Bentonite polymer composite for water purification

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Abstract. A polyethylene glycol (PEG)–bentonite (BT) composite was prepared by direct polymerization of PEG in suspensions of BT. Based on detailed analyses using field-effect scanning electron microscopy, X-ray diffraction, surface area measurements and chemical methods, the obtained product was mainly composed of Ca-BT with a specific surface area of $4.13 \text{ m}^2 \text{ g}^{-1}$. The optimal conditions for adsorption of Pb^{2+} and Cd^{2+} ions were found to be a PEG content of 0.1% and a contact time of 60 min. The sorption experiments were performed under various operating variables, including polymer concentration, pH and temperature. For both Pb^{2+} and Cd^{2+} , the adsorption equilibrium was described by the Freundlich model, which confirmed the presence of a heterogeneous system with irregular filling of the active centres. The maximum sorption capacities of BT–PEG for removal of Pb^{2+} and Cd^{2+} were found to be 22 and 18 mg g^{-1} , respectively. The rate constants calculated for the sorption of Pb^{2+} and Cd^{2+} were 6.29 and $6.67 \text{ g mg}^{-1} \text{ min}^{-1}$, respectively, at 25°C . This study shows that the obtained sorbents based on BT may be used for treatment of waste water and could help resolve environmental protection issues.

Keywords. Bentonite clay; polyethylene glycol; lead; cadmium; sorption; composite materials.

1. Introduction

Lead and cadmium are considered as highly toxic substances. The negative effects of both metals on the human body are manifested even at very low concentrations, for example at 0.25 and 0.005 mg l^{-1} for Pb and Cd in the blood, respectively. An excessive and long-term intake of cadmium in the body leads to development of chronic disease in which the urinary and reproductive systems are affected. Lead is known as a toxic substance for almost 5000 years; its inorganic compounds are enzyme inhibitors and disrupt metabolism [1–4]. Anthropogenic release of heavy metals into the environment is much more significant than natural sources. Huge amounts of lead and cadmium wastes are produced in the automobile, metallurgic, printing and chemical industries, in mining and processing factories and in workshops of metal plating. Major sources for such wastes in Kazakhstan include the Ust-Kamenogorsk lead-zinc plant, copper smelters located in central Kazakhstan, the Petropavlovsk heavy engineering plant, the Aktobe plant of chromium compounds and refineries and other plants. For instance, waste water from the steel and mining industries shows that flotation and enrichment of lead and cadmium ores produce concentrations as high as $5\text{--}10 \text{ mg l}^{-1}$ [5]. Chronic poisoning from water

containing heavy metal ions, such as lead and cadmium, leads to gradually impaired renal function and nervous system, to water deficiency and to anaemia.

Ion exchange and sorption methods are widely used for purification of waste water [6–8]. These methods are based on the use of solid adsorbents and are effective for the purification of water from various metals. Solid adsorbents for purification of waste water are typically produced by simple synthesis at relatively low cost and exhibit high sorption characteristics [9–11]. Many adsorbents, such as clay materials, activated carbon, cellulose and its derivatives and metal oxides, have a high capacity for sewage treatment and have been used as adsorbents for water purification [12–14]. Activated carbon is considered to be a particularly competitive and efficient sorbent for the removal of heavy metal ions [14]. Nevertheless, the use of activated carbon is not suitable in certain cases due to the high costs associated with its production and regeneration. In this work, we used clay sorbents, which play a significant role in purification processes applied to aqueous solutions of inorganic and organic pollutants [15,16]. However, in a natural state, many clay sorbents do not have high adsorption capability, so they are usually modified to provide improved adsorptive and catalytic properties. Thermal activation, acid and alkali processing and various complexing

agents such as polymers and organic substances are widely used methods for activation of natural sorbents [17–19]. Semi-synthetic sorbents, which contain donor atoms, are composite materials that are prepared from natural minerals, for example by chemisorption of organic or inorganic compounds or by precipitation on simple or complex oxides. As a result, sorbents are obtained with different kinds of surfaces and pore structures. For instance, semi-synthetic organo-bentonite (BT), a natural montmorillonite clay, was pillared by polyhydroxyl ferric and aluminium, MnCl_2 , TiCl_4 , chitosan and other means; polyacrylamide, polycarboxylic acid, poly(2-hydroxyethyl methacrylate) and other polymers can serve as a continuous phase in the composite [20–22].

The aim of this work was to establish the physical and chemical characteristics of modified clay sorbent based on BT and to study the sorption of lead and cadmium ions. In our work, the BT clay was modified with a polymeric ligand, namely polyethylene glycol (PEG), which is a non-toxic and widely available reagent [23]. PEG is polar, miscible in water and compatible with aqueous clay mineral suspensions, and interacts at the molecular level. The hydroxyl groups present on montmorillonite and the water bound to the exchangeable cations readily form hydrogen bonds with the hydroxyl groups of the PEG chains [24].

2. Experimental

2.1 Materials

The following materials were used in this work: Ca-montmorillonite (BT) from Dinosaur deposits (95% purity), purchased from the B-clay company (Kazakhstan); water-soluble PEG, produced by AppliChem GmbH (Germany) with molecular weight of 6000 g mol^{-1} ; $\text{Pb}(\text{NO}_3)_2$ and $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$. All chemicals were of analytical grade.

2.2 Preparation of composite BT-PEG

The modification of BT clay was conducted with several concentrations of PEG by standard procedure [25]. For this purpose, five samples of sorbent were prepared: 20 g natural BT was dispersed in 100 ml of 0.1, 0.5, 1.0, 2.0 and 5.0% aqueous solutions of PEG, respectively, under continuous stirring. This dispersion was stirred at 25°C for 1 h and left for 24 h at ambient temperature. The prepared BT-PEG was separated by paper filtration, washed several times with deionized water and dried at 100°C for 4 h. Obtained sorbents were ground to a powder of $70 \mu\text{m}$ in size using a porcelain mortar.

2.3 Sorbent characterization

The morphology and particle dispersion were investigated by field-emission scanning electron microscopy (FE-SEM, FEI QUANTA 3D 200i). The chemical composition of the modified BT was measured by energy-dispersive X-ray

spectroscopy (EDX) performed in a SEM. Structural features were investigated by X-ray diffraction (XRD) spectroscopy (AXS D-8 Advance, Bruker) with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV/40 mA. The textural features were also measured by nitrogen sorption (Quantachrome NOVA 4200e) at -196°C . The specific surface area (S_{BET}) was calculated according to the Brunauer–Emmett–Teller (BET) theory up to a relative nitrogen pressure of 0.2. Sorbent moisture was determined by mass difference from the initial sample weight of 1 g after drying at 110°C for 1 h in a weighing bottle [26]. Ash content was determined by mass difference from the initial sample weight of 1 g after calcination at 900°C for 2 h [27]. The total gross porosity of water and acetone was determined by absorption for 30 min at room temperature [28]. Adsorption activity of iodine was determined by titration with sodium thiosulphate according to the ASTM procedure [29].

2.4 Adsorption experiments

The sorption process was investigated in static conditions. The adsorption of heavy metals was performed by mixing 1 g of adsorbent with a 100 ml solution of known solute (Pb^{2+} or Cd^{2+} at $2\text{--}250 \text{ mg l}^{-1}$) at constant temperature until equilibrium was reached. The equilibrium time was determined from curves of changes in adsorption capacity with contact time. Samples were taken every 30 min from the aqueous solution for determination of metal content; the metal concentration was determined by an atomic absorption spectrometer (Shimadzu 6200). The sorption capacity q (mg g^{-1}) was obtained as follows:

$$A = \frac{C_0 - C_e}{m} V \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg l^{-1}) of metal ions in the aqueous solution, respectively, V is the volume of the metal ion solution (l) and m is the weight of sorbent (g). To study the effect of pH on the sorption, 1 g of sorbent was dispersed in 100 ml solutions containing 100 mg l^{-1} of each heavy metal ion at 25°C . The initial pH values were adjusted from 2 to 6 by adding HCl from a 0.1 N solution, and pH measurements were performed using a pX-150MI pH-meter.

3. Results and discussion

3.1 Characterization of the sorbent

The obtained BT-PEG sorbent was thoroughly characterized by EDX, FE-SEM, XRD and BET analysis. Existence of Ca (55.54% w/w), Si, Al, Mg, Na, Fe and O was observed by elemental analysis (see supplementary table S1 of the Supporting Information). High calcium content in the original and modified BT-PEG sorbent indicates effective sorption capability [30]. After modification, a slight increase in carbon and

oxygen content and decrease in calcium content can be seen, which confirm the successful synthesis of BT-PEG.

Physico-chemical and textural characterization of the initial and modified BT sorbent is summarized in table 1. BT in its dry state was shown to have a moisture content of around 8.6% and ash content of 6.4%. Moreover, the data show that modification of the initial BT clay leads to a significant reduction in the total pore volume of acetone (from 29.05

to 19.12%), which indicates a reduction in the number of mesopores. In addition, the increase in iodine adsorption (from 30.60 to 40.00%) indicates an improvement in the microporous structure. Water sorption measurements indicated that the total pore volume decreased as a result of the polymer modification. Hence, we conclude that the modification of BT by PEG leads to a predominance of meso- and micro-pores in the sorbent structure, which significantly enhance the adsorption of heavy metal ions.

Figure 1 shows typical FE-SEM images of non-modified BT and modified BT-PEG after sorption of Pb^{2+} and Cd^{2+} ions. Non-modified BT (figure 1A) had significantly uniform texture provided primarily by micropores with a diameter in the range of 1–4 μm . Needle-shaped growths of the polymer can be seen in this image (figure 1B), which indicates the impregnation of PEG. The near absence of crystallinity after loading the sample with Pb^{2+} and Cd^{2+} ions (figure 1C and D) indicates that there was no crystalline phase transformation after sorption.

Table 1. Textural characterization of BT and BT-PEG.

Characterization	BT	BT-PEG
Moisture, %	8.6	4.9
Ash content, %	6.4	23.3
The total pore volume of acetone, %	29.05	19.12
Adsorption activity on iodine, %	30.60	40.00
The total pore volume of water, $cm^3 g^{-1}$	0.010	0.009

Figure 1. SEM images of sorbents: (A) BT, (B) BT-PEG, (C) BT-PEG-Pb and (D) BT-PEG-Cd.

Figure 2. Schematic illustration of BT modification by PEG.

Figure 3. XRD patterns of: (A) natural BT and (B) BT-PEG.

It is known that montmorillonite is the main mineral of BT; it has a 2:1 layer structure, consisting of an octahedral alumina sheet sandwiched between opposing tetrahedral silica sheets [31]. The bonding between the two silica sheets is very weak, allowing water and exchangeable ions to enter. It was assumed that adsorption of PEG can occur on both external surface and interlayer spaces (figure 2). Then, the adsorption proceeds according to the ion-exchange mechanism, which is presented for BT and PEG in equations (2 and 3) as follows:

The XRD patterns of raw BT (A) and modified BT (B) are shown in figure 3. The raw BT contains characteristic diffraction peaks of montmorillonite (M), which are located at $2\theta = 20.49, 32.64$ and 62.54 and quartz (Q), where the characteristic peaks are located at $2\theta = 37.14, 39.02$ and 50.85 , respectively. The other peaks are impurities corresponding to cristobalite, field spar and illite [32]. However, as can be seen in the diffraction pattern of BT-PEG shown in figure 3, while there is a change in the intensity of the peaks, the appearance

of new peaks is not detected. This might be due to the low concentration of the modifying agent or the high dispersion of polymer particles in the BT matrix. EDS data showing PEG particles fixed onto the surface of BT are given in supplementary table S1 of the Supporting Information.

Adsorption isotherms enable us to draw conclusions about the surface area, the porosity of the adsorbent and the nature of the interaction between the sorbent and the sorbate. Figure 4 shows N_2 adsorption–desorption isotherms indicating that the surface area, total pore volume and average pore diameter decreased significantly by modifying the BT by PEG, from 4.13 to $3.67 \text{ m}^2 \text{ g}^{-1}$, 0.0131 to $0.0082 \text{ cm}^3 \text{ g}^{-1}$ and 222 to 186 nm , respectively. This reduction in the values of the characteristic attributes of the BET theory was assumed to arise due to the introduction of the polymer in the pores of the initial BT. However, from figure 4c, we can see that the modified BT has a narrow pore size distribution of about $2\text{--}4 \text{ nm}$.

3.2 Removal of Pb^{2+} and Cd^{2+} BT-PEG

3.2a Effect of modifier (PEG) concentration and sorbent dose: First, we studied the effect of the polymer concentration in the BT-PEG material on the adsorption of the metal ions. The effect of the PEG concentration was studied at 25°C , and the results are presented in figure 5. It was found that increasing the concentration of polymer in the BT-PEG material increases the amount of adsorbed metal ions. This behaviour might be due to the fact that at higher polymer concentrations, metal ions are adsorbed onto the sorbent surface not only by the mechanism of physical sorption, but also by functional groups of PEG. The saturation period of the sorbent is defined by the nature of both adsorbent and sorbate. The sorption equilibrium of lead and cadmium ions occurs within 60 min ; this short time period required to attain equilibrium suggests an excellent affinity of the metal ions for the BT-PEG composite.

Based on these graphs, regardless of the quantity of the modifying polymer, all sorbents almost completely adsorbed the lead and cadmium ions. Therefore, for economic efficiency, the sorbent containing the minimum quantity of PEG (0.1%) was selected for further studies.

Supplementary figure S1 of the Supporting Information reveals the effect of the adsorbent dose on the adsorption characteristics. Comparative analysis shows that the optimal dose of adsorbent for removal of lead and cadmium ions is 10 g l^{-1} . This dose is quite high, but due to the low-cost and non-toxic properties of BT-PEG, this composite can be applied.

3.2b Effect of pH: It is known that at pH values above 6, most of the heavy metals tend to form hydroxides, which can mask the ‘true’ degree of adsorption. Therefore, the dependence of the adsorption on the acidity of the metal ion solutions was studied at pH values ranging from 2 to 6. The effect of pH on adsorption of lead and cadmium ions onto pure BT was investigated earlier [25]. For BT-PEG, the effect of pH is shown in figure 6. At pH values ranging from 3 to 5,

Figure 4. N_2 adsorption–desorption isotherms of: (A) BT, (B) BT-PEG and (C) Barrett–Joyner–Halenda (BJH) pore size distribution plot of the BT-PEG.

Figure 5. Effect of PEG concentration on the extent of adsorption of: (A) Pb^{2+} and (B) Cd^{2+} ions onto BT-PEG (adsorbent dose = $10 g l^{-1}$; pH = 6; temperature = $25^\circ C$).

the adsorption capacity of Cd^{2+} is higher than Pb^{2+} , while at pH 6, both ions showed similar adsorption capacity.

At low pH values, which correspond to a high proton concentration, there is competition between the H^+ and the Pb^{2+} and Cd^{2+} ions for the negatively charged surface of the sorbent [33].

3.3 Adsorption isotherms

The effect of the initial concentration of metal ions on their adsorption was studied at $25^\circ C$ in a broad range of 2–250 $mg l^{-1}$. According to the obtained isotherms (figure 7), the modified sorbent showed maximum adsorption of 22 and

Figure 6. Effect of pH on heavy metal adsorption by BT-PEG (initial metal ion concentration = 100 mg l^{-1} ; adsorbent dose = 10 g l^{-1} ; temperature = 25°C).

Figure 7. Adsorption isotherms on (A) Pb^{2+} , (B) Cd^{2+} ions onto BT and (C) Pb^{2+} and (D) Cd^{2+} onto BT-PEG (contact time = 180 min; adsorbent dose = 10 g l^{-1} ; pH = 6; temperature = 25°C).

18 mg g^{-1} for lead and cadmium ions, respectively, whereas pure BT showed considerably lower maximum adsorptions of 13 and 6 mg g^{-1} for lead and cadmium, respectively. Sorption isotherms are important for describing the adsorption process, as they show how the metal ions are distributed between the adsorbent and liquid phase at equilibrium depending on the concentration. In this work, to describe the sorption of heavy metal ions by the investigated sorbent, the two of the most commonly used models were applied: the Langmuir and Freundlich isotherms. The following isotherm constants were calculated: K the equilibrium constant of the adsorption process, A_∞ the limiting adsorption, β the the Freundlich parameter and $1/n$ the heterogeneity factor. It can be seen from table 2, the Langmuir isotherm does not conform to either of the two metal sorption processes, as evidenced by the values of the R^2 correlation coefficient, which were 0.886 and 0.703 for Pb^{2+} and Cd^{2+} ions, respectively.

Table 2. Characterization of adsorption isotherms of metal ions at 25°C .

Metal ion	Langmuir model			Freundlich model		
	$K, \text{ mg l}^{-1}$	$A_\infty, \text{ mg g}^{-1}$	R^2	β	$1/n$	R^2
BT						
Pb^{2+}	0.05	1.35	0.397	14.45	1.187	0.979
Cd^{2+}	0.18	0.26	0.541	15.35	0.393	0.604
BT-PEG						
Pb^{2+}	1.35	4.46	0.886	3.82	0.91	0.919
Cd^{2+}	2.45	3.34	0.703	2.30	0.53	0.915

The data from adsorption studies are best described by the Freundlich isotherm (figure 8, $R^2 = 0.919$ for lead and $R^2 = 0.915$ for cadmium). Therefore, the sorption of metal ions by BT-PEG proceeds in good agreement with the Freundlich isotherm model in which the extraction of metal ions occurs in a heterogeneous system with uneven filling of the active centres and the visible forces of interaction between the adsorbed particles.

3.4 Adsorption kinetics

In the present study, pseudo-first-order and pseudo-second-order kinetic models were employed to test the experimental data [34]. The pseudo-first-order and pseudo-second-order models are described by the following equations, respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

where q_e and q_t are the amounts of adsorbate (mg g^{-1}) on the adsorbent at the beginning and at time t , and k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) are the rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

The kinetic data were linearized using the pseudo-first-order and pseudo-second-order models and plotted as $\ln(q_e - q_t)$ vs. t and t/q_t vs. t , respectively.

The constants were calculated from the slope and intercept of the plots and are given in table 3 and shown in figure 9. The results in table 3 indicate that while the pseudo-first-order model applies for pristine BT, better correlation coefficients were obtained for the composite BT-PEG using the pseudo-second-order model, which thus explains the adsorption process better.

To determine the influence of the temperature, the sorption was carried out at 25 and 35°C . Furthermore, the kinetics was characterized and the activation energy was calculated using

Figure 8. Freundlich isotherm model of heavy metal ion adsorption onto (A) BT and (B) BT-PEG.

Table 3. Kinetic characterization of Pb^{2+} and Cd^{2+} sorption onto BT-PEG.

Metal	C_0 , mg l ^{−1}	A_{max} , mg l ^{−1}	T , K	Pseudo-first order model		Pseudo-second order model		E_a , kJ mol ^{−1}
				k_1 , min ^{−1}	R^2	k_2 , g mg ^{−1} min ^{−1}	R^2	
BT								
Pb ²⁺	5	0.16	298	0.015	0.937	0.027	0.919	—
Cd ²⁺	5	0.10	298	0.021	0.976	0.166	0.866	—
BT-PEG								
Pb ²⁺	5	0.52	298	0.065	0.853	6.29	1	−10.38
	5	0.49	308	0.089	0.933	5.49	1	
Cd ²⁺	5	0.46	298	0.036	0.753	6.67	1	−34.21
	5	0.32	308	0.004	0.481	4.26	0.999

Figure 9. Plots of kinetics of heavy metal ions by (A) pure BT and (B) BT-PEG (initial metal ions concentration = 5 mg l^{-1} ; adsorbent dose = 10 g l^{-1} ; pH value = 6; temperature = 25°C).

the following Arrhenius equation:

$$E_a = \frac{RT_1 T_2 \ln(k_{T_2}/k_{T_1})}{T_2 - T_1} \quad (6)$$

where R is the gas constant ($\text{J mol}^{-1} \text{K}^{-1}$), T_1 and T_2 are the temperatures (K) at which the sorption was carried out and k_{T_1} and k_{T_2} are the rate constants at temperatures T_1 and T_2 .

The obtained results are presented in table 3, showing that the rise in temperature has a negative impact on the rate of sorption of both ions. The physical sorption mechanism is supported by the negative value of the activation energy. In addition, the rapid achievement of the equilibrium state (equilibrium time = 60 min) also supports a physical adsorption mechanism.

4. Conclusions

In summary, BT-PEG sorbent was prepared successfully from BT of the Dinosaur field and used as an adsorbent for removing Pb^{2+} and Cd^{2+} from aqueous solutions. SEM, XRD and BET analysis indicate intercalation of the PEG polymer into the initial structure of the BT. The surface area, total pore volume and average pore diameter of BT-PEG were calculated to be $3.67 \text{ m}^2 \text{ g}^{-1}$, $0.0082 \text{ cm}^3 \text{ g}^{-1}$ and 186.3 nm , considerably lower than the corresponding values for BT. The adsorption of Pb^{2+} and Cd^{2+} was found to be dependent on the metal ion concentration, pH and temperature. The adsorbed amounts of both metal ions increased with increasing PEG concentration, pH. The adsorption equilibrium for both Pb^{2+} and Cd^{2+} can be described by the Freundlich model, which confirmed the presence of a heterogeneous system with irregular filling of the active centres. The maximum sorption capacities for Pb^{2+} and Cd^{2+} shown by BT-PEG were 22 and 18 mg g^{-1} , respectively. The rate constants for Pb^{2+} and Cd^{2+} sorption were found to be 6.29 and $6.67 \text{ g mg}^{-1} \text{ min}^{-1}$, respectively, at 25°C .

The results clearly show that the BT-PEG composite is a highly effective sorbent for the extraction of lead and cadmium ions. This facile method of BT clay modification provides a low-cost sorbent, which can be used for purification of waste water at the industrial level.

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