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STUDIES ON REMOVAL OF NI(II), CU(II), ZN(II), PB(II) AND AMMONIUM IONS FROM SEDIMENTARY WATERS FROM MUNICIPAL SEWAGE-TREATMENT PLANTS WITH NATURAL INORGANIC SORBENTS

BADANIA NAD USUNIĘCIEM NI(II), CU(II), ZN(II), PB(II) ORAZ JONÓW AMONOWYCH Z WÓD OSADOWYCH MIEJSKICH OCZYSZCZALNI ŚCIEKÓW Z UŻYCIEM NATURALNYCH SORBENTÓW NIEORGANICZNYCH

Abstract

Removal of Ni(II), Cu(II), Zn(II), and Pb(II) ions from wastewater from municipal sewage treatment plants was investigated. Adsorption and ion exchange methods are most commonly used for removal of heavy metal ions from wastewater. Bentonite and palygorskite from a large number of sorbents are specially interesting because of their physicochemical properties. Sorption process of the above mentioned ions was investigated with SEM and TEM methods.

Keywords: heavy metals, ammonium ion, wastewater, inorganic sorbents

Streszczenie

Przedmiotem badań jest usuwanie jonów Ni(II), Cu(II), Zn(II), Pb(II) z wód osadowych z komunalnych oczyszczalni ścieków. Do usuwania jonów metali ciężkich ze ścieków najczęściej wykorzystuje się metody adsorpcyjne i wymianę jonową. Z dużej grupy sorbentów na szczególną uwagę ze względu na swoje właściwości fizykochemiczne zasługują bentonit i pałygorskit. Proces sorpcji wyżej wymienionych jonów badano metodą SEM oraz TEM.

Słowa kluczowe: metale ciężkie, jon amonowy, ścieki, sorbenty nieorganiczne

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1. Introduction

Dispersion limitation of organogenic elements and heavy metal ions in the environment has a profound effect on the reduction of eutrophication pressure in water and soil ecosystems. Nitrogen is the basic nutrient for all life forms as a structural element of amino acids, proteins and genetic material. Although it is an indispensable nutrient for living organisms it can become toxic depending on its content. For example, ammonium ions at very low concentrations about 0.2 mg/dm^3 are toxic for fish and other forms of water life. Heavy metal ions can be carcinogenic and teratogenic and cause other diseases and in agricultural ecosystems they can also reduce biological value of products and plant raw materials.

Adsorption and ion exchange methods [2–4] are most commonly used for the removal of heavy metal and ammonium ions. Natural inorganic sorbents are used for the processes because of their high adsorption capacity, molecular sieve properties, high selectivity in relation to heavy metal and ammonium ions and resistance to acids and higher temperatures. In recent years the content of heavy metal ions in wastewater has had a decreasing tendency but ammonium ions are a big problem because their content in sewage exceeds often 400 mg/dm^3. Ammonia nitrogen amount recycled with wastewater is a considerable load for the biological part of a sewage treatment plant, which substantially increases oxygen consumption and leads to efficiency reduction of the wastewater treatment process and its economics. It is also connected with the necessary application of additional alkaline agents and external source of organic carbon required in denitrification process.

2. Experimental

2.1. Sorbent characteristics

Bentonite and palygorskite were ground and sieved into fractions. Samples were washed with distilled water to remove contaminations and then dried at room temperature. Fractions 0.1–0.3 mm were used for analyses. Table 1 shows chemical composition [%] of the sorbents. The investigated samples of wastewater were taken from municipal sewage treatment plant in Puławy. The chemical composition before and after the sorption process (after equilibration) is presented in Table 2.

Table 1

Content of selected elements in analysed sorbents

Analysed sorbent	**Content [%]**								
	H_2O	Al	Si	Fe	Ca	K	Mg	Na	Mn
Palygorskite	10.60	5.57	30.47	5.76	0.32	0.69	3.61	0.06	0.09
Bentonite	7.97	7.15	30.61	4.89	0.73	0.06	0.83	0.08	0.02

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Table 2

Chemical composition of wastewater from municipal sewage treatment plant in Puławy before and after sorption process

Component	Content before sorption [mg/dm³]	Content after sorption on palygorskite [mg/dm³] (1 g pal. per 100 cm³)	Content after sorption on bentonite [mg/dm³] (1 g bent. per 100 cm³)
Cu(II)	1.0	0.20	0.017
Zn(II)	4.06	0.068	0.076
Ni(II)	5.2	0.059	0.029
Pb(II)	1.0	0.051	0.037
K(I)	142.0	142.3	159.0
Na(I)	137.0	139.2	189.0
NH_4^+	388.0	89.0	82.0
Mg(II)	29.0	31.0	30.0
Ca(II)	91.0	91.6	92.8

2.2. Microscopic examination with SEM and TEM methods

A scanning electron microscope (SEM), Zeiss, the Ultra Plus model, was used for the examination of heavy metal and ammonium ion samples before and after sorption from wastewater. The samples were placed in a chamber of 12.5 mm in diameter and then a pressure of 5×10^{-4} Pa was exerted on it. The electron beam had energy of 20 keV. An energy dispersive X-ray detector (EDX), where radiation was analysed, was produced by Brucker AXS, the 125 eV model, and it was used with Quantax software. EDX spectra were recorded and photos of the surfaces of investigated sorbents were taken.

3. Results

3.1. SEM and TEM methods

Energy dispersive X-ray spectroscopy is very helpful in determination of many physical and chemical properties of aluminosilicates which were investigated. Figures 1–4 present EDX spectra of bentonite and palygorskite before and after the sorption process of heavy metal and ammonium ions from model solutions and after sorption of the ions from sedimentary waters.

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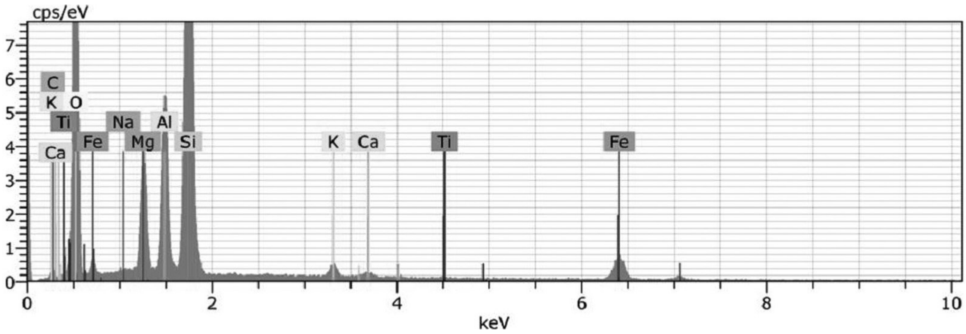

Fig. 1. EDX spectrum of palygorskite before sorption process

Rys. 1. Widmo EDX pałygorskitu przed procesem sorpcji

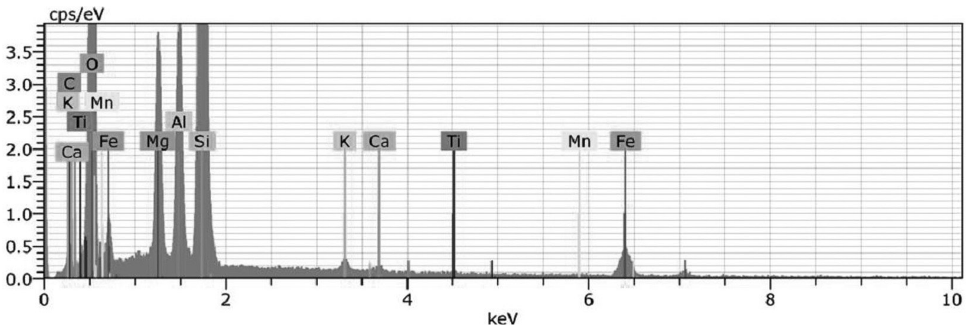

Fig. 2. EDX spectrum of palygorskite after sorption process of NH_4^+ and investigated heavy metal ions from sedimentary waters

Rys. 2. Widmo EDX pałygorskitu po procesie sorpcji jonów NH4+ i badanych jonów metali z wód osadowych

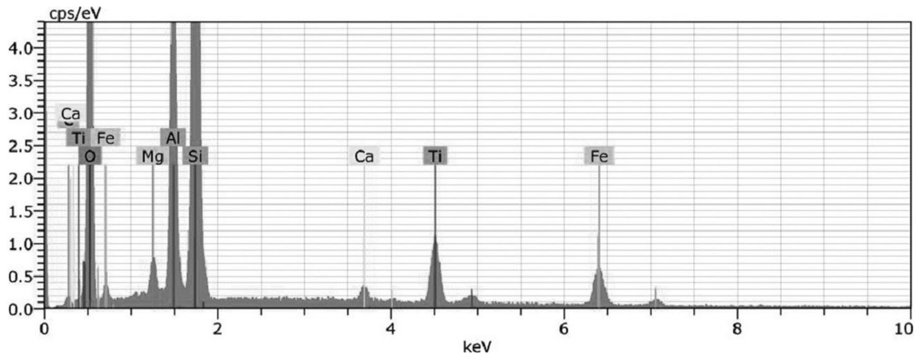

Fig. 3. EDX spectrum of bentonite before sorption process.

Rys. 3. Widmo EDX bentonitu przed procesem sorpcji

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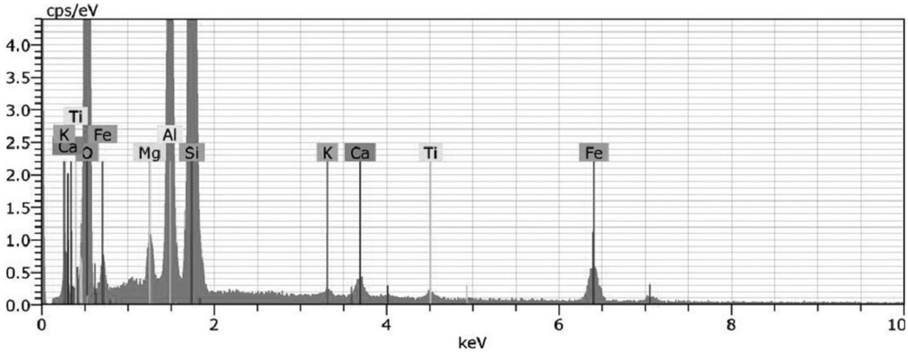

Fig. 4. EDX spectrum of bentonite after sorption process of NH_4^+ and heavy metal ions from sedimentary waters

Rys. 4. Widmo EDX bentonitu po procesie sorpcji jonów NH4 + i jonów metali ciężkich z wód osadowych

SEM method results indicate that the Si/Al ratio has changed, which results from structural changes in bentonite and palygorskite. The greatest changes in Si/Al ratio took place during Cu(II) ion sorption where Si/Al ratio in bentonite before sorption process was 3.01 and after that it decreased to 2.38 because of silicon content reduction. Sorption of Ni(II) ions had the lowest effect on changes of Si/Al ratio in bentonite. SEM results for palygorskite indicate that changes of Si/Al ratio are accompanied by changes in its structure. The sorption of Pb(II) ions caused greatest changes in palygorskite where Si/Al ratio before the process was 2.47 and after that it increased to 3.95 as a result of aluminium (III) content reduction. The sorption of Zn(II) ions had the lowest effect on changes of Si/Al ratio the value of which was 3.22 after the process.

Sorption of all investigated heavy metal and ammonium ions resulted in the reduction of exchanged ion content, i.e. Mg(II), Na(I), K(I), and Ca(II). They evolved from sedimentary waters in amounts not exceeding the set limits.

4. Conclusions

The investigated sorbents can reduce the content of heavy metal and ammonium ions in wastewater from municipal sewage treatment plants very effectively. Sedimentary waters and sludge formed in the sorption process are safe for the environment.

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