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Utilization of Bentonite and Its Modification for Sorption

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1. Introduction

The problem of removing pollutants from water is an important process and is becoming more important with the increase of industrial activities. There are several methods to treat metal contaminated effluent. Adsorption is one of the more popular methods for the removal of heavy metals from wastewater. Low cost adsorbents are preferred in the purification process. For this reason, industrial wastes and mining by-products are used.

Bentonite is a raw material extracted during brown coal mining in the Czech Republic. Bentonite has optimal sorption properties for its use as an adsorbent. This approach ensures the improvement of the economic effectiveness of mining and helps prevent its accumulation in the environment.

Intercalation with octadecylamine in different weight ratios and natrification by 1M solution of sodium chloride were used for improving the sorption properties (the interlayer space, surface area, ion-exchange capacity) of bentonite sample.

Prepared materials – modified samples of bentonite and its raw form – were tested as potential adsorbents for heavy metals adsorption. This paper summarizes the results of lead and copper adsorption on a raw bentonite sample and its modifications. These samples were used for the adsorption of Pb^{2+} and Cu^{2+} from the synthetically prepared waste water.

2. Experiment

2.1. Materials and methods

A sample of bentonite from the Branany – Cerny Vrch locality was used for experiments. The X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses were carried out on an URD-6 (Freiberger Präzissionsmechanik/Seifer Roentgen) and a SPECTROSCAN MACK-GV, respectively. The specific surface area was measured by a GEMINI 2360 (Micrometrics).

This sample was physically treated by crushing and grinding, then sieved with the intention of obtaining two fractions: <0.1 mm and 0.1 – 0.5 mm. These two fractions (without chemical treatment) were measured as standards. Chemical treatment included a natrification (by 1M NaCl/100g of sample) and an intercalation (by octadecylamine – ODA). These treatments provided a change of the bentonite structure. Intercalations in different weight ratios were used: 100 g of sample and 75 g of ODA (1:0.75), 100 g of sample and 100 g of ODA (1:1) and 100 g of sample and 150 g of ODA (1:1.5). The specific preparation of the bentonite modifications can be seen in Fig. 1.

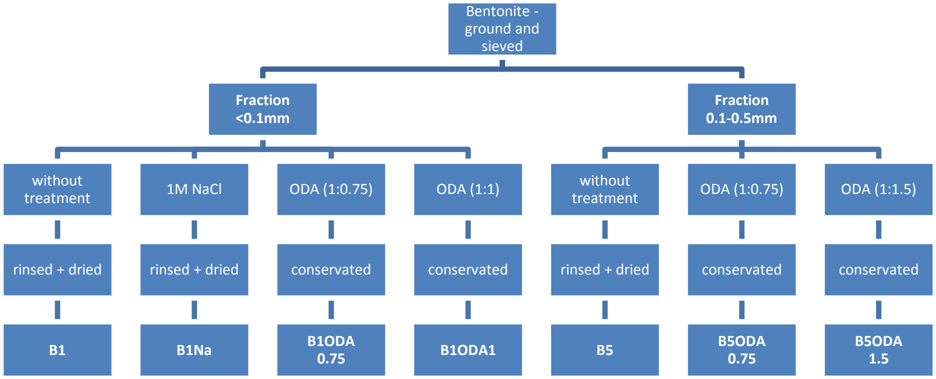

Fig. 1. Scheme of preparation of the bentonite modifications
Rys. 1. Schemat przygotowania modyfikacji bentonitu

2.2. Sorption studies

Batch sorption tests were conducted at temperature of 25 °C, by mixing 1.000 g of the sample of bentonite and modified bentonite with 50 mL of model solutions containing the desired concentration of heavy metal ions (Pb^{2+} and Cu^{2+}). The mixture was agitated in 80 mL polypropylene (PPE) plastic bottles in a tumbling mill at 120 rev./min for the time necessary to achieve an adsorption equilibrium and then filtered, using filter papers (Fluka, Germany). All the samples were analysed by Flame Atomic Absorption Spectrophotometer (FAAS) – Varian, Australia. Each experiment was carried out in duplicate and the average results are presented in this study.

The adsorbed metal concentrations were obtained from the difference between the initial (c_0) and final (c_r) metal concentration in the model solution. The percentage removal (E) was calculated as (1):

$$E(\%) = \frac{(c_0 - c_r)}{c_0}.100 \tag{1}$$

To study equilibrium of metal removal by bentonite, individual initial metal concentrations were determined. The required initial concentrations were 500, 1000, 1500, 2000 and 2500 mg Pb^{2+}/L and 300, 600, 900, 1200 and 1500 mg Cu^{2+}/L. All tests were conducted with constant agitation, with samples filtered and analysed by FAAS. The adsorption data can be interpreted using several relationships. The Langmuir (1) and Freundlich models (2) are commonly used to fit experimental data.

$$a = a_m \cdot \frac{b \cdot c_r}{1 + b \cdot c_r} \tag{2}$$

$$a = K \cdot c_r^{\frac{1}{n}} \tag{3}$$

where a is an adsorption capacity (mg/g), a_m is a maximal adsorption capacity (mg/g), b a Langmuir constant (L/mg), c_r a final concentration of the solution, K a Freundlich constant for characterising maximal adsorption capacity (L/g), n a Freundlich constant for characterising maximal intensity of adsorption.

3. Results and discussion

XRD analysis of the sample of bentonite showed that the main compound is a group of amorphous minerals 85.90% (there was counted also montmorillonite because the internal standard method was used; volcanic glass and organic fraction). The other compounds are quartz (8.33%), siderite (2.49%), anatase (1.91%) and calcite (1.41%). The basal diffraction of this sample was 15.25 Å.

The crystallochemical formula calculated after XRF analysis using base 10 structural O and 2 OH was:
$(Ca_{0.18}Na_{0.09}K_{0.08})(Al_{0.98}Fe_{0.54}Mg_{0.31}Ti_{0.11})(Si_{3.70}Al_{0.30})O_{10}(OH)_2 \cdot 7.72H_2O$.

The value of the specific surface area was 73.77 m^2/g.

The sorption equilibrium of Pb^{2+} for samples without chemical treatment (B1, B5) was achieved after 7 hours, for sample B1Na 5 hours and for samples after treatment with ODA after 3 hours. The sorption equilibrium of Cu^{2+} for modified samples was achieved in the same time as for Pb^{2+}. Samples B1 and B5 achieved the equilibrium at 12 and 9 hours, respectively.

The maximal metal decrease of Pb^{2+} and Cu^{2+} for each sample is shown in Fig. 2. In the case of Pb^{2+} adsorption the samples modified by ODA reached high values – maximal adsorption of Pb^{2+} from the metal solution was measured with using B1ODA0.75 (87.00%). The maximal adsorption of Cu^{2+} was seen in the sample B5ODA1.5 (92.57%). The best sample in fraction <0.1 mm was B1ODA1 where the maximal adsorption of Cu^{2+} was 85.94%.

Models of adsorption isotherms were constructed for understanding a mechanism of adsorption. Langmuir and Freundlich parameters were calculated by nonlinear regression using OriginPro 8. Final parameters of the isotherm models are shown in Tab. 1 and Tab. 2.

The maximum value of adsorption capacity Pb^{2+} calculated by the Langmuir model was detected by B5ODA1.5 (117.22 mg Pb^{2+}/g). Other samples modified by ODA also achieved high values of adsorption capacity of Pb^{2+}. A sample modified by natrification showed 76.99 mg Pb^{2+}/g, which represented a slightly higher value than a sample without modification – B1 (72.68 mg Pb^{2+}/g). The lowest value was calculated at sample B5 (62.03 mg Pb^{2+}/g). In conclusion all modifications contributed to the higher value of maximal adsorption.

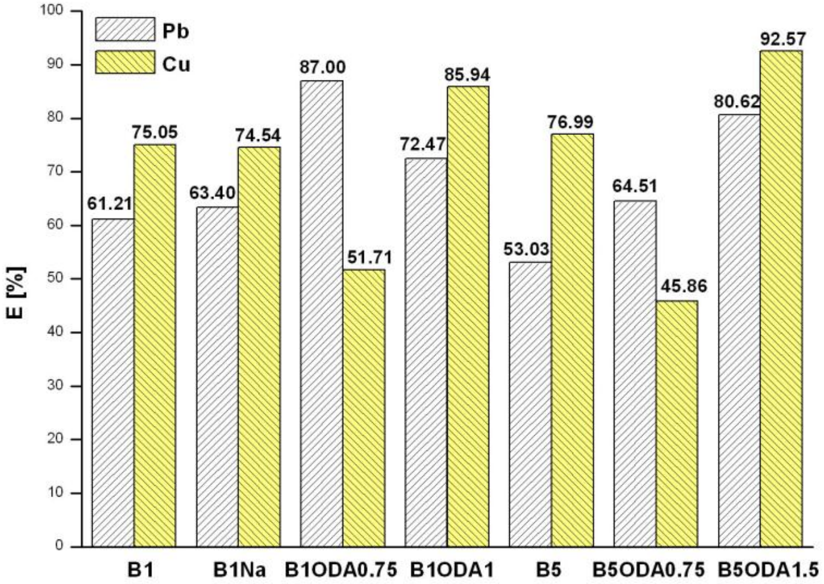

Fig. 2. The maximum metal decrease of Pb^{2+} and Cu^{2+} for bentonite samples
Rys. 2. Maksymalne obniżki Pb^{2+} and Cu^{2+} dla próbek bentonitu

Table 1. Final parameters of the adsorption isotherms Pb^{2+} for bentonite samples calculated by nonlinear regression
Tabela 1. Końcowe parametry izoterm adsorpcji Pb^{2+} dla próbek bentonitu obliczone za pomocą regresji nieliniowej

Sample	Parameters of adsorption isotherms					
	Langmuir			Freundlich		
	a_m	b	Correlation coefficient	K	1/n	Correlation coefficient
B1	72.68	0.15	0.79704	35.69	9.00	**0.99817**
B1Na	76.99	4.29	**0.99366**	43.52	10.49	0.95515
B1ODA0.75	97.15	0.06	0.86517	28.23	4.64	**0.96616**
B1ODA1	82.80	2.45	0.90136	44.54	9.06	**0.98339**
B5	62.03	0.11	0.90976	19.88	5.59	**0.97943**
B5ODA0.75	94.82	0.01	**0.96756**	11.94	3.38	0.88285
B5ODA1.5	117.22	0.01	0.89828	23.53	4.26	**0.95081**

Table 2. Final parameters of the adsorption isotherms Cu^{2+} for bentonite samples calculated by nonlinear regression
Tabela 2. Końcowe parametry izoterm adsorpcji Cu^{2+} dla próbek bentonitu obliczone za pomocą regresji nieliniowej

Sample	Parameters of adsorption isotherms					
	Langmuir			Freundlich		
	a_m	b	Correlation coefficient	K	1/n	Correlation coefficient
B1	50.44	2.02	0.93417	24.52	7.25	**0.94379**
B1Na	50.23	1.88	**0.95176**	24.36	7.22	0.94897
B1ODA0.75	1.37E6	3.94E-8	0.95344	0.01	0.83	**0.96444**
B1ODA1	62.62	13.98	**0.97743**	42.32	10.64	0.84872
B5	70.86	0.01	0.88607	10.10	3.51	**0.94863**
B5ODA0.75	772449.47	5.60E-8	0.92752	0.02	0.88	**0.93226**
B5ODA1.5	66.92	7.41	**0.97896**	42.66	8.54	0.85415

The values of maximal adsorption capacity of Cu^{2+} for samples B1ODA0.75 and B5ODA0.75 calculated by the Langmuir model showed an error. In this case these samples cannot be described by the Langmuir model. Taking into consideration the other samples the maximum value of adsorption capacity Cu^{2+} calculated by the Langmuir model was detected by B5 (70.85 mg Cu^{2+}/g). Samples modified by ODA – B1ODA1 and B5ODA1.5 – achieved values of 62.62 mg Cu^{2+}/g and 66.92 mg Cu^{2+}/g, respectively. Samples B1 and B1Na were calculated with the same values (50.44 mg Cu^{2+}/g and 50.23 mg Cu^{2+}/g, respectively). In conclusion, only modification by ODA contributed to the higher value of maximal adsorption. No increase of this value was observed in the sample modified by natrification.

Correlation coefficients showed a suitability of the Langmuir or Freundlich isotherm models. For adsorption of Pb^{2+} the Langmuir model fitted the B1Na and B5ODA0.75 samples and the Freundlich model fitted the B1, B1ODA0.75, B1ODA1, B5 and B5ODA1.5 samples. For adsorption of Cu^{2+} the Langmuir model fitted the B1Na, B1ODA1 and B5ODA1.5 samples and the Freundlich model fitted the B1, B1ODA0.75, B5 and B5ODA0.75 samples. The most suitable isotherms for adsorption of Pb^{2+} and Cu^{2+} are constructed in Figs. 3 and 4 respectively. Using different models of isotherms showed that there were different types of adsorption process; to understand the process of the adsorption mechanism other analyses will be carried out – determination of the iodometric number, ion exchange capacity etc. – and this will explain the behaviour of the modifications of the bentonite samples.

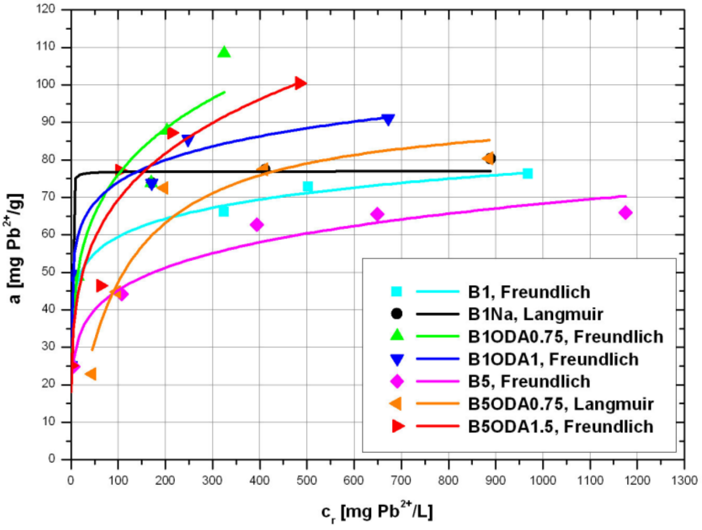

Fig. 3. The most suitable models of isotherms for adsorption of Pb^{2+} for bentonite samples

Rys. 3. Najbardziej pasujące modele izoterm adsorpcji Pb^{2+} dla próbek bentonitu

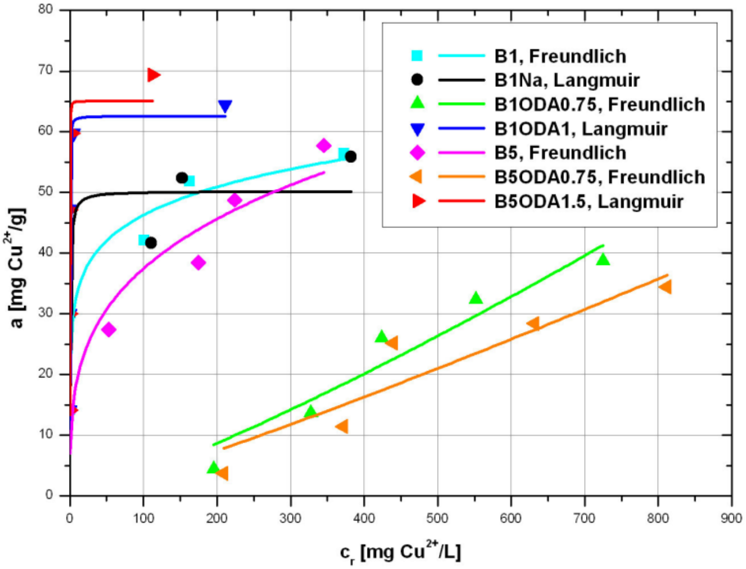

Fig. 4. The most suitable models of isotherms for adsorption of Cu^{2+} for bentonite samples

Rys. 4. Najbardziej pasujące modele izoterm adsorpcji Cu^{2+} dla próbek bentonitu

4. Conclusions

The experiments have shown that bentonite from the Branany – Cerny Vrch locality and its modifications are suitable for the adsorption of Pb^{2+} and Cu^{2+}. Sorption properties were affected by the action of chemical reagents – ODA and the 1M NaCl solution. After modelling the isotherms it has been found that the best sorption values for adsorption of Pb^{2+} were shown by the B5ODA1.5 sample and for adsorption of Cu^{2+} were shown by the B5 sample.

It is significant that bentonite as an associated raw material extracted during brown coal mining can be used for adsorption. An effort to utilize raw materials more effectively is still important.

Acknowledegements

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Zastosowanie bentonitu i jego modyfikacji do procesu sorpcji

Streszczenie

Badania dotyczyły możliwości usuwania jonów Pb^{2+} and Cu^{2+} z roztworów wodnych w procesie sorpcji na bentonicie oraz możliwości modyfikacji tego procesu. Próbki bentonitu pochodziły ze złoża Branany – Cerny Vrch w Republice Czeskiej. Próbki składały się głównie z montmorylonitu, kwarcu i syderytu; właściwości sorpcyjne były modyfikowane w procesie interkalacji (kompleksowanie za pomoca octadecylaminy) oraz za pomoca 1M NaCl. Dla opisu procesu sorpcji wykorzystano modele Langmuira i Freundlicha opisując izotermy sorpcji Pb^{2+} i Cu^{2+} na próbkach bentonitu surowego i modyfikowanego.