STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LIV, 3, 2009

HEAVY METAL IONS REMOVAL FROM MODEL WASTEWATERS USING ORAŞUL NOU (TRANSILVANIA, ROMANIA) BENTONITE SAMPLE

ANDRADA MĂICĂNEANU[a], HOREA BEDELEAN[b], SILVIA BURCĂ[a], MARIA STANCA[a]

ABSTRACT. A bentonite sample from Oraşul Nou deposit, (Transilvania, Romania), was used to remove heavy metal ions (Zn^{2+}, Pb^{2+}, Cd^{2+}) from model monocomponent wastewaters. A representative sample of bentonite (ON) was characterised using, wet chemical analyses, XRD, BET and FTIR. The bentonite deposit from Oraşul Nou formed by alteration of rhyolites and perlites. Mineralogically, they contain clay minerals (montmorillonite, and subordinately kaolinite, illite), cristobalite, carbonates, zeolites (clinoptilolite), iron oxi-hydroxides and relics of primary minerals such as quartz and feldspar.The bentonite sample was used as powder, (d < 0.2 mm), without any chemical treatment. We studied the influence of the working regime, static and dynamic, concentration, and solid : liquid ratio over the process efficiency. We used monocomponent synthetic wastewaters containing zinc, lead and cadmium ions. The bentonite sample proved to be efficient for the removal of the considered heavy metal ions, removal efficiencies up to 100% (lead and zinc removal) were reached. First-order, pseudo- second-order and Elovich models were used to study the adsorption kinetic of zinc ions on the bentonite sample.

Keywords: *bentonite, montmorillonite, zinc, lead, cadmium, removal*

INTRODUCTION

Heavy metals such as Cd, Pb and Zn are usually found in Earth's crust mainly as minerals and are mobilised by soil erosion, volcanic activities and forest fires (natural sources). Heavy metals concentration in the environment increased drastically due to intense human activities (anthropogenic sources).

Cadmium, lead and zinc can be found in air (eroded particles), water (in ionic form, from wastewaters insufficient treated or mobilised from polluted soils) and soil (adsorbed on soil particles) in different combinations. Heavy metals exposure can take place by inhalation (contaminated air, cigarette

---

[a] *Universitatea Babeş-Bolyai, Facultatea de Chimie şi Inginerie Chimică, Str. Kogălniceanu Nr.1, RO-400084 Cluj-Napoca, România, andrada@chem.ubbcluj.ro*

[b] *Universitatea Babeş-Bolyai, Facultatea de Biologie şi Geologie, Str. Kogălniceanu Nr. 1, RO-400084 Cluj-Napoca, România, bedelean@bioge.ubbcluj.ro*

smoke, working exposure), ingestion (water and contaminated food) and dermal (contact with contaminated soil, heavy metal compounds) exposures. With exception of Zn, which in small quantities is nutritive elements, heavy metals are toxic to humans, animals and plants. Heavy metal ions have the tendency to accumulate in living organisms causing a variety of disorders [1-3].

Heavy metal ions can be removed from the environment using a variety of methods such as precipitation, solvent extraction, vacuum evaporation, membrane technologies, adsorption or ionic exchange, the selection of a method depending mainly upon the heavy metal ion concentration. Adsorption is used when concentration of heavy metal ions is small, but is higher that the allowable concentration according to environmental legislation.

Low-cost adsorbents such as natural zeolites, clay minerals (kaolinite, montmorillonite), chitosan, peat moss, fly ash, coal, natural oxides (aluminium oxide, ferric oxide), industrial waste (waste slurry, iron (III) hydroxide, lignin, furnace slag, sawdust, activated red mud, bagasse fly ash, brewery waste biomass), rice husk, coconut shell, agricultural waste, etc. were all considered as adsorbents for heavy metal ions (cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, zinc) removal from wastewaters [4,5]. Due to their availability and low costs, natural materials such as zeolites and clay minerals became object of many research papers in the last years.

In Romania, most studies related to the identification of new materials used in environmental protection, concerned natural zeolites (zeolitic volcanic tuffs), which were used in various applications based on their properties [6]. Clays, especially bentonite clays, are present in large amounts in Romania. Bentonite collected from Transilvanian deposits, Petreşti, Oraşul Nou and Valea Chioarului were considered for heavy metal ions (Petreşti), ammonium ions (Petreşti, Valea Chioarului, Oraşul Nou) and organics (Petreşti, Oraşul Nou) removal from wastewaters [7-9].

Clay minerals are aluminium hydrosilicates, crystallized in monoclinic system, characterized by planar reticular structures. Stratified structure of mineral clays is determined by the combination in one reticular plan (structural unit) of two cationic layers, one layer in which silicon is coordinated tetrahedric with O·OH (tetrahedric level Te) and one layer in which aluminium is coordinated octahedric with O·OH (octahedric level Oc). These layers are bonded between them with van der Waals bonds forming the structural unit. According to the numbers of Te and Oc layers, clay minerals are classified in 1Te:1Oc (e.g. kaolinite), 2Te:1Oc (e.g. montmorillonite) and 2Te:2Oc (e.g. chlorite). The layered structure of the clay minerals and presence of isomorphous replacement of Si^{4+} with Al^{3+} (negative charge compensated by Na^{+}, K^{+}, Ca^{2+} and/or Mg^{2+}) determines their main properties: swelling, water and organic compounds adsorption and ionic exchange capacity [4,10].

Bentonites are clay rocks formed by devitrification and chemical alteration of a glassy igneous material, usually a tuff or volcanic ash. Bentonites are composed mainly of smectite group minerals. This group includes dioctahedral minerals such as montmorillonite, beidellite and nontronite and trioctahedral minerals such as hectorite and saponite. The main mineral from smectite group is montmorillonite, a hydrated sodium calcium aluminum magnesium silicate hydroxide.

The purpose of this study was to characterise the bentonite from Oraşul Nou (ON) deposit, Satu Mare County, Romania and to evaluate its heavy metal ions (Zn^{2+}, Pb^{2+}, Cd^{2+}) removal capacity. Also, first, pseudo second and Elovich kinetic models were used to study the adsorption kinetics of zinc ions on the betonite sample.

RESULTS AND DISCUSSION

Bentonite characterization

The bentonite deposit from Oraşul Nou (Satu Mare County) is located about 30 km north-west of the city of Baia Mare, in the Oaş Basin, Maramureş Depression. The area consists of sedimentary rocks and volcanic rocks. Sedimentary formations are of marine origin (marls, fine sandstones) of Neogene age. Volcanic rocks outcrops are up to 300 m in thickness and consist of rhyolite and rhyolitic tuffs, andesitic tuffs, perlites, dacite and pyroclastic rocks. The bentonite deposit from Oraşul Nou formed by alteration of rhyolites and perlites.

Bentonite bodies are lens-like shaped, ranging between 3 and 8 m in thickness, 100 to 400 m in length and 50 to 250 m in width.

In Mujdeni area, from where we collected the samples used for our experiments, a rhyolite basement is covered by altered perlites gradually passing into bentonites. The bentonite layers are followed by unaltered perlites, clay and the soil. The bentonitization of perlites and rhyolites is a process connected to solutions' complex circulation favoured by the porosity of the rhyolites in the basement and by the small, concentric fissures within the perlites.

As a rule, bentonites are white in colour, fine grained or compact, the perlitic structure being more or less preserved.

Mineralogically, they contain clay minerals (montmorillonite, and subordinately kaolinite, illite), cristobalite, carbonates, zeolites (clinoptilolite), iron oxi-hydroxides and relics of primary minerals such as quartz and feldspar. The ratio between the montmorillonite and kaolinite-group minerals varies according to the degree of transformation of the original rock. Thus, the minerals from the kaolinite group are clearly dominant as compared to montmorillonite in the areas where bentonitization was not completed, while in the intervals with bentonite montmorillonite represents the major phase.

The chemical composition of the bentonites from Oraşul Nou is presented in the table 1. It is worthy to note the relatively high Al_2O_3 and relatively low Na_2O contents.

Semi-quantitative mineralogical composition of clay raw material realised by means of X-ray diffraction analysis, figure 1, indicated that in all bentonite samples, smectite (montmorillonite) is the most abundant clay mineral. Identified minerals were: smectite (montmorillonite), cristobalite, quartz, feldspars. The basal space was recorded at 15 Å, indicating the precence of Ca-montmorillonite [11].

The montmorillonite amount varies between 20-85%, according to the alteration degree of the rock; locally, it may even reach values of 95%.

Table 1. Chemical composition of the bentonite samples from Oraşul Nou (Satu-Mare County).

Oxides, [%]	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**TiO_2**	**L.O.I.**
Oraşul Nou	60.62 -71.46	15.40 -23.55	0.84 -2.34	1.18 -1.86	0.54 -2.05	0.00 -0.30	0.25 -2.16	0.15 -0.36	8.69 -12.4

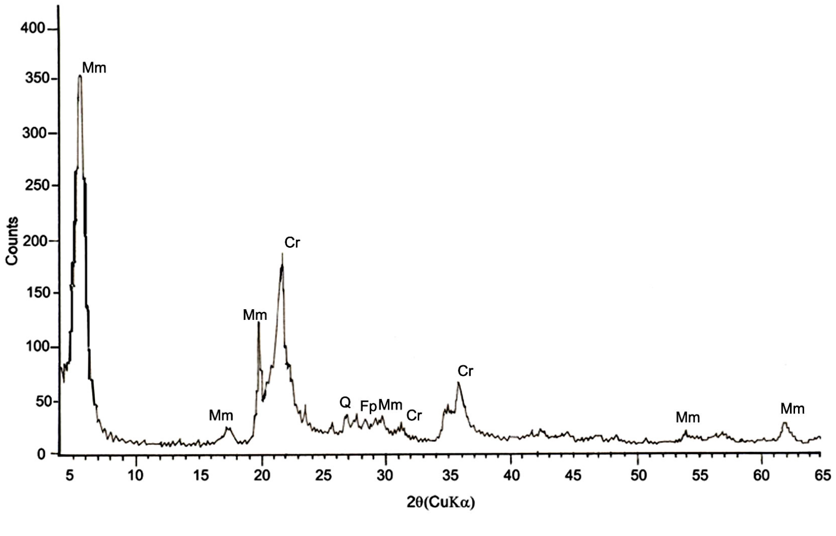

Figure 1. Powder X-ray diffractogram of the Oraşul Nou bentonite sample; Mm- montomorillonite, Cr-cristobalite, Q-quartz, Fp-feldspar.

Examination of IR spectra of the bentonite sample (figure 2), indicates the presence of specific 2:1 clay mineral peaks (montmorillonite) with peaks in 600-700 cm^{-1} region that could be attributed to illite, clinoptilolite or opal CT accompanying minerals [12-19]. The identified peaks can be attributed as follows: 3631.30 cm^{-1} – stretching vibrations of isolate hydroxyls and OH less firmly bond to the tetrahedrical outer layer, 3448.10 cm^{-1} – stretching vibrations of the structural OH and also of the hydration water, 1639.20 cm^{-1} – angular deformation of hydroxyls from adsorbed water molecules (held in interlayers), 1095.37 and 1047.53 cm^{-1} – main bands corresponding to the stretching vibrations of Si,Al-O, 794.53 and a shoulder at 620.97cm^{-1} – weak bands corresponding to the stretching vibrations of Si,Al-O (there are not specific peaks for montmorillonite and could be attributed to the accompanying minerals), and 474.40 and 524.54 cm^{-1} bending vibrations of Si-O-M bonds (M can be Mg, Al, Fe).

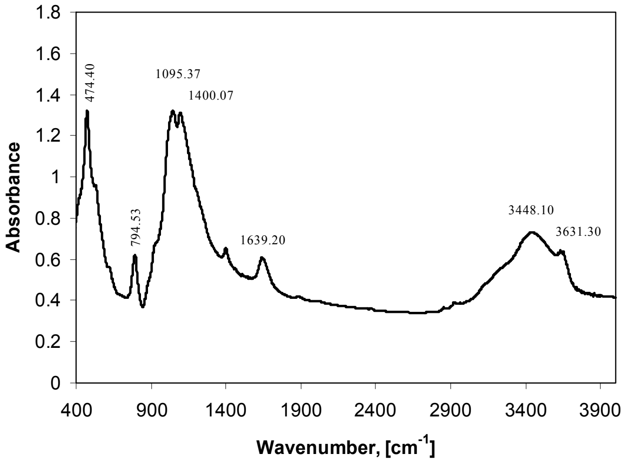

Figure 2. FTIR spectrum of the bentonite sample from Oraşul Nou deposit.

Heavy metal ions removal results

The results obtained in case of **zinc removal** from monocomponent model solutions are presented and discussed in terms of removal efficiency and adsorption capacity.

In figure 3, evolution of zinc removal efficiency in time is presented for the experiment conducted in static regime (C_i = 125 mg Zn^{2+}/L, 2 g bentonite, 20 ml zinc solution). A closer inspection of this evolution led to the conclusion that in the first 24 hours, concentration of zinc ions drops significantly from the initial value to 1.68 mg Zn^{2+}/L, leading to high removal efficiency (98.71%). Equilibrium was reached in 48 hours, when concentration of zinc ions in solution drops to 0 (100% efficiency) and adsorption capacity increased up to 1.3003 mg Zn^{2+}/g bentonite.

The experiments realised in dynamic regime (3D shaker) were conducted with the modification of the initial concentration of zinc in model solutions, and bentonite quantity. Results are presented in figures 4 to 7 in terms of removal efficiency and adsorption capacity.

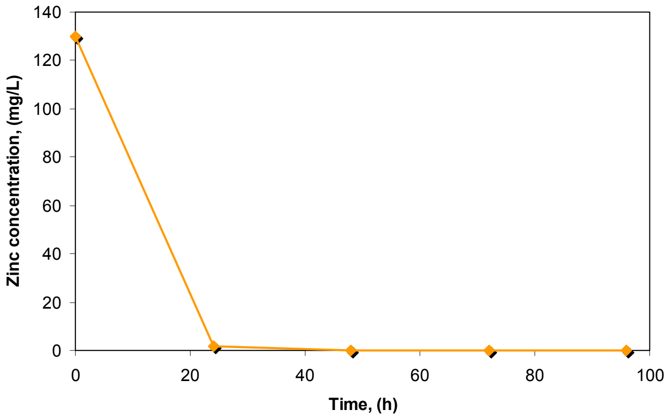

Figure 3. Removal efficiency evolution in time during zinc removal process on Oraşul Nou bentonite sample in static regime (C_i = 125 mg Zn^{2+}/L, 2 g bentonite).

From figure 4, where we presented the *influence of the initial zinc concentration* over the evolution of the removal efficiency it can be concluded that an increase of the initial concentration led to a decrease of the removal efficiency. Also in terms of time evolution of the removal efficiency, we observed that trends are similar. Equilibrium was reached after around 45 minutes. Maximum removal efficiencies were as follows 100, 83.48, and 71.65 for 125, 250, and 525 mg Zn^{2+}/L initial concentrations respectively. Adsorption capacities calculated for the three experiments are presented in figure 5. It is easy to observe, that with an increase in the initial concentration, zinc quantities retained on the bentonite sample increase. The highest adsorption capacity was calculated to be 3.8171 mg Zn^{2+}/g bentonite in case of the highest initial concentration (525 mg Zn^{2+}/L).

Influence of the *bentonite quantity* over the zinc removal efficiency is presented in figure 6 as evolution in time and in figure 7 as maximum values. If we follow the evolution of the removal efficiency in time we can observe that as the bentonite quantity increase the removal efficiency has higher values and equilibrium is reached faster. When we used 3 g of bentonite the equilibrium was reached in 15 minutes, with a maximum removal efficiency of 100%. In case of 2 g, equilibrium was reached in 45 minutes with 100% removal efficiency, while in case of 1 g, equilibrium was reached in 60 minutes with a removal efficiency of 98.71%.

At a closer inspection of the results obtained in case of the bentonite quantity influence we can conclude that an increase in the adsorbent quantity has to be implemented in an industrial scale process only after the realisation of the economic calculations, taking in account that an increase from 1 to 2 g of bentonite led to an increase of just 1.29 points (from 98.71 to 100%) of the removal efficiency, but with a decrease from 2.5671 to 1.3003 mg of the Zn^{2+} retained on the adsorbent unit (g).

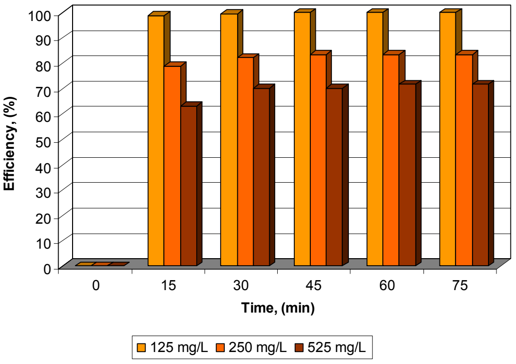

Figure 4. Influence of the initial zinc concentration over the removal efficiency evolution in time, during zinc removal process on 2 grams of Oraşul Nou bentonite sample in dynamic regime (3D shaker).

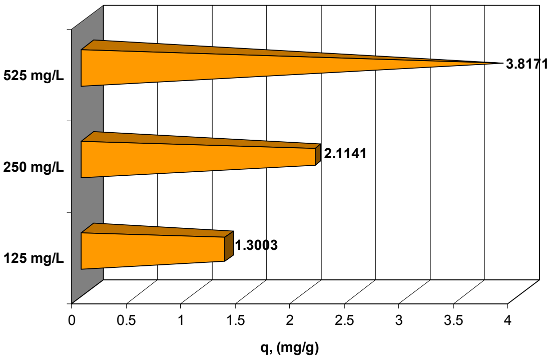

Figure 5. Influence of the initial zinc concentration over the adsorption capacity, in zinc removal process on 2 grams of Oraşul Nou bentonite sample in dynamic regime (3D shaker).

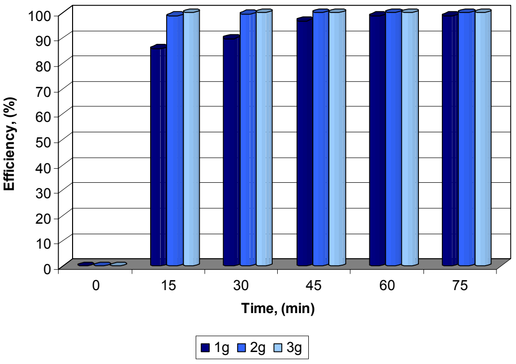

Figure 6. Influence of the bentonite quantity over the removal efficiency evolution in time, during zinc removal process on Oraşul Nou bentonite sample in dynamic regime (3D shaker), C_i = 125 mg Zn^{2+}/g.

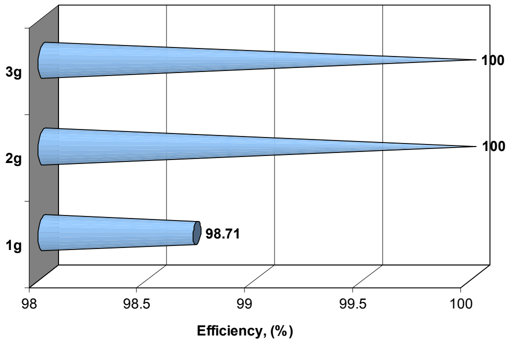

Figure 7. Influence of the bentonite quantity over the maximum removal efficiency, in zinc removal process on Oraşul Nou bentonite sample in dynamic regime (3D shaker), $C_i = 125$ mg Zn^{2+}/g.

In order to design and optimise a wastewater treatment process is also important to know the *adsorption kinetic models*, which can correlate the adsorbate up-take rate with the bulk concentration of the adsorbate. First-order (Lagergren), pseudo-second-order and Elovich models were used to study the adsorption kinetic of zinc ions on the bentonite sample [20]. Linear regression was used to determine the best fitting kinetic rate equation (correlation coefficients, R^2) [21].

Lagergren suggested a first-order equation for the adsorption of liquid/ solid system based on solid capacity, which can be expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (1)$$

Integrating eq. (1) from the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (2)$$

where,

q_e and q_t are the amounts of zinc adsorbed (mg/g) at equilibrium and time t, respectively

k_1 is the rate constant of first-order adsorption (1/min).

In order to determine the rate constant and equilibrium zinc uptake, the straight line plots of $\ln(q_e-q_t)$ against t, eq. (2), were made at four different initial zinc concentrations. Correlation coefficients between 0.8080 and 0.9500 were obtained (figure not shown), therefore zinc adsorption on bentonite cannot be classified as first-order.

The pseudo-second-order kinetic model is derived on the basis of the adsorption capacity of the solid phase, expresses as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (3)$$

Integrating eq. (3) from the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{4}$$

where,

q_e and q_t are the amounts of zinc adsorbed (mg/g) at equilibrium and time t, respectively

k_2 is the rate constant of first-order adsorption (g/mg·min).

Equation (4) can be rearranged in linear form, as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

In order to determine the rate constant and equilibrium zinc uptake, the straight line plots of t/q_t against t, eq. (5), were made at four different initial zinc concentrations. Correlation coefficients between 0.9867 and 1.0000 were obtained (figure 8 and table 1), therefore zinc adsorption on bentonite can be classified as pseudo-second-order.

Elovich equation that is widely used to describe the kinetics of chemisorption of gas and solids can also be applied to liquid/solid systems and can give information about the possibility that chemical adsorption or chemical adsorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate to be rate determining step [20]. The Elovich equation was derived from the Elovich kinetic equation:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t} \tag{6}$$

Integrating eq. (6) from the boundary conditions t = 0 to t = t and $q_t = 0$ to $q_t = q_t$, gives:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t + t_0) \tag{7}$$

where,

α and β are the parameters of the equations, and

$t_0 = 1/(\alpha\beta)$

α represents the rate of chemisorption at 0 coverage, (mg/g·min),

β is related to the extent of surface coverage and activation energy for chemisoprtion, (g/mg) [20].

When $t_0 << t$, then eq. (7) is replaced by:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{8}$$

In order to determine equations parameters, the straight line plots of q_t against ln(t), eq. (8), were made at four different initial zinc concentrations. Correlation coefficients between 0.8562 and 0.9188 were obtained (figure not shown), therefore zinc adsorption on bentonite cannot be classified as chemisorption.

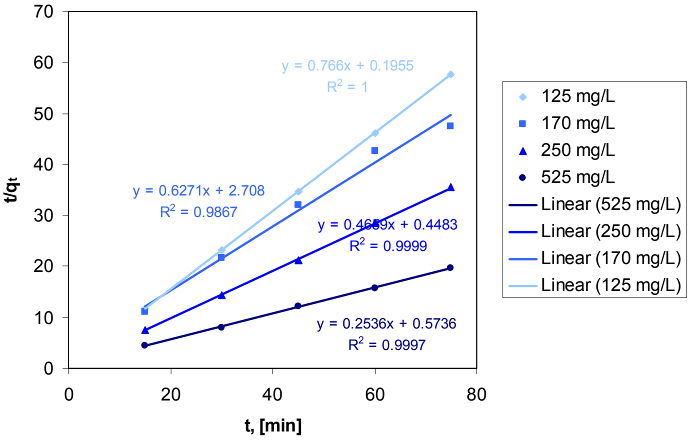

Figure 8. Plots of the second-order model, at different initial zinc concentrations (dynamic regime, 2 g bentonite, 20 ml zinc solution).

Table 1. Second order adsorption rate constants, and calculated and experimental q_e values for zinc adsorption using different initial concentrations.

C, (mg Zn^{2+}/L)	**q_e (exp), (mg Zn^{2+}/g)**	**k_2, (g/mg·min)**	**q_e (calc), (mg Zn^{2+}/g)**	**R^2**
125	1.3003	3.0013	1.3005	1.0000
170	1.5772	0.1452	1.5946	0.9867
250	2.1141	0.4842	2.1464	0.9999
525	3.8171	0.1121	3.9432	0.9997

The results obtained in case of **lead and cadmium removal** from monocomponent model solutions are also presented and discussed in terms of removal efficiency and adsorption capacity.

Lead removal process was realised in static and dynamic (3D shaker) regimes using 2 g of bentonite and 20 ml solution of 54 mg Pb^{2+}/L. In both static and dynamic regime the initial concentrations drops significantly in the first 24 h and 15 min, from the initial 54 to 3.73 and 0.01 mg Pb^{2+}/L, respectively, indicating a favourable diffusion process in case of dynamic conditions. Maximum efficiency reached 99.99% in both cases, while the adsorption capacity was calculated to be 0.5390 mg Pb^{2+}/g bentonite. Removal efficiency evolution in time during lead removal process on Oraşul Nou bentonite sample in dynamic regime is presented in figure 9. Equilibrium was reached in 72 h in static regime and 60 minutes in dynamic regime.

Cadmium removal process was realised in static regime using a 2150 mg Cd^{2+}/L model solution, 20 ml, and 2 g of bentonite. Maximum removal efficiency value was calculated to be 48.08% corresponding to an adsorption capacity of 10.3418 mg Cd^{2+}/g. Equilibrium was reached in 48 h. Evolution of removal efficiency in dynamic regime (C_i = 25 mg Cd^{2+}/L, 2 g bentonite, 20 ml solution) is presented in figure 10. Removal efficiency increases slowly in the first 60 minutes, until 62.37%, value obtained at equilibrium (60 min). At equilibrium, adsorption capacity was calculated to be 0.1589 mg Cd^{2+}/g. The adsorption capacity values obtained, ranging between 0.1589 and 10.3418 mg Cd^{2+}/g indicates that our bentonite sample has high adsorption capacities, therefore it can be used to remove cadmium ions from diluted as well as more concentrated solutions.

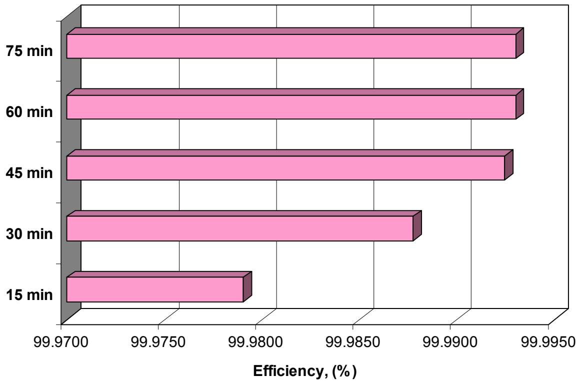

Figure 9. Removal efficiency evolution in time during lead removal process on Oraşul Nou bentonite sample in dynamic regime (3D shaker), C_i = 54 mg Pb^{2+}/L, 2 g bentonite, 20 ml solution.

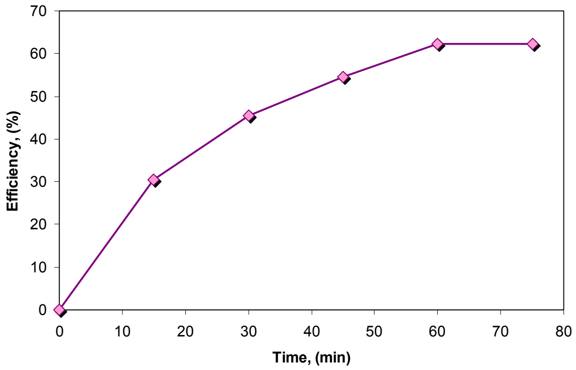

Figure 10. Removal efficiency evolution in time during cadmium removal process on Oraşul Nou bentonite sample in dynamic regime (3D shaker), C_i = 25 mg Cd^{2+}/L, 2 g bentonite, 20 ml solution.

CONCLUSIONS

A bentonite sample from Oraşul Nou deposit, (Transilvania, Romania), was used to remove heavy metal ions (Zn^{2+}, Pb^{2+}, Cd^{2+}) from model monocomponent wastewaters.

Physico-chemical and mineralogical analyses of the bentonite from Oraşul Nou, Satu Mare County, Romania indicated that our sample is a smectitic clay mineral, containing Ca-montmorillonite (up to 85%).

The considered bentonite sample proved to be efficient in heavy metal ions removal process. Efficiencies up to 100% in case of Zn^{2+} (C_i = 125 Zn^{2+} mg/L), 99.99% in case of Pb^{2+} (C_i = 54 mg Pb^{2+}/L) and 62.37% in case of Cd^{2+} (C_i = 25 Cd^{2+} mg/L) in dynamic regime, were obtained.

First-order, pseudo-second-order and Elovich models were used to study the adsorption kinetic of zinc ions on the bentonite sample. We conclude that zinc adsorption on Oraşul Nou bentonite sample can be classified as pseudo-second-order.

EXPERIMENTAL SECTION

Bentonite compositional investigations

Representative bulk rock samples of bentonite were collected from open bentonite pits in Oraşul Nou area (Satu Mare County, Romania).

The analyses of whole-rock chemistry were performed at ICEI (Physico-Chemical Analises Center) Cluj-Napoca using usual analytical methods for silicate materials (wet chemistry).

X-ray diffraction analyses on random powders were performed using a Siemens Bruker unit with Cu Kα anticathode. The diffractograms were recorded from 10° to 70° 2θ. The analytic conditions are 40 A, 40 kV, step of 2 degrees. A semi-quantitative X-ray diffraction method to determine mineral composition was used.

Specific surface area of the bentonite sample was determined using Brunauer-Emmett-Teller (BET) method using a home made apparatus. BET specific surface area was determined to be 72 m^2/g.

FTIR spectrum of the bentonite sample was recorded using a Jasco 615 spectrophotometer, 400-4000 cm^{-1}, resolution 2 cm^{-1}.

Heavy metal ions removal procedure

Heavy metal ions (Zn^{2+}, Pb^{2+}, Cd^{2+}) removal was realised on a representative bentonite sample from Oraşul Nou (ON) deposit, Satu Mare County, Romania. The bentonite sample was used as powder, particles with grain size smaller than 0.2 mm, without any chemical treatment.

For the heavy metal ions removal study we used synthetic monocomponent solutions containing zinc ions (125-525 mg Zn^{2+}/L), lead ions (54 mg Pb^{2+}/L) and cadmium ions (25-2150 mg Cd^{2+}/L) prepared from $ZnSO_4{\cdot}7H_2O$, $(CH_3OO)_2Pb{\cdot}3H_2O$ and $Cd(NO_3)_2{\cdot}4H_2O$ salts (analytical purity reagents). Cadmium and lead ions in solution were determined using an ion selective electrode and a pH meter (Jenway 3330), while in case of zinc ions we used a spectrophotometric method (potassium ferrocyanure, λ = 420 nm, Jenway 6305 spectrophotometer). Experiments were carried out without any modification of the temperature (the experiments were realised at room temperature, 20°C) and pH of the synthetic solutions.

Heavy metal ions removal process was realised in a batch reactor in static and dynamic (3D shaker) regimes, using 1, 2 and 3 grams of bentonite in contact with 20 ml heavy metal ion solution. In order to determine the exact concentration of heavy metal ions, water samples were taken every 24 hours in static regime and every 15 minutes in dynamic regime, until the equilibrium was reached.

We studied the influence of the working regime, static and dynamic (3D shaker), initial concentration and bentonite quantity (zinc) over the process efficiency and adsorption capacity.

Removal efficiencies (%) and adsorption capacities (mg M^{n+}/g) were calculated in order to establish the effectiveness of the considered bentonite sample in the heavy metal ions removal process (the calculated values of removal efficiencies and adsorption capacities should be regarded according to the precision of the determination methods we used).

First-order, pseudo-second-order and Elovich models were used to study the adsorption kinetic of zinc ions on the bentonite sample.

ACKNOWLEDGMENTS

This work was realized with financial support from Romanian National University Research Council, Grant CNCSIS A 1334.

REFERENCES

1. H. Abadin, A. Ashizawa, Y. W. Stevens, F. Llados, G. Diamond, G. Sage, M. Citra, A. Quinones, S. J. Bosch, S. G. Swarts, “Toxicological profile for lead”, U.S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, **2007**.
2. J. Taylor, R. DeWoskin, F. K. Ennever, “Toxicological profile for cadmium”, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, **1999**.

3. N. Roney, C. V. Smith, M. Williams, M. Osier, S. J. Paikoff, “Toxicological profile for zinc”, U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, **2005**.
4. K. G. Bhattacharyya, S.S. Gupta, *Advances in Colloid and Interface Science*, **2008**, *140*, 114.
5. S. Babel, T. A. Kurniawan, *Journal of Hazardous Materials*, **2003**, *B97*, 219.
6. A. Măicăneanu, H. Bedelean, M. Stanca, “Zeoliții naturali. Caracterizare şi aplicații în protecția mediului”, Presa Universitară Clujeană, **2008**, Cluj-Napoca, chapter 1-3, 6.
7. H. Bedelean, A. Măicăneanu, S. Burcă, M. Stanca, *Clay Minerals*, **2009**, in press.
8. H. Bedelean, A. Măicăneanu, S. Burcă, M. Stanca, Sesiunea Ştiinţifică anuală GEO 2009 a Facultății de Geologie şi Geofizică, în parteneriat cu Societatea Geologică a României şi Societatea Română de Geofizică, **2009**, Bucureşti.
9. M. Stanca, A. Măicăneanu, S. Burcă, H. Bedelean, International Conference, Sustainable Development in the Balkan Area: Vision and Reality, **2007**, Alba-Iulia.
10. D. Rădulescu, N. Anastasiu, “Petrologia rocilor sedimentare”, Editura Didactică şi Pedagogică, **1979**, Bucureşti, chapter 6.
11. N. Anastasiu, “Minerale şi roci sedimentare, Determinator, Editura Tehnică, **1977**, Bucureşti, chapter 3.
12. D. Haffad, A. Chambellan, J. C. Lavalley, *Catalysis Letter*, **1998**, *54*, 227.
13. A. Bakhti, Z. Derriche, A. Iddou, M. Larid, *European Journal of Soil Science*, **2001**, *52*, 683.
14. W. P. Gates, J. S. Anderson, M. D. Raven, G. J. Churchman, *Applied Clay Science*, **2002**, *20*, 189.
15. P. Komadel, *Clay Minerals*, **2003**, *38*, 127.
16. K. A. Carrado, (S.M. Auerbach, K.A. Carrado, P.K. Dutta, editors), in *Handbook of layered materials*, Marcel Dekker Inc., **2004**, New-York, chapter 1.
17. R. J. Hu, B. G. Li, *Catalysis Letter*, **2004**, *98*, 43.
18. A. Meunier, *Clays*, Springer-Verlag, **2005**, Berlin, chapter 1.
19. S. Ozcan, O. Gok, A. Ozcan, *Journal of Hazardous Materials*, **2009**, *161*, 499.
20. C. Namasivayam, D. Sangeetha, *Adsorption*, **2006**, *12*, 103.
21. J. Febrianto, A. N. Kosasih, J. Sunarsao, Y. Ja, N. Indraswati, S. Ismadji, *Journal of Hazardous Materials*, **2009**, *162*, 616.