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Sorption of cadmium (II) from aqueous solution by magnetic clay composite

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ABSTRACT

The objective of this work is to compare the removal of cadmium (II) by the natural bentonite and composite, prepared by magnetic modification of the clay. Both, the bentonite and the composite material were characterized with the aim to describe their structural and surface properties by the X-ray diffraction, FE–TEM method and low nitrogen adsorption method. The surface charge of the materials was studied by the zeta potential measurement. The sorption properties were examined under the different conditions such as pH of the model solutions, contact time and initial metal ion concentration. The optimal pH for the removal of cadmium (II) was found equal 5. The equilibrium data was analyzed using the linearized Langmuir isotherm. The maximum adsorption capacities obtained from the sorption experiments realized in initial concentration range 10–750 mg L^{-1} were 61.35 and 63.29 mg g^{-1} for the bentonite and composite, respectively. Refining the initial metal concentration range to 1–10 mg L^{-1}, the sorption efficiency of composite achieved more than 98%.

Keywords: Natural bentonite; Composite material; Cadmium (II); Sorption

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1. Introduction

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous also at low concentrations. Examples of heavy metals include mercury, cadmium, arsenic, chromium, thalium and lead. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air.

Cadmium is a natural, usually minor constituent of surface and groundwater. It may exist in water as the hydrated ions, as inorganic complexes such as carbonates, hydroxides, chlorides or sulphates, or organic complexes with humic acids. Cadmium enters to fresh waters from industrial sources and is rapidly adsorbed by particulate matter, and later is emitted to the aquatic environment from the sediments. Rivers containing excess of cadmium can contaminate surrounding land, either through irrigation for agricultural purposes, dumping of dredged sediments or flooding. It has also been demonstrated that rivers can transport cadmium for considerable distances, up to 50 km, from the source.

The toxicological properties of cadmium are derived from its chemical similarity to zinc an essential micronutrient for plants, animals and humans. It is biopersistent and, once absorbed by an organism, remains resident for many years (over decades for humans)

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although it is eventually excreted. In humans, long-term exposure is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer. Cadmium may also produce bone defects in humans and animals.

Some naturally occurring clay minerals may serve as cost-effective sorbents for the removal of heavy metals. In spite of their lower sorption capacity with respect to the synthetic sorbents, these materials could provide an inexpensive substitute for the treatment of waste waters. To enhance their sorption capacity, the clays are modified in various ways, such as acidic treatment [1–3], treatment by inorganic or organic compounds, intercalation and pillaring [4–8].

In the last decades the interest of the scientists is aimed at the synthesis of magnetic nanoparticles due to their wide utilization for example in magnetic fluids [9], bionanocomposites [10] and in remediation of oil spill [11]. Surface decoration of the aluminosilicate minerals with different metallic, semiconducting or magnetic nanoparticles had led to a new class of composite materials [12,13], which could be also used for the environmental purposes [14,15].

This article deals with the composite material prepared by magnetic modification of the natural clay used as a potential sorbent of cadmium (II). Bentonite, known for its good sorption properties was used as a support material for iron oxides precipitation. The influence of the parameters such as pH, contact time, sorbent dose and initial metal ion concentration on the sorption process was investigated. The Langmuir isotherm model was used to evaluate the equilibrium adsorption data.

2. Materials and methods

2.1. Sorbents

The natural bentonite originated from Jelšový potok (Slovakia) was treated by the sedimentation method [16] with the aim to obtain almost monomineral fraction of the montmorillonite with particle size below 20 μm. The composite material was prepared by the method of precipitation of the iron oxide on the bentonite surface from the solution of ferrous and ferric salts ($Fe^{2+}/Fe^{3+} = 0.5$) in acidic condition by continuous stirring for 0.5 h in the nitrogen atmosphere at the ambient temperature [17]. The natural bentonite was added to the solution shortly before the precipitation of iron oxide particles by NH_4OH. The weight ratio of the bentonite to the synthesized iron oxide was 5:1. The final product was washed with water several times to remove free ions. To interpret reliably the changes in the structure and surface of the composite material, the pure iron oxide particles were also synthesized by the same reaction.

2.2. Structural and surface properties

Powder X-ray diffraction (XRD) patterns were collected using a PW1820 diffractometer (Philips, The Netherlands) equipped with a CuKα radiation (40 kV, 40 mA). The JCPDS PDF database was used for the phase identification.

Morphology of the composite sample was observed by the scanning electron microscope (SEM) of type JSM-6400 (JEOL Ltd., Japan) and field-emission scanning transmission electron microscope (FE–STEM) of type JEM-2100F (JEOL Ltd., Japan).

Adsorption and desorption isotherms were measured with the Micrometrics ASAP 2400 apparatus (USA) by the method of physical adsorption of nitrogen at 77 K. Experimental data were processed by the BET (Brunauer, Emmett, Teller) isotherm [18] in the range of relative pressure 0.05–0.2 p/p_0. The micropore volume V_{micro} and the external surface area S_t were calculated from the t-plot method using Harkins-Jura standard isotherm [19,20]. The value of total pore volume V_a was estimated from the maximum adsorption at relative pressure close to the saturation pressure. The pore size distribution was obtained from the BJH (Barret–Joyner–Halenda) method [21].

2.3. Electrokinetic measurements

The surface charge of the natural bentonite, composite material and synthesized iron oxides dispersed in distilled water was evaluated as a function of pH by using the laser-Doppler electrophoretic light scattering (ZetaPlus, Brookhaven Instruments, USA). To modify the pH of the dispersions, concentrated NaOH and HCl solutions were added in water dropwise. The measured ELS spectra were analyzed and electrophoretic mobilities of the dominant peaks were converted into zeta (ζ) potentials according to the Smoluchowski formula (i.e. without any other corrections). This is applicable for relatively coarse particles of bentonite whose size (of faces) exceeds their double-layer thickness (inverted Debye length). However, the nanometric iron oxide particles were also expected to be of the same concern due to their spontaneous agglomeration (no special care was taken in this respect). The same is true for the composite sample.

2.4. Metal solutions

All the reagents used in this study were of the analytical grade. A $Cd(NO_3)_2$ solution was used in the

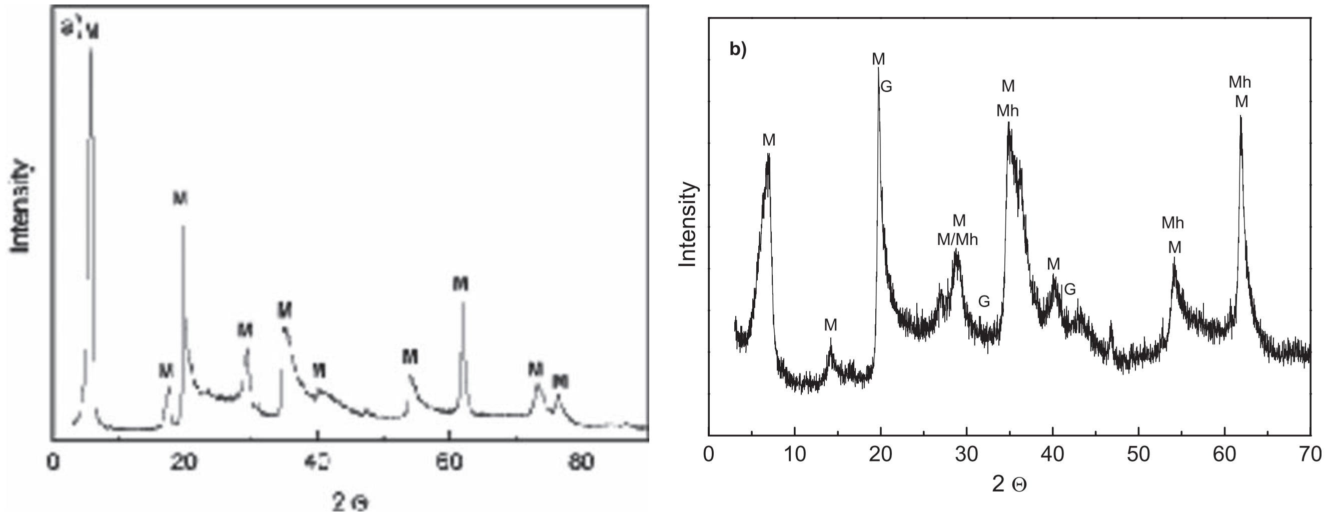

Fig. 1. (a) XRD pattern of the natural bentonite (M – montmorillonite) and (b) XRD pattern of the composite material (Mh – maghemite, G- goethite).

batch experiments. Different concentrations between 1 and 700 mg L^{-1} were prepared. The pHs of the solutions were adjusted by adding diluted NaOH and HCl solutions.

2.5. Experimental methods

Different pH solutions (from 2 to 9) were used to study the pH effect on the sorption capacity for both sorbents. The initial metal ion concentration (C_0) for this experiment was 100 mg L^{-1} and sorbents concentration (m_s) was 2 g L^{-1}. The stability of the iron oxide particles in the composite material during this sorption process was studied, too.

Kinetic study was carried out in different time intervals during 100 min.

A volume of 15 cm^3 of cadmium solutions with 0.015 g of the sorbents was placed into a plastic tube to start the experiments. The initial metal ion concentration of model solutions ranged among 10–700 mg L^{-1}, then 1–50 mg L^{-1} and finally 1–10 mg L^{-1}. The batch adsorption experiments were conducted at pH 5. The stirring speed was 30 rpm during the test at the room temperature. The experiments were completed after 24 h.

A quantitative analysis of cadmium in solution was made by the atomic absorption spectroscopy (AAS, Varian 240 RS/2400). The linearized Langmuir model was used for the analyses of the sorption isotherms.

Finally, the stability of the adsorbed metal on the composite material was tested using desorption during the 24 h period.

3. Results

3.1. Structural and surface properties

The XRD measurement of the natural bentonite confirmed the dominant montmorillonite phase in the sample, Fig. 1a. Phase analysis of the composite material showed besides the montmorillonite the presence of two Fe oxidized phases in the sample: maghemite, γ-Fe_2O_3, and goethite, α-FeOOH, Fig. 1b [22].

A detail of the morphology of the composite material observed by SEM is shown in Fig. 2a. The COMPO mode was used for the separation of the composition contrast, Fig. 2b, where white spots points to the presence of the iron oxide particles covering the bentonite surface. FE-STEM (Fig. 3a) shows the general morphology of the agglomerates created by the maghemite particles, which carry, locally, needle-like particles of goethite, noticed at high magnification (Fig. 3b).

The surface properties were also studied by the low temperature nitrogen adsorption method. Hysteresis loop between the adsorption and desorption branches of the investigated samples is an evidence of the presence of mesopores in the structures of the natural bentonite and composite. Hysteresis loop observed for the pure iron oxide is similar to type H1, according to the IUPAC report [23], which is typical for materials with tendency to create agglomerates and the loop is a result of additional sorption process into the interparticles space. Due to the presence of the iron oxide particles, higher volume of the adsorbed gas is observed for the composite material than for the natural bentonite in the

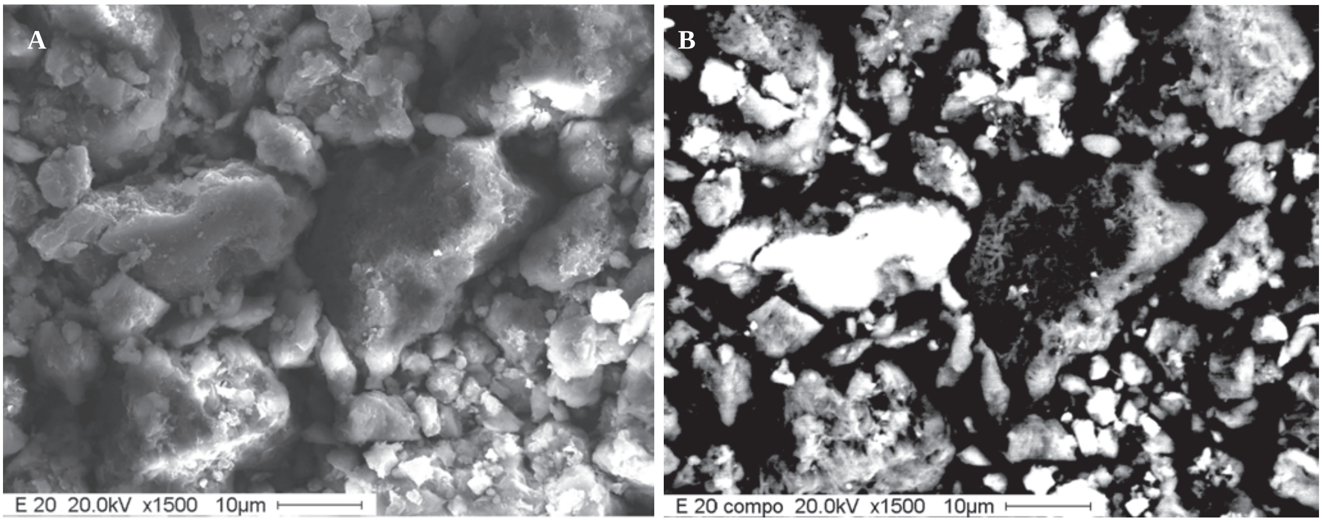

Fig. 2. (a) Morphology of the composite sample observed by SEM. (b) COMPO mode used for the separation of the composition contrast of the composite sample.

whole range of p/p_0, Fig. 4. The shape of the final parts of the adsorption isotherms of the bentonite and composite is related to the occurence of macropores.

It can be seen in Table I, that S_{BET} value of the composite material is more than twice higher in comparison to that of bentonite. The value of the micropore volume for composite material is lower than for natural bentonite (Table 1), probably due to restrained access of the nitrogen molecules into some of micropores filled by the agglomerated iron oxide nanoparticles.

Pore size distribution of the investigated samples obtained from the desorption isotherms by the BJH method confirmed their mesoporous character, Fig. 5. For the composite material, an increase of the adsorbed volume in the range 2–50 nm was observed, what is an evidence of the agglomerated particles precipitated on the bentonite surface.

3.2. *ζ-potential determinations*

The ζ-potential of bentonite, iron oxides and composite as a function of pH is shown in Fig. 6. Apparently the particles of the natural bentonite are almost constantly negatively charged. The only exception is a rather abrupt increase in the negative ζ value between pH 6 and 7. There is no isoelectric point, as it is usual for the most montmorillonites [24]. On the

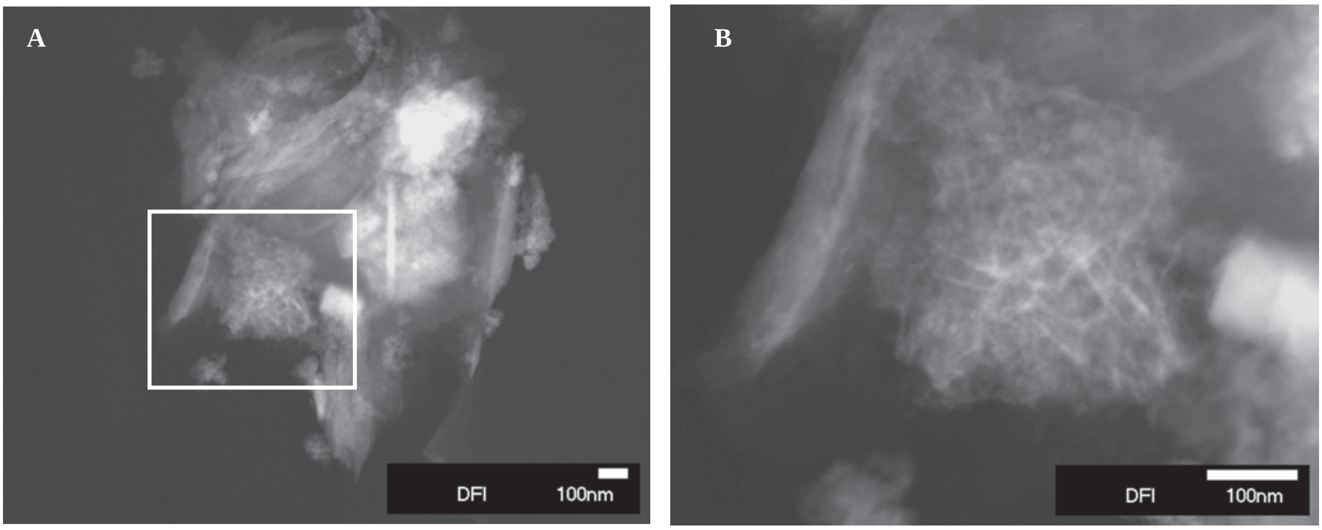

Fig. 3. FE-STEM micrographs exhibiting: (a) the morphology of the composite sample, (b) needle-like particles. The latter are seen in a close-up of the marked area of a.

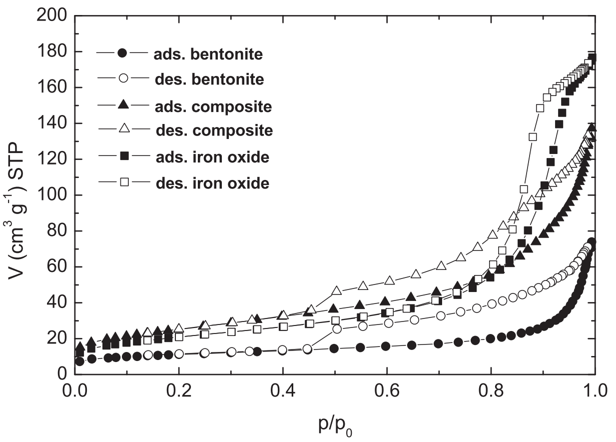

Fig. 4. Adsorption and desorption isotherms of the investigated samples obtained from the plot of adsorbed volume of the nitrogen to the relative pressure.

other hand, the iron oxide particles manifest two isoelectric points, at pH 5.07 and 5.67. This phenomenon is possibly connected with a low concentration of the particles in the dispersions prepared for the electrokinetic experiments. Fig. 6 shows that the electrokinetic response of the composite, being characterized by a net negative charge (ζ above−15 mV) at all pHs, is the lowest in comparison to the natural bentonite and synthesized iron oxide in the range of pH from 4.5 to 6.5.

3.3. Effect of pH

Batch equilibrium studies were carried out at different initial pH values ranging from 2 to 9. The results presented in Fig. 7a showed that stable uptake of Cd(II) was observed in the range of pH from 4.5 to 6, at initial metal ion concentration 100 mg L^{-1} and sorbent dose 2 g L^{-1}. In solutions with higher pH (pH 8 and 9), the sorption capacity of sorbents increased, due to the precipitation of $Cd(OH)_2$ [25], what was also observed using different sorbents like dead tea fungus [26] or sulphuric acid-treated wheat bran [27]. It followed from Fig. 7a and zeta potential measurement that the optimal pH for the sorption experiments is equal 5. The same pH of the solution was chosen for the Cd(II) removal by the iminodiacetate chelating resins [28]. Fig. 7b shows the good stability of the composite material in solutions with pH higher than 4.

Table 1
Surface parameters of the investigated samples obtained from the low temperature nitrogen adsorption method

Sample	S_{BET} [m^2 g^{-1}]	V_a [cm^3 g^{-1}] STP	V_{micro} [cm^3 g^{-1}] STP	S_t [m^2 g^{-1}]
Bentonite	39.44	0.096	0.006	25.43
Composite	90.68	0.187	0.002	84.23

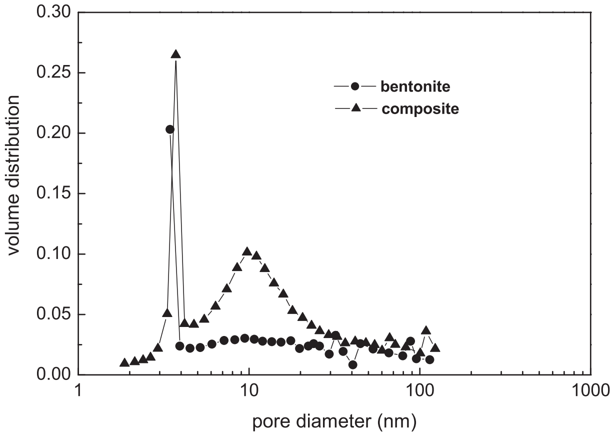

Fig. 5. Pore size distribution of the natural bentonite and composite material.

3.4. Adsorption kintetics

The kinetics of the Cd(II) sorption on the bentonite and composite material was studied during 100 min. The metal uptake was analyzed in eight different time intervals, Fig. 8a.

Bedoui et al. presented in their work, that the contact time for the Cd(II) sorption equilibrium on the pure clay was 6 h and for the ion exchange resin Lewatite S 100 2 h [29]. It followed from the Fig. 8a that the amount of removed Cd(II) by the composite is almost stable in the whole studied time interval. The amounts of adsorbed ions q_t for bentonite fluctuate during the first minutes of the sorption. It can be observed that the maximum adsorption capacity was achieved after 40 min for both sorbents.

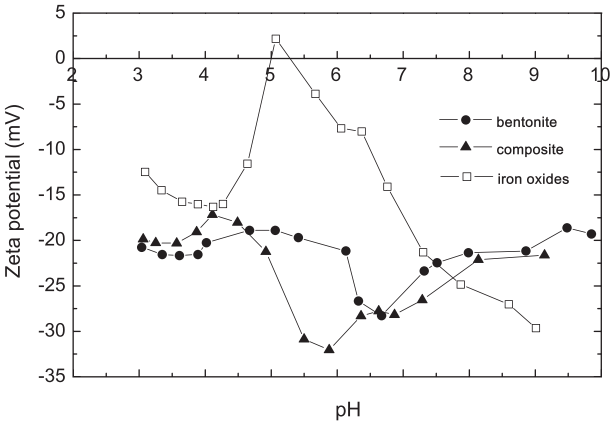

Fig. 6. ζ vs. pH dependence of bentonite, iron oxide and composite.

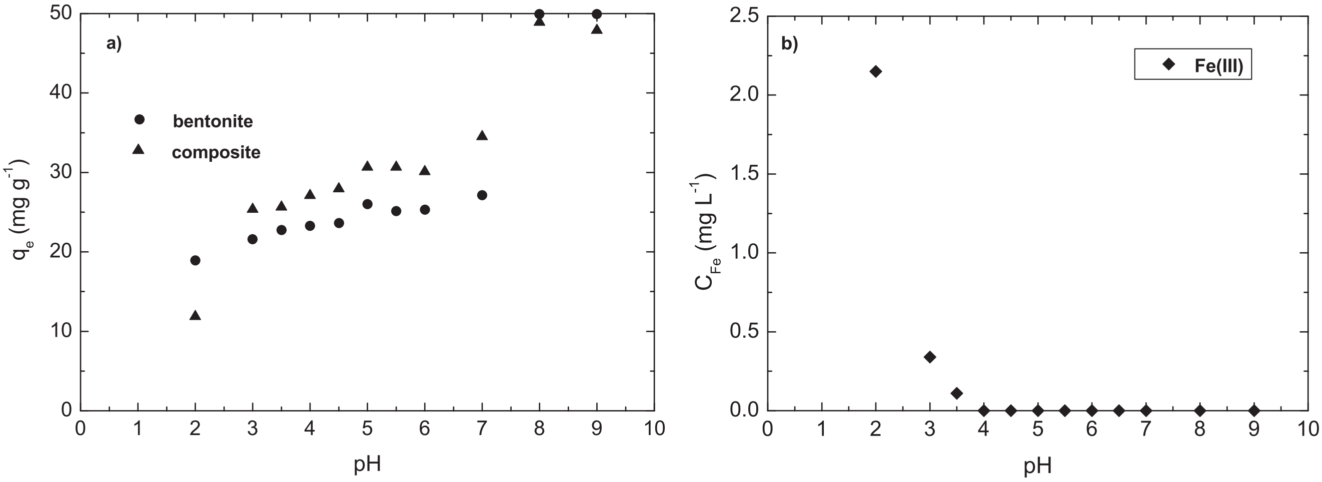

Fig. 7. (a) Effect of pH on Cd(II) ions removal by the natural bentonite and composite material. Initial metal ion concentration 100 mg L^{-1}and sorbents dose 2 g L^{-1}. (b) Stability of iron oxide particles in the composite material in dependence on pH of the solution (C_{Fe} – concentration of Fe(III) in the solution).

To analyze the kinetics of the sorption, some models have been studied. It was found that the pseudo first-order kinetic model is not suitable to describe the adsorption system (not shown here). Therefore the pseudo-second-order model was used to interpret the experimental data:

$$\frac{t}{q_t} = \frac{1}{k\,q_e^2} + \frac{1}{q_e}\,t,$$

where q_e and q_t are the amounts of metal ions adsorbed per unit mass (mg g^{-1}) at equilibrium and at any time t, respectively, k is the rate constant for the adsorption process (g mg^{-1} min^{-1}) [30].

The plots of the applied model to the experimental data are shown in Fig. 8b. The kinetic parameters for cadmium sorption on bentonite and composite material are given in Table 2. These results indicate that the sorption is governed by the pseudo-second order reaction and the rate limiting step may be a chemical sorption.

It follows from Table 2 that the cadmium sorption on composite is more favourable than on bentonite.

3.5. *Effect of initial metal ion concentration*

The batch type experiments with natural bentonite and composite material were conducting using the metal ion solutions ranging from 10 to 700 mg L^{-1} at pH 5. Sorbent dose was 1 g L^{-1}. The sorption

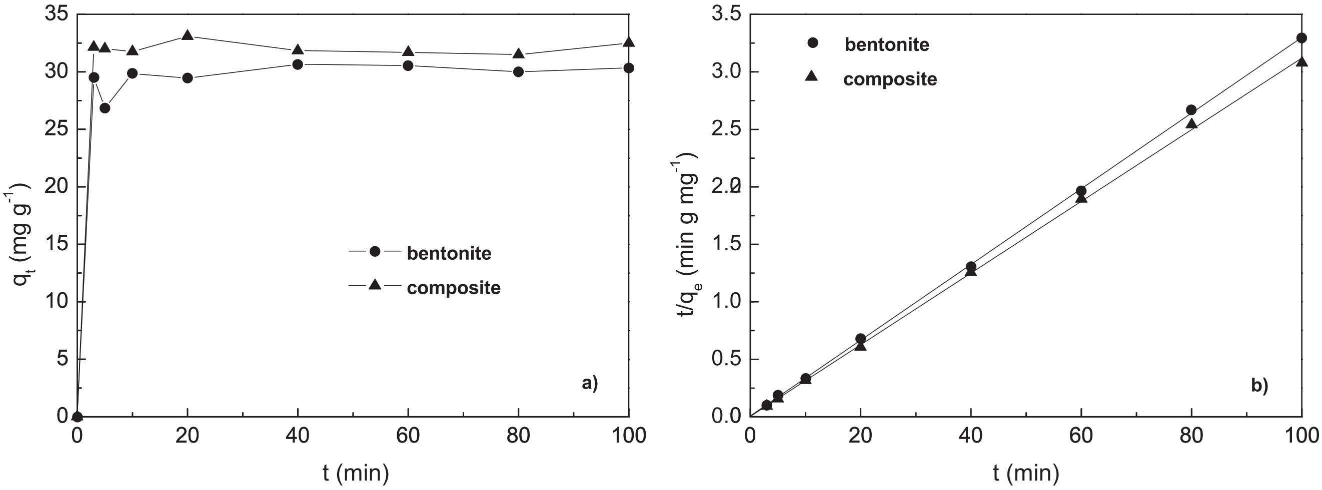

Fig. 8. (a) Amount of cadmium removed by the bentonite and composite material versus time. Initial metal ion concentration 100 mg L^{-1}, sorbent dose 1 g L^{-1}and initial pH 5. (b) Pseudo-second-order kinetic plots for the adsorption of cadmium (II) onto bentonite and composite material.

Table 2
Kinetic parameters of pseudo-second-order model for the adsorption of cadmium (II) onto bentonite and composite material

Sample	k [g mg^{-1} min^{-1}]	q_e [mg g^{-1}]	R^2
Bentonite	0.124	30.40	0.9998
Composite	0.487	32.05	0.9995

equilibrium was reached for initial concentration $C_0 >$ 400 mg L^{-1}, Fig. 9.

3.6. Adsorption isotherms

Analyses of the equilibrium data were done using linearized adsorption Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0},$$

where C_e and q_e are equilibrium solute concentration and equilibrium adsorption capacity, respectively, Q_0 is Langmuir constant representing maximum adsorption capacity (amount of adsorbed metal ions per 1 gram of sorbent) and b is sorption equilibrium constant [31].

The calculated Langmuir constants are presented in Table 3. Higher value (63.291 mg g^{-1}) was obtained for the composite material. The coefficients of determination R^2 suggested that the Langmuir linearized model is very suitable for fitting, Fig. 10.

3.7. Effect of low initial metal ion concentration

Different adsorption rates of natural bentonite and composite material apparent at low concentrations (Fig. 9) evoked the further study of the sorption efficiency at lower C_0 concentrations: 1–50 mg L^{-1} and finally 1–10 mg L^{-1}.

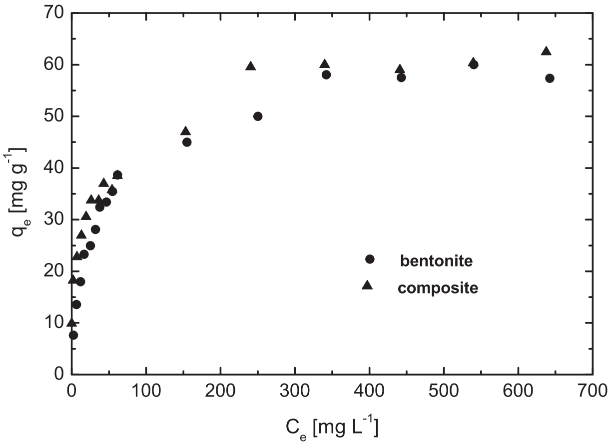

Fig. 9. Comparison of the sorption isotherms of Cd(II) ions on the natural bentonite and composite material. Initial metal ion concentration range 10–700 mg L^{-1}, sorbents dose 1 g L^{-1}, initial pH 5, contact time 24 h.

Table 3
Langmuir constants for sorption of Cd(II) by the natural bentonite and composite material

Sample	Q_0 [mg g^{-1}]	b [L mg^{-1}]
Bentonite	61.350	0.030
Composite	63.291	0.042

Removal of heavy metals at low concentrations from aqueous environment is generally difficult. In very low metal concentrations, processes such as precipitation (addition of a base to precipitate hydroxides) are not adequate and sufficient [32]. Due to the complexation with inorganic and organic ligands of the water, the final dissolved concentrations are above those expected according to the thermodynamic solubility products of the precipitates [33]. On the other hand, sorption on the commercially activated carbon is effective, but very expensive [34].

The batch type experiments were realized at pH 5 and sorbents dose 1 g L^{-1}. It could be seen in Fig. 11 that equilibrium adsorption capacities q_e of the composite material are higher in the whole investigated concentration range in comparison to the bentonite. The next experiment, Fig. 12, conducted in concentration range 1–10 mg L^{-1} showed, that the efficiency of composite material is 98.7%, while of bentonite is 80.9%.

3.8. Desorption experiment

The composite sample with adsorbed metal ions (approx. 30 milligrams of Cd(II) per 1 gram of the sorbent) was put into the distilled water with the pH

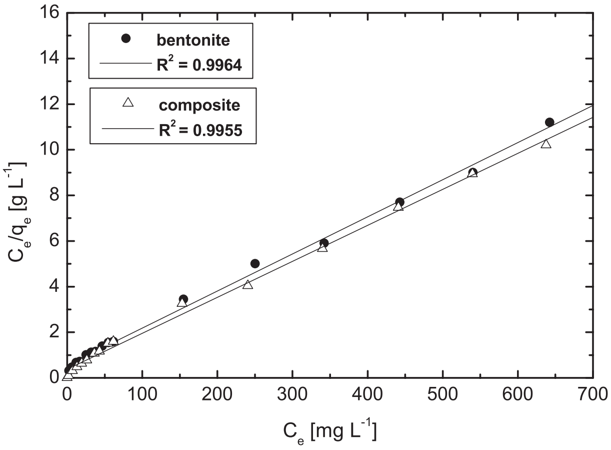

Fig. 10. Linearized Langmuir adsorption isotherms of Cd(II) ions on the natural bentonite and composite.

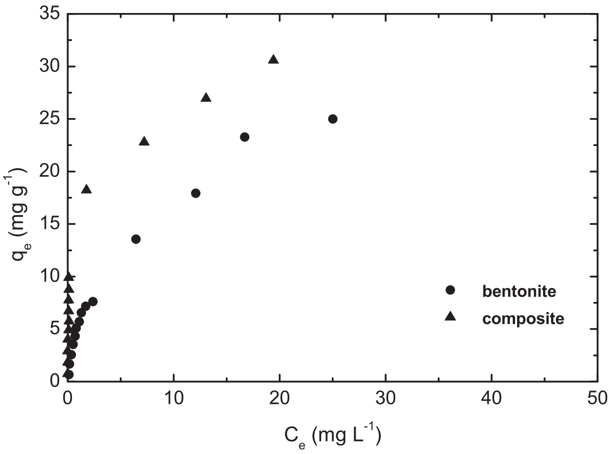

Fig. 11. Comparison of the sorption isotherms of Cd(II) ions on the natural bentonite and composite material. Initial metal ion concentration range 1–50 mg L^{-1}, sorbents dose 1 g L^{-1}, initial pH 5, contact time 24 h.

adjusted by addition of diluted nitric acid (0.01 M) to the value equal 5. Three takings of the solution after 20 min, 2 and 24 h were done and the amount of the dissolved metal was determined by the AAS method. It was found, that the sorbent with the adsorbed metal is well-stable, only approx. 1 milligram of Cd(II) ions was dissolved in 1 liter of the solution.

4. Conclusion

In this work the possibility to use the magnetically modified bentonite for removal of cadmium (II) from aqueous solutions is presented. The structural and surface study showed that the surface properties of the composite were affected by the precipitation of maghemite and goethite in the agglomerated form.

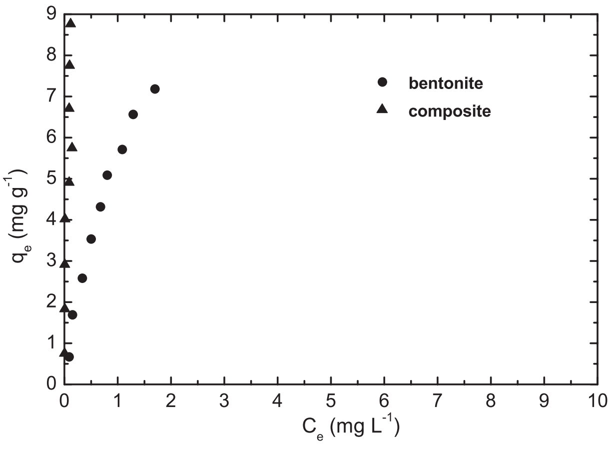

Fig. 12. Sorption of Cd(II) ions on the natural bentonite and composite material in the low initial metal ion concentration range 1–10 mg L^{-1}, sorbents dose 1 g L^{-1}, initial pH 5, contact time 24 h.

The composite showed higher adsorption capacity as compared with the bentonite. The adsorption of cadmium (II) was found to depend on the pH of the solution as well as the concentration of ions. The highest efficiency of the composite material was observed at low ion concentrations from 1 to 10 mg L^{-1}. The desorption experiments pointed to the good stability of the composite sorbent.

From the obtained results it can be stated that the composite material should be convenient in disposal of metals from aqueous solution, where its concentration is very low, but still harmful, as well as for the final purification of pre-treated waste waters.

The magnetic properties of the composite can be utilized at easy separation of the sorbent from the medium, applying magnetic field [35].

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List of symbols

p/p_0	relative pressure (hydrostatic pressure/saturation pressure) [–]
V	adsorbed volume of the nitrogen at the corresponding pressure [cm^3 g^{-1}]
S_{BET}	specific surface area [m^2 g^{-1}]
V_{micro}	micropore volume [cm^3 g^{-1}]
S_t	external surface area [m^2 g^{-1}]
V_a	total pore volume [cm^3 g^{-1}]
C_0	initial metal ion concentration [mg L^{-1}]
m_s	sorbent concentration [g L^{-1}]
C_e	equilibrium metal ion concentration [mg L^{-1}]
q_e	amount of metals adsorbed at equilibrium [mg g^{-1}]
q_t	amount of metal ions adsorbed at various times t [mg g^{-1}]
t	time [min]
k	rate constant of the pseudo-second-order model for the adsorption process (g mg^{-1} min^{-1})
R^2	coefficient of determination [–]

Q_0	Langmuir constant representing maximum adsorption capacity [mg g^{-1}]
b	Langmuir sorption equilibrium constant [L mg^{-1}]

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