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PREPARATION OF BENTONITE/nAg NANOCOMPOSITES

In this work results of the preparation of bentonite/nAg nanocomposites were presented. In the first stage, the bentonite sorption properties were determined, including the equilibrium and kinetics parameters of the sorption process of silver ions on the bentonite. The study analyzed the filler sorption properties for different concentrations of silver ions in solution. The equilibrium sorption data were analyzed using Freundlich, Langmuir and Temkin equations. It was found that the best fit is given by the Freundlich equation. Analysis of the kinetics of the sorption process showed that the pseudo-second-order equation was characterized by the best fit for the experimental data, suggesting the chemical character of the adsorption process. In order to obtain a nanocomposite, silver ions contained in the composite were subjected to a reduction process using tannic acid with stabilizing and reducing properties. The obtained bentonite/nAg nanocomposites contained silver nanoparticles in the range of 162÷266 mg/g. The structures of the nanomaterials were studied by XRD and SEM methods.

Keywords: adsorption, bentonite, equilibrium, kinetics, nanocomposite, silver

OTRZYMYWANIE NANOKOMPOZYTU BENTONIT/nAg

Celem niniejszej pracy była analiza równowagi i kinetyki procesu sorpcji jonów srebra na powierzchni napelnacza oraz otrzymanie nanokompozytu bentonit/nAg. W badaniu analizowano właściwości sorpcyjne napelnacza dla różnych stężeń jonów srebra w roztworze. Do opisu równowagi sorpcji analizowanych jonów zastosowano równania Langmuira, Freundlicha oraz Temkina. Stwierdzono, że najlepsze dopasowanie daje równanie Freundlicha. Celem badania było również określenie kinetyki sorpcji. Równanie pseudodrugiego rzędu uzyskało lepsze dopasowanie do danych doświadczalnych, co świadczy o chemicznym charakterze sorpcji. W celu otrzymania nanokompozytu jony srebra zawarte w kompozycie poddano procesowi redukcji przy użyciu kwasu taninowego, charakteryzującego się właściwościami stabilizująco-redukującymi. Otrzymano nanokompozyt bentonit/nAg o zawartości nanocząstek srebra 162÷266 mg/g.

Słowa kluczowe: adsorpcja, bentonit, równowaga, kinetyka, nanokompozyt, srebro

INTRODUCTION

Nanotechnology holds great promise for revolutionizing material use in the 21st century [1]. Adding nanoparticles to raw materials improves or creates new material properties. Nanocomposite materials consist of two or more phases with different properties, with at least one additive being in the nanometer size. Nanocomposites have better properties compared to the individual components included in the composite. Nano-scale additions are characterized by greater efficiency in the use of such materials compared to additions introduced on the macro scale. The components of the nanocomposite, fulfilling filler properties, can improve the physical and chemical properties of the final material, and uniformly distribute the nanoadditives throughout the composite. Depending on the used nanoadditives, new material properties can be obtained, for example the addition of metal oxides TiO₂ and ZnO improve the photocatalytic and hydrophilic properties [2], nanome-

tal additions such as Ag and Cu improve the antibacterial properties of the material [3, 4].

Commonly used composites are aluminosilicates with additions of metal and metal oxide nanoparticles. Aluminosilicates due to their construction and properties are a characteristic group of fillers used especially in construction. The materials are built with hydrated silicates with a packet structure. The basis of the packages are silicon and aluminum (or magnesium). The group of aluminosilicates includes: kaolinite, montmorillonite, bentonite and vermiculite [5, 6]. Due to the physical properties of clay, they are used in the chemical, food and building industry as an additive to mortars and concrete walls, for constructing waterproof aluminum liners and as a component of paints [7, 8]. One of the basic properties of clay minerals is their good ability to adsorb ions from aqueous solutions and the ability of ion exchange, which results from their specific surface

area [9, 10]. In this way, it is possible to directly form combinations of a silicate-nanoadditive, which greatly simplifies production methods and reduces the production costs of such materials.

Currently, silver is one of the most commonly used additives with antibacterial properties. Silver nanoparticles show specific chemical, optical and mechanical properties [3, 11]. The nanometric dimensions of nanosilver and the ability to immobilize another element or its chemical compound on the particles make it an ideal addition for modifying polymeric materials [12]. Silver nanoparticles, compared to silver ions, show greater antibacterial effectiveness [2]. The antibacterial activity results from their larger active surface, which makes nanosilver more biologically and chemically reactive [11, 13].

The aim of the research was to obtain a bentonite/nAg nanocomposite. The nanocomposite formed in the process can be successfully used, among others, as an addition to paints, which improves the antimicrobial properties of the product. In order to determine the sorption properties of the filler, its equilibrium and sorption kinetics were determined depending on the initial concentration of silver ions.

EXPERIMENTAL

Materials

The initial solution of Ag(I) was prepared using AgNO₃ (POCH) by dissolving appropriate amounts of salts in deionised water to obtain the desired concentration ranging from 1000 to 5000 mg/dm³. Bentonite was used as a filler. The reducer and stabilizer of the silver nanoparticles was tannic acid (Sigma-Aldrich). The concentration of metal ions in aqueous solutions was determined with silver-sulphate and reference electrodes combined (Hydromet Company) with the Elmetron CX-701 Multifunction Meter.

Instrumental methods

The surface microstructures and elemental composition were characterised by Scanning Electron Microscopy (Vegall-Tescan Company). The study was supplemented with micro area analysis using the EDS detector. The bentonite was analysed to determine the phase composition of the material and to identify crystalline phases using X-ray analysis. Before and after the silver reduction process the material was characterised. A Philips X'Pert camera with a PW 1752/00 CuKα monochromator was used in the study.

Silver ions sorption process onto bentonite

The adsorption of silver ions on bentonite was studied using batch mode experiments. 30 cm³ of the silver ions solution (1000, 2000, 3000, 4000 and 5000 mg/dm³) was added to 1 g of the material. The

solutions were stirred for 2, 4, 6, 10, 20, 30 and 40 min (rpm = 300) at 293 K. Then, the solution was filtered and the concentration of metal ions was measured. The amounts of adsorbed metal ions q [mg/g], were calculated from the dependence:

$$q_e = \frac{(C_0 - C_e)V}{1000 \cdot m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium silver ion concentration [mg/dm³] in solution, V is the solution volume [cm³], and m is the mass of the adsorbent [g].

Sorption equilibrium

The adsorption equilibrium is reached when the rate of adsorption processes equals the desorption rate of the adsorbed particles. In order to characterise the adsorption equilibrium of silver ions onto bentonite, it is essential to establish the most appropriate correlation for the equilibrium curve. Three models were tested: Langmuir, Freundlich and Temkin.

Langmuir model

One of the basic models of adsorption is the Langmuir model. The main assumption is that the substance is adsorbed to form a monolayer and the number of active sites on which the processes can run is constant. All the centres are identical, which means that all the active sites have an equal affinity for the adsorbate. In addition, the adsorbed molecules do not react with each other and there is no interaction between the active centres themselves. The maximum amount of adsorbed molecules equals the number of active sites on the adsorbent surface [14]. The Langmuir isotherm equation in nonlinear form is shown below [15]:

$$q_e = q_m K_L \frac{C_e}{1 + K_L C_e} \quad (2)$$

where: q_e - equilibrium sorption capacity [mg/g], q_m - maximum sorption capacity [mg/g], K_L - Langmuir constant, C_e - equilibrium concentration of silver ions [mg/dm³].

Freundlich model

The Freundlich model is one of the simplest models used to describe the adsorption equilibrium. The model represents reversible physical adsorption where the adsorbates create a multilayer. The amount adsorbed is the summation of adsorption on all sites (each having bond energy), with the stronger binding sites occupied first, until the adsorption energy is exponentially decreased upon completion of the adsorption process [16, 17]. The Freundlich isotherm equation is shown as:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where: q_e - equilibrium sorption capacity [mg/g], $K_F, 1/n$ - Freundlich constants related to adsorption

capacity, C_e - equilibrium concentration of silver ions [mg/dm^3].

Temkin model

The Temkin model is a 2-parameter equation representing the adsorption process, assuming even distribution of the adsorbent-adsorbate interactions, in which, as the molecules move away from the surface of the molecule, the heat of adsorption decreases linearly [18]. The isothermic Temkin equation is in the form [19]:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (4)$$

where: q_e - equilibrium sorption capacity (mg/g), K_T - Temkin constant [dm^3/g], b_T - constant related to heat of adsorption [J/mol], R - gas constant ($8.314 \text{ J}/\text{mol}$), T - temperature [K], C_e - equilibrium concentration of silver ions [mg/dm^3].

Sorption kinetic

To describe the sorption kinetics, the pseudo-first order equation and the pseudo-second equation were used. In the pseudo-first-order kinetics model, the reaction rate is proportional to the difference of the adsorbent solid phase equilibrium solids concentration and the instantaneous phase concentration in the solid phase. The pseudo-first order model describes the sorption process of a physical nature. The linear form of the pseudo-first-order kinetic model may be represented by [20, 21]:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (5)$$

In the pseudo-second order kinetics model, the sorption rate is directly proportional to the square difference of the equilibrium and instantaneous concentration in the adsorbent phase [22]. The pseudo-second order model is suitable for chemical sorption. The linear form of the model is shown below [23]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where q_e and q_t are the amounts of adsorbate [mg/g] at equilibrium and at time t [min], respectively, k_1 and k_2 are the rate constants of pseudo-first-order adsorption [min^{-1}] and pseudo-second-order adsorption [$\text{g mg}^{-1} \text{ min}^{-1}$].

Reduction of silver ions with tannic acid

The nanocomposite production process consisted in the reduction of silver ions directly onto the surface of bentonite using tannic acid as a reducing agent. 110 cm^3 of silver nitrate solution with concentrations 3000, 4000 and $5000 \text{ mg}/\text{dm}^3$ were added to 10 g of bentonite. The solutions were stirred for 40 min ($\text{rpm} = 300$) at 293 K.

Then, the solutions were filtered and the concentration of metal ions was measured. The test was repeated three times for each concentration. An aqueous solution of tannic acid acting as reducer of silver ions and forming a stabilizer of silver nanoparticles was added to the obtained precipitates. The molar ratio of tannic acid to silver ions was 0.2:1. The solutions with material were mixed for 2 min. The samples were filtrated and the products were dried at about 50°C .

RESULTS AND DISCUSSION

Sorption process

Table 1 shows the results of the silver sorption process on bentonite. The adsorbent capacity to absorb silver ions changes over the entire concentration range of $1000\div 5000 \text{ mg}/\text{dm}^3$. The adsorption capacity increases as the concentration of silver ions increases. At the lowest initial concentration of $1000 \text{ mg}/\text{dm}^3$, it was $29 \text{ mg}/\text{g}$, while at the highest concentration, $5000 \text{ mg}/\text{dm}^3$ was $119 \text{ mg}/\text{g}$. The sorption equilibrium was reached after 40 minutes.

TABLE 1. Results of sorption process for silver ions on bentonite

TABELA 1. Wyniki procesu sorpcji dla jonów srebra na bentonicie

Time [min]	Concentration of silver ions [mg/dm^3]									
	1000		2000		3000		4000		5000	
2	156	455	1017	1215	1781	2130	2070	2030	3170	3560
4	55	123	856	1100	1554	1783	1768	1820	2280	2040
6	45.6	76.3	710	799	1470	1531	1550	1614	1960	1820
10	28.7	45.8	613	705	1200	1312	1533	1499	1701	1719
20	38.7	40.1	444	572	990	1148	1501	1450	1616	1650
30	30.2	39.0	377	403	980	997	1485	1317	1549	1499
40	29.2	37.6	242	312	708	754	963	1140	1294	1317
C_e	33.4		277		731		1052		1036	
q_e	29		52		68		88		119	

Equilibrium sorption

In order to characterise the adsorption equilibrium of silver ions on bentonite, it is essential to establish the most appropriate correlation for the equilibrium curve. Table 2 compares the adsorption equilibrium models used in the study, the form of their nonlinear equations. The graphs show the approximations of the models combined with the experimental results (Fig. 1).

The experimental points for silver ion adsorption are best described by the Freundlich model. This model yielded the highest adjusted R-square (0.9546). Parameter n is lower than one, which suggests the chemical character of the adsorption process.

TABLE 2. Langmuir, Freundlich and Temkin isotherm constants and correlation coefficients for adsorption of silver ions onto bentonite

TABELA 2. Stałe oraz współczynniki korelacji dla modeli równowagi Langmuira, Freundlicha oraz Temkina dla procesu adsorpcji jonów srebra na bentonicie

Adsorbed metal ions	Isotherm	Parameters	Non-linear regression
Ag(I)	Langmuir	q_{max} [$mg\ g^{-1}$]	134.3 ± 138.4
		K_L [$dm^3\ mg^{-1}$]	2.12 ± 6.04
		R^2	0.7488
	Freundlich	K_F [$mg^{1-(\frac{1}{n})} L^{\frac{1}{n}} g^{-1}$]	89.95 ± 17.15
		n^{-1}	0.424 ± 0.304
		R^2	0.9546
	Temkin	A_T [$dm^3\ g^{-1}$]	94.18 ± 301
		B	126.3 ± 104.8
		R^2	0.7742

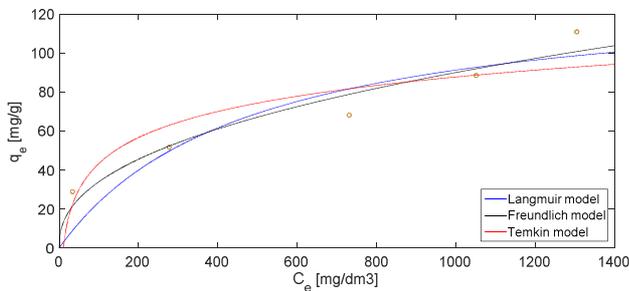


Fig. 1. Isotherm plots of adsorption on bentonite for Ag(I)
 Fig. 1. Izotermy adsorpcji jonów srebra na bentonicie

Kinetic sorption

A series of measurements was carried out to investigate the kinetics of the silver ion sorption process on bentonite. The results are summarised in Table 3. The pseudo-first order and pseudo-second order models were used to describe the kinetic parameters of adsorption. The graphs show the approximate straightforwardness of the models combined with the experimental results (Fig. 2).

The pseudo-second-order model fit better than the pseudo-first-order model, which confirmed the chemical nature of the process. Constantino et al. [24] analysed the Ag(I) sorption process onto bentonite clays. The process was based on pseudo-second order kinetics, suggesting that a similar mechanism confirms the consistency of the results. The obtained R^2 values for the pseudo-second order kinetic model were the highest. The experimental q value is very close to the theoretical value in the pseudo-second-order model, which confirms the compatibility of the fit with the model.

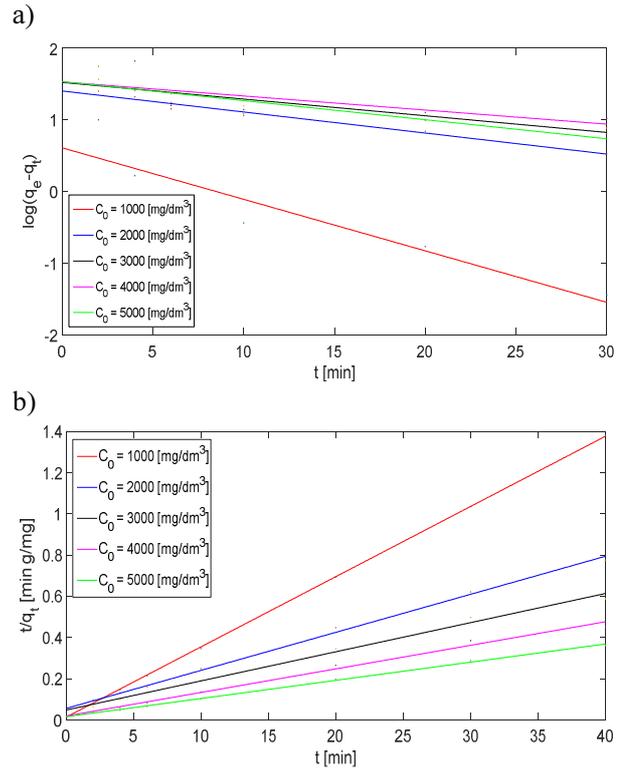


Fig. 2. Plots of kinetic models of sorption process of silver ions onto bentonite: a) pseudo-first-order model, b) pseudo-second-order model

Fig. 2. Wykresy kinetyki pseudopierwszego rzędu oraz kinetyki pseudo drugiego rzędu procesu sorpcji jonów srebra na bentonicie

TABLE 3. Kinetic parameters of Ag(I) adsorption onto bentonite

TABELA 3. Parametry kinetyki procesu sorpcji jonów Ag(I) na bentonicie

Models	Parameters	1000 $\frac{mg}{dm^3}$	2000 $\frac{mg}{dm^3}$	3000 $\frac{mg}{dm^3}$	4000 $\frac{mg}{dm^3}$	5000 $\frac{mg}{dm^3}$
First order kinetic model	k_1 [min^{-1}]	0.1654 ± 0.0916	0.0676 ± 0.0148	0.0536 ± 0.0201	0.0452 ± 0.0623	0.0612 ± 0.0472
	q_{max} [$mg\ g^{-1}$]	4.08 ± 5.82	25.34 ± 5.88	33.35 ± 10.50	33.91 ± 32.86	34.25 ± 25.18
	R^2	0.8285	0.9692	0.9140	0.3808	0.7055
Second order kinetic model	k_{II} [$g\ mg^{-1}\ min^{-1}$]	0.0866 ± 0.0780	0.0061 ± 0.0028	0.0042 ± 0.0032	0.0070 ± 0.0041	0.0051 ± 0.0026
	q_{max} [$mg\ g^{-1}$]	29.34 ± 0.50	54.16 ± 3.58	70.72 ± 6.63	87.43 ± 9.49	113.3 ± 5.8
	R^2	0.9997	0.996	0.9921	0.9894	0.9976
Exp. data	q_{exp} [$mg\ g^{-1}$]	29.00	51.69	68.07	88.45	110.83

Preparation of nanocomposite

Table 4 presents the results of the analysis of silver concentration after the sorption process and after the reduction process in the solutions and the composite.

TABLE 4. Content of silver ions and nanoparticles of silver in solutions and the composites

TABELA 4. Zawartość srebra oraz nanocząstek srebra w roztworach i kompozycje

Concentration of Ag^+ in solution $\left[\frac{mg}{dm^3}\right]$	3000	4000	5000
Average Ag^+ concentration after sorption $\left[\frac{mg}{g}\right]$	899	966	1797
Concentration of Ag^+ in composite $\left[\frac{mg}{dm^3}\right]$	210	303	320.3
Concentration of nanosilver in solution $\left[\frac{mg}{g}\right]$	486	498	543
Concentration of nanosilver in composite $\left[\frac{mg}{dm^3}\right]$	162	254	266

Analysis of the results (Table 4) shows that the highest content of silver nanoparticles in the composite was 266 mg/g, while the lowest was 162 mg/g. The limited sorption capacity of the material can affect on the amount of silver adsorbed onto the material. Due to the occurring silver ion reduction process on the surface of bentonite, the possibility of contact between reagents is limited. After exceeding the initial concentration of silver ions above 4000 mg/dm³, the state of equilibrium of the process was reached, hence, despite the increase in silver concentration, no significant increase in nanosilver on the bentonite was observed.

Instrumental analysis

Bentonite was used as the adsorbent in the studies. The study of its phase composition was performed using an X-ray diffractometer (Fig. 6). XRD analysis showed that the components of bentonite are halloysite (Al₂H₈O₁₁Si₂), aluminum oxide (Al₂O₃), tridymite (SiO₂) and metahalosite (Al₂H₄O₉Si₂) (Fig. 3a). Figure 3b shows a diffractogram of bentonite with adsorbed silver ions (from a solution of 5000 mg/dm³) and Figure 3c presents a diffractogram of bentonite after the reduction of silver ions. XRD analysis showed the presence of silver in the material under study. The peaks present in the 38° and 44° regions are characteristic for silver [25].

Scanning electron microscopy (SEM) analysis was used to characterise the morphology and structure of the adsorbent. Figure 4 shows the surface morphology of bentonite with marked points on the basis of which the analysis of chemical composition was performed by the EDS method. Analysis indicated that the material contained approximately 24% silicon and the rest of the element, i.e. carbon, sodium, magnesium, aluminium, sulphur, potassium, titanium, manganese, iron, oxygen and copper.

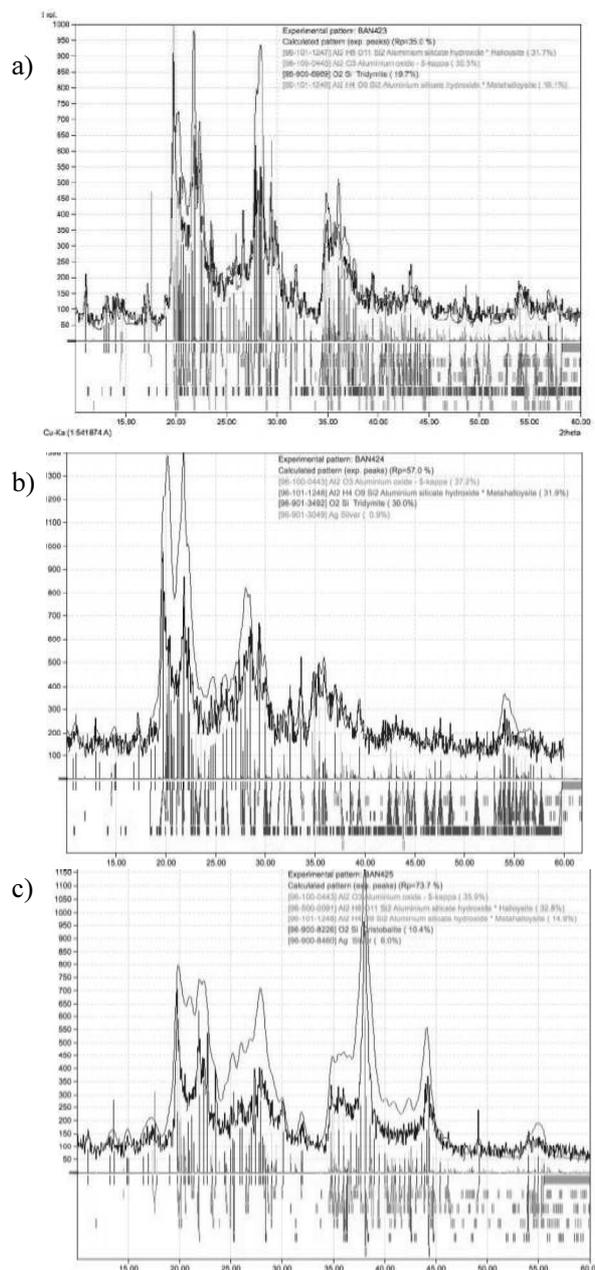


Fig. 3. X-ray diffraction: a) raw bentonite, b) after Ag⁺ adsorption on bentonite, c) bentonite/nAg

Fig. 3. Dyfraktogramy XRD: a) surowego bentonitu, b) bentonitu po adsorpcji jonów srebra, c) kompozytu bentonit/nAg

The results of the SEM-EDS analysis for bentonite with adsorbed silver ions (for a solution with an initial silver concentration of 5000 mg/dm³) and bentonite after reduction of the silver ions are shown in Figure 5. SEM-EDS analysis confirms the presence of ionic silver after the sorption process and silver nanoparticles after the process reduction on the surface of bentonite. Silver ions evenly distributed over the entire surface of the sample are visible on the surface of the sample. Analysis of the bentonite/nAg nanocomposite sample showed the presence of silver nanoparticles on the surface of bentonite, which are unevenly distributed, forming larger clusters. This may indicate aggregation of the resulting nanoparticles [26, 27].

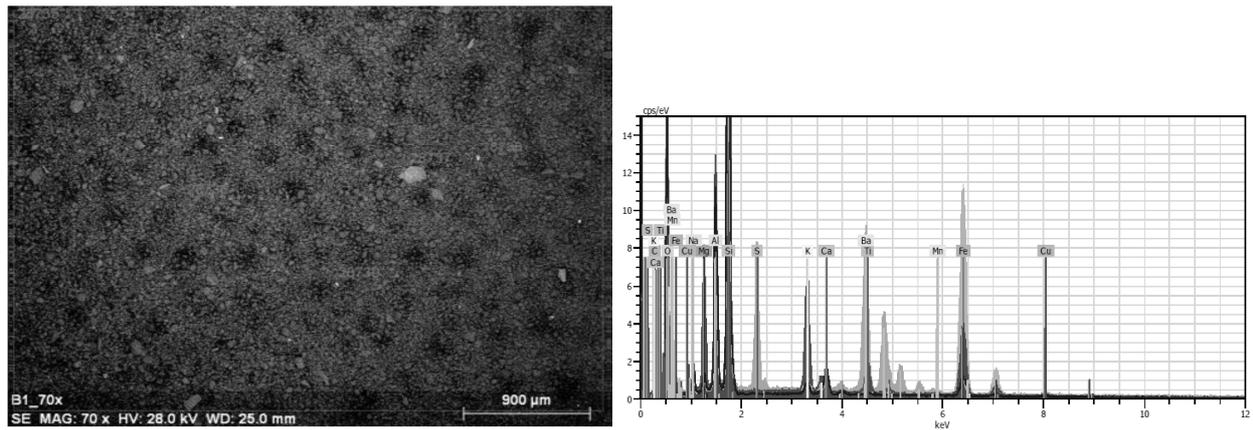


Fig. 4. Results of SEM-EDS analysis of raw bentonite

Rys. 4. Wyniki analizy SEM-EDS bentonitu

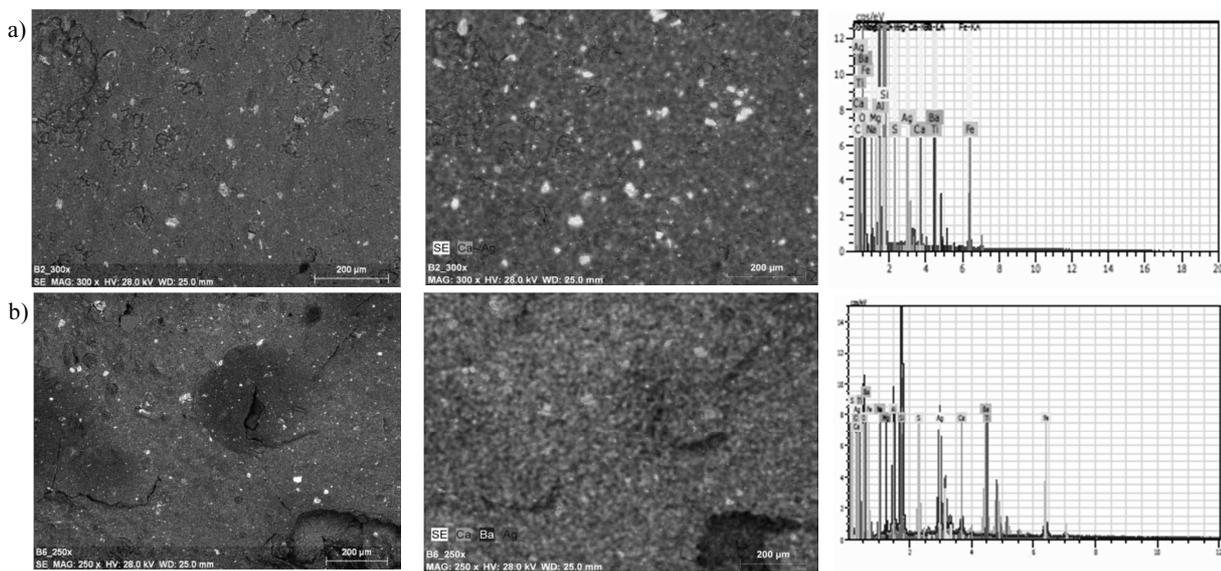


Fig. 5. SEM image and EDS patterns: a) bentonite after silver ions sorption process, b) composite bentonite/nAg

Rys. 5. Analiza SEM i EDS: a) bentonit po procesie sorpcji jonów srebra, b) kompozyt bentonit/nAg

CONCLUSION

The nanocomposites were obtained by the reduction process, using tannic acid as the reducer agent. The bentonite/nAg nanocomposite contained silver nanoparticles in the amount of 162-266 mg/g. The nanoparticles contained in the composite were characterized by a high degree of crystallinity. As the concentration of silver ions increases, the adsorption capacity of bentonite increases. The equilibrium for the adsorption of Ag(I) was best described by the Freundlich model. The kinetics of adsorption of Ag(I) by bentonite follows pseudo-second-order kinetics, suggesting monolayer coverage and a chemisorption process. On the basis of the conducted research it can be concluded that bentonite can be used as a material on which it is possible to adsorb silver ions and then reduce them with tannic acid. The created nanocomposite can be used, among others, as an addition to paints, affecting the antimicrobial properties of the product.

REFERENCES

- [1] Wei B., Shi Z., Xiao J., Xu Y., Lv L., In vivo and in vitro antibacterial effect of nano-structured titanium coating incorporated with silver oxide nanoparticles, *J. Biomater. Tissue Eng.* 2017, 7, 418-425.
- [2] Lu P.-J., Huang S.-C., Chen Y.-P., Chiueh L.-C., Shih D.Y.C., Analysis of titanium dioxide and zinc oxide nanoparticles in cosmetics, *J. Food Drug Anal.* 2015, 23, 587-594.
- [3] Ortega-Morales B.O., Reyes-Estebanez M.M., Gaylarde C.C., Camacho-Chab J.C., Sanmartín P., Chan-Bacab M.J., Granados-Echegoyen C.A., Pereañez-Sacarias J.E., Antimicrobial properties of nanomaterials used to control microbial colonization of stone substrata, [in:] *Advanced Materials for the Conservation of Stone*, Springer International Publishing, Cham 2018, 277-298.
- [4] Peszke J., Dulski M., Nowak A., Balin K., Zubko M., Sułowicz S., Nowak B., Piotrowska-Seget Z., Talik E., Wojtyniak M., Mrozek-Wilczkiewicz A., Malarz K., Szade J., Unique properties of silver and copper silica-based nanocomposites as antimicrobial agents, *RSC Adv.* 2017, 7, 28092-28104.

- [5] Mnatsakanyan N., Trchounian A., Nanocomposite filter made from porous mineral tuff with absorbed silver nanoparticles and its application for disinfection of water, *J. Water Supply Res. Technol. - Aqua jws* 2018, 161.
- [6] Tahervand S., Jalali M., Sorption and desorption of potentially toxic metals (Cd, Cu, Ni and Zn) by soil amended with bentonite, calcite and zeolite as a function of pH, *J. Geochemical Explor.* 2017, 181, 148-159.
- [7] Monteiro M.K.S., dos Santos F.K.G., Leite R.H. de L., Aroucha E.M.M., Vitoriano J.O., Oliveira V.R.L., Hydrophilicity, solubility and optical properties in composite films of gelatin and bentonite clay in its natural form or modified, *Mater. Sci. Forum* 2018, 912, 136-140.
- [8] Pramanik S., Karak N., Polymer Nanocomposites for Adhesive, Coating, and Paint Applications, [in:] *Properties and Applications of Polymer Nanocomposites*, Springer, Berlin - Heidelberg 2017, 173-204.
- [9] Putro J.N., Santoso S.P., Ismadji S., Ju, Y.-H., Investigation of heavy metal adsorption in binary system by nanocrystalline cellulose - Bentonite nanocomposite: Improvement on extended Langmuir isotherm model, *Microporous Mesoporous Mater.* 2017, 246, 166-177.
- [10] Rihayat T., Salim S., Zaini H., Salmiyah, Rahmawati, C.A., Kurniati, Irawan, Y., Zaimahwati, Synthesis, characterization and microbial protection of palm oil based polyurethane / bentonite / chitosan as paint and coating material, 2nd International Conference Sustainable and Renewable Energy Engineering (ICSREE), IEEE 2017, 10-13.
- [11] Zhang X.-F., Liu, Z.-G., Shen, W., Gurunathan, S., Silver nanoparticles: Synthesis, characterization, properties, applications, and therapeutic approaches, *Int. J. Mol. Sci.* 2016, 17, 1534.
- [12] Hannon J.C., Kerry J.P., Cruz-Romero M., Azlin-Hasim S., Morris M., Cummins E., Kinetic desorption models for the release of nanosilver from an experimental nanosilver coating on polystyrene food packaging, *Innov. Food Sci. Emerg. Technol.* 2017, 44, 149-158.
- [13] Zhang C., Hu Z., Deng B., Silver nanoparticles in aquatic environments: Physicochemical behavior and antimicrobial mechanisms, *Water Res.* 2016, 88, 403-427.
- [14] Yakout S.M., Elsherif E., Batch kinetics, isotherm and thermodynamic studies of adsorption of strontium from aqueous solutions onto low cost rice-straw based carbons, *Carbon - Sci.* 2010, 1, 144-153.
- [15] Langmuir I., The constitution and fundamental properties of solids and liquids. Part I. Solids, *J. Am. Chem. Soc.*, 1916, 38, 2221-2295.
- [16] Freundlich H., Over the adsorption in solution, *Z. Phys. Chem.* 1906, 57, 385-470.
- [17] Chen C., Evaluation of equilibrium sorption isotherm equations, *The Open Chemical Engineering Journal* 2013, 7, 24-44.
- [18] Temkin M.I., Pyzhev V., Kinetics of ammonia synthesis on promoted iron catalysts, *Acta Physicochim.* 1940, 12, 327-356.
- [19] Dada A.O., Olalekan A.P., Olatunya A.M., Dada O., Langmuir. Freundlich. Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} unto phosphoric acid modified rice husk, *IOSR Journal of Applied Chemistry* 2012, 3, 38-45.
- [20] Banach M., Bukała A., Pulit-Prociak J., Staroń P., Equilibrium and kinetics of nanosilver sorption from aqueous solutions, *J. Nanosci. Nanotechnol.* 2016, 16, 7898-7909.
- [21] Md Ariff N.F., Megat Hanafiah M.A.K., Wan Ngah W.S., Adsorption of Cu(II) onto cross-linked chitosan coated bentonite beads: Kinetic and isotherm studies, *Key Eng. Mater.* 2017, 753, 243-248.
- [22] Ghaedi M., Sadeghian B. Amiri Pebdani A., Sahraei R., Daneshfar A., Duran C., Kinetics, thermodynamics and equilibrium evaluation of direct yellow 12 removal by adsorption onto silver nanoparticles loaded activated carbon, *Chemical Engineering Journal* 2012, 187, 133-141.
- [23] Freitas E.D., Carmo A.C.R., Almeida Neto A.F., Vieira M.G.A., Binary adsorption of silver and copper on Verde-lodo bentonite: Kinetic and equilibrium study, *Appl. Clay Sci.* 2017, 137, 69-76.
- [24] Constantino L.V., Quirino J.N., Monterio A.M., Abrão T., Parreira P.S., Urbano A., Santos M.J., Sorption and desorption of silver ions by bentonite clays, *Environmental Science and Pollution Research* 2017, 24, 11349-11359.
- [25] Zhirong L., Azhar Uddin M., Zhanxue S., FT-IR and XRD analysis of natural Na-bentonite and Cu(II)-loaded Na-bentonite, *Spectrochim. Acta Part A, Mol. Biomol. Spectrosc.* 2016, 79, 1013-1016.
- [26] Tomacheski D., Pittol M., Ferreira Ribeiro V., M. Campomanes Santana M.R., Efficiency of silver-based antibacterial additives and its influence in thermoplastic elastomers, *J. Appl. Polym. Sci.* 2016, 133, 1-10.
- [27] Tomacheski D., Pittol M., Simões D.N., Ribeiro V.F., Santana R.M.C., Effects of silver adsorbed on fumed silica, silver phosphate glass, bentonite organomodified with silver and titanium dioxide in aquatic indicator organisms, *J. Environ. Sci. (China)* 2017, 56, 230-239.