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SORPTION CAPACITY OF SEWAGE SLUDGE FOR IONS OF SELECTED METALS

ZDOLNOŚCI SORPCYJNE WYBRANYCH METALI PRZEZ OSADY ŚCIEKOWE

Abstract: The study was conducted to determine the sorption capacity of excessive and fermented sewage sludge with respect to nickel(I) and lead(II). The sorption capacity of the sludge was found to be dependent on the content of organic matter and the iodine adsorption value. Samples of fermented sludge exhibited higher sorption capacity for both metals.

Keywords: waste sludge, sorption, heavy metals

Sewage sludge produced from the treatment of municipal wastewater amounts to approximately 400 000 Mg d.m. per year [1]. Treated sludge is classified as waste, and the principles of waste management are applied. One of the options to manage sludge is land application, when sludge is released into the environment.

As can be seen from the data provided in [2], sewage sludge shows considerable sorption capacity for halogens. It is desirable to establish whether sludge will show sorption capacity for ions of heavy metals. If the answer is positive, sludge can be used as a substance immobilizing heavy metal ions in the environment and limiting their migration.

This study focused on the sorption capacity of sludge for the ions of two selected metals: nickel and lead. Since the sorption capacity of natural sorbents such as soils is dependent on the content of organic matter [3], the analysis was conducted for sewage sludge material differing in the content of organic matter.

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Experimental part

1. Material

The sewage sludge samples used in the tests were obtained from different municipal wastewater treatment plants. Two types of sludge were analyzed: surplus sludge from sites I and II, and stabilized and fermented sludge from site III.

2. Determining the sludge properties

2a. Determining the content of organic matter

The content of organic matter was determined using the Tiurin method [4].

The sludge samples of 0.25 g were dried in the air prior to testing. Then, they were ground in a mortar, passed through a 0.25 mm sieve and placed in a flask. Each sample was submerged in 15 cm^3 of 0.4 N $K_2Cr_2O_7$ to which 0.1g of Ag_2SO_4 was added. The flask content was heated to boiling for five minutes under a reflux condenser. After cooling, the samples were transferred quantitatively into conical flasks, dissolved in 250 cm^3 of distilled water and titrated with 0.2 N solution of Mohr salt in the presence of diphenylamine.

The carbon content was calculated applying the following formula:

$$\%\, C = \frac{(V_1 N_1 - V_2 N_2) \cdot 0.003}{p} \cdot 100$$

where: V_1 – volume of $K_2Cr_2O_7$ added to the sample,
N_1 – $K_2Cr_2O_7$ titre,
V_2 – volume of Mohr salt used for titration with surplus $K_2Cr_2O_7$,
N_2 – Mohr salt titre,
0.003 – carbon milligram equivalent,
p – weighed amount of sludge [g].

The carbon content was then converted into the content of organic matter % I_{om}, using the following relationship:

$$\%\ I_{om} = \%\ C \cdot 1.724$$

where: 1.724 – conversion coefficient.

2b. Determining dry residue and water content

Dry residue and water content were determined following the EN 12 880:2000 standard [5]. Sludge samples of 5 g were dried in a dryer at 105 ^oC. The samples were dried until the material attained dry mass.

The content of dry residue, w_{dr} [%], was calculated from the following relationship:

$$w_{dr} = [(m_c - m_a) / (m_h - m_a)] \cdot 100$$

and the content of water, w_w [%], was calculated from

$$w_w = [(m_h - m_c) / (m_h - m_a)] \cdot 100$$

where: m_a – mass of an empty evaporator [g],
m_b – mass of an evaporator with a non-dried sludge sample [g],
m_c – mass of an evaporator with a dried sludge sample [g].

2c. Determining the iodine adsorption value

The iodine adsorption value was determined according to the PN-83/C-97 515.04 [6] standard adjusted to sewage sludge.

A sample of non-dried sludge in the amount equivalent to 0.2 g of dry mass was treated with 4 cm^3 of 1 M HCl solution and 20 cm^3 of 0.2 M iodine solution. The sample submerged in the solutions was shaken for five minutes using a laboratory shaker (300 rev./min). Once the sludge was mechanically separated from the solution, iodine was titrated with 0.1 M solution of sodium thiosulphate using a starch indicator. The iodine (adsorption) value, *LJ*, was calculated from the following relationship:

$$LJ = \frac{(V_0 - V_1) \cdot c_1 \cdot 126.92}{m} \quad \text{[mg/g d.m.]}$$

where: V_0 – volume of the 0.1 M $Na_2S_2O_3$ solution used for a blank titration [cm^3],
V_1 – volume of the 0.1 M $Na_2S_2O_3$ solution used for titration of a sample [cm^3],
c_1 – concentration of the $Na_2S_2O_3$ solution [M],
126.92 – mass of 1 mol of (1/2 I_2) iodine [g],
m – mass of a sludge sample converted into dry mass [g].

3. Analyzing the sorption capacity of the sludge material for nickel(II) and lead(II)

3a. Determining the sorption kinetics for nickel(II) and lead(II) ions

The analysis was conducted under static conditions. Sewage sludge samples 5 g were placed in eight flasks and treated with 50 cm^3 of 0.1 M solution of lead nitrate(V) or nickel nitrate(V). The samples were then shaken in a GFL-3005 shaker at a rotational speed of 300 rev./min. The shaking time ranged from 5 minutes to 20 hours. The

solutions of metal salts separated from the sludge were tested for the concentration of lead(II) and nickel(II). The metal equilibrium concentration was determined using a spectrophotometric method included in Merck's procedures [7,8]. The spectrophotometric measurements were taken by means of a Merck Nova 60.

The sorption capacity was calculated using the following expression:

$$A = \frac{v(c_0 - c)}{m}$$

where: A – proper sorption [mg/g],
c_0 – initial concentration of the metal salt solution [mg/dm^3],
c – equilibrium concentration of the metal salt solution [mg/dm^3],
v – volume of solution [dm^3],
m – sorbent mass [g].

3b. Determining the sorption isotherms

The sorption isotherms for nickel(II) and lead(II) were determined under static conditions. Five sewage sludge samples, 2.0, 5.0, 7.5, 10.0 and 12.5 g, were placed in five conical flasks, respectively. Each was treated with 50 cm^3 of 0.1 M solution of lead nitrate(V) or nickel nitrate(V). The samples were shaken in a laboratory shaker for four hours. The next steps were the same as in section 3a.

Results and discussion

The first objective of the analysis was to determine selected physical and chemical properties of the sewage sludge samples (Table 1).

Table 1

Properties of the sewage sludge material

Treatment plants	Content of organic matter [%]	Content of water [%]	*LJ* [%]	Content of dry residue [%]
I N	46.96	81.06	412	18.94
II C	41.12	86.13	424	13.87
III P	57.25	48.63	473	51.37

The fermented sludge (sample III) showed the highest content of dry residue (51.37 %) and the highest amount of organic matter (57.25 %). The surplus sludge (sample II), on the other hand, had the lowest content of dry residue (13.87 %) and organic matter (41.12 %). The changes in the content of dry residue and organic matter were represented by the iodine adsorption value. The iodine (adsorption) value, which was used for determining the sorption capacity of the sludge material,

was the highest for the fermented sludge (sample III) with the highest amount of organic matter and dry residue. The iodine adsorption value, ranging from 412 to 473 mg I/g d.m., was several times lower for soil samples (approx. 100–150 mg I/g d.m.) and twice as low as those for WD-extra activated carbon (920 mg I/g d.m.) [9, 10]. The iodine (adsorption) value showed that the sewage sludge material possessed relatively high sorption capacity.

The next objective was to determine the sorption kinetics for nickel and lead salts. As can be seen from the sorption curves in Figs. 1 and 2, the sorption equilibrium was achieved after four hours. The contact time was determined from the sorption isotherms (Figs. 3 and 4). For lead, the highest sorption capacity, ie 385 mg/g, was obtained for the samples fermented in a closed fermentation chamber. The sorption capacity was reported to be lower for the surplus sludge samples; it was 54 mg/g for sample I and 86 mg/g for sample II. For nickel, the best sorption of 266 mg/g was observed also for the

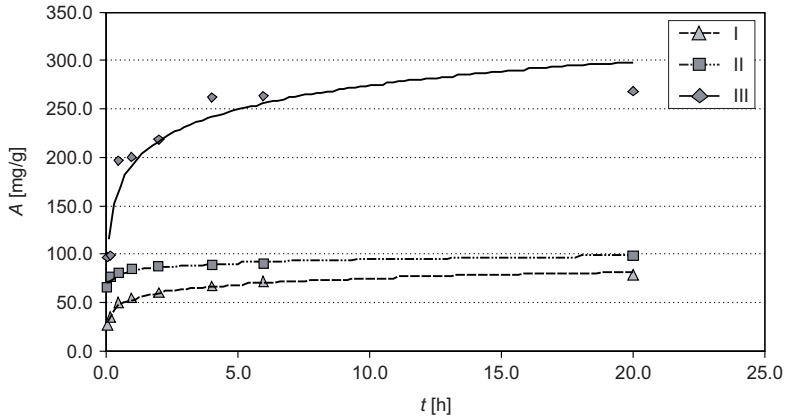

Fig. 1. Adsorption vs time for nickel

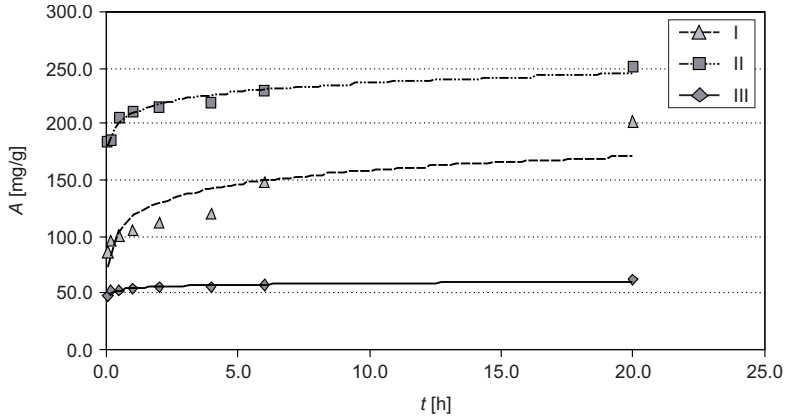

Fig. 2. Absorption vs time for lead

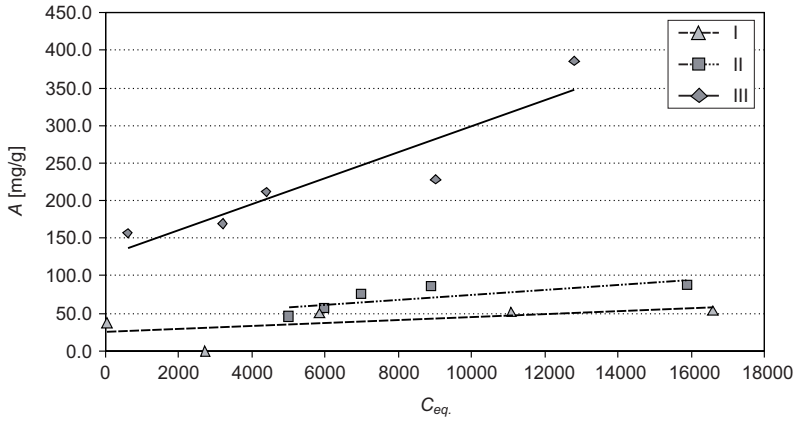

Fig. 3. Nickel sorption isotherms

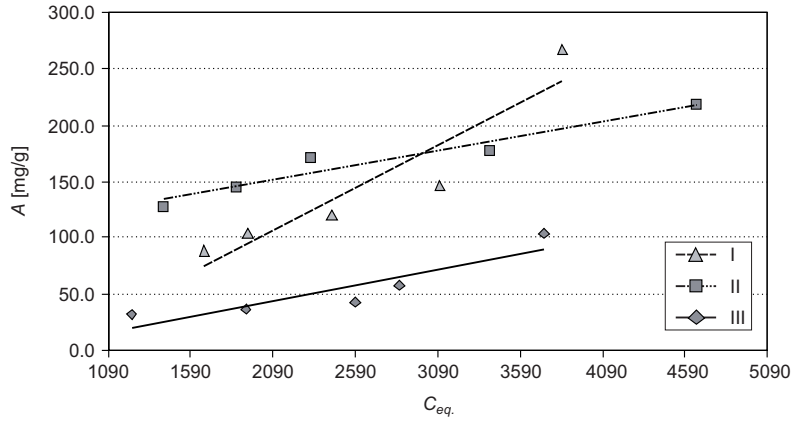

Fig. 4. Lead sorption isotherm

material fermented in a closed fermentation chamber; the surplus sludge had a sorption of 218 (sample II) and 104 (sample I).

The changes in the sorption capacity were consistent with the data provided in the literature [3, 9]. The highest sorption of nickel and lead was reported for the sludge samples with the highest content of organic matter and the highest iodine (adsorption) value. The sorption equilibrium was described through the Freundlich isotherm, $A = \mathrm{k} \cdot c_{\mathrm{eq.}}^{1/n}$ [11], which, as Weber suggests [3], well describes the sorption of hydrophobic substances in soil assuming that it occurs mainly for an organic fraction of soil. Parameter k reflects the sorption capacity of a sorbent for a sorbate, while $1/n$ reflects the energy of binding of the sorbent by the sorbate.

Table 2 presents the values of parameters k and n and the coefficient of determination calculated by using version 7.0 of STATISTICA. The values of the coefficient of determination higher than 0.9 confirm that the Freundlich isotherms were suitable for describing the test results.

Table 2

Estimators of the parameters of the function $A = k \cdot c^{1/n}$ describing the Freundlich isotherms used in the analysis

Treatment plants	Pb			Ni		
	R	K	*n*	R	K	*n*
I	0.9237	9.287	5.354	0.9451	0.022	0.897
II	0.8425	0.357	1.703	0.9687	6.845	2.462
III	0.9126	43.194	5.375	0.8944	0.021	0.997

Conclusions

1. The sludge material demonstrated good sorption capacity for ions of heavy metals such as nickel and lead.

2. From the analysis it is clear that sewage sludge can be used as a substance immobilizing heavy metal ions in the environment.

3. The sorption capacity of a sludge material is dependent on the content of organic matter; the higher the amount of organic matter, the higher the sorption capacity.

4. The sorption capacity of sludge can be assessed using the iodine (adsorption) value.

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ZDOLNOŚCI SORPCYJNE WYBRANYCH METALI PRZEZ OSADY ŚCIEKOWE

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Abstrakt: Zbadano zdolności sorpcyjne jonów niklu(II) i ołowiu(II) przez osady ściekowe nadmierne i przefermentowane. Stwierdzono, że zdolności sorpcyjne osadów zależą od zawartości w nich materii organicznej i od wartości liczby jodowej. Wyższe zdolności sorpcyjne dla obu metali miały próbki osadów przefermentowanych.

Słowa kluczowe: osady ściekowe, sorpcja, metale ciężkie