



## Removal of nickel(II) and cadmium(II) ions from aqueous solutions using an oxide adsorbent of MgO·SiO<sub>2</sub> type

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### ABSTRACT

The principal aim of the present work was to obtain an inorganic oxide system, MgO·SiO<sub>2</sub>, with unique physicochemical and electrokinetic properties which would enable its use as an effective adsorbent of nickel(II) and cadmium(II) ions. An important component of the work was involved in determining, how the pH and the quantity of adsorbent affect the efficiency of the process for the removal of nickel(II) and cadmium(II) ions from model aqueous solutions. The effectiveness of the adsorption process was evaluated using various analytical techniques, including atomic absorption spectroscopy and energy dispersive X-ray spectroscopy. Nickel or cadmium elution was also tested, in order to determine the durability of the bonds between adsorbent and adsorbate. At the next stage, Langmuir's and Freundlich's models were used to describe the equilibrium adsorption isotherms, applying the method of nonlinear regression. The experimental data were found to fit well with Langmuir's isotherm model. The maximum adsorption capacity of an MgO·SiO<sub>2</sub> monolayer was 56.59 mg (Ni<sup>2+</sup>)/g and 35.86 mg (Cd<sup>2+</sup>)/g, which indicates that the synthesized material acts as a highly effective adsorbent of nickel(II) as well as cadmium(II) ions.

*Keywords:* Synthetic oxide adsorbents; Adsorption; Nickel; Cadmium; Adsorption isotherms

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### 1. Introduction

Increasing urbanization and industrialization lead to a growing problem of pollution of the environment with organic and inorganic substances. Particularly hazardous are inorganic pollutants, including toxic hazardous metal ions. This is a collective term applied to a group of metals which exhibit toxic properties. Particularly noteworthy are metals such as lead, mercury, cadmium, copper, chromium, nickel, and others [1,2].

Due to the increasing problem of water pollution, it becomes extremely important to apply effective techniques to remove toxic compounds occurring in water as pollutants. It is therefore important to seek even more economically and environmentally favourable technological solutions which can contribute to reducing the quantity of heavy metals in municipal- and industrial waste water. One of the most effective methods of removing ions of heavy metals from aqueous solutions is the process of adsorption. In view of its numerous advantages, over recent years this process

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has become an alternative to traditional water purification techniques [3–5].

Scientific reports are currently providing a great deal of information concerning various adsorbents capable of selectively removing hazardous metal ions from aqueous solutions. Researchers have shown increasing interest over recent years in adsorbents of natural origin. Natural sorbents are materials that occur in the environment, and whose use does not bring about any further pollution. The category of selective adsorbents of natural origin includes such substances as sedimentary rocks, coffee grounds, peat, olive stones, lignin, and various minerals [6–12].

The efficiency of the adsorption of a specified group of heavy metals from aqueous solutions is affected not only by the type of sorption material used, but also by process conditions such as temperature, contact time of reagents, concentration of the precursor of heavy metal ions, quantity of adsorbent, and pH [13–15]. It is therefore important to determine the parameters of the process in order to achieve the maximum efficiency of removal of heavy metal ions from aqueous solutions.

In an era of constant technological development, synthetic adsorbents—which can also be used in the process of heavy metal ions removal from aqueous solutions—are enjoying increasing popularity. Selective synthetic adsorbents include alumina, titania, and chitosan–TiO<sub>2</sub> composite [16–18]. The possibility of designing the physicochemical parameters of materials of this type at the stage of their preparation enables the attainment of very high efficiency in the adsorption process, as a result of their highly developed porous structure and selectivity with respect to heavy metal ions.

Among the most hazardous pollutants of water systems are nickel compounds. Compounds of this metal have mutagenic and carcinogenic effects on living beings. Ajmal [19] reports that nickel(II) ions can be effectively removed using an adsorbent such as orange peel, while Singhon et al. [20] used a composite of chitosan and silica (SiO<sub>2</sub> + CS) as an effective nickel(II) adsorbent. It is thus important to apply adsorbents which are effective and selective with respect to this group of pollutants, which occur in both industrial and municipal waste water. Cadmium is also known to be one of the most hazardous metals, both to humans and to the natural environment. A source of environmental contamination is the liquid wastes produced by various industries. It should be noted that even relatively small quantities of this element in drinking water can have a significant effect on human health. The maximum permitted concentration of cadmium and its inorganic compounds is 0.05 mg (Cd<sup>2+</sup>)/dm<sup>3</sup>. Cadmium enters the body via the digestive tract (2–6%) along with food (primarily

grains and vegetables; cadmium contamination of agricultural crops is mainly a result of physicochemical properties of the soil, including its pH, and the use of fertilizers), as well as via the respiratory tract (30–64%) in air polluted with dust or tobacco smoke. The toxic action of cadmium is chiefly a consequence of its ability to accumulate in the body. The element is deposited mainly in the liver, kidneys, bones, and testicles; the body is able to eliminate only a small percentage [21,22].

Many projects have been undertaken with the chief goal of developing methods of neutralizing this hazardous material [23–26]. Nonetheless, the use of an inorganic sorbent would appear to be a highly desirable solution.

Consequently, in the present work, an attempt was made to apply the synthetic oxide system MgO·SiO<sub>2</sub> in the role of an adsorbent of nickel(II) or cadmium(II) ions.

## 2. Experimental

### 2.1. Preparation of the adsorbent

The basic raw material used to obtain magnesium silicate was an aqueous solution of sodium silicate (Na<sub>2</sub>O·mSiO<sub>2</sub>·xH<sub>2</sub>O—water glass produced by Vitrosilicon SA). Synthetic magnesium silicate was obtained by co-precipitation (Fig. 1). The precipitating agent used was hydrated magnesium sulfate (Chempur). The white precipitate obtained in this way was a synthetic adsorbent (magnesium silicate), which was separated from the post-reaction mixture by a process of vacuum filtration. The precipitate was washed several times with water. The product was then dried at a temperature of 105 °C for 24 h. The oxide system prepared in this way was used in subsequent experiments as an adsorbent of nickel(II) and cadmium(II) ions from model aqueous sulfate solutions.

### 2.2. Adsorption experiments and analytical measurements

In the adsorption process an inorganic salt, hexahydrated nickel sulfate NiSO<sub>4</sub>·6H<sub>2</sub>O or 3CdSO<sub>4</sub>·8H<sub>2</sub>O (POCh SA), was used as a precursor of nickel(II) or cadmium(II) ions. Model solutions were prepared with the following concentrations of nickel(II) and cadmium(II) ions: 15, 30, 75, 100, and 150 mg/L. An adsorption process was carried out using synthetic magnesium silicate as an adsorbent (Fig. 2) at different pH values. This was done in order to determine the effect of that parameter on the efficiency of the process of adsorption of nickel(II) or cadmium(II) ions from the model aqueous solutions. For the specified concentrations of nickel(II) and cadmium(II) ions,

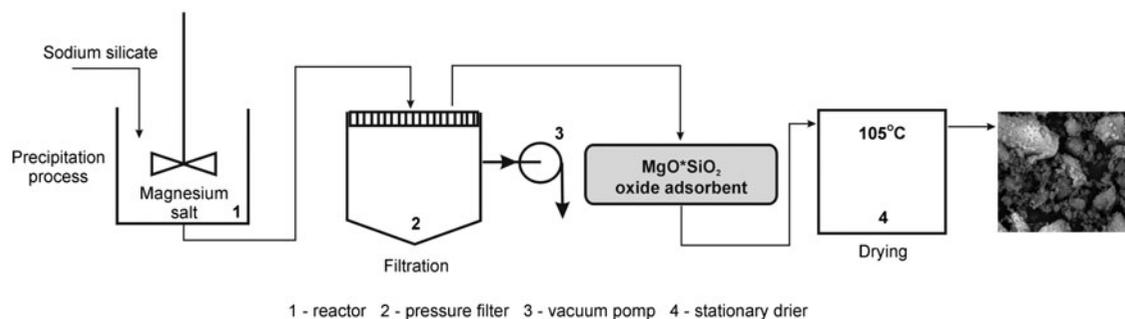


Fig. 1. Diagram of the process for obtaining an oxide adsorbent of MgO·SiO<sub>2</sub> type.

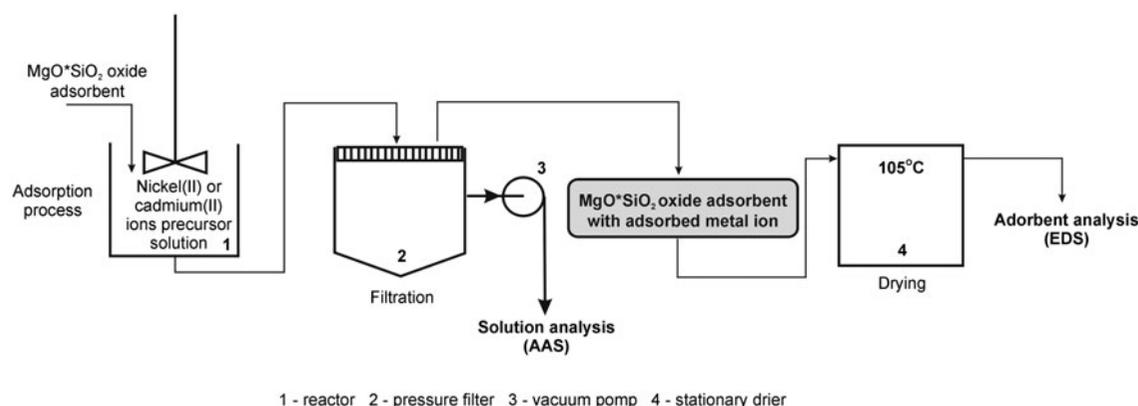


Fig. 2. Methodology for the process of nickel(II) or cadmium(II) ions adsorption.

adsorption process was carried out at pH values of 2, 4, 6, 7, 9, and 11. The prepared solutions of nickel(II) and cadmium(II) salts (0.1 L) in different concentrations were placed in conical flasks, and 5 g of the adsorbent was added to the solution. Next, sodium hydroxide or sulfuric acid was added to obtain the desired pH value, which was monitored using a pH-meter (CP-401, Elmetron). After the pH stabilized at the correct value, the system was mixed using a magnetic stirrer (Ika Werke Labor Technik GmbH) for 60 min. After this time the resulting mixture was filtered under reduced pressure using specialist apparatus and filters (Sartorius). The precipitate obtained was dried for 2 h at a temperature of 105°C. Further analysis was carried out on both the precipitate and the filtrate obtained at each stage of the adsorption process.

Another important component of the work involved determining the effect of the quantity of adsorbent on the efficiency of the process for removal of nickel(II) or cadmium(II) ions from aqueous solutions. For this purpose, the process of adsorption of nickel(II) or cadmium(II) ions in a concentration of

30 mg/L was carried out using different quantities of MgO·SiO<sub>2</sub> (1–8 g) for 60 min.

In the estimation of adsorption isotherms, 0.5 g of MgO·SiO<sub>2</sub> and 0.05 L of nickel(II) or cadmium(II) ion solutions of different concentrations (15–350 mg/L) were shaken for 60 min at an initial pH of 7.0. Atomic absorption spectroscopy (AAS) analysis enabled precise determination of the quantity of nickel(II) or cadmium(II) ions remaining in the filtrate after the adsorption process. The quantity of nickel(II) or cadmium(II) ions adsorbed at equilibrium,  $q_e$  (mg/g), was calculated by the following formula:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where  $q_e$  is the quantity of nickel(II) or cadmium(II) ions adsorbed at equilibrium (mg/g),  $V$  is the volume of nickel(II) or cadmium(II) ions solution (L),  $C_0$  is the initial concentration of nickel(II) or cadmium(II) ions (mg/L),  $C_e$  is the equilibrium nickel(II) or cadmium(II) ions concentration (mg/L), and  $m$  is the mass of adsorbent (g). The experimental data obtained were

used to determine Langmuir [27] and Freundlich [28] adsorption isotherms.

### 2.3. Elution tests

To evaluate the durability of the bonds between the adsorbent and adsorbate, and to investigate the effectiveness of the removal of nickel(II) or cadmium(II) ions from the surface of the adsorbent (desorption), elution tests with water were performed at the next stage of the experiment. These were performed on the adsorbents obtained following the adsorption process. For the purpose of the elution tests, 1 g of the adsorbent obtained after the adsorption process was placed in a flask with 50 mL of distilled water. The mixture obtained was stirred using a magnetic stirrer for 60 min. The resulting system was filtered under reduced pressure using specialist apparatus and filters. The filtrate was then subjected to further tests in order to determine the quantity of nickel(II) or cadmium(II) ions present in it. A process diagram of the elution tests is shown in Fig. 3. The concentrations of eluted nickel(II) or cadmium(II) ions in aqueous solutions were determined using AAS analysis.

## 2.4. Evaluation of adsorption efficiency

### 2.4.1. Atomic absorption spectroscopy

AAS analysis was used to determine the quantity of nickel(II) or cadmium(II) ions present in the filtrate after the adsorption process and after the elution tests. This is one of the most precise methods of quantitative analysis. The tests were carried out using a Z-8200 spectrometer (Hitachi). Before the samples were analyzed, it was necessary to configure the calibration curve in the spectrometer's software, enabling calculation of the concentration of nickel(II) or cadmium(II)

ions in the filtrate. The results obtained using AAS analysis were used for calculations relating to the efficiency of the process of removal of nickel(II) or cadmium(II) ions from aqueous solutions. The following formula was used:

$$\% \text{ Removal} = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\% \quad (2)$$

where  $C_0$  and  $C_e$  are respectively the initial and equilibrium concentrations of nickel(II) or cadmium(II) ions (mg/L).

### 2.4.2. Evaluation of physicochemical properties of the adsorbent before and after the process

It was necessary to perform a thorough physicochemical analysis of the adsorbent before the adsorption process, in order to obtain a full characterization of the synthetic  $\text{MgO} \cdot \text{SiO}_2$  oxide system. In turn, analysis of the adsorbents after the adsorption process made it possible to confirm indirectly the effectiveness of the removal of nickel(II) or cadmium(II) ions from aqueous solutions.

Dispersive characteristic of the oxide adsorbent was determined by a Mastersizer 2000 apparatus (Malvern Instruments Ltd), using the laser diffraction method and measuring particles of sizes from 0.2 to 2,000  $\mu\text{m}$ . The resolution of determination of the effective particle diameter was 0.1  $\mu\text{m}$ . Measurements of particle size were repeated at least 10 times for each sample. The morphology and microstructure of the adsorbent obtained were analyzed using a Zeiss EVO40 scanning electron microscope. The observations permitted the evaluation of the degree of dispersion, the structure of the particles and their tendency to aggregate or agglomerate. The surface area  $A_{\text{BET}}$

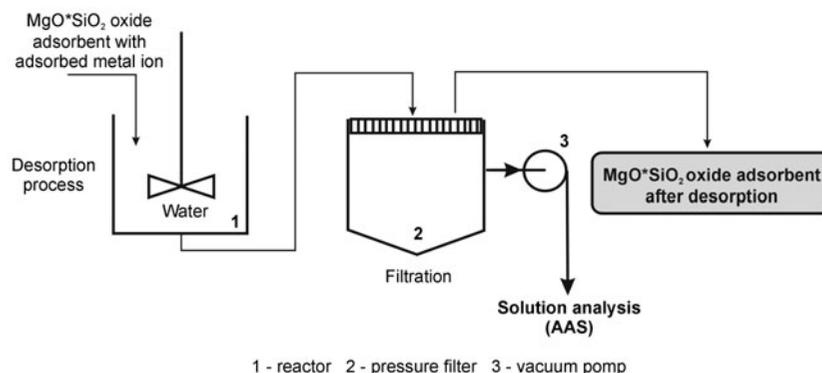


Fig. 3. Methodology for testing of elution of nickel(II) or cadmium(II) ions from the adsorbent surface using water.

(based on the BET equation) was estimated using low-temperature adsorption of nitrogen. The isotherms of nitrogen adsorption/desorption were measured at  $-196^{\circ}\text{C}$  using an ASAP 2020 apparatus (Micromeritics Instrument Co.). With regard to the high accuracy of the instrument ( $\pm 0.001 \text{ m}^2/\text{g}$ ), the surface area values were rounded up to whole numbers, and the mean pore size ( $S_p$ ) and total pore volume ( $V_p$ ), calculated by the BJH method, were taken to one and two decimal places, respectively. The surface composition of the oxide adsorbents was analyzed by energy-dispersive X-ray microanalysis (EDS). With a Zetasizer Nano ZS (utilizing the non-invasive back scattering method), it was also possible to measure the electrophoretic mobility using laser Doppler velocimetry, and indirectly the zeta potential (the Zetasizer Nano ZS software provides the ability to convert electrophoretic mobility values to the zeta potential based on the Smoluchowski model). The electrokinetic potential in the presence of 0.001 M NaCl electrolyte was measured over the whole pH range, which permitted the determination of the electrokinetic curves.

### 3. Results and discussion

#### 3.1. Adsorbent characteristics

The results of physicochemical analysis of the synthetic MgO-SiO<sub>2</sub> oxide system as a potential adsorbent of heavy metal ions made it possible to obtain a thorough description of that material (Table 1).

First, the parameters of the porous structure were determined. The synthetic oxide adsorbent used in the tests has a large surface area of  $427 \text{ m}^2/\text{g}$ , a pore volume of  $V_p = 0.49 \text{ cm}^3/\text{g}$  and a pore diameter of  $S_p = 4.5 \text{ nm}$ . In numerous literature reports, the surface

Table 1  
Physicochemical properties of the synthetic MgO-SiO<sub>2</sub> oxide system

Properties	Value
<i>Porous structure parameters</i>	
Surface area $A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	427
Mean pore volume $V_p$ ( $\text{cm}^3/\text{g}$ )	0.49
Pore diameter $S_p$ (nm)	4.5
<i>Dispersive parameters (<math>\mu\text{m}</math>)</i>	
$d$ (0.1)	3.9
$d$ (0.5)	18.8
$d$ (0.9)	62.3
$D$ [4.3]	36.8
<i>Chemical composition (%)</i>	
SiO <sub>2</sub>	54.10
MgO	20.43
H <sub>2</sub> O	19.85

area has been determined for various synthetic oxide systems used in the role of adsorbent. For example, for TiO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and ZnO the  $A_{\text{BET}}$  value was measured at 208, 240 and  $147 \text{ m}^2/\text{g}$ , respectively [29–31], these being markedly smaller values than that for the system obtained by the present method.

Analysis of the size of particles of the synthetic oxide adsorbent made it possible to obtain information about the dispersion, grain morphology and nature of agglomeration. It was found that the synthetic oxide adsorbent has 90% of its particles with diameters of less than  $62.3 \mu\text{m}$ , and only 10% with diameters less than  $3.9 \mu\text{m}$ . The dominant particle diameter of the inorganic oxide system is  $36.8 \mu\text{m}$ . This is confirmed by SEM image of the MgO-SiO<sub>2</sub> oxide system (Fig. 4). The photograph shows the differently sized particles of the adsorbent, and also their irregular shape. The dispersion parameters influence the potential areas of application of materials of this type, and also determine other physicochemical properties such as surface area and electrokinetic properties.

In turn, based on analysis of the chemical composition of the oxide system, its structure was confirmed to contain the two dominant components—SiO<sub>2</sub> (54.10%) and MgO (20.42%)—as well as H<sub>2</sub>O (19.85%), consisting of physically bound water and water of crystallization, which is a consequence of the method used to obtain the MgO-SiO<sub>2</sub> system.

Fig. 5 shows a graph of the zeta potential as a function of pH for an analyzed sample of the synthetic oxide system.

It can be concluded from the electrokinetic curve obtained that the zeta potential of the oxide system is strongly dependent on the ambient pH. The synthetic adsorbent has negative zeta potential values in the range pH 3–11. The electrokinetic potential of the sample ranges from  $-4$  to  $-39 \text{ mV}$ , which may suggest that the surface of the synthetic oxide system exhibits a negative charge. These properties are of great importance in the case of adsorption of positively charged heavy metal ions at the specified pH values, and also to determine the stability of the oxide systems in aqueous systems. The analysis carried out to determine physicochemical and electrokinetic properties confirms the significant possibilities for applications of the synthetic MgO-SiO<sub>2</sub> oxide system as an effective adsorbent of hazardous metal ions.

#### 3.2. Influence of pH

Tests were carried out to determine the effect of pH on the efficiency of the adsorption of nickel(II) or cadmium(II) ions from model aqueous solutions by the synthetic oxide adsorbent MgO-SiO<sub>2</sub>. The results

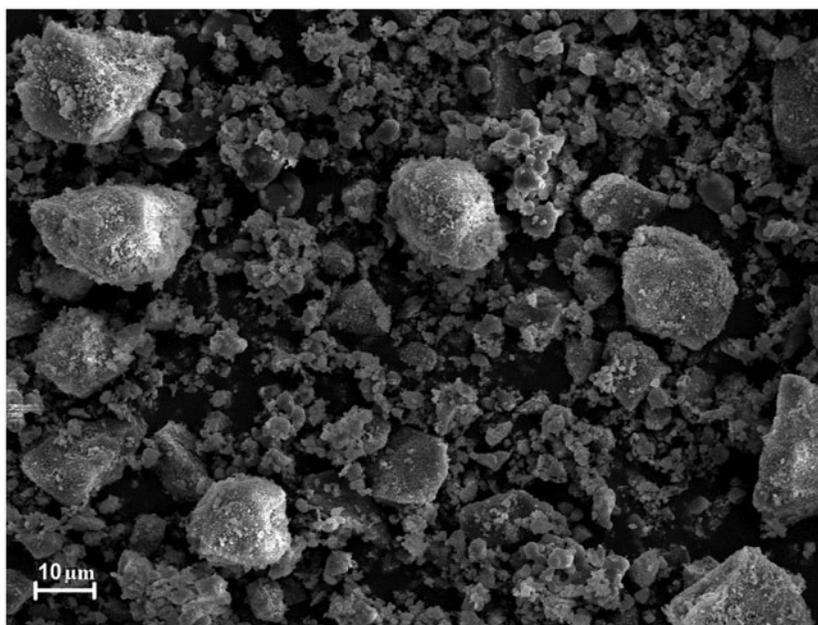


Fig. 4. SEM image of MgO-SiO<sub>2</sub>.

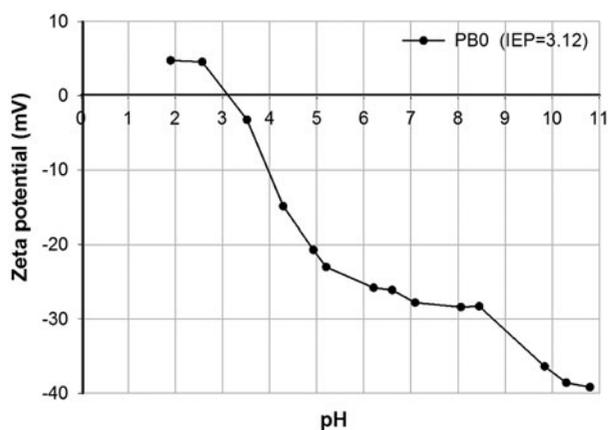


Fig. 5. Graph of zeta potential as a function of pH for the MgO-SiO<sub>2</sub> oxide system.

illustrated in Fig. 6(a) confirm the prior assumption that the synthetic oxide system MgO-SiO<sub>2</sub> can be used successfully as an effective adsorbent of nickel(II) ions. The results lead to the conclusion that the pH and the concentration of the precursor of nickel(II) ions have a significant influence on the efficiency of the process of their adsorption.

When the adsorption process was carried out in an acidic environment (particularly at pH 2) the lowest efficiencies of adsorption of nickel(II) ions were obtained: 34, 73, and 76% respectively for the model solution concentrations 15, 75, and 150 mg/L. These

efficiency values are markedly lower than those obtained at neutral and basic pH. In a neutral environment the efficiencies of the adsorption process were respectively 86, 89, and 93% proportionally for increasing concentrations of nickel(II) ions of 15, 75, and 150 mg/L. When the adsorption process took place in a basic environment the efficiencies were of the order of 98–99%, a result of the presence of negligible quantities of nickel(II) ions in the analyzed filtrates and the significant affinity of surface groups of the adsorbent to the nickel(II) ions. The same pattern was observed for every analyzed concentration of nickel(II) ions.

Analysis of the results for efficiency of adsorption of cadmium(II) ions depending on the pH of the system led to the graphical interpretation of the process shown in Fig. 6(b). The relationships found also enabled consideration of how the pH affects the adsorption of cadmium(II) ions from sulfate solutions. Analogously to the case of nickel(II) ions adsorption, it was found that as the alkalinity of the system increases, there is an increase in the efficiency of removal of the metal from aqueous solutions on an inorganic oxide system. It should be noted that when the adsorption process was carried out in an acidic environment (particularly at pH 2), the lowest efficiencies of the adsorption of cadmium(II) ions were obtained: 40, 39, and 31%, respectively, for the model solution concentrations 15, 75, and 150 mg/L. When the process was carried out in a neutral environment

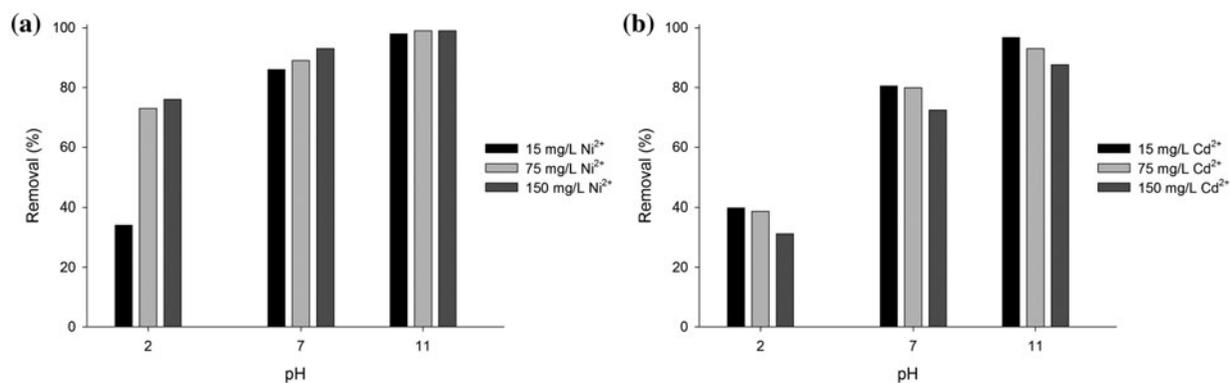


Fig. 6. Efficiency of removal of nickel(II) (a) or cadmium(II) (b) ions for different concentrations of model solutions and pH of the reaction system.

(pH 7), with metal ion solution concentrations of 15, 75, and 150 mg/L, the efficiencies attained were 81, 80, and 72%, respectively. Carrying out the adsorption of cadmium(II) ions in the most highly alkaline system, produced efficiencies in the range 88–97%. It should be noted that in the case of adsorption of cadmium(II) ions, irrespective of the pH of the reaction system, the efficiency of the process was found to decrease as the concentration of metal ions increased.

In summing up the results of the experiments, it can be stated that the efficiency of the process of adsorption of nickel(II) or cadmium(II) ions on the synthetic oxide adsorbent MgO-SiO<sub>2</sub> is significantly influenced by the pH of the reaction system. For every analyzed concentration of nickel(II) or cadmium(II) ions (15–150 mg/L), the lowest efficiencies were obtained when the process took place in an acidic environment (pH 2), and the highest in a basic environment (pH 11). The results obtained for a process carried out in a neutral environment (pH 7) also proved satisfactory.

For additional confirmation of the effectiveness of the process of adsorption of nickel(II) or cadmium(II) ions on the synthetic oxide adsorbent, EDS was performed on selected adsorbents used in the experiments (see Table 2). In the EDS analysis, it was significant that the presence of nickel or cadmium was confirmed in the structure of the adsorbents following the completed adsorption process. The results of the EDS analysis confirmed the high effectiveness of the adsorption process. Analogously as in the case of the previous analysis, the smallest quantities of nickel or cadmium on the surface of the synthetic adsorbent, amounting to 0.09, 0.18, 0.27% (Ni) and 0.03, 0.14, 0.21% (Cd) by mass for metal ion concentrations of 15, 75, and 150 mg/L, respectively, were obtained when the adsorption process took place in an acidic environment (pH 2). The largest quantities of the element,

respectively 0.20, 0.59, 1.01% (Ni) and 0.1, 0.39, 0.87% (Cd) by mass for increasing metal ion concentrations, were obtained when the adsorption process took place in a basic environment (pH 11). On interpreting all of the EDS results, it can be stated that the quantity of nickel or cadmium adsorbed is significantly influenced by the pH value of the reaction system in which the process takes place. When the adsorption process occurs in an acid environment (pH 2), the quantity of nickel or cadmium adsorbed on the surface of the adsorbent is the smallest. When adsorption takes place in a basic environment (pH 11) it is possible to obtain the greatest quantities of nickel in the structure of the adsorbent.

It should also be noted that adsorption carried out in a neutral environment (pH 7), which is the most favorable from an ecological point of view, also enables a significant level of removal of nickel or cadmium from model solutions, which confirms the high effectiveness of the process when carried out in such conditions. In most cases the results obtained using EDS corresponded to the previous results for adsorption efficiency (AAS analysis).

Table 3 shows the parameters of the porous structure of synthetic adsorbents after the process of adsorption of nickel(II) or cadmium(II) ions from model sulfate solutions, depending on the pH of the reaction system, carried out in order to confirm the effectiveness of the process.

The effectiveness of the process is confirmed by the fact that the values obtained for the  $A_{\text{BET}}$  surface area of the adsorbents after the completed process are significantly smaller than for the initial sample. In every case, independently of the process pH and the concentration of the model solutions, the surface area was found to decrease relative to the model sample ( $A_{\text{BET}} = 427 \text{ m}^2/\text{g}$ ).

Table 2  
Chemical composition of oxide adsorbents after adsorption of Ni(II) or Cd(II) ions

Metal ion concentration (mg/L)	Element	pH		
		2	7	11
		Mass contribution (%)		
<i>Nickel(II)</i>				
15	Mg	6.87	5.87	7.87
	Si	38.78	39.78	40.04
	O	53.98	53.01	51.85
	Ni	0.09	0.14	0.20
75	Mg	6.45	4.99	5.09
	Si	40.71	41.09	41.87
	O	51.99	52.87	51.87
150	Ni	0.18	0.41	0.59
	Mg	4.98	7.99	8.22
	Si	42.32	37.87	39.25
	O	52.45	53.25	51.35
	Ni	0.27	0.84	1.01
<i>Cadmium(II)</i>				
15	Mg	6.87	5.87	7.87
	Si	38.78	39.78	40.04
	O	53.98	53.01	51.85
	Cd	0.03	0.11	0.17
75	Mg	6.45	4.99	5.09
	Si	40.71	41.09	41.87
	O	51.99	52.87	51.87
150	Cd	0.14	0.23	0.39
	Mg	4.98	7.99	8.22
	Si	42.32	37.87	39.25
	O	52.45	53.25	51.35
	Cd	0.21	0.54	0.87

Table 3  
Porous structure parameters of synthetic oxide adsorbent after adsorption of nickel(II) and cadmium(II) ions from aqueous model solutions at different pH values

Metal ion concentration (mg/L)	pH	Porous structure parameters					
		Surface area $A_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )		Pores volume $V_p$ ( $\text{cm}^3/\text{g}$ )		Pores diameter $S_p$ (nm)	
–	–	427		0.49		4.5	
15		Ni <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>
	2	395	394	0.26	0.29	2.7	2.8
	7	394	398	0.25	0.27	2.8	2.8
	11	365	388	0.27	0.28	2.7	2.7
75	2	413	410	0.28	0.28	2.7	2.8
	7	386	382	0.25	0.27	2.8	2.7
	11	368	375	0.27	0.27	2.8	2.8
150	2	405	407	0.28	0.28	2.7	2.8
	7	390	399	0.27	0.26	2.8	2.7
	11	358	374	0.27	0.27	2.8	2.7

When the adsorption process took place in an acidic environment (pH 2), the smallest surface areas of adsorbents were obtained, amounting to 395, 413, and 405 m<sup>2</sup>/g, respectively, for model solutions with nickel (II) ions concentrations of 15, 75, and 150 mg/L. When it took place in a neutral environment (pH 7), the surface areas of the adsorbents after the process were smaller (at 394, 386, and 390 m<sup>2</sup>/g, respectively) than when it took place at pH 2. When the adsorption process occurred in a basic environment (pH 11), the smallest surface area of the adsorbent, equal to 358 m<sup>2</sup>/g, was obtained, using a solution with a nickel(II) ions concentration of 150 mg/L as the adsorbate. It is significant that in most cases, with an increase in the pH of the reaction system and in the concentration of the nickel (II) ions precursor, the surface area was found to decrease, which provides indirect evidence of the effectiveness of the process and confirms the relationships described above.

In determining the parameters of the porous structure of the adsorbents, a measurement was also made of the total volume and average diameter of the pores, before and after the process. The data in Table 3 show that, in each case, irrespective of the pH of the reaction system and the concentration of the solutions of nickel(II) ions, there is a decrease in pore volume (to values of  $V_p = 0.25\text{--}0.28\text{ cm}^3/\text{g}$ ) and in pore diameter (to values of  $S_p = 2.7\text{--}2.8\text{ nm}$ ) compared with the model sample ( $V_p = 0.49\text{ cm}^3/\text{g}$  and  $S_p = 4.5\text{ nm}$ ).

Analogous results concerning the porous structure of the adsorbents were obtained in the case of adsorption of cadmium(II) ions from aqueous solutions (see Table 3). As the alkalinity of the system increased, there was a reduction in the surface area of adsorbents. When the process was performed in the most acidic environment, the surface areas of the adsorbents were respectively 394, 410, and 407 m<sup>2</sup>/g using a model solutions with cadmium(II) ions concentrations of 15, 75, and 150 mg/L, respectively. The surface areas of the adsorbents, when the process took place at pH 7, were smaller (394, 386, and 399 m<sup>2</sup>/g) than when it took place in the most acidic environment. As in the case of the adsorption of nickel(II) ions, the smallest surface areas were obtained for a basic environment (pH 11); these lies in the range 374–388 m<sup>2</sup>/g.

The data given in Table 3 show that when the process of cadmium(II) ions adsorption took place on an oxide adsorbent of MgO·SiO<sub>2</sub> type, there was a reduction in pore volume to  $V_p = 0.26\text{--}0.29\text{ cm}^3/\text{g}$ , and in pore diameter to  $S_p = 2.7\text{--}2.8\text{ nm}$ , compared with the standard sample ( $V_p = 0.49\text{ cm}^3/\text{g}$  and  $S_p = 4.5\text{ nm}$ ).

The parameters of the porous structure of the synthetic oxide adsorbent following the process of adsorption of nickel(II) and cadmium(II) ions carried

out over different pH ranges provide indirect confirmation of the effectiveness of the process.

An analysis was made in [32] of the effect of pH on the efficiency of the process of adsorption of nickel (II) and cadmium(II) ions, using an inorganic oxide system (SiO<sub>2</sub>·TiO<sub>2</sub>) as adsorbent. The study focused on determining how the pH (2–8), the duration of adsorption process, and the metal ion concentration affected the efficiency of their adsorption. The pH proved to be the most significant factor affecting the efficiency of the process of adsorption on the inorganic oxide system SiO<sub>2</sub>·TiO<sub>2</sub>. In the pH 2 case, the efficiency of adsorption was 30–35% but as the system became more basic (pH 8), it approached ≈100%.

In another report, bentonite was combined with iron oxide in order to obtain an adsorbent of heavy metals from aqueous solutions. The prepared composite was used as an adsorbent of heavy metals from aqueous solutions to determine the effect of pH on the stability of the system. Measurements were made over the range pH 1–11. It was found that the efficiency of adsorption increases in the order Ni(II) < Cu(II) < Cd(II) < Zn(II) for a sample of adsorbent with a 2:1 ratio of bentonite to iron(III) oxide. It should be noted that the most favorable results were obtained at pH 9, and above that limit, a state of equilibrium was reached [33].

Cheng et al. [34] also carried out a study focused on determining the effect of pH on the efficiency of the process of adsorption of lead(II), copper(II), cadmium(II), and chromium(III). The adsorbent of heavy metal ions used was metakaolin (geopolymer). The results showed pH to be a very important parameter controlling the adsorption process. Experiments were performed over a pH range of 2–5, which made it possible to calculate accurately the effect of that parameter on the efficiency of the process of removal of selected heavy metal ions from aqueous solutions. It was found that as the pH value increases, the efficiency of the adsorption of the aforementioned metal ions also increases. A significant improvement in adsorption capacity was recorded for the lead(II) and cadmium (II) ions (at pH values of 4–5). For copper(II) ions the increase in efficiency was much smaller, while for chromium(III) the increase in pH did not have a significant effect on the efficiency of the process of removal of the metal from aqueous solutions, and the results obtained were thus unsatisfactory.

### 3.3. Effect of quantity of MgO·SiO<sub>2</sub>

The effectiveness of the removal of nickel(II) or cadmium(II) ions from model solutions is also significantly

affected by the quantity of adsorbent used; this was proved experimentally as shown in Fig. 7.

Adsorption process was carried out for 60 min from model solutions with a nickel(II) or cadmium(II) ions concentration of 30 mg/L. The effectiveness of the removal of nickel(II) or cadmium(II) ions increases rapidly as the quantity of adsorbent used increases, this being linked to an increase in the surface of contact between the synthetic oxide adsorbent and the adsorbate solution. The highest efficiency of removal of nickel(II) ions was obtained using 7 and 8 g of adsorbent, which agrees with other data reported in the literature [35,36]. In the case of adsorption of cadmium(II) ions, there is a continuous rise in the effectiveness of the process with increasing mass of the oxide material.

### 3.4. Adsorption isotherms

An important aspect to be considered in the realization of the process of removing heavy metal ions from aqueous solutions is the matching of the experimental data obtained to a corresponding adsorption isotherm model. The selected model can be used for detailed description and design of the process. Fig. 8 shows a plot of  $q_e$  vs.  $C_e$  for the adsorption isotherms of nickel(II) and cadmium(II) onto MgO·SiO<sub>2</sub> at 25°C.

The experimental data were applied to the two-parameter isotherm models of Langmuir [21] and Freundlich [22]. The constant parameters of the isotherm equations of Langmuir and Freundlich were calculated using nonlinear regression analysis. Table 4 shows the correlation coefficients, the calculated parameters of the adsorption equation and the

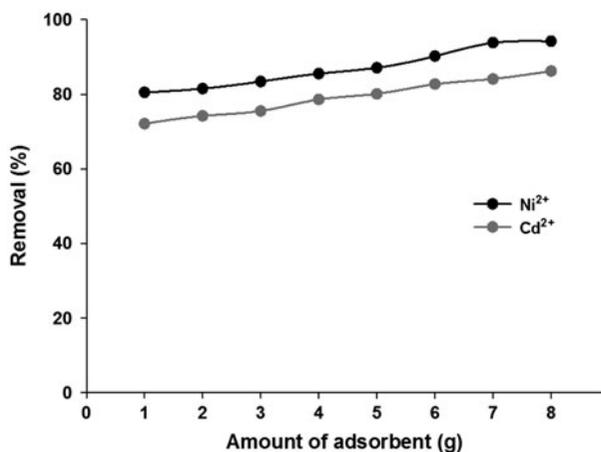


Fig. 7. Effect of quantity of MgO·SiO<sub>2</sub> on nickel(II) and cadmium(II) ions removal efficiency.

quantity of nickel(II) or cadmium(II) ions adsorbed at equilibrium concentration ( $q_e$ ).

#### 3.4.1. Langmuir isotherm

Langmuir's isotherm model is based on the assumption that there are active centers on the surface of the adsorbent, and that only one molecule of adsorbate can be adsorbed at each of these centers. The bond between the adsorbate and adsorbent may be of a physical or chemical nature. The molecules adsorbed on the surface layer do not interact with each other. All of these features entail a case of monolayer (monomolecular) adsorption. The nonlinear equation of the Langmuir isotherm model is expressed as follows [27]:

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

where  $C_e$  is the equilibrium concentration of the solution (mg/L), and  $q_m$  and  $K_L$  are the Langmuir constants, representing the maximum adsorption capacity. The fundamental coefficient describing the affinity of the adsorbate to the adsorbent is the separation factor or dimensionless equilibrium ( $K_L$ ). It is computed as follows:

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (4)$$

where  $K_L$  is the Langmuir constant and  $C_0$  is the initial concentration of nickel(II) ions. The  $R_L$  value indicates the shape of the adsorption isotherm to be irreversible ( $R_L=0$ ). If  $R_L=1$ , then the adsorption process takes a favorable course, but if  $R_L=1$  the course of the process can be said to be unfavorable and incompletely characterized. The calculated separation parameter values were found to be between 0.711 and 0.096 for initial nickel(II) ions concentrations of 15–350 mg/L, which indicates favourable adsorption. In the case of the adsorption of cadmium(II) ions the corresponding values were 0.797 and 0.097. The maximum monolayer adsorption capacity of MgO·SiO<sub>2</sub> was found to be 56.59 mg of nickel(II)/g and 35.86 mg of cadmium(II)/g. The equilibrium data for adsorption of nickel(II) and cadmium(II) over a range of concentrations from 15 to 350 mg/L were correlated with the Langmuir isotherm (Fig. 8).

#### 3.4.2. Freundlich isotherm

The Freundlich isotherm model describes adsorption on heterogenic surfaces. It is a type of empirical

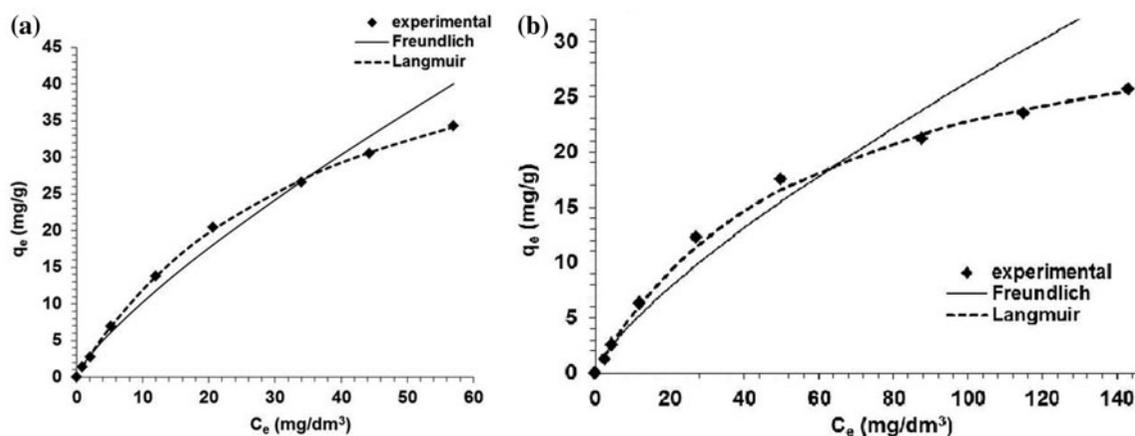


Fig. 8. Nonlinear adsorption isotherms for nickel(II) (a) and cadmium(II) (b) ions adsorbed onto MgO·SiO<sub>2</sub>.

Table 4  
Langmuir and Freundlich isotherms constants for nickel(II) and cadmium(II) ions adsorbed onto MgO·SiO<sub>2</sub> at 25°C

Adsorbed metal ion	Langmuir parameters			Freundlich parameters		
	$R^2$	$q_m$ (mg/g)	$b$ (L/mg)	$R^2$	$K_F$ (mg/g)	$n$
Ni <sup>2+</sup>	0.995	56.59	0.027	0.988	0.849	1.28
Cd <sup>2+</sup>	0.990	35.86	0.017	0.970	0.803	1.32

adsorption isotherm. This model ideally describes the process of adsorption on microporous adsorbents. The formula for Freundlich's isotherm has the following form [28]:

$$q_e = K_F \cdot C_e^{\frac{1}{n}} \quad (5)$$

where  $K_F$  is the Freundlich constant related to the bonding energy,  $1/n$  is the heterogeneity factor, and  $n$  (g/L) is a measure of the deviation from linearity of adsorption. This value indicates the degree of nonlinearity between solution concentration and adsorption as follows: if  $n < 1$ , then chemical adsorption is taking place, while  $n > 1$  implies physical adsorption. The value  $n$  calculated from Freundlich's equation for the adsorption of nickel(II) ions on a synthetic adsorbent of MgO·SiO<sub>2</sub> type is 1.28, and for cadmium(II) ions 1.32, which may indicate the physical nature of the adsorption process.

### 3.4.3. Comparison of adsorption isotherms

Based on the correlation coefficients obtained (Table 4) for the respective isotherm models, it can be

stated that the experimental data fit better to Langmuir's isotherm model ( $R^2 = 0.995$  for Ni<sup>2+</sup> and  $R^2 = 0.990$  for Cd<sup>2+</sup>) than to Freundlich's model ( $R^2 = 0.988$  for Ni<sup>2+</sup> and  $R^2 = 0.970$  for Cd<sup>2+</sup>).

The maximum adsorption capacity of MgO·SiO<sub>2</sub> calculated using Langmuir's isotherm model was compared with the adsorption capacities of other adsorbents (Table 5). Analysis of the reported results

Table 5  
Comparison of Langmuir capacity ( $q_m$ ) with some reported data on nickel(II) or cadmium(II) ions adsorption from aqueous solution by various adsorbents

Adsorbent	$q_e$ (mg/g)	Ref.
Alumina	83.33 Ni <sup>2+</sup>	[37]
MgO·SiO <sub>2</sub>	56.59 Ni <sup>2+</sup>	This study
Citrus peels	43.12 Cd <sup>2+</sup>	[38]
MgO·SiO <sub>2</sub>	35.86 Cd <sup>2+</sup>	This study
Barley straw	35.80 Ni <sup>2+</sup>	[39]
<i>Tectona grandis</i> L.f.	29.94 Cd <sup>2+</sup>	[40]
Montmorillonite	28.40 Ni <sup>2+</sup>	[41]
Hydrous titanium(IV) oxide	22.07 Ni <sup>2+</sup>	[42]
<i>Raphanus sativus</i> peels	19.82 Cd <sup>2+</sup>	[13]
Olive cake	10.56 Cd <sup>2+</sup>	[43]

Table 6  
Desorption of nickel(II) and cadmium(II) ions from MgO-SiO<sub>2</sub> adsorbent

	Removal efficiency (%)		Recovery of metal ions (%)	
	Ni <sup>2+</sup>	Cd <sup>2+</sup>	Ni <sup>2+</sup>	Cd <sup>2+</sup>
15	84.9	80.5	0.3	0.3
30	88.8	80.1	0.5	0.4
75	88.5	79.9	0.6	0.7
100	92.4	78.7	0.8	0.7
150	92.8	72.4	0.9	0.8

leads to the conclusion that the synthetic oxide system MgO-SiO<sub>2</sub> has high sorption capacity in comparison with other frequently used adsorptive materials.

### 3.5. Elution tests

The results of the analysis of the degree of elution of nickel from the surface of the adsorbent using water (Table 6) show its value to be practically zero. This holds for all concentrations of model solutions (15–150 mg/L) used in the first stage of the adsorption process, for both nickel(II) or cadmium(II) ions. This fact provides evidence of the high durability of the bonds between the heavy metal and the adsorbent, and is in agreement with the relationships noted above.

## 4. Conclusions

It was shown in this study that the pH of the reaction system and the quantity of adsorbent used have a significant effect on the efficiency of the process of adsorption of nickel(II) or cadmium(II) ions from model aqueous solutions of its salts, on a synthetic oxide adsorbent (MgO-SiO<sub>2</sub>). Adsorption was least effective when the process was carried out in an acidic environment, while the highest values for the efficiency of the process were recorded for the adsorption of nickel or cadmium in a basic environment (pH 11). Adsorption of nickel(II) or cadmium(II) ions in a neutral environment also gave satisfactory results.

Irrespective of the pH of the reaction system and the concentration of nickel(II) ions, the bonds obtained between adsorbent and adsorbate were found to be highly durable, as is shown by the elution tests.

The effectiveness of removal of nickel(II) or cadmium(II) ions from model solutions is significantly influenced by the quantity of adsorbent used. The

effectiveness of removal of nickel(II) and cadmium(II) ions increases rapidly as the dose of adsorbent increased. The highest efficiency of the process of removal of nickel(II) ions was obtained using 7 and 8 g of adsorbent.

Using the data obtained, a determination was made of the optimum adsorption isotherm model describing the process of removal of nickel(II) or cadmium(II) ions using the synthetic oxide adsorbent MgO-SiO<sub>2</sub>. The experimental data correspond to a significant degree with Langmuir's isotherm model. The maximum adsorption capacity of the MgO-SiO<sub>2</sub> monolayer was 56.59 mg(Ni<sup>2+</sup>)/g and 35.86 mg(Cd<sup>2+</sup>)/g.

Analysis of the results of the experiments and other theoretical aspects indicate unambiguously the effectiveness of the process of adsorption of nickel(II) or cadmium(II) ions from model sulfate solutions using the synthetic oxide system MgO-SiO<sub>2</sub>. In this study it was possible to determine the optimum conditions for that process, which will undoubtedly facilitate its practical realization with liquid waste systems containing nickel(II) or cadmium(II) among other ions.

It is planned to investigate the use of the tested adsorbent for the removal of other hazardous metals, such as lead, mercury, and zinc.

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