AGNIESZKA BOŻĘCKA*, STANISŁAWA SANAK-RYDLEWSKA*

SORPTION OF Cd^{2+} IONS FROM AQUEOUS SOLUTIONS ON ORGANIC WASTES

SORPCJA JONÓW Cd^{2+} Z ROZTWORÓW WODNYCH NA ODPADACH ORGANICZNYCH

This article presents the results of research on the Cd^{2+} ions sorption from model aqueous solutions on sunflower hulls, walnut shells and plum stones. The effect of various factors, such as mass of the natural sorbent, the pH, the time and the temperature was studied. The process of Cd^{2+} ions sorption on studied sorbents was described by the Langmuir model. The best sorption capacity has been achieved for sunflower hulls. The maximum sorption capacity for this material was 19.93 mg/g.

Keywords: Sorption, cadmium ions, organic wastes

W artykule przedstawiono wyniki badań, które dotyczyły usuwania jonów Cd^{2+} z modelowych roztworów wodnych za pomocą odpadów organicznych, takich jak: łuski słonecznika, łupiny orzecha włoskiego i pestki śliwek. Wykazano, iż badane materiały mogą być skutecznie wykorzystywane do usuwania jonów Cd^{2+} z modelowych roztworów wodnych w układach jednoskładnikowych.

Dla badanego zakresu stężeń i przyjętych warunków procesu sorpcji w układach jednoskładnikowych, największą wydajność sorpcji jonów Cd^{2+}, osiągnięto dla łuszczyn słonecznika. Wyniosła ona 81,75-93,02%. Dla pozostałych materiałów sorpcja jest nieco niższa, ale również zadowalająca.

W pracy podano interpretację otrzymanych wyników w oparciu o jeden z najpopularniejszych modeli izoterm adsorpcji − Langmuira, który potwierdził, iż najlepszym sorbentem jonów Cd^{2+}, spośród badanych, są łuszczyny słonecznika. Materiał ten cechuje się największą wartością parametrów q_{max} i b izotermy Langmuira. W tym przypadku stała q_{max}, wyrażająca pojemność monowarstwy, przyjęła wartość 19,93 mg/g, a parametr b, określający powinowactwo do usuwanych jonów wynosi 0,2264 dm^3/mg (Rys. 5, Tab. 1).

Udowodniono również, że proces sorpcji jonów Cd^{2+} na badanych sorbentach organicznych zależy od masy sorbentu. Dla wszystkich materiałów stopień usunięcia jonów Cd^{2+} z roztworów wodnych rośnie ze wzrostem masy sorbentu, aż do uzyskania maksimum przy naważe 0,5 g (Rys. 1).

Otrzymane wyniki potwierdzają ścisłą zależność między wartością pH oczyszczanych roztworów, a skutecznością usuwania jonów Cd^{2+} na badanych sorbentach. We wszystkich przypadkach maksimum sorpcji osiągnięto przy pH równym 4,0. Wydajność procesu sorpcji w roztworach o pH poniżej i powyżej 4,0 jest niższa (Rys. 2).

* AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, FACULTY OF MINING AND GEOENGINEERING, AL. A. MICKIEWICZA 30, 30-059 KRAKÓW, POLAND. CORRESPONDING AUTHOR: E-MAIL: gala@agh.edu.pl

Badania kinetyki sorpcji wskazują, iż równowaga badanych procesów ustala się po 60 minutach (Rys. 3).

Wykazano również, że dla wszystkich badanych materiałów, wraz ze wzrostem temperatury w zakresie od 293 K do 313 K następuje obniżenie ich zdolności sorpcyjnych (Rys. 4).

Słowa klucze: sorpcja, jony kadmu, odpady organiczne

1. Introduction

Non-ferrous metal ores, coal and phosphate minerals are a main natural source of cadmium in the nature (Kabata-Pendias & Pendias, 1999; Krzywy et al., 2010). But emissions of this element from natural sources are not a threat to the environment. The potential source of pollution are processes of raw materials processing and manufacturing of products containing cadmium. Increased concentration level of cadmium in the atmosphere occurs mainly in industrial areas, the source of which are metals industry and combustion of coal and oils.

This element coexists with lead and it accumulates in the dusts and sludges during the processing of zinc-lead ores. It is also used for the preparation of galvanic protective coatings, for the production of nickel-cadmium batteries, and cobalt catalysts. Cadmium is also used as a pigment in paints, dyes, varnishes. It is a stabilizer of plastics and component of many kinds of alloys (Krzywy et al., 2010; Ostrowska et al., 2008).

Cadmium gets to the surface water mainly from mine wastewater (Dojlido, 1995). Galvanized pipes may also be one of the causes of cadmium pollution in drinking water. According to the Ministry of Healthy Regulation the maximum concentrations of Cd in drinking waters can't be higher than 0.005 g/m^3 (Dz. U.07.61.417, 2007).

The main source of cadmium in soils are nitrogenous and phosphorus fertilizers. Their use leads to the accumulation of heavy metals in plants and also in the human body (Czeczot & Skrzycki, 2010). For example, ammonium sulfate may contain from 2 to 37 mg Pb/kg, and from 0.05 to 8.5 mg of Cd/kg (Jaworska, 2009).

Cadmium compounds gets into human body by ingestion and inhalation. Especially a lot of cadmium is absorbed by smokers (Seńczuk, 2005). Cereal products and vegetables may also contain cadmium compounds which are accumulated in the cells of the small intestine and they can get into the bloodstream from there. The liver is most exposed to the harmful effects of cadmium acute poisoning but in case of chronic poisoning, kidneys are the most vulnerable.

Considering the valency of cadmium, it may substitute elements such as iron, zinc, calcium, magnesium in the human body, which are necessary for its proper functioning. This element is placed by International Agency for Research on Cancer (IARC) in the group of carcinogenic elements (Czeczot & Skrzycki, 2010).

2. Aim of the study

The aim of this study was to experimentally confirm the possibility of using sunflower hulls (*Helianthus L.*), ground walnut shells (*Juglans regia L.*) and plum stones (*Prunus domestica L.*) for removing Cd^{2+} ions from aqueous solutions. For studied sorbents, the best physico-chemical parameters of the sorption process, such as sorbent mass, equilibrium time, pH and temperature of solutions, were selected and determined. The results obtained for sunflower hulls and plum

stones were compared to that of walnut shells which were published before (Gala & Sanak-Rydlewska, 2012).

3. Methods of the study

3.1. Preparation of sorbents

Sunflower hulls (*Helianthus L.*), walnut shells (*Juglans regia L.*) and plum stones without the kernels (*Prunus domestica L.*) were used for the study as natural sorbents. The sorption experiments were carried out on the fraction with a particle size below 0.5 mm. For the preparation of sorbents samples for studies, selected organic waste were washed, dried, crushed and sieved through appropriate sieve. Next, materials were purified (treatment with 10^{-3} mol/L mineral acids solutions, washing with reverse osmosis water until the pH attained that of pure reverse osmosis water (about 6.0)), and then dried in temperature up to 323K (Gala & Sanak-Rydlewska, 2010, 2011a, 2011b, 2012).

3.2. Study of the sorption process of Cd^{2+} ions from aqueous solutions

The effect of selected factors, such as sorbent mass, stirring time, pH of solution and temperature on the studied sorption process of Cd^{2+} ions from monocomponent aqueous solutions, was examined. Experiments were performed for all selected sorbents. They were based on placing a known mass of sorbent (sample weight from 0.3 g to 1.0 g) in the beakers with 100 mL solutions of cadmium(II). The range of the studied initial concentration of the Cd^{2+} ions was from 6.25 to 109.38 mg/L. Metal was introduced into the solution in the form of salt − $Cd(NO_3)_2 \cdot 4H_2O$ p.p.a. All experiments were performed at a fixed ionic strength value equal 0.02 mol/L. The ionic strength was controlled with a 0.04 mol/L solution of potassium nitrate (V). The pH was studied in the range from 2.0 to 5.0 (±0.1). For each solution, the pH value was measured before and after the experiment. The pH was controlled with a 0.02 mol/L solution of nitric acid.

The solutions with the sorbent were continuously stirred with a mechanical stirrer at 120 rpm at the constant temperature equal 298±0.5 K. The studies of temperature effect were performed for a range of 293 to 313±0.5 K. In all experiments, the samples for analysis were taken after one hour (in this time the system reached equilibrium) (Gala & Sanak-Rydlewska, 2010, 2011a, 2011b, 2012).

3.3. Used instrumental methods

The final concentration of Cd^{2+} ions in the solutions was determined by flow-through coulometry using EcaFlow 150 GLP apparatus manufactured by POL-EKO. Before measurements, all samples were filtered to remove solid particles. Three measurements were performed for each sample. The values of equilibrium concentrations shown in the tables are the arithmetic average of three measurements.

The sorption capacity was determined as the amount of metal ions contained in the dry weight of sorbent according to the concentration in the aqueous solution. It was calculated from

formula presented below:

$$Q = \frac{V(c_0 - c_{eq})}{m}$$

(1)

where:

Q — amount of the Cd^{2+} ions in mg per gram of the sorbent, mg/g,

V — is the volume of the solution, L,

c_o and c_{eq} — are the initial and final concentrations of Cd^{2+} ions, mg/L,

m — is the quantity of dry mass of the adsorbent, g.

4. Discussion of the results

4.1. The effect of the sorbent mass on the sorption of Cd^{2+} ions from aqueous solutions

The study of the sorption as a function of sorbent mass is shown in Fig. 1. The curves show that the highest sorption capacity of Cd^{2+} ions was obtained for sunflower hulls. It was 90.31-91.27%. For plum stones and the studied mass range from 0.3 g to 1.5 g of sorbent, the efficiency of Cd^{2+} ions sorption was in range from 73.46 to 78.25%. While, for walnut shells the reduction of Cd^{2+} in the solutions was 35.17-70.61%.

For all sorbents, the reduction degree of Cd^{2+} ions from the solutions increases with increasing of sorbent mass until it reaches a maximum at a sorbent mass of 0.5 g. Further increasing of mass of studied sorbents samples does not significantly modify the reduction degree of studied ions. This is most likely due to the phenomenon of aggregation of sorbent's particles in the solution, which can block the access of metal ions to functional groups on the sorbent surface (Uluozlu et al., 2008). Consequently, further study was continued at a sorbent mass of 0.5 g (Gala & Sanak-Rydlewska, 2010, 2011a, 2011b, 2012).

4.2. The effect of pH on the sorption of Cd^{2+} ions from aqueous solutions

The dependence of the sorption of Cd^{2+} ions efficiency as a function of pH, obtained for the sunflower hulls, walnut shells and plums stones is shown in Fig. 2. The obtained results confirm the close relationship between the pH of the treated solutions and the efficiency of Cd^{2+} removal on the studied sorbents. For all used materials, the sorption increases in pH range from 2.0 to 4.0, reaching a maximum at pH value 4.0 ($\pm$ 0.1) (Fig. 2). The value of this maximum was 92.93% for sunflower hulls, 70.43% for walnut shells and 76.02% for plum stones. While, in solutions with pH value 5.0 ($\pm$ 0.1) a significant reduction in sorption was observed for all studied materials.

Probably, the observed decrease in sorption in solutions at pH below and above 4.0, is connected with a different charge on the sorbents surface. The type and size of this charge depends on pH value of solutions and the functional groups present on the sorbent surface (e.g., carboxyl, hydroxyl groups) (Bansal & Goyal, 2009).

In more acidic solutions the studied sorbent surface is positively charged. The reason for this phenomenon is very strong functional groups protonation. Therefore, the studied metal cations
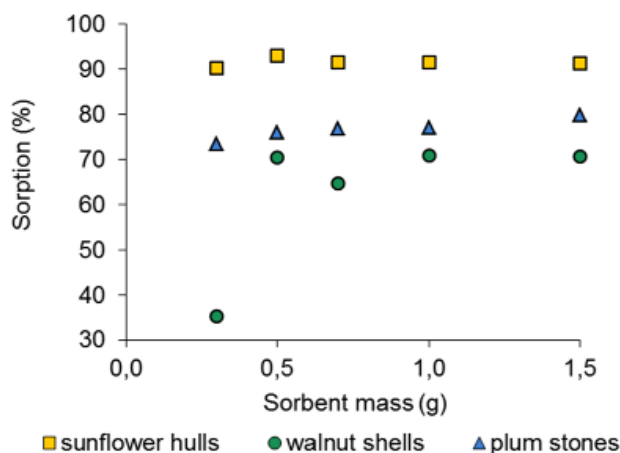
Fig. 1. The influence of the sorbent mass on the sorption of Cd^{2+} ions on sunflower hulls, walnut shells and plum stones (c_o = 15.63 mg/L; pH of 4.0±0.1; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; temperature (298±0.5) K; time of sorption 1 h; mixing speed 120 rpm.)
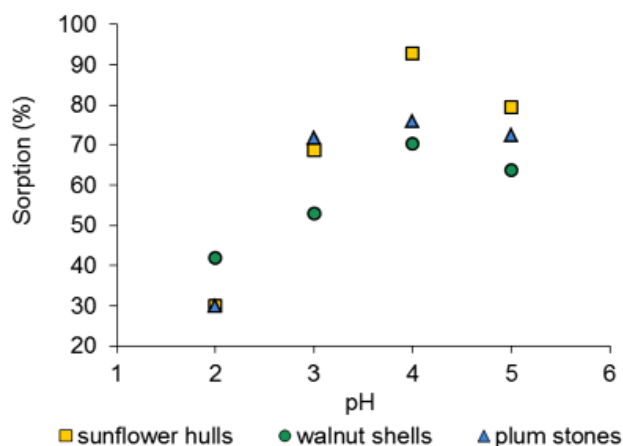

Fig. 2. The effect of pH on the sorption of Cd^{2+} ions on sunflower hulls, walnut shells and plum stones (c_o = 15.63 mg/L; sorbent mass 0.5 g; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; temperature (298±0.5)K; time of sorption 1 h; mixing speed 120 rpm.)

have limited access to the sorbents surface and this can lead to the reduction of the Cd^{2+} ions sorption due to the competitive interaction between metal ions and the hydrogen ions (due to electrostatic attraction forces) (Gala & Sanak-Rydlewska, 2010, 2011a, 2011b, 2012).

The gradual increase in the pH values causes the deprotonation of groups and thus the increasing of the sorption efficiency. When the sorbents surface is negatively charged due to the ionization of acidic groups, the electrostatic attraction between metal ions and the sorbents sur-

face occurs, which increases sorption. Additionally, with an increase of pH, the solution contains less hydrogen ions and the competition for Cd^{2+} ions decreases, thus increasing the efficiency of sorption process (Gala & Sanak-Rydlewska, 2010, 2011a, 2011b, 2012).

The pH value also determines the type and concentration of the studied ions in the solution. In highly acidic solutions, cadmium is present mainly in the form of cations. A gradual increase in pH leads to the formation of complex ions and precipitation of cadmium hydroxides.

4.3. The effects of contact time between the sorbent and solution on the sorption of Cd^{2+} ions from aqueous solution

In order to determine the time at which the studied systems reached equilibrium of adsorption, experiments of Cd^{2+} ions sorption were performed after 5, 15, 30, 45 and 60 minutes. Obtained results are shown in Fig. 3.

The kinetic study of sorption shows that, for all sorbents, the degree of removal of Cd^{2+} ions from solutions increases with the lengthening of the contact time between the sorbent and solution in the range from 5 to 45 minutes (Fig. 3). After 45 minutes no significant changes in the efficiency of Cd^{2+} ions sorption. So it can be concluded that the equilibrium of studied processes began to establish. It was also observed that for plum stones the system reaches equilibrium after 60 minutes. It is connected with a small difference (about 1%) between the sorption capacity after 45 and 60 minutes. Therefore, it was assumed that the equilibrium is determined after 60 minutes.
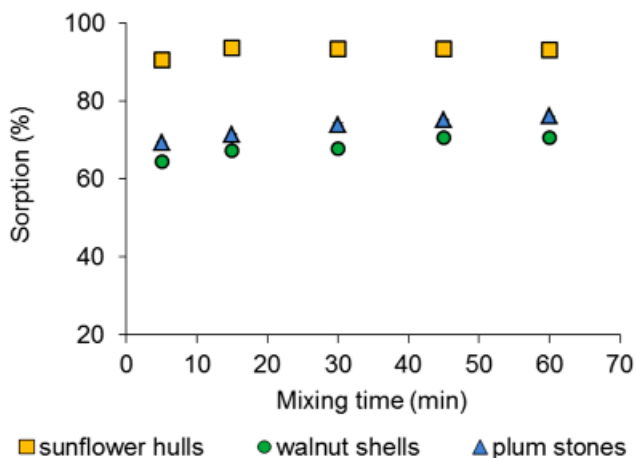

Fig. 3. The influence of the mixing time on the sorption of Cd^{2+} ions on sunflower hulls, walnut shells and plum stones (c_o = 15.63 mg/L; sorbent mass 0.5 g; pH of 4.0±0.1; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; temperature (298±0.5) K; mixing speed 120 rpm)

4.4. The effect of temperature on the sorption of Cd^{2+} ions from aqueous solution

In order to study the effect of temperature on Cd^{2+} sorption on selected sorbents, sorption experiments were performed in the range from 293 to 313K. Other conditions remained the same as in previous experiments.

For all sorbents it was observed that their sorption capacity decreases with the increasing of the temperature (Fig. 4). Such a result confirms the exothermic nature of studied processes. The observed decrease of sorption capacity may result from damage of active sites on the sorbents surface or the shift of the process equilibrium towards desorption of Cd^{2+} ions from the surface to the solution (Uluozlu et al., 2008). Moreover, the kinetic energy of the molecules increases at higher temperatures, which may hamper their attachment to the surface (Gala & Sanak-Rydlewska, 2010, 2011a, 2011b, 2012).
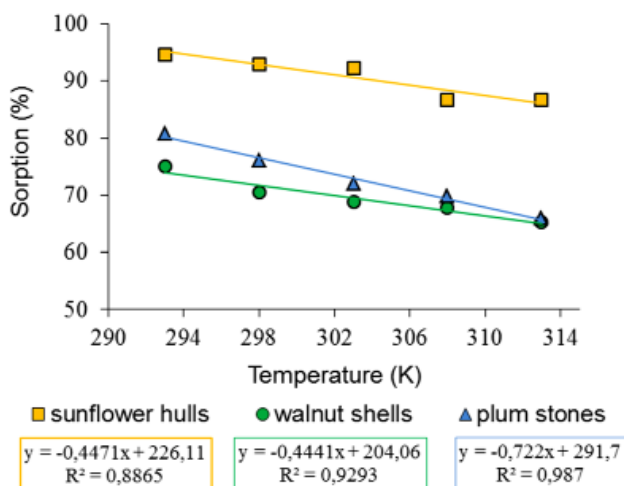
Fig. 4. The influence of the temperature on the sorption of Cd^{2+} ions on sunflower hulls, walnut shells and plum stones ($c_o = 15.63$ mg/L; sorbent mass 0.5 g; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; pH of 4.0±0.1; time of sorption 1 h; mixing speed 120 rpm.)

4.5. The interpretation of the results of Cd^{2+} ions sorption based on the Langmuir adsorption model

In order to determine the maximal sorption capacity of studied sorbents toward Cd^{2+} ions, the common Langmuir adsorption model was used.

Langmuir theory assumes that on the adsorbent surface there are specified quantity of adsorption centers, and each of them is able to adsorb only one molecule. Energy state of each adsorbed individual is the same in all places on the surface of the adsorbent. The localized adsorption takes place, which means that particles cannot move freely on the surface. This is the monolayer adsorption on the homogeneous surface. The obtained layer reduces the forces of

adsorption interaction preventing formation of subsequent layers (Bansal & Goyal, 2009; Pigoń & Ruziewicz, 1993; Ignatowicz, 2008).

This model is described by the following equation:

$$Q = \frac{q_{max} b \cdot c_{eq}}{(1 + b \cdot c_{eq})} \qquad (2)$$

where: q_{max} (mg/g) and b (L/mg) are Langmuir isotherm coefficients.

The parameter q_{max} is the maximum sorption capacity of the sorbent i.e. the maximum amount of metal ions needed to form a complete monolayer (Han at al., 2005). The constant b represents the energy of adsorption. This parameter is very useful, because it determines the sorbents affinity toward removed substances. The higher the value of the constant b the higher the affinity of the sorbent towards metal ions and the steeper the Langmuir isotherm. In general, a good sorbent should be characterised by a high value of both q_{max} and b constant (Davis et al., 2003; Meena et al., 2008; Gala & Sanak-Rydlewska, 2012).

The values of coefficients q_{max} and b in the Langmuir equation were determined based on the linear form of this isotherm:

$$\frac{1}{Q} = \frac{1}{q_{max} b} \cdot \left(\frac{1}{c_{eq}} + b \right) \qquad (3)$$

The results of the study described with the Langmuir equations were shown in Fig. 5. The values of coefficients q_{max} and b in the Langmuir equation were determined based on the linear form of these equations 3. All the parameters and their uncertainties were calculated using Microsoft EXCEL. The calculated values of adsorption isotherm coefficients and the correlation coefficients R are presented in table 1.
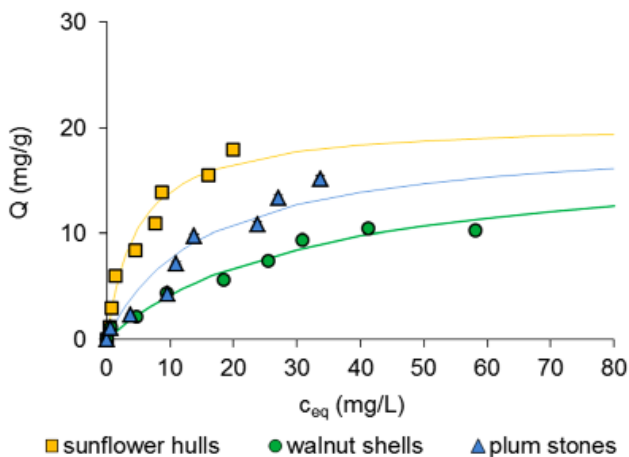

Fig. 5. Langmuir isotherms for Cd^{2+} ions adsorption on sunflower hulls, walnut shells and plum stones (sorbent mass 0.5 g; sorbent's particle size class < 0.5 mm; ionic strength 0.02 mol/L; pH of 4.0±0.1; time of sorption 1 h; temperature (298±0.5) K; mixing speed 120 rpm.)

Langmuir isotherms coefficients and their uncertainties

Studied material	q_{max} (mg/g)	Δq_{max} (mg/g)	b (L/mg)	Δb (L/mg)	R
Sunflower hulls	19.93	0.51	0.2264	0.0002	0.9869
Walnut shells	17.17	0.54	0.03272	0.00008	0.9485
Plum stones	17.98	0.39	0.0777	0.0001	0.9613

Analysis of the dependencies presented in Fig. 5 shows that the sorption capacity of the studied materials rapidly increases until the equilibrium adsorption is reached. The obtained results confirm that the sunflower hulls have the highest value of the parameter q_{max} equal 19.93 mg/g (Table 1, Fig. 5). Moreover, sunflower hulls are characterized by the largest affinity for Cd^{2+} ion, compared with the other studied materials. The constant b of the Langmuir isotherm has a value of 0,2264 L/mg for sunflower hulls. Walnut shells and plum stones show a slightly worse sorption capacity toward Cd^{2+} ions equal 17.98 mg/g and 17.17 mg/g, respectively. In turn, the value of the parameter b was 0.0777 L/mg for plum stones and 0,0327 L/mg for walnut shells. It follows that the walnut shell has the lowest affinity for Cd^{2+} ions.

5. Summary

Based on the performed experiences it can be concluded that:
1. Sorption of Cd^{2+} ions on the studied organic sorbents depends on the sorbent mass (regardless of the sorbent type).
2. It was shown that the best sorption of Cd^{2+} ions is at pH 4.0±0.1.
3. The study also showed that as the temperature increases (from 293 to 313 K) the sorption of Cd^{2+} ions gradually decreases for all studied sorbents.
4. Among studied materials, the sunflower hulls show the best sorption capacity toward Cd^{2+} ions. The sorption efficiency ranges from 82% to 93%.
5. The best values of the Langmuir isotherm parameters such as: the monolayer capacity (q_{max}) and the constant (b) represents the affinity of the sorbent towards Cd^{2+} ions, confirm the validity of the above statements.

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