Study of Cadmium Sorption on Na-Montmorillonite

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In order to characterize the sorption process of Cd(II) on Na – montmorillonite, the influence of the following set of operational variables was investigated: initial cadmium cations concentration, clay particle size and solution ionic strength. Equilibrium isotherms have been measured and analyzed using a Langmuir isotherm model. The metals were predominantly adsorbed on the permanent charge sites, but there was also evident a substantial involvement of the hydroxyl groups on the edges of Na-montmorillonite in specific adsorption of the cations especially at higher pH. In low ionic strength (0.01 M $NaNO_3$*) solutions, the fixation of* Cd^{2+} *appears to be controlled by a mechanism indicated of the ionic exchange. Important cadmium uptake occurred in the first ten minutes of reaction. In contrast, at high ionic strength (0.1 M* $NaNO_3$*), metal cation uptake rate was much slower. Using the shrinking core model the internal diffusion of cadmium sorption process was proposed as the rate-limiting step.*

Keywords: cadmium, sorption, montmorillonite

The removal of heavy metals from water and industrial effluents is compulsory due to their extreme toxicity towards aquatic life and humans [1].

Cadmium (Cd) is one of those heavy metals that have received the most attention with regard to accumulation in soils, uptake by plants, and contamination of groundwater.

It is found everywhere in the environment including air, water, soil, sediments, and food. An industrially important compound, cadmium's main uses are battery production; as a weathering and ultraviolet light stabilizer in polyvinyl chloride (PVC) plastic; as a pigment in artists paints, ceramics, plastics; in metal plating; and in soldering compounds and alloys [2]. It is desirable in these industries because it is highly resistant to rusting and corrosion under alkaline and saline conditions, photoconductive and electroluminescent. It is produced as a coproduct during smelting of ores, most commonly zinc (~0.3 kg of cadmium for each ton of zinc). Cadmium occurs in nature predominantly as cadmium sulfide, a stable solid compound. Small amounts are released naturally during weathering of minerals, forest fires, and volcanic emissions, but most releases are a result of human activities. In general, the major pathways through which cadmium is released to the environment are to the atmosphere during fuel combustion, smelting, incineration of trash; to water via sewage and wastewater discharging (water contamination during battery, paint, plastics production, during soldering) point and nonpoint source runoff associated with the application of phosphate fertilizers and biosolids (product of sewage sludge); and as leachate from soils, landfills, and groundwater. Cadmium is also released to air, water, and land during mining operations. Cadmium can be leached from refuse material, especially under aerobic conditions and leaching is accentuated in the presence of brine solutions. The release via incineration and smelting processes produces fine airborne particles that attach quickly to dry or wet particles that can then be transported relatively long distances (miles) away from the source. Cadmium is a probable carcinogen and is associated with lung cancer. The primary sources of cadmium to humans are through food and cigarette smoke. Aquatic and terrestrial plants take up cadmium that then can be taken up by animals and humans and concentrates in the liver and kidney and can cause kidney disease. Plants such as tobacco, fruits, grains, and vegetables readily take up and retain cadmium, which, in turn, is taken up and retained by humans. Smokers tend to have higher concentrations of cadmium due to the cadmium associated with tobacco leaves. The retention of cadmium from inhalation is twice as high as the retention from food. Shellfish and organ meats are also sources of cadmium. The toxicity of cadmium is variable depending on the chemical and physical form. Recent research has found that cadmium can mimic estrogen's impact on cells, altering the reproductive systems of rats, and cadmium may also disrupt DNA repair.[3] Virtually every case of Cd poisoning is associated with occupational exposure, and the main health problems have been associated with kidney disease. Cadmium tends to continuously accumulate until the age of 50 to 60, and then concentrations begin to decline; however, the effects on the kidney and liver already have occurred and are irreversible. Cadmium is also associated with brittle bones and under very high doses can cause death.

According to a World Health Organization recommendation, the daily intake of cadmium should not exceed 1 μg per kg of body weight. For this reason, it has been recommended that the upper limit of this metal in drinking water should be 5μg dm^{-3}.

Taking into account all the above, we have considered of great interest to study the sorption process of cadmium on mineral clays.

Sorption is an efficient method for the removal of metal ions from dilute aqueous solutions. Among the different sorptive materials that have been used to remove metal ions from aquatic solutions one can mention hydroxides and oxides [6], molecular sieves [7], fly ash [8], bone char [9], biomass [10, 11] and clays [12-17].

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Clays are abundant and inexpensive layered aluminosilicate minerals with adsorbent properties due to their large surface areas and negative layer charge. In general, chemical species can interact with clays either by ion exchange [12] or physisorption [18], both being reversible processes.

Among the mineral clays, smectites, especially montmorillonite, deserve special attention. Montmorillonite is a widespread mineral of weathering formation and sediment [19], that possesses a large specific surface area and a high structural charge (up to 1000 meq/ kg) which enable it to sorb organic and inorganic cations. Exchangeable cations were shown by X-ray diffraction to be located in the clay interlayer[20]. Many studies using electron-spin resonance (ESR), X-ray photoelectron spectroscopy, and extended X-ray adsorption fine structure (EXAFS) spectroscopy further indicated that many exchangeable divalent cations keep a complete hydration sphere in water- saturated media. Outer sphere (OS) surface complexes are thus formed near the basal plane of smectites [21-23]. More recently, studies of cation sorption performed at low cation concentration showed that uptake increases with pH, especially under high ionic strength conditions [24, 25]. This *p*H-dependent uptake results in proton release, as for metal ion sorption on hydroxide mineral surfaces [26], and was interpreted in terms of inner sphere (IS) complex formation on surface sites at the edges of mineral clay [27-28].

The present paper aims at clarifying the equilibrium and kinetic features of, Cd(II) sorption on Na- montmorillonite.

Experimental part

The adsorbent used in this study was Na-montmorillonite, with 99% of the clay particles < 10 μm as was supplied by I.C.P.M "MINESA - S.A." Cluj Napoca.

The cation exchange capacity of the mineral clay (CEC) measured at *p*H 6 by Cs^+ exchange, was equal to 0.92 $meqg^{-1}$. Specific surface area (SSA) of montmorillonite was obtained by N_2 adsorption at 77K using a Carlo Erba Sorptomatic equipment. By applying the BET method, the calculated SSA was $72.4 m^2g^{-1}$.

Homoionic aqueous solutions of Cd^{2+} were prepared from the nitrate salt of the metal, $Cd(NO_3)_2 \cdot 4H_2O$ (p.a. Fluka). Exact concentration of these stock solutions were determined by flame atomic absorption spectrometry. All metal solutions were diluted to the required concentration in bidistilled water.

As background electrolyte $NaNO_3$ has been used. In all the Cd sorption experiments, the concentration of Na-montmorillonite in liquid phase was $C_M = 1 g\ L^{-1}$.

Sorption experiments

Sorption of Cd on Na-montmorillonite was determined in batch experiments. The experiments were performed at 20.0 ± 0.1° C in glass vessels immersed in a thermostatic water bath.

In order to obtain sorption isotherms twenty milligrams of Na- montmorillonite were mixed with 10 mL of $2 \cdot 10^{-2}$ M $NaNO_3$ and 10 mL of $Cd(NO_3)_2 \cdot 4H_2O$ aqueous solutions with metal concentrations ranging from 0.1 to 1.2 mmol L^{-1}.

A rotating magnetic bar ensured vigorous stirring of the suspension. The sorption experiments were carried out for three pH values: 4.5, 5.5, 6.5. The lowest was value imposed by the possible dissolution of Na-montmorillonite (at *p*H<4). The upper *p*H limit was imposed by the necessity to avoid the precipitation of pure or mixed Cd carbonates or hydroxides (at *p*H > 7.5 for Cd^{2+}).

The *p*H values were adjusted by adding small volumes of 10^{-2} M NaOH or 10^{-2} M HNO_3 solutions and monitored by the means of a *p*H electrode (Metrohm 6.0204.100) connected to a pH meter (Metrohm 713). The electrode was calibrated with buffer solutions (Merk, titrisol).

According to a previous kinetic study a 24-h reaction period – with continuous stirring – was chosen in order to reach the equilibrium. After the equilibrium was reached, the clay was separated from solution using a Beckman J-2-21 laboratory centrifuge at 10000 rpm for 30 min. The supernatant cadmium concentration was determined by atomic absorption spectroscopy (Perkin-Elmer 1100B atomic absorption spectrometer). The amount of adsorbed metal was calculated as a difference between the initial and final solution concentration.

Metal solutions without adsorbent were also stirred for 24 h and used as reference ones.

Kinetic studies

The effect of montmorillonite particle size, initial cadmium concentration and solution ionic strength on sorption kinetic of Cd(II) was studied.

A series of sorption experiments were carried out for three different initial concentration of heavy metal (0.1; 0.2; 0.4 mmol L^{-1}).

Experiments were conducted at 20±0.1°C in glass vessels immersed in a thermostatic water bath, without CO_2 elimination.

A suspension of $1 g \cdot L^{-1}$ montmorillonite was obtained by mixing the appropriate amounts of montmorillonite stock suspension and $NaNO_3$ solution. Kinetic experiments were initiated by adding an aliquot of $0.1 \cdot 10^{-4}$ $0.2\ 10^{-4}$ or $0.4\ 10^{-4}$ M cadmium solution, respectively.

The *p*H of the suspensions was maintained at 5.50± 0.05, below the precipitation level for this metal by adding small volumes of 0.1M NaOH or 0.1 M HNO_3 solutions. The *p*H was monitored by a *p*H electrode (Metrohm 6.0204.100) connected to a pH meter (Metrohm 713). The concentration of background electrolyte solution was 0. 01M.

A rotating magnetic bar ensured vigorous stirring of the suspension.

After a given time 5-mL samples were withdrawn from the reaction vessel and immediately centrifuged.

The cadmium concentration in the supernatant was determined by atomic absorption spectroscopy. The amount of adsorbed metal was calculated making the difference between the initial and the final solution concentration.

Sorption studies were conducted likewise but for three different particle sizes of minus 2 μm, (4-6) μm and (8-10) μm.

The initial concentration of cadmium in suspension was $4 \cdot 10^{-4}$ M.

The kinetic of Cd(II) sorption on Na-montmorillonite was investigated in a similar way but for two concentration of background electrolyte 0.01M and 0.1M, respectively.

The amount, q_t, of metal ion sorbed at time *t*, is calculated from the mass balance equation:

$$q_t = (C_0 - C_t)V/M \qquad (1)$$

where:

C_0 – represents the initial metal concentration;
C_t – final metal concentration;
V – volume of solution;
M – mass of sorbent.

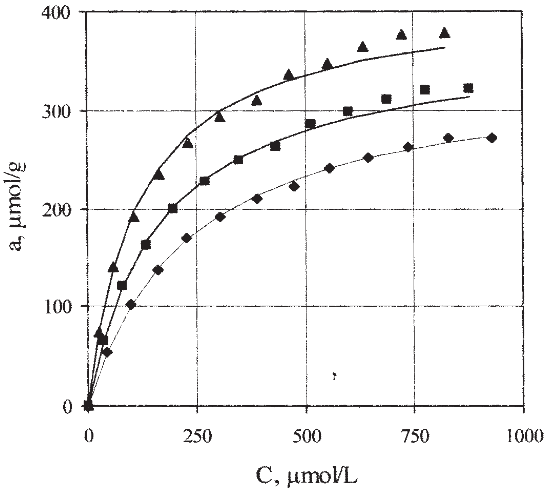

Fig. 1.Cd(II) adsorption isotherms
Symbols represent experimental data points, whereas lines are the Langmuir-fit adsorption curves.
*p*H= 5.50 ± 0.05; T= 20.00.1°C; I= 10^{-2} M $NaNO_3$; C_M= 1g·L^{-1}
♦pH= 4..50 ± 0.05; ■ *p*H= 5.50 ± 0.05;
▲*p*H= 6.50 ± 0.05

Results and discussion

Equilibrium of sorption process

Cadmium adsorption isotherms are presented in figure1.

The maximum amounts of cadmium sorbed onto montmorillonite, at equilibrium, increase with pH increasing, resulting, respectively 273.9, 319.8 and 363.4 mmol kg^{-1}.

The heavy metal sorption data were well described by the Langmuir equation:

$$a = a_m \frac{bC}{1+bC} \qquad (2)$$

where:

a – represents the equilibrium concentration of adsorbed metal;

C – equilibrium concentration of metal in solution;

a_m – the maximum concentration of adsorbed metal;

b – equilibrium constant.

Langmuir equation can be written as:

$$\frac{C}{a} = \frac{C}{a_m} + \frac{1}{a_m b} \qquad (3)$$

and therefore a plot of *C*/*a* vs. C represents a straight line of slope $1/a_m$ and intersect point $1/ba_m$.

The straight line through the marked data is usually obtained by a linear least – square fitting procedure.

The equilibrium parameters for cadmium sorption on montmorillonite are shown in table 1.

Sorption experiments showed that the amounts of cadmium adsorbed on Na-montmorillonite at equilibrium, was higher at a higher *p*H level of the solution.

Kinetic of sorption process

The influence of the initial concentration of cadmium cations on the sorption rate is shown in figure 2.

Increasing of the initial Cd(II) concentration one obtain the increase of the amount of cation uptake.

The effect of the Na-montmorillonite particle size was investigated.

As shown in figure 3 the overall sorption rate of Cd(II) on mineral clay is dependent on montmorillonite particle size used.

The amount of cadmium cations sorbed on Na – montmorillonite increases while the clay particle size decreases.

External and internal mass transfer resistance by the clay particle is of concern for the sorption dynamics.

The sorption of Cd(II) on Na-montmorillonite at various ionic strengths is presented in figure 4. The amount of cadmium cations sorbed on mineral clay decreases while the ionic strength of solution increases.

At a low ionic strength (0.01M $NaNO_3$) about 60% from total amount of Cd(II) sorbed on mineral clay occurred in the first 8 min . Following this fast reaction step, sorption at low ionic strength went at a much slower rate. At high ionic strength (0.1M $NaNO_3$) the first stage represented by rapid cation sorption was far less pronounced than at low ionic strength. The cadmium uptake by Na-montmorillonite in this stage represents only 25% from total amount sorbed at equilibrium.

As illustrated in figures 2-4, the sorption rate could be divided into two stages, the fast initial rate followed by a much slower rate [29-31].

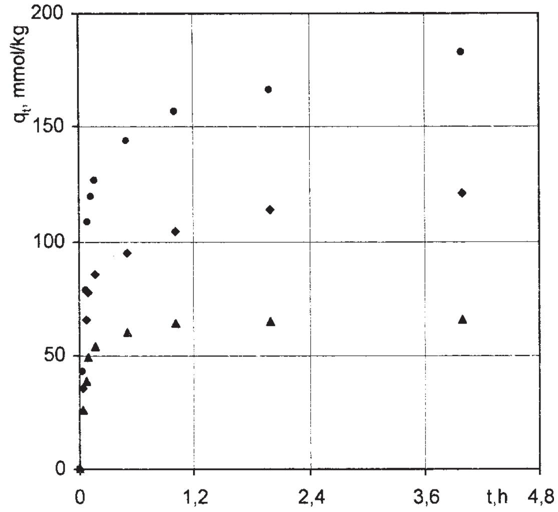

Fig. 2.Dependence of Cd(II) concentration in solid phase on the contact time, for different initial concentrations
T=20.0±0.1° C; *p*H= 5.50±0,05; C_M =1g·L^{-1}; I=10^{-2}M $NaNO_3$
● C_i =4·10^{-4}M;♦C_i =2·10^{-4}M; ▲C_i =10^{-4}M

Table 1

EQUILIBRIUM PARAMETERS, a_m AND *b*, for Cd^{2+} ADSORPTION ON Na – MONTMORILLONITE, AT DIFFERENT *p*H VALUES

pH	a_m [mmol kg^{-1}]	b [L $mmol^{-1}$]	*r*
4.5	344 ± 10	4 ± 1	0.999
5.5	373 ± 20	6 ± 1	0.999
6.5	416 ± 8	8 ± 2	0.998

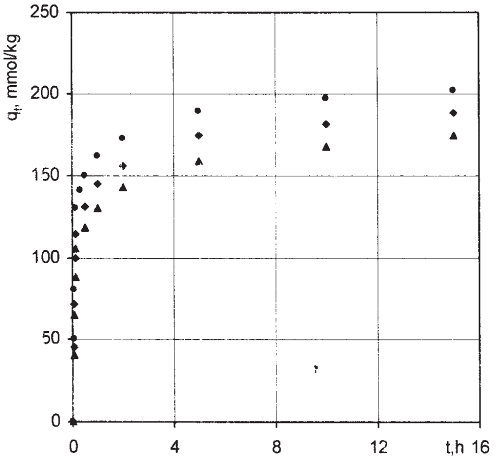

Fig. 3. Dependence of Cd(II) concentration in solid phase on the contact time, for different clay particle size
T=20.0±0.1° C; *p*H= 5.50±0,05; C_i =4·10^{-4}M; C_M =1g·L^{-1}
I=10^{-2} M $NaNO_3$; •D < 2 µm; ♦ 4µm <D,6µm;
▲8µm <8, 10µm

The first stage is represented by an initial rapid Cd(II) uptake in the first 8 min. A cation exchange mechanism is presumably responsible for this fast cation uptake [32]. It is likely that this cation exchange occurred on sites located on (001) basal planes of clay particles [33].

The second stage is much slower and took a few hours to reach the sorption equilibrium. Following this fast reaction step, sorption went at a much slower rate. This sorption rate observed within this second step is too slow to be accounted for cation exchange, which suggests the existence of a second uptake mechanism. Divalent cations adsorbed on exchange sites are known to form outer sphere surface complexes [21, 22]. The sorption observed for t > 8 min, coinciding with proton release, can be connected to specific uptake of Cd(II) with formation of Inner Sphere surface complexes on the edge of montmorillonite particles. EXAFS studies [29] reveal that the reactivity of edge sorption sites is not altered when the ionic strength is modified.

Mathematical Model

In this research the sorption of cadmium cations onto Na-montmorillonite was studied using the shrinking core model. The model was elaborated first by Yagi and Kunii [34], for gas-solid reactions and developed by Levenspiel [35]. Only the fundamental equations are presented in the following section.

An assumption of this model is that the adsorption rate is controlled by external or internal pore mass transfer resistance or by cation exchange reaction. The mechanism may be described as follows:

The mass transfer in the external liquid phase can be written as:

$$-\frac{1}{4\pi R^2}\frac{dN_A}{dt} = K_L[C_A^0 - C_{A(S)}] = K_L\, C_A^0, \qquad (4)$$

where $C_{A(S)}$ is practically zero.

The liquid diffusion in the pore occurs according to Fick's law:

$$-\frac{1}{4\pi r^2}\frac{dN_A}{dt} = D\frac{dC_A^0}{dr} \qquad (5)$$

The velocity of the concentration-front obtained from the mass balance on a spherical element is shown below:

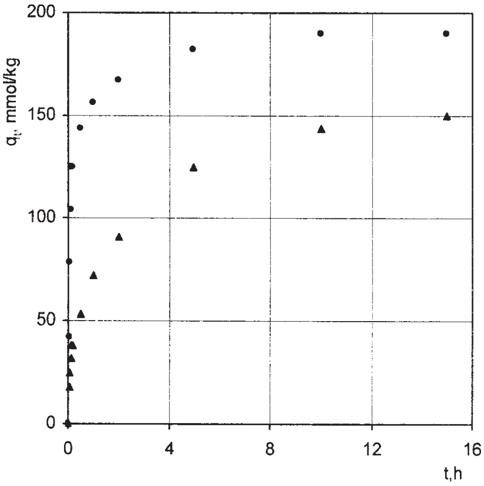

Fig.4. Dependence of Cd(II) concentration in solid phase on the contact time, for different ionic strength
T=20.0±0.1° C; pH= 5.50±0,05; C_i =4·10^{-4}M; C_M =1g·L^{-1};
•I=10^{-2}M; ▲I=10^{-1} M

$$-\frac{1}{4\pi r_n^2}\frac{dN_A}{dt} = KC_A^0 \qquad (6)$$

Using the notation:

$$\eta = \frac{reactedcationicmass}{totalcationicmass} = \frac{4/3C_c\pi R^3 - 4/3C_c\pi r r_n^3}{4/3C_c\pi R^3} = 1-(\frac{r_n}{R})^3 \qquad (7)$$

Solving equations 1,2 and 3 one obtain:

$$\eta = \frac{3K_L C_A^0}{C_c R}t \qquad (8)$$

$$1-3(1-\eta)^{2/3} + 2(1-\eta) = \frac{6DC_A^0}{C_c R^2}t \qquad (9)$$

$$1-(1-\eta)^3 = \frac{KC_A^0}{C_c R}t \qquad (10)$$

In the equations (4) –(10), the following notations have been used:

R – particle radius, m;
r_n – unreacted particle radius, m;
r – variable particle radius, m;
V – unreacted core volume, m^3;
C_c – cation exchange capacity, Kmol·m^{-3};
C_A^0 - initial metal cation concentration in liquid – phase, Kmol·m^{-3};
$C_{A(S)}$ – liquid-phase concentration at particle surface, Kmol·m^{-3};
N_A – Kmol of liquid phase, equivalent/s;
K_L – mass transfer coefficient in liquid-phase, m·s^{-1};
D – pore diffusion coefficient, m^2·s^{-1};
t – time, s.

The sorption kinetics data were analyzed using the equations of shrinking core model.

Taking into account the kinetic controlling processes, the equations (8)-(10) written as:

$$F(\eta) = \eta = \frac{t}{t_0} \text{ for external diffusion} \qquad (11)$$

$$F(\eta) = 1-3(1-\eta)^{2/3} + 2(1-\eta) = \frac{t}{t_0} \text{ for internal diffusion} \qquad (12)$$

$$F(\eta) = 1-(1-\eta)^{1/3} = \frac{t}{t_0} \text{ for chemical reaction} \qquad (13)$$

have been tested.

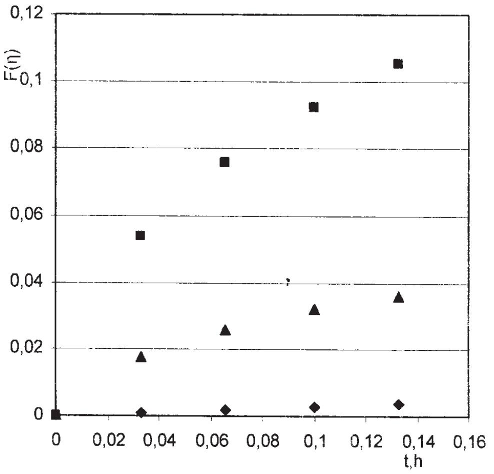

Fig. 5. Equation test of shrinking core model for Cd(II) sorption on Na-montmorillonite
C_i = 0,1 mmol/L;T = 20 ± 0,1°C; *p*H = 5,50±0,05; I = 0,01M $NaNO_3$; C_M = 1g/L
■ η ▲1- $(1-\eta)^{1/3}$ ♦1-3$(1-\eta)^{2/3}$ + 2(1- η)

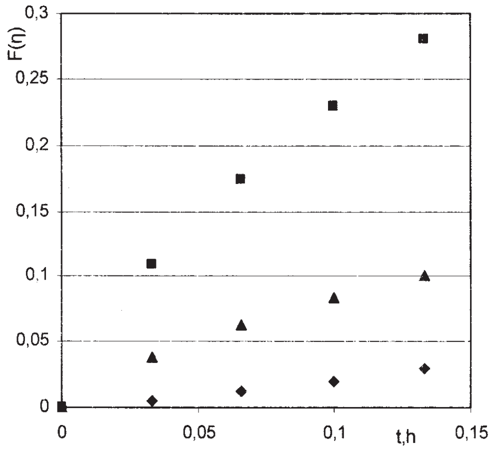

Fig. 6. Equation test of shrinking core model for Cd(II) sorption on Na-montmorillonite
C_i = 0,4 mmol/L;T = 20 ± 0,1°C; *p*H = 5,50±0,05; I = 0,01M $NaNO_3$; C_M = 1g/L ■ η ▲1-$(1-\eta)^{1/3}$ ♦ 1-3$(1-\eta)^{2/3}$ + 2(1- η)

In figures 5- 6 are illustrated the dependences F(η) - t for cadmium sorption at different initial concentration of metal aqueous solutions.

The equations (8)-(10) were used only for short periods of time, corresponding to ion exchange processes.

The straight line dependence in F(η) - t diagramme suggest the internal diffusion as rate limiting step [36].

The internal diffusion coefficients were determined according to equation (9) written as:

$$\lg[1-3(1-\eta)^{2/3}+2(1-\eta)] = -\lg\frac{1}{6}\frac{CECR^2}{D_{Me}C_{Me}^0}+\lg t \quad (14)$$

Where:

t – represents the contact time, s

CEC – cation exchange capacity, equivalent m^{-3};

R – particle radius, m;

D_{Me} – diffusion coefficient, $m^2\ s^{-1}$;

C_{Me}^0 –initial concentration of cadmium solution;

η – cation exchange efficiency.

The values of pore diffusion coefficients for different clay particle sizes are shown in table 2.

Table 2

DIFFUSION COEFFICIENTS FOR CADMIUM SORPTION ON Na-MONTMORILLONITE

d, μm	D_{Cd}
2	$2.7\ 10^{-14}$
6	$1.99\ 10^{-13}$
10	$4.15\ 10^{-13}$

Conclusions

This study confirms the possibility to use efficiently the Na-montmorillonite as adsorbent for cadmium cations removing. The sorption of cadmium cations on the mineral clay can be characterized using Langmuir isotherm equation. The efficiency of this material in removing metal cations would allow to develop a convenient way to use Na-montmorillonite as adsorbent.

Soil minerals are often negatively charged and similar effects as observed for montmorillonite are expected; a mobilizing effect should occur for heavy metals in soil with high pH values.

The results obtained in this study are roughly consistent with those previously attained by other authors on heavy metal sorption experiments on mineral clay. The sorption rate was divided into two stages, a fast initial one followed by a much slower sorption rate. A cation exchange mechanism is presumably responsible for this fast cation uptake, while the slower stage may be explained by the specific uptake of Cd(II), with the inner sphere surface complexes appearing on the edge of montmorillonite particles.

Using the shrinking core model it was established that the rate-limiting step for the cadmium sorption process is the internal diffusion.

The heavy metals removal from industrial waters have been also studied by other authors [41-44].

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