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Influence of ultrasound irradiation on cadmium cations adsorption by montmorillonite

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ABSTRACT

The objective of this work is study of the influence of ultrasound irradiation on adsorption properties of montmorillonite, contained in bentonite, mined in the Slovak deposit. First, structural properties of the adsorbent were characterized by Mössbauer spectroscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. For the adsorption experiments, cadmium, as a heavy metal ion, was selected. The adsorption has been studied by a batch method using an ultrasound device and a rotary shaker. The montmorillonite adsorption properties have been tested under different conditions such as pH of the solution, initial metal ions concentration and temperature. It was observed that sonication markedly influenced the adsorption capacity of montmorillonite and its value increased by approximately 40% in comparison with the corresponding capacity of the non-sonicated material. No evident effect of temperature on the adsorption capacity of montmorillonite was proved.

Keywords: Montmorillonite; Adsorption; Ultrasound; Cadmium

1. Introduction

Due to the rapid increase in global industrial activities, heavy metal pollution became serious. Naturally occurring clays and clay minerals are of paramount importance in the field of environmental and waste management [1,2]. Amongst various treatment technologies, bentonites are commonly used as inexpensive adsorbents for the treatment of wastewater [3–14]. Bentonites are a group of natural nanomaterials composed predominantly from crystalline mineral particles from the group of dioctahedral smectites—montmorillonite. The adsorption properties of bentonites are determined by their chemical and mineralogical composition, value of cation exchange capacity and specific surface area. There are several studies dealing with the cadmium (II) removal by bentonite, studying the sorption equilibrium, isotherms, effect of pH, ionic strength or temperature on the sorption process [15–20]. Removal of Pb(II), Cd (II), Zn(II) and Cu(II) from aqueous solution using the adsorption process on bentonite was studied by Bereket et al. [21]. The rate of attending equilibrium of adsorption of metals ions followed the order Zn(II) > Cu(II) > Cd(II) > Pb(II). Higher removals for all heavy metal cations were observed in the lower temperature range. The maximum removal for Cd(II), (55.5%), was reached at 20°C. Investigation of the adsorption

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properties of granular bentonite in the removal of Hg (II), Cd(II) and Pb(II) showed the selectivity of the sorbent towards these salts in order Pb(II) > Cd(II) > Hg(II). The adsorption capacity of granular bentonite towards cadmium was 13.05 mg g^{-1} [22]. Also, various ways of modifications and treatments were performed with the aim to enhance the adsorption properties of bentonites [23–36]. The sorption of Cd(II) and other selected metal ions on the sodium form of montmorillonite was studied in the work of Abollino et al. [37]. Effect of pH and presence of ligands on the sorption capacity were investigated. Acid activation of the bentonite clay increased its maximum adsorption capacity towards Cd(II) from 48.2 to 57.88 mg g^{-1} [38]. Magnetic adsorbent, where adsorption features of bentonite with the magnetic properties of iron oxide were combined, was synthezised and studied by Oliveira et al. [39]. The adsorption capacity of clay/iron oxide composite was higher in comparison with bentonite and increased for studied metal cations in following order: Ni(II) < Cu(II) < Cd(II) < Zn(II).

Ultrasound is the wave at the frequency above 16 kHz. When ultrasound is irradiated through a liquid, an alternating adiabatic compression and rarefaction cycle of the medium occur. Acoustic cavitations provide unusual conditions in the sorption process which are different from common method for the removing of pollutants. In the past years, several researchers studied the role of ultrasound in the adsorption and desorption processes. The ultrasonic waves had a greater efficiency for interface mixing than conventional agitation [40–51].

Cadmium receives wide attention by environmentalists as one of the most toxic heavy metals. Its presence in the environment is increasing due to its use in electroplating, smelting, plastics, pigments, ceramics, battery, fertilizers and mining. 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. 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 although it is eventually excreted. For its removal from waters and wastewaters, various methods have been developed, from which adsorption has been shown to be most promising option.

Entezari and Bastami showed in their study [52] that the intensity of ultrasound as well as sorbate/sorbent concentration ratio was two important factors for removal of Cd(II) by adsorption process. Simultaneous removal of Cd(II) and Pb(II) ions from binary aqueous solutions in the presence of ultrasound was also studied by Entezari and Soltani [53]. In the presence of ultrasound, lower amount of adsorbent was required to maximum removal. In the presence of Pb (II), the adsorption of Cd(II) decreased. In the case of Pb(II) adsorption, the temperature effect was negligible, but it was important for Cd(II) removal. Discarded tyre rubber was used as a cheap adsorbent for the removal of cadmium. The maximum metal adsorption capacity was found to be greater in the presence than in the absence of ultrasound [54]. Hamdaoui also showed that the amount of cadmium adsorption increased in the presence of ultrasound, where acoustic power was an important parameter for the enhancement of the adsorption [55]. The combination of stirring and ultrasound led to an intensification of the process.

The work deals with an investigation of influence of ultrasound irradiation on the adsorption properties of locally available clay. The effect of various parameters like pH, contact time, initial metal ion concentration and temperature on the adsorption behaviour was studied and compared with the results obtained from the conventional method—adsorption in a rotary shaker.

2. Materials and methods

2.1. Adsorbent and adsorptive

Bentonite, containing the calcium—magnesium montmorillonite with crystalochemical formula: $[Si_{7.95} Al_{0.05}]$ $[Al_{3.03}$ $Fe_{0.22}$ $Mg_{0.75}]$ O_{20} $(OH)_4$ $(Ca_{0.42}Mg_{0.04}Na_{0.01}K_{0.01})$, originated from the Slovak deposit Jelšový potok [56]. The sample used for the investigation was isolated from the 4% water suspension of bentonite and treated by sedimentation method [57] with the aim to obtain the monomineral fraction of montmorillonite with the particle size below 20 μm.

Analytical grade metal salt ($Cd(NO_3)_2$. $4H_2O$) was used without further purification. Stock solutions (1,000 and 100 mg L^{-1}) of Cd(II) were prepared by dissolving the appropriate amounts of nitrate in deionized water. The stock solutions were diluted to obtain standard solutions containing 10–600 mg L^{-1} of Cd(II).

2.2. Adsorbent characterization

Room temperature Mössbauer measurement was made in transmission geometry. A^{57}Co/Rh-ray source was used. The velocity scale was calibrated relative to ^{57}Fe in Rh. Mössbauer spectral analysis software

"Recoil" [58] was used for the quantitative evaluation of the spectra. The Voigt-based fitting method was applied.

Fourier transform infrared (FT-IR) spectrum was taken on a spectrometer AVATAR 330 (Thermo Nicolet Corp., USA) equipped with a DTGS/KBr detector at a resolution 4 cm^{-1}. The spectrum was collected with spectral resolution in the region from 4,000 to 400 cm^{-1} on potassium bromide (KBr) pellets.

Morphology of the montmorillonite sample was observed by the scanning electron microscope (SEM) of type JSM-6400 (JEOL Ltd., Japan).

Surface parameters, characterizing the surface properties of the adsorbent, like specific surface area, total pore volume, micropore volume and external surface area were determined from the low-temperature adsorption measurements and were presented earlier in [59].

2.3. Adsorption procedures

The adsorption measurements were made by a batch technique at room temperature using the ultrasonic device and rotary shaker. The ultrasonic irradiation was carried out by the commercial device Kraintek K10E (Slovakia), operating at 40 kHz, working with the power of 180 W, equipped with a temperature regulator. Known amount of the montmorillonite was added into the plastic tubes containing 15 ml of Cd(II) solution of known concentration and pH. The tubes were placed into the carrier installed in the water basin of the ultrasound device. A circulating bath was used to maintain a constant temperature during the ultrasound irradiation. Conventional experiments were performed in the rotary shaker with operating speed 30 rpm (conventional method). All experiments were carried out at pH 5 (except when the effect of pH was studied). The pH of the dispersions was adjusted to the desired value by diluted solutions of NaOH and HCl added dropwise. The suspensions were sonicated or shaken for a given time period to reach equilibrium. The operating frequency and the rotation speed were kept constant. The suspensions were subsequently filtered using the filter paper, and the supernatant solutions were analysed by the atomic absorption spectroscopy (AAS, Varian 240 RS/2400). The linearized Langmuir model was used for the analyses of the adsorption isotherms. Through the study, the pH varied from 2 to 9, initial Cd(II) concentration from 10 to 600 mg L^{-1}. The amount of adsorbent mass was stable 1 g L^{-1}. Influence of the temperature on the adsorption was studied only under the sonication at 25, 50 and 70˚C.

3. Results and discussion

3.1. Adsorbent characterization

The presence of monomineral montmorillonite phase in the bentonite sample was proved by X-ray diffraction method, shown in previous study [60]. For detailed investigation of its structure, the Mössbauer spectroscopy was applied. The room temperature Mössbauer spectrum (Fig. 1), was asymmetric, consisting of two doublets suggesting two different iron cations positions in montmorillonite structure. Therefore, it was fitted by two spectral components [61]. On the basis of the obtained hyperfine parameters: isomer shifts $IS_1 = 0.28\,\mathrm{mm\,s^{-1}}$, $IS_2 = 0.23\,\mathrm{mm\,s^{-1}}$; quadrupole splittings $QS_1 = 1.39\,\mathrm{mm\,s^{-1}}$, $QS_2 = 0.52\,\mathrm{mm\,s^{-1}}$; relative intensities $I_1 = 33.7\%$, $I_2 = 66.3\%$, it can be stated that iron cations in the montmorillonite are trivalent [62].

The absorption band at the position about 3,626 cm^{-1} is due to the stretching vibrations of structural OH groups of the montmorillonite (Fig. 2). The bands corresponding with the AlAlOH and AlMgOH bending vibrations were observed at 916 and 840 cm^{-1}, respectively. A complex band at 1,040 cm^{-1} related with the stretching vibrations of Si–O groups, whilst the bands at 523 and 470 cm^{-1} are due to the Al–O–Si and Si–O–Si bending vibrations, respectively. The band at the position 625 cm^{-1} was assigned to the couple Al–O and Si–O out of the plane vibrations. Water in montmorillonite gave a broad band at about 3,420 –3,450 cm^{-1} corresponding with the H_2O-stretching vibrations. The shoulder close to 3,330 cm^{-1} is due to an overtone of the bending vibration of water observed at 1,635 cm^{-1} [63].

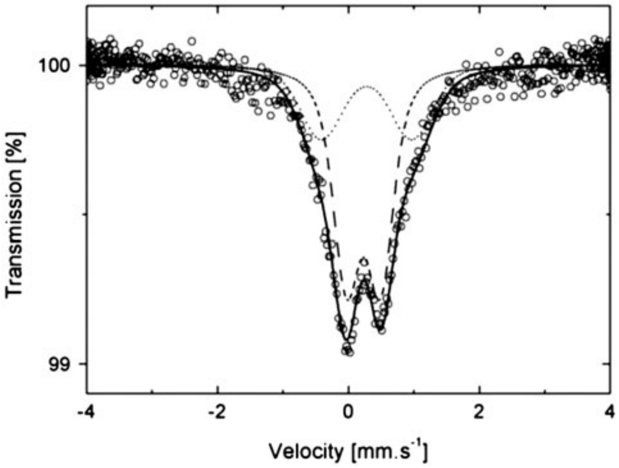

Fig. 1. Mössbauer spectrum of the montmorillonite (dash and dot lines represent two positions of trivalent iron cations in the montmorillonite structure, solid line fits Mössbauer spectrum).

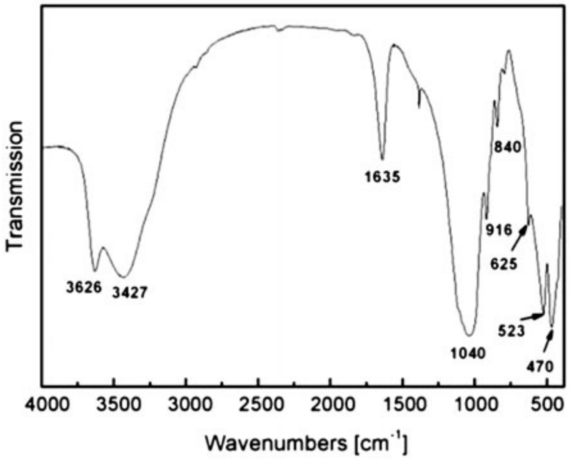

Fig. 2. IR spectrum of the montmorillonite.

The SEM micrograph showed the sheet structure — leaf-like crystals forming a dense aggregate [64] (Fig. 3).

3.2. *Adsorption procedures*

3.2.1. *Effect of pH*

The pH of the metal ions solution influences their adsorption by adsorbent. For this experiment, initial metal ion concentration 100 mg Cd(II) L^{-1} was used. The Cd(II) adsorption had similar behaviour during the ultrasonic assisted experiment as the adsorption in the rotary shaker (Fig. 4). The metal ion uptake did not markedly change in the pH range from 3 to 7, but higher adsorbed amount was observed for the adsorption under the sonication. In the solutions with pH 8 and 9, the adsorption capacity of the montmorillonite increased, due to the precipitation of $Cd(OH)_2$ [65–67]. It followed from this experiment and the zeta potential measurement [68] that the optimal pH for the next adsorption experiments was equal 5.

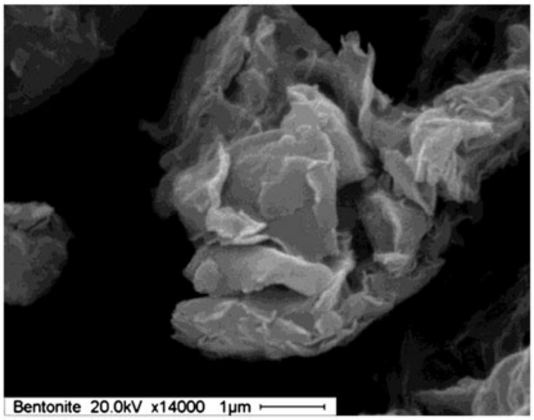

Fig. 3. SEM micrograph of the montmorillonite.

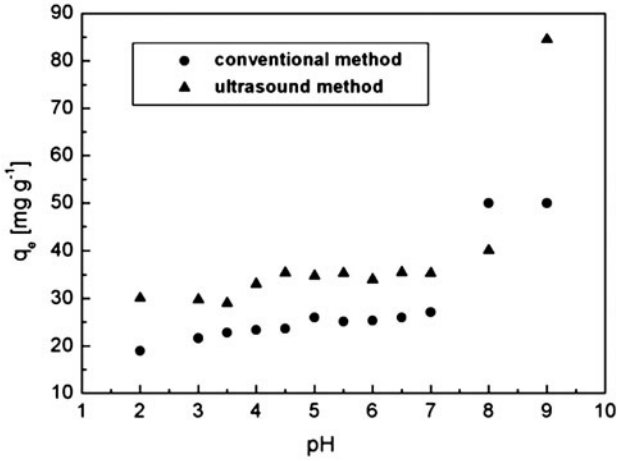

Fig. 4. Effect of pH on Cd(II) removal by montmorillonite using the conventional and ultrasound assisted method ($C_0 = 100$ mg Cd(II) L^{-1}).

3.2.2. *Effect of initial Cd(II) concentration and adsorption isotherms analyses*

In the initial stages of the adsorption, the amount of the cadmium cations adsorbed at the equilibrium increased rapidly with the increasing initial cations concentration, especially for the ultrasonic assisted adsorption, then slowly, until the saturation of the montmorillonite was reached (Fig. 5). The higher values of equilibrium adsorption capacities were observed for adsorption under the ultrasound irradiation in the whole studied concentration range. The saturation of the adsorbent was reached at the initial concentration 400 mg Cd(II) L^{-1} for both methods.

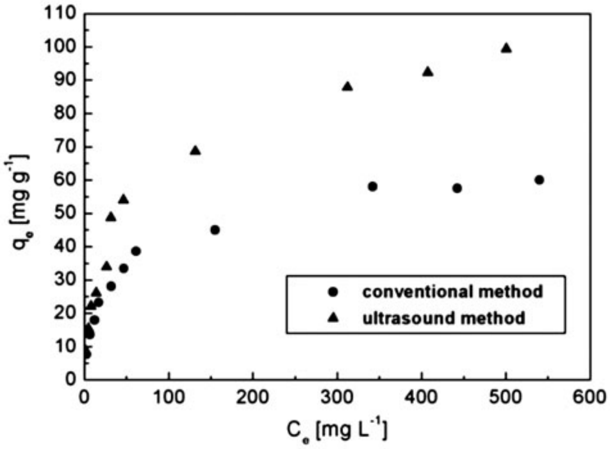

Fig. 5. Adsorption isotherms for Cd(II) removal using the conventional and ultrasound assisted method.

Adsorption isotherm is basically important to describe how solutes interact with adsorbents. Langmuir model, often applied by various workers for the adsorption of variety of compounds, properly fitted the experimental data in the studied range of the initial concentrations (Fig. 6). Its linear form is represented by the below Equation:

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

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 gm of sorbent) and b is adsorption equilibrium constant [69].

As it is shown in Table 1, the higher maximum adsorption capacity of montmorillonite was obtained in the presence of ultrasound irradiation. This indicated that under the sonication new sites of sorption were appeared by disruption of adsorbent particles.

Table 1
Langmuir constants and correlation coefficient for the Cd (II) adsorption by montmorillonite

	Q_o [mg g^{-1}]	b [L mg^{-1}]	R^2
Conventional	62.5	0.030	0.9963
Ultrasound	102.0	0.026	0.9927

3.2.3. Effect of temperature

According to Fig. 7, there is no difference in the adsorption isotherms obtained at 25 and 50°C. The increase in the values of equilibrium adsorption capacities was observed only at 70°C. Also, the maximum adsorption capacities calculated from the Langmuir model are equal for experiments carried out at 25 and 50°C, 102 mg Cd(II) g^{-1}. A little bit more effective seems to be the process realized at 70°C, where the calculated maximum adsorption capacity was 110 mg Cd(II) g^{-1}.

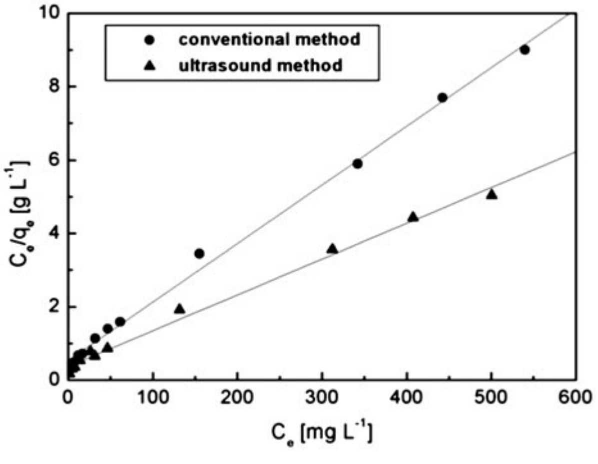

Fig. 6. Linearized Langmuir isotherms for Cd(II) adsorption by montmorillonite using the conventional and ultrasound assisted method.

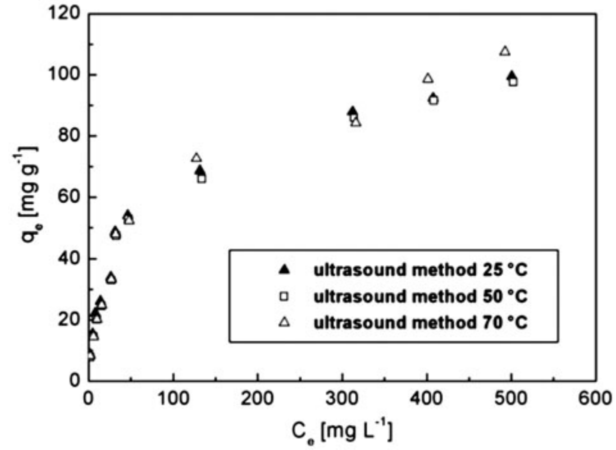

Fig. 7. Adsorption isotherms for Cd(II) removal under the ultrasound assistance at different temperatures.

From these results, it can be stated that the amount of adsorbed Cd(II) was appreciably higher in the presence of ultrasound, hence the effect of temperature was negligible. The sonication enhances the adsorption of the metal ions through the extreme conditions generated by cavitation bubbles. The non-thermal effect is mostly produced by the microstreaming of the acoustic vortex, by the high-speed microjets and high-pressure shockwaves induced by acoustic cavitation.

3.2.4. Thermodynamic parameters of adsorption

From the following equation, it is possible to calculate the Gibbs energy changes for the adsorption process at different temperatures:

$$\Delta G^\circ = -RT \ln K \tag{2}$$

where R is the gas constant, K is the equilibrium constant at the temperature T. Numerical values of the equilibrium constant were calculated from:

$$K = \frac{C_{Be}}{C_{Ae}}, \tag{3}$$

Table 2
Thermodynamic parameters of Cd(II) adsorption by the montmorillonite under the sonication

T [K]	ΔG° [J mol^{-1}]	ΔH° [J mol^{-1}]	ΔS° [J mol^{-1}]
298	−381.3	−1279.7	−2.991
323	−303.4		
343	−250.4		

where C_{Be} and C_{Ae} are the equilibrium concentrations of heavy metal cations on adsorbent and in solute, respectively.

The enthalpy (ΔH°) and entropy changes (ΔS°) of the adsorption can be determined through the slope and intercept of the plot ln K vs. $1/T$ (Van't Hoff equation).

The negative values of ΔG° indicated the spontaneous nature of the adsorption process (Table 2). Entropy was defined as a degree of chaos of the system. During the adsorption, the cadmium cations became associated on the montmorillonite surface. Negative value of ΔS° pointed at their stable arrangement. The enthalpy showed the exothermic nature of the adsorption process [70,71].

4. Conclusion

The Cd(II) removal by montmorillonite was investigated under the different experimental conditions in the presence and absence of ultrasound. This study showed that the adsorption properties of the montmorillonite could be enhanced by the sonication due to the cavitation process. The Cd(II) adsorption from the solution was fast and effective. The adsorption process provided in the ultrasound device was exothermic and of spontaneous nature. The obtained numerical value of the entropy indicated good stability of adsorbed cadmium cations on the montmorillonite surface. No temperature effect on the adsorption properties of montmorillonite was observed.

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List of symbols

IS — isomer shift [mm s^{-1}]
QS — quadrupole splitting [mm s^{-1}]
I — relative intensity [%]
C_0 — initial metal ion concentration [mg L^{-1}]
m_s — adsorbent concentration [g L^{-1}]
C_e — equilibrium metal ion concentration [mg L^{-1}]
q_e — amount of metals adsorbed at equilibrium [mg g^{-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}]
ΔG° — Gibbs energy changes [J mol^{-1}]
R — gas constant [J mol^{-1} K^{-1}]
T — temperature [K]
K — equilibrium constant at the temperature T [−]
C_{Be} — equilibrium concentrations of heavy metal cations on adsorbent [mg L^{-1}]
C_{Ae} — equilibrium concentrations of heavy metal cations in solute [mg L^{-1}]
ΔH° — enthalpy changes [J mol^{-1}]
ΔS° — entropy changes [J mol^{-1}]

References

[1] M. Galamboš, O. Rosskopfová, J. Kufčáková, P. Rajec, Utilization of Slovak bentonites in deposition of high-level radioactive waste and spent nuclear fuel, J. Radioanal. Nucl. Chem. 288 (2011) 765–777.

[2] J.H. Potgieter, S.S. Potgieter-Vermaak, P.D. Kalibantonga, Heavy metals removal from solution by palygorskite clay, Miner. Eng. 19 (2006) 463–470.

[3] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.

[4] K.G. Bhattacharyya, S.S. Gupta, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite, A review, Adv. Colloid Interface Sci. 140 (2008) 114–131.

[5] V. Copcia, C. Hristodor, C. Luchian, N. Bilba, I. Sandu, Ammonium nitrogen removal from aqueous solution by natural clay, Rev. Chím. 61 (2010) 1192–1196.

[6] A. Kaya, A.H. Ören, Adsorption of zinc from aqueous solutions to bentonite, J. Hazard. Mater. B125 (2005) 183–189.

[7] G.N. Pshinko, S.A. Kobets, A.A. Bogolepov, V.V. Goncharuk, Treatment of waters containing uranium with saponite clay, J. Water Chem. Technol. 32 (2010) 10–16.

[8] A.G. Sanchez, E.A. Ayuso, O.J. De Blas, Sorption of heavy metals from industrial waste water by low-cost mineral silicates, Clay Miner. 34 (1999) 469–477.

[9] S.S. Tahir, R. Naseem, Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay, Sep. Purif. Technol. 53 (2007) 312–321.

[10] C.C. Wang, L.C. Juang, C.K. Lee, T.C. Hsu, J.F. Lee, H.P. Chao, Effects of exchanged surfactant cations on the pore structure and adsorption characteristics of montmorillonite, J. Colloid Interface Sci. 280 (2008) 27–35.

[11] S. Kocaoba, Adsorption of Cd(II), Cr(III) and Mn(II) on natural sepiolite, Desalination 244 (2009) 24–30.

[12] M.M. Nassar, M.S. El-Geundi, A.A. Al-Wahbi, Equilibrium modeling and thermodynamic parameters for adsorption of cationic dyes onto Yemen natural clay, Desalin. Water Treat. 44 (2012) 340–349.

[13] C. Tansakul, S. Laborie, C. Cabassud, Membrane hybrid processes for pretreatment before seawater reverse osmosis desalination, Desalin. Water Treat. 9 (2009) 279–286.

[14] J.S. Al-Jariri, F. Khalili, Adsorption of Zn(II), Pb(II), Cr(III) and Mn(II) from water by Jordanian bentonite, Desalin. Water Treat. 21 (2010) 308–322.

[15] G.P.CH. Rao, S. Satyaveni, A. Ramesh, K. Seshajah, K.S.N. Murthy, N.V. Choudari, Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite, J. Environ. Manage. 81 (2006) 265–272.

[16] S.A. Al-Jlil, Removal of heavy metals from industrial wastewaters by adsorption using local bentonite clay and roasted date pits in Saudi Arabia, Trends Appl. Sci. Res. 5 (2010) 138–145.

[17] N. Zahra, S.T. Sheikh, K. Javed, Batch adsorption studies of cadmium in wastewater on bentonites, J. Chem. Soc. Pak. 30 (2008) 797–799.

[18] M. Hamidpour, M. Kalbasi, M. Afyuni, K. Shariatmadari, Kinetic and isothermal studies of cadmium sorption onto bentonite and zeolite, Int. Agrophys. 24 (2010) 253–259.

[19] Y.G. Chen, W.M. Ye, X.M. Yang, F.Y. Deng, Y. He, Effect of contact time, pH and ionic strength on Cd(II) adsorption from aqueous solution onto bentonite from Gaomiaozi, China, Environ. Earth Sci. 64 (2011) 329–336.

[20] F.A. Dawodu, G.K. Akpomie, I.C. Ogbu, Isotherm modeling on the equilibrium of cadmium (II) from solution by Agbani Clay, Int. J. Multi. Sci. Eng. 3 (2012) 9–14.

[21] G. Bereket, A.Z. Aroğuz, M.Z. Özel, Removal of Pb(II), Cd(II), Cu(II) and Zn(II) from aqueous solutions by adsorption on bentonite, J. Colloid Interface Sci. 187 (1997) 338–343.

[22] Y.F. Nava, M. Ulmanu, I. Anger, E. Marañón, L. Castrillón, Use of granular bentonite in the removal of mercury (II), cadmium (II) and lead (II) from aqueous solutions, Water Air Soil Pollut. 215 (2011) 239–249.

[23] M.C. Brum, J.L. Capitaneo, J.F. Oliveira, Removal of hexavalent chromium from water by adsorption onto surfactant modified montmorillonite, Miner. Eng. 23 (2010) 270–272.

[24] Y. Chen, B. Zhu, D. Wu, O. Wang, Y. Yang, W. Ye, J. Guo, Eu (III) adsorption using di(2-thylhexly) phosphoric acid-immobilized magnetic GMZ bentonite, Chem. Eng. J. 181–182 (2012) 387–396.

[25] V. Copcia, C. Hristodor, N. Bilba, E. Popovici, Use of natural and modified clay for Zn^{2+} removal, Rev. Chím. 62 (2011) 195–198.

[26] M. Galamboš, M. Daňo, O. Rosskopfová, F. Šeršeň, J. Kufčáková, R. Adamcová, P. Rajec, Effect of gamma-irradiation on adsorption properties of Slovak bentonites, J. Radioanal. Nucl. Chem. 292 (2012) 481–492.

[27] S. Karahan, M. Yurdakoç, S. Yoldaş, K. Yurdakoç, Removal of boron from aqueous solution by clays and modified clays, J. Colloid Interface Sci. 293 (2006) 36–42.

[28] T. Vengris, R. Binkien, A. Sveikauskait, Nickel, copper and zinc removal from waste water by a modified clay sorbent, Appl. Clay Sci. 18 (2001) 183–190.

[29] C. Volzone, L.B. Garrido, Retention of chromium by modified Al–bentonite, Cerâmica 48 (2002) 153–156.

[30] G. Wang, K. Chen, W. Li, T. Liu, L. Qi, X. Zhang, Y. Zhang, L. Jiang, H. Zhu, Y. Zhu, J. Wang, Preparation of nano magnetic modified bentonite materials for reclamation of coking wastewater, ICMREE2011—Proc. International Conference on Materials for Renewable Energy and Environment 1 (2011) 1027–1030.

[31] W.Q. Wang, Q.M. Feng, F. Dong, H. Li, X. Zhao, Preparation and properties of Fe3O4/clinoptilolite magnetic composite, Wuji Cailiao Xuebao/J. Inorg. Mater. 25 (2010) 401–405.

[32] W. Wenjuan, Ch. Changwei, W. Xin, S. Li, Effect of the structure and acidic property of activated bentonite on removal of olefin aromatics, China petroleum process, Petrochem. Technol. 4 (2009) 23–26.

[33] N. Bouchenafa-Saïb, K. Khouli, O. Mohammedi, Preparation and characterization of pillared montmorillonite: application in adsorption of cadmium, Desalination 217 (2007) 282–290.

[34] L.G. Yan, X.Q. Shan, B. Wen, G. Owens, Adsorption of cadmium onto Al(13)-pillared acid-activated montmorillonite, J. Hazard. Mater. 156 (2008) 499–508.

[35] J.X. Lina, L. Wang, Treatment of textile wastewater using organically modified bentonite, Desalin. Water Treat. 25 (2011) 25–30.

[36] R. Huang, D. Zheng, B. Yang, B. Wang, Preparation and simultaneous sorption of CTMAB–HTCC bentonite towards phenol and Cd(II), Desalin. Water Treat. 44 (2012) 276–283.

[37] O. Abollino, M. Aceto, M. Malandrino, C. Sarzanini, E. Mentasti, Adsorption of heavy metals on Na–montmorillonite, effect of pH and organic substances, Water Res. 37 (2003) 1619–1627.

[38] S. Budsaereechai, K. Kamwialisak, Y. Ngernyen, Adsorption of lead, cadmium and copper on natural and acid activated bentonite clay, KK Res. J. 17 (2012) 800–810.

[39] L.C.A. Oliveira, R.V.R.A. Rios, J.D. Fabris, K. Sapag, V.K. Garg, R.M. Lago, Clay-iron oxide magnetic composites for the adsorption of contaminants in water, Appl. Clay Sci. 22 (2003) 169–177.

[40] M. Breitbach, D. Bathen, Influence of ultrasound on adsorption processes, Ultrason. Sonochem. 8 (2001) 277–283.

[41] M.H. Entezari, T.R. Bastami, Sono-sorption as a new method for the removal of lead ion from aqueous solution, J. Hazard. Mater. B137 (2006) 959–964.

[42] M.H. Entezari, Z.S. Al-Hoseini, Sono-sorption as a new method for the removal of methylene blue from aqueous solution, Ultrason. Sonochem. 14 (2007) 599–604.

[43] M.H. Entezari, T. Soltani, Simultaneous removal of copper and lead ions from a binary solution by sono-sorption process, J. Hazard. Mater. 160 (2008) 88–93.

[44] O. Hamdaoui, E. Naffrechoux, Adsorption kinetics of 4-chlorophenol onto granular activated carbon in the presence of high frequency ultrasound, Ultrason. Sonochem. 16 (2009) 15–22.

[45] J. Laurent, M. Casellas, Ch. Dagot, Heavy metals uptake by sonicated activated sludge: Relation with floc surface properties, J. Hazard. Mater. 162 (2009) 652–660.

[46] D.D. Milenković, P.V. Dašić, V.B. Veljković, Ultrasound-assisted adsorption of copper(II) ions on hazelnut shell activated carbon, Ultrason. Sonochem. 16 (2009) 557–563.

[47] O. Hamdaoui, M. Chiha, E. Naffrechoux, Ultrasound-assisted removal of malachite green from aqueous solution by dead pine needles, Ultrason. Sonochem. 15 (2008) 799–807.

[48] M. Karimi, M.H. Entezari, M. Chamsaz, Sorption studies of nitrate ion by a modified beet residue in the presence and absence of ultrasound, Ultrason. Sonochem. 17 (2010) 711–717.

[49] O. Korkut, E. Sayan, O. Lacin, B. Bayrak, Investigation of adsorption and ultrasound assisted desorption of lead (II) and copper (II) on local bentonite: A modelling study, Desalination 259 (2010) 243–248.

[50] G. Jing, Z. Zhou, L. Song, M. Dong, Ultrasound enhanced adsorption and desorption of chromium (VI) on activated carbon and polymeric resin, Desalination 279 (2011) 423–427.

[51] O. Hamdaoui, Intensification of the sorption of Rhodamine B from aqueous phase by loquat seeds using ultrasound, Desalination 271 (2011) 279–286.

[52] M.H. Entezari, T.R. Bastami, Influence of ultrasound on cadmium ion removal by sorption process, Ultrason. Sonochem 15 (2008) 428–432.

[53] M.H. Entezari, T. Soltani, Cadmium and lead ions can be removed simultaneously from a binary aqueous solution by the sono-sorption method, Ultrason. Sonochem. 16 (2009) 495–501.

[54] M.H. Entezari, N. Ghows, M. Chamsaz, Ultrasound facilitates and improves removal of Cd(II) from aqueous solution by the discarded tire rubber, J. Hazard. Mater. B131 (2006) 84–89.

[55] O. Hamdaoui, Removal of cadmium from aqueous medium under ultrasound assistance using olive leaves as sorbent, Chem. Eng. Process. 48 (2009) 1157–1166.

[56] K. Jesenák, Ľ. Kuchta, L. Guller, J. Fúsková, Physico-chemical Properties of Bentonite "Stará Kremnička - Jelšový potok": I. Particle Size Distribution, Mineralia Slovaca 29 (19797) 439–442.

[57] K. Jesenák, V. Hlavatý, Laboratory device for sedimentation of fine bentonite fractions, Scripta Fac. Sci. Nat. Univ. Masarik. Brun. Geol. 28–29 (2000) 33–36.

[58] K. Lagarec, D.G. Rancourt, Recoil-Mössbauer spectral analysis software for Windows, Version.02, University of Ottawa, Department of Physics, Ottava, 1998.

[59] A. Mockovčiaková, Z. Orolínová, Adsorption properties of modified bentonite clay, Cheminė Technologija 50 (2009) 47–50.

[60] Z. Orolínová, A. Mockovčiaková, Sorption of cadmium (II) from aqueous solution by magnetic clay composite, Desalin. Water Treat. 24 (2010) 284–292.

[61] E. Murad, J.H. Johnston, Iron oxides and oxyhydroxides, In: G.J. Long (Ed), Mössbauer Spectroscopy Applied to Inorganic Chemistry, vol. 2, Plenum Press, New York, pp. 507–582, 1987.

[62] E. Murad, The characterization of soils, clays and clay firing products, Hyperfine Interact. 111 (1998) 251–259.

[63] E. Eren, B. Afsin, An investigation of Cu(II) adsorption by raw and acid-activated bentonite: a combined potentiometric, thermodynamic, XRD, IR, DTA study, J. Hazard. Mater. 151 (2008) 682–691.

[64] J. Konta, Textural variation and composition of bentonite derived from basaltic ash, Clays, Clay Miner. 34 (1986) 257–265.

[65] V. Arámbula-Villazana, M. Solache-Ríos, M.T. Olguín, M.T, Sorption of cadmium from aqueous solutions at different temperatures by mexican HEU-type zeolite rich tuff, J. Inclusion Phenom. Macrocyclic Chem. 55 (2006) 229–236.

[66] Y.-n. Chen, D.-ch. Zhang, M, Chen, Y.-ch. Ding, Biosorption properties of cadmium (II) and zinc(II) from aqueous solution by tea fungus, Desalin. Water Treat. 8 (2009) 118–123.

[67] A. Özer, H.B. Pirinççi, The adsorption of Cd(II) ions on sulphuric acid-treated wheat bran, J. Hazard. Mater. B137 (2006) 849–855.

[68] A. Mockovčiaková, Z. Orolínová, J. Škvarla, Enhancement of the bentonite sorption properties, J. Hazard. Mater. 180 (2010) 274–281.

[69] Y.S. Ho, W.T. Chiu, Ch. Wang, Regression analysis for the sorption isotherms of basic dyes on sugarcane dust, Bioresour. Technol. 96 (2005) 1285–1291.

[70] T. Shahwan, H.N. Erten, Thermodynamic parameters of Cs^+ sorption on natural clays, J. Radioanal. Nucl. Chem. 253 (2002) 115–120.

[71] D. Xu, X.L. Tan, C.L. Chen, X.K. Wang, Adsorption of Pb(II) from aqueous solution to MX-80 bentonite: Effect of pH, ionic strength, foreign ions and temperature, Appl. Clay Sci. 41 (2008) 37–46.