capacity of kaolin for cobalt ions at temperatures of 298, 313 and 333 K

The mechanism of adsorption of cobalt and nickel ions occurs as a result of ion exchange. From the literature data [Distanov et al., 1999, Voyutsky, 1975] it is known that the ions having the same charge are adsorbed the better the greater their effective radius. The ions of a larger radius are hydrated to a lesser extent, – hence, their ability to

be attracted by the surface of the polar adsorbent increases [Lurie, 1979]. The obtained values of specific adsorption of manganese, cobalt and nickel can be arranged in the following series: 0.091 nm, 0.078 nm, 0.074 nm [Poloshchuk et al., 2019].

The process of adsorption on kaolin is due to the nature of the interaction of heavy metal ions

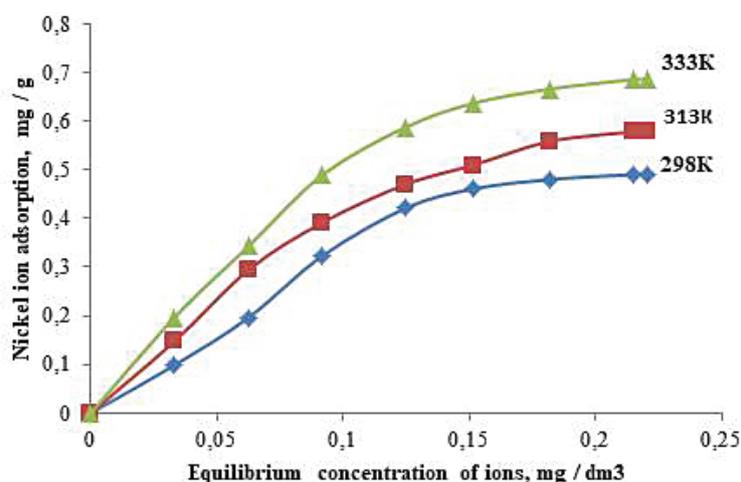


Figure 5. Adsorption capacity of kaolin for nickel ions at temperatures of 298, 313 and 333 K

with the hydroxyl groups of the adsorbent. The ion exchange capacity is related to the reactivity of silane groups ( $\equiv\text{Si-OH}$ ) and their quantity, which depends on the degree of hydration of silica. The adsorption properties of siliceous rocks are directly dependent on the size of the specific surface and the volume of the adsorption space represented by the macropores of the mineral [Kalyukova et al., 2010].

Figure 6 shows the IR spectrum of kaolin obtained as a tablet with sodium bromide. The absorption bands in the region  $3600\text{--}3800\text{ cm}^{-1}$  correspond to the valence fluctuations of OH groups. The present intense peak at  $730\text{--}780\text{ cm}^{-1}$  corresponds to the presence of Al-O bonds, the peak at  $830\text{--}950\text{ cm}^{-1}$  indicates the presence of Si-O bonds. The IR spectrum for the kaolin sample is consistent with the data described in the literature [Lurie, 1979]. The IR spectrum confirms the mechanism of adsorption of the studied metals.

The maximum capacity of kaolin (mg/g) with increasing temperature for ions is: manganese 0.060 (298K), 0.092 (313K), 0.11 (333 K); cobalt

0.055 (298K), 0.69 (313K), 0.84 (333 K); Nickel 0.49 (298K), 0.058 (313K), 0.68 (333 K).

The average content of manganese in natural sources of Tyumen is recorded at the level of 1.7 (17 MPC)  $\text{mg/dm}^3$ , the content of nickel and cobalt – at the level of 0.072 (3.6 MPC) and 0.53 (5.3 MPC) respectively [Pimneva, Zagorskaya, 2019]. The use of 1 g of sorbent as a supplement to the existing reagents of drinking water treatment at the existing natural water treatment plant demonstrates an efficiency of 10%, 100% and 3%, respectively (Fig. 7).

## CONCLUSIONS

On the basis of the data obtained, we can draw the following conclusions:

1. As the temperature rises, the sorption efficiency increases, which makes it difficult to use the sorbent without modification for the purification of natural waters in autumn and winter, when the temperature of the purified water ranges from 8 to 10 °C.

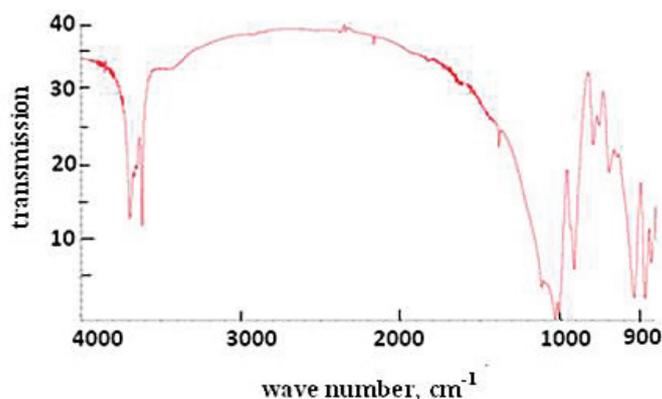
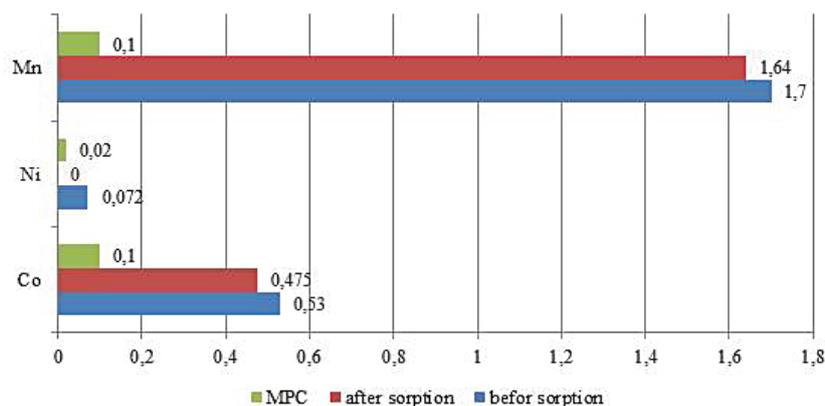


Figure 6. The IR spectrum of kaolinite



**Figure 7.** Changes in concentrations of manganese, nickel and cobalt ions after treatment with kaolinite ( $T = 298K$ )

- The maximum sorption capacity is observed during the extraction of nickel ions, which indicates the possibility of using natural kaolin as the main reagent to reduce the nickel concentrations in natural waters.
- For manganese, the extraction efficiency did not exceed 10% in relation to the initial concentration of solutions, which means that the use of kaolin in the practice of extracting manganese from natural waters is possible only at the stage of additional purification.
- The sorption efficiency for cobalt was 3%, which implies the replacement of kaolin with another clay material, if it is necessary to extract cobalt ions.

On the basis of these findings, we can say with confidence that kaolinite can be used as the main reagent for the extraction of nickel, and in the case of manganese and cobalt, only as a post-treatment reagent.

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