The Adsorption Study of the Cyanides Using Solid Adsorbents

OANA MIHAI[1], CATALINA CALIN[1]*, CATALINA MARINESCU[2], NATALIA NATU[2], OCTAV PANTEA[1], DORINA MATEI[1]
[1] Petroleum-Gas University of Ploiesti, 39 Bucuresti Blvd., 100520, Ploiesti, Romania
[2] S.C. Zecasin S.A., 202 Splaiul Independentei, 060021, Bucharest, Romania

The adsorptive potential of bentonite for removing cyanide from wastewaters was studied. The adsorptive treatments of the wastewaters were studied by using solid adsorbents such as bentonite with/without surfactants. The bentonite samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM) methods. The study was performed over a range of pH values between 8 to 10.5.The contact time was kept at 2 hrs and various cyanide concentrations of 10, 100 and 300 ppm were employed for experiments. The optimum conditions for removal of the cyanide from the contaminated waters could be achieved at concentrations of 10 ppm, adsorbent loading of 15 g/L, in the absence of surfactant. The advantageous pH for adsorption reaction was found to be 8 - 9. The results showed that the adsorption behavior of cyanide on bentonite was strongly dependent on pH and adsorbent loading.

Keywords: cyanide, bentonite, adsorbents, adsorption

Wastewaters generated from various processes such as petrochemical and coke-processing plants, precious metals milling operations contain free and metal-complexes cyanides at various concentrations and are dangerous to humans and aquatic life. Before releasing into the environment, cyanides must be subjected to a rigorous treatment in order to preserve water resources and the environment. U.S. Environmental Protection Agency reveals the water quality criterion for cyanide of 5.2μg/L (in case of the freshwater aquatic life), and 1 μg/L (for marine aquatic life and wildlife) [1].

The investigation of the wastewaters contaminated with the cyanides compounds is effectively employed by different methodologies such as sedimentation, chemical treatment, and oxidation, biological and electrical processes [2, 3].

The most widely used method for the removal of the chemical compounds, especially cyanides from wastewaters is the physical-chemical adsorption, which is referred to that process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings. Various solid adsorbents such as alumina, silica gel, zeolites, activated carbon are considered to be promising materials for the removal of chemical species from wastewaters [2-4].

Among those natural adsorbents, clays are being extensively studied as conventional materials specially because its low cost, available in abundance, relatively high purity and having good sorption properties. The adsorption efficiency of clays result from a net negative charge on the structure of minerals, which gives clay the capability to adsorb positively, charged species. Bentonite is an aluminium phyllosilicate (clay) consisting mostly of montmorillonite, having the ability to absorb water molecules between its sheets. The crystal structure of montmorillonite is composed of two tetrahedral layers of silica with a central alumina octahedral layer between them. The distance between the layers is not fixed and the layers can expand [7-9]. Bentonites have high specific surface areas, in theory ranging from 700 to 850 m^2/g and from 20 to 130 m^2/g using BET method [10, 11].

Due to their hydrophilicity, bentonites are usually not effective in adsorbing organic compounds. The development of technologies for the decontamination of waters polluted by various organic compounds has encouraged research into the use of anionic and cationic surfactants as potential agents for the enhanced solubilization and removal of contaminants. The activation by adsorption of surfactants may cause structural changes (such as pore structure, surface properties, and adsorptive behavior) on solid adsorbents and their adsorption capacity can be improved by surface-modification. The anionic (NaOH) and cationic (e.g. mineral acids) activation of the bentonites can be used in order to improve their specific properties [10, 12].

The main goal of this work is to study the effect of various adsorption factors on cyanide uptake such as solution *p*H, initial concentration of the adsorbent, the cyanide concentration and the presence or absence of the surfactants in the composition of the adsorbent.

Experimental part

Materials and methods

Natural bentonite samples used in this work are originated from Hunedoara County, located in the Gurasada region which represents one of the largest bentonite reserves in Romania [13]. The content of Ca-based montmorillonite is 64-88%. The bentonite composition also consists of cristobalite (8-11%), quartz (1.6 -3.6%), and rarely feldspar, calcite, kaolinite were found. Small amounts of Fe_2O_3 (1.4-1.6%) were found in its composition and the clay fraction is lower compared to other bentonites materials [14, 15]. The studied bentonite samples with the particle size less than 200 ìm from Na-bentonite were provided by CHIMFOREX-BMI Gurasada. The typical composition of the Gurasada bentonite is presented in Table 1 [11].

Adsorption tests were performed using 50 mL solution of sodium cyanide (NaCN) at ambient temperature under continuous stirring. The adsorbent and the prepared cyanide solution were mixed in a beaker under rigorous stirring.

**email: catalina.calin20@yahoo.com; Tel. +4 (0) 722 738775*

Oxides, %	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	L.O.I.
Bentonite Gurasada	70,40-72,99	0,10-0.27	12,60-14.65	0,53-1,69	1.60-2,73	2.62-3,69	0.0-1,11	0,0-1,0	6,29-9,69

Table 1
THE CHEMICAL COMPOSITION OF THE BENTONITE ORIGINATED FROM GURASADA AREA

The contact time between cyanide aqueous solution and solid adsorbent was kept at 2 h during all series of experiments.

The obtained solutions were then centrifuged in a SIGMA 1-6 P instrument with 1400 rpm for 15 min. After centrifugation, two phases were observed: solid phase (bentonite) and liquid phase. The *p*H values of the liquid phase were then measured by using a glass electrode connected to an electronic meter that measures and display the *p*H reading (Cyberscan PCD 6500 instrument). A stock cyanide solution of 1000 ppm was prepared for making the calibration curve. Different dilutions of stock solution were also prepared in order to obtain the concentrations in the range from 10 to 300 ppm.

Fresh bentonite (namely in this study as NaB) has been modified with aqueous solutions containing a cationic surfactant, namely, cetyltrimethylammonium bromide (CTAB, Merck) by ion-exchange impregnation at 25°C under continuous stirring for 1 h. Various concentrations of the surfactant (from 100 to 240 mmol/L) have been used during the synthesis. The optimal ratio CTAB/NaB was 10/1 mL/g [17]. Different amounts of Na-Bentonite of 10, 15 and 20 g/L were used during tests. The modified bentonite sample is named as NaB-M.

Characterization of the bentonites samples

Infrared spectra of the materials were taken in a Varian Resolutions Pro 3100 spectrometer in the range of 4000-400 cm^{-1}. The instrument was equipped with a horizontal attenuated total reflectance (ATR) accessory which consisted of a diamond crystal. The spectrometer was software-controlled by the Varian Resolutions Pro software. XRD patterns were recorder between 2° and 40° (2θrange) using a Bruker D8 instrument (λ = 0.154 nm, 40 kV and 40 mA) with CuKα radiation. Scanning electron microscopy (SEM) of the bentonites samples was performed on Hitachi S-3400 SEM instrument at the chamber pressure of 40 Pa and working distance of 5.3 mm. Images of samples were recorded at different magnifications at an operating voltage of 30 kV.

Results and discussions

The IR spectra of the raw-bentonite (NaB) are given in figure 1 and figure 2. The spectra were taken at various wavenumber range. No peaks have been observed in the range of 4000 to 3600 cm^{-1} for NaB sample and the IR results are not shown in figure 1. The structural OH stretching vibrations generally appear in the range of 3400-3500 cm^{-1}, as is observed in figure 1. In addition, the wavenumber of 3457 cm^{-1} may be attributed to OH frequencies of the water molecule. The peaks corresponding to the wavenumber of 3661 - 3725 cm^{-1}(as is shown in figure 3 for NaB-M sample) originates from the Al_2OH stretching. The Si–O–Si and Al–O–Si stretching peaks of tetrahedral layer were seen at the wavenumber of 1011 and 1001, or 515 and 511 cm^{-1}, respectively, as is shown in figures 2 and 4 [18-20].

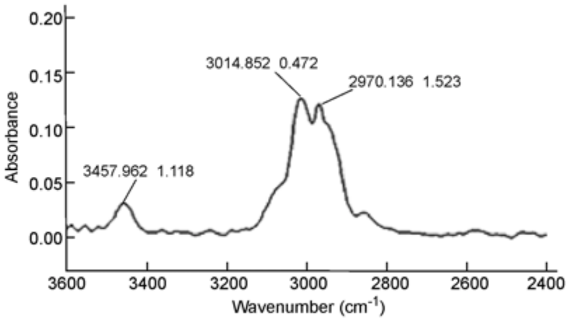

Fig.1. IR spectra of NaB bentonite (fresh) between the ranges of 3600-2400 cm^{-1}

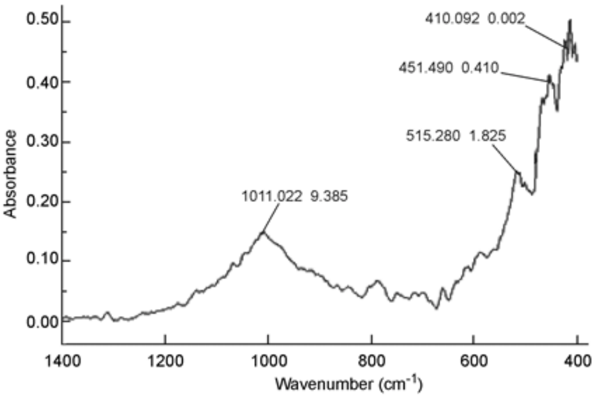

Fig.2. IR spectra of NaB sample (fresh) between the ranges of 1400-400 cm^{-1}

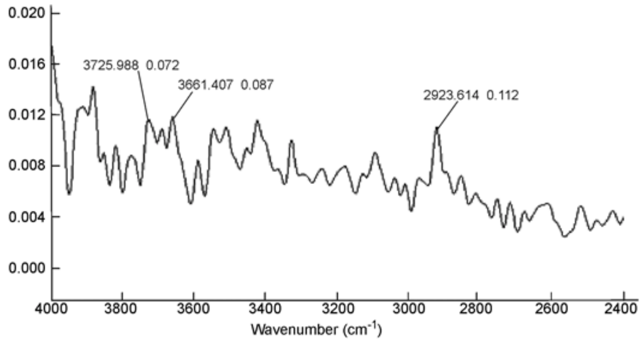

Fig.3. IR spectra of NaB-M sample (modified) for wavenumber of 4000-240cm^{-1}

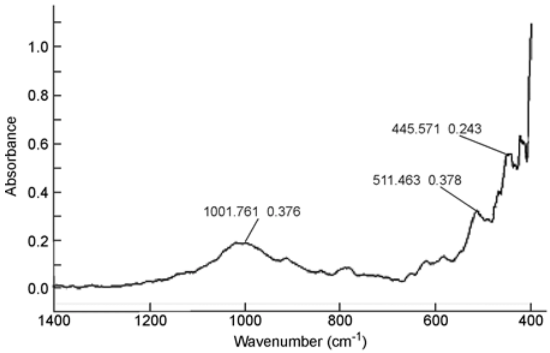

Fig.4. IR spectra of NaB-M sample (modified) for wavenumber of 1400-400 cm^{-1}

The XRD patterns of the untreated and treated bentonites (NaB and NaB-M) are showed in figures 5 and 6. Both diffractograms show a typical XRD peak at 2θ= 5 - 6°, corresponding to the main montmorillonite component which is present in the bentonite structure. Montmorillonite is the most abundant mineral present in bentonite, and its presence was confirmed by identification of peaks at certain values of 2-theta. The XRD spectra of the treated bentonite (fig. 6) reveals the additional peaks at 2θ= 21 - 22°, at 2θ= 27 - 28°, which can be assigned to the presence of the cristobalite and quartz, respectively [18, 21, 22].

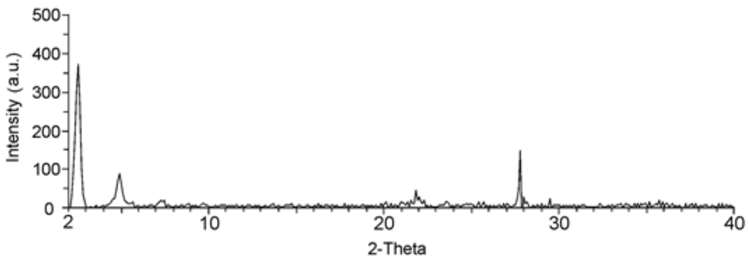

Fig.5. XRD diffraction patterns of the NaB bentonite

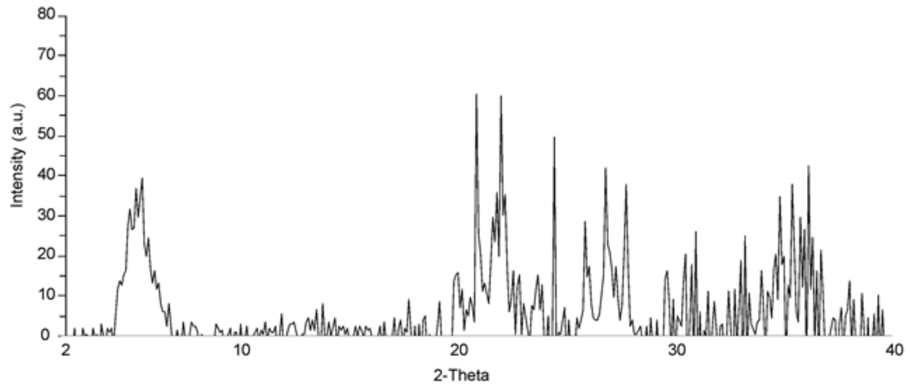

Fig 6. XRD spectra of the NaB-M bentonite

SEM microphotographs of powdered untreated and treated bentonites samples at different magnifications are shown in figures 7 and 8. The bentonites particles appear nonuniformly and partially agglomerated. SEM images of the impregated raw-bentonite samples (fig. 8) do not show difference than parent bentonite regarding the particle size.

The adsorption capacity of bentonite depends on several physicochemical factors related to the sorbate, the sorbent, and the liquid phase characteristics including the solution *p*H, initial metal concentration in the solution, presence of other cations, ionic strength, temperature, mineral type, grain size and concentration, and agitation speed.

The efficiency of adsorption means the capacity of adsorbent (e.g. bentonite) to remove the metal complexes cyanide from aqueous solution and it was calculated using the following equation:

$$E(\%) = \frac{C_i - C_f}{C_i} \times 100$$

where:

C_i = the initial concentration of cyanide solution (g/L)

C_f = the final concentration after desired contact time of 2 h (g/L)

Effect of cyanide concentration

A study of cyanide concentration effect was carried out and the results are presented in figure 9. In this study, the initial cyanide concentrations were 10, 100 and 300 ppm. Figure 9 shows that the increase in the cyanide concentration leads to decrease of the adsorption capacity of the bentonite at various *p*H values.

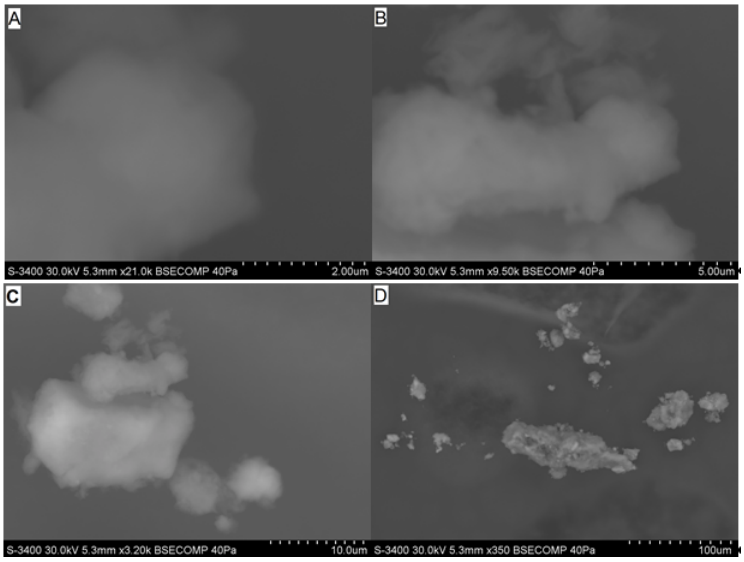

Fig.7. SEM images of NaB bentonite with 2µm magnification (A), 5 µm (B), 10 µm (C) and 100 µm (D)

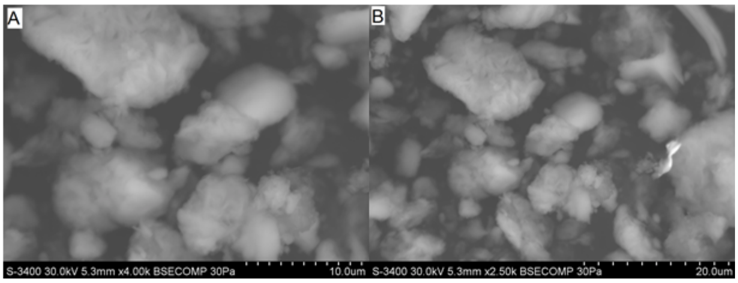

Fig.8. SEM images of treated NaB-M bentonite with 10 µm magnification (A), 20 µm (B).

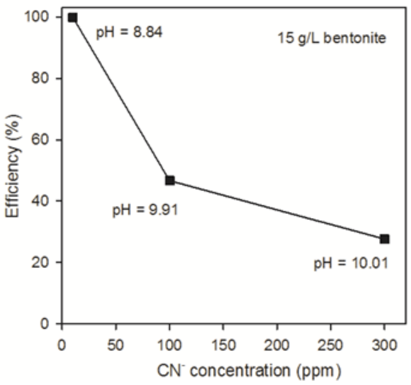

Fig.9. Influence of the cyanide concentration on the adsorption efficiency of NaB. Concentration of NaB = 15 g/L. The contact time = 2h

The variation of solution pH

*p*H measures either the acidity (*p*H < 7) or basicity (*p*H > 7) of the aqueous solution. The *p*H factor is very important in the adsorption process especially for cyanide adsorption.

The efficiency of bentonite was affected by the variation of *p*H solution from 8 to 10.5, as is shown in figure 10. At high pH solution, the positive charge at the solution interface decreases and the adsorbent surface appears negatively charged. Ramirez et al. [16] show that bentonite might be stable up to *p*H of 12.6, depending of the originated region. The adsorption capacity of bentonite decreases with increase in *p*H solution for 10 g/L bentonite loading.

A relatively stable high efficiency is observed with the increasing of the bentonite leading up to 15 g/L for *p*H range of 8 - 9.

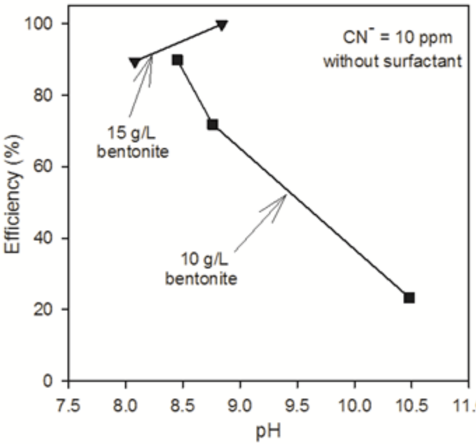

Fig.10. Effect of *p*H on the adsorption efficiency of NaB. Cyanide concentration = 10 ppm. The contact time = 2h. The NaB was not activated with surfactant

The influence of Na-bentonite loading

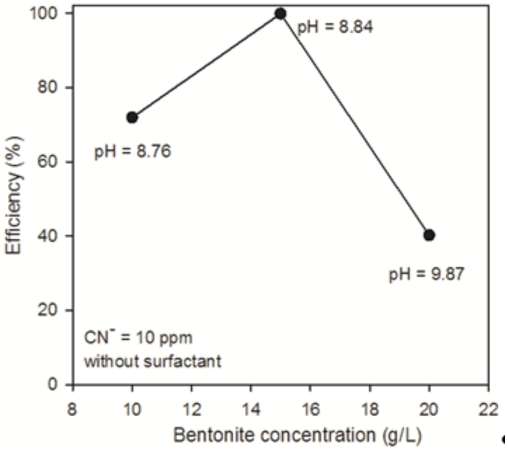

Fig.11. Adsorption capacity as function of the NaB concentration. The cyanide concentration = 10 ppm. The contact time = 2h.

The presence/absence of surfactants into bentonite composition

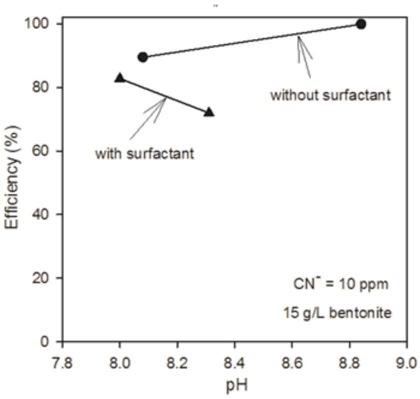

Fig.12. Influence of the surfactant presence / absence on the efficiency of NaB. Concentration of NaB = 15 g/L. The cyanide concentration = 10 ppm

Relatively high efficiency of bentonite adsorption is revealed either with/ without presence of surfactant in its composition.

Conclusions

The removal of cyanide from waste waters by sorption onto bentonite gained a great attention. Bentonite as a natural clay is able to remove cyanides species from wastewater very effectively. Three cyanide concentrations were used for tests: 10, 100 and 300 ppm.

The study was performed in the *p*H range of 8 to 10.5. It was found that the increase of CN^- concentration lowers the adsorption capacity of the bentonite for studied *p*H domain, and as consequence the efficiency decreases. The optimum concentration for adsorption is 10 ppm.

In the case of 10 g/L bentonite concentration, its adsorption capacity decreases with the increasing of *p*H. Highest efficiency has been observed for the concentration of 15g/L, and a *p*H range of 8-9 and without the surfactant presence.

References

1.MORAN, R., Cyanide Uncertainties: Observations on the Chemistry, Toxicity, and Analysis of Cyanide in Mining-Related Waters, Mineral Policy Center, Protecting Communities and the Environment, Issue Paper No. 1, 1998.

2.PAPADIMITRIOU, C.A., SAMARAS, P., SAKELLAROPOULOS, G.P., Comparative study of phenol and cyanide containing wastewater in CSTR and SBR activated sludge reactors, Bioresources Technology, 100, 2009, p. 31.

3.GUPTA, V.K., SUHAS, Application of low-cost adsorbents for dye removal – A review, Journal of Environmental Management, 90, 2009, p. 2313.

4.DESAI, J.D., RAMAKRISHNA, C., PATEL, P.S., AWASTHI, S.K., Cyanide wastewater treatment and commercial applications, Chem. Eng. World, 33, 1998, p. 115.

5.McKAY, G., OTTERBURN, M.S., AGA, J.A., Fuller earth and fired clay as adsorbents for dyestuffs – equilibrium and rate studies, Water Air Soil Pollut, 24, 1985, p. 307.

6.BROWN, B., CURLISS, D.,VAIA, V., Chem. Matter., 14, 2002, p. 3376.

7. K.G. BHATTACHARYYA, S.S. GUPTA, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review, Advanced Colloid Interface Science, 140, 2008, p. 114.

8.NAGY, N.M., KONYA, J., Interfacial Chemistry of Rocks and Soils, CRC Press, Taylor & Francis, New York, 2009.

9.VIRARAGHAVAN, T., KAPOOR, A., Adsorption of mercury from wastewater by bentonite, Applied Clay Science, 9, 1994, p. 31-49.

10.BERGAYA, F.,THENG, B.G.K., LAGALY, G., Handbook of Clay Science, Developments in Clay Science (1st ed.), Chapter 7.1, P. KOMADEL, J.

MADEJOVA, Acid activation of clay minerals, Elsevier Science, New York, 2006, p. 263.

11.KAUFHOLD, S., DOHRMANN, R., KLINKENBERG, M.,SIEGESMUND, S., UFER, K., N_2-BET specific surface area of bentonites, J. Colloid Interface Sci., 349, 2010, p. 275.

12.BERGAYA, F., THENG, B.G.K., LAGALY,G., Handbook of Clay Science, Developments in Clay Science (1st ed.), Chapter 11.1, G.J. CHURCHMAN, W.P. GATES, B.K.G. THENG, G. YUAN, Clays and clay minerals for pollution control, Elsevier Science, New York, 2006, p. 625.

13.CONSTANTINA, C., SZAKACS, A., PECSKAY,Z., Petrography, geochemistry and age of volcanic rocks in the Gurasada area, sothern Apuseni Mts, Carpathian Journal of Earth and Environmental Sciences, 4, 2009, p. 31.

14.BEDELEAN, H., MAICANEANU, A., STANCA, M., BURCA,S., Raport de Cercetare, Grant: A 1334 – Aplicatii ale rocilor argiloase in procese de epurare, Univ. Babes-Bolyai, Cluj Napoca.

15.BEDELEAN, H., MAICANEANU, A., BURCA, S., STANCA, M., Removal of heavy metal ions from wastewaters using natural clays, Clay minerals, 44, 2009, p. 487.

16.RAMIREZ, S., CUEVAS, J., VIGIL, R.,LEGUEV,S., Hydrothermal alteration of La Serrata bentonite (Almeria, Spain) by alkaline solutions, Applied Clay Science, 21, 2002, p. 257.

17.BOMBOS, D., GANEA, R., MATEI, V., MARINESCU, C., BONDAREV, A., MIHAI, S., NATU, T., TAMAS, I., Modified Bentonite for Purification of Dyeing Waste Water, Rev. Chim. (Bucharest), **65**, no. 8, 2014, p. 976.

18.TABAK, A., YILMAZ, N., EREN, E., CAGLAR, B. AFSIN, B., SARIHAN, A., Structural analysis of naproxen-intercalated bentonite (Unye), Chemical Engineering Journal, 174, 2011, p. 281.

19.ONAL, M., SARIKAYA, Y., Preparation and characterization of acid-activated bentonite powders, Powder Technology, 172, 2007, p. 14.

20.ALABARSE, F.G., CONCEICAO, R.V., BALZARETTI, N.M., SCHENATO ,F., XAVIER, A.M., In-situ FTIR analyses of bentonite under high-pressure, Applied Clay Science, 51, 2011, p.202.

21.YERMIYAHU, Z., LAPIDES, I., YARIV,S., Thermo-XRD-analysis of montmorillonite treated with protonated Congo-red. Curve fitting, Applied Clay Science, 30, 2005, p. 33.

22.RANDELOVIC, M.S., PURENOVIC, M.M., MATOVIC, B.Z., ZARUBICA, A.R.,. MOMCILOVIC, M.Z., PURENOVIC, J.M.,Structural, textural and adsorption characteristics of bentonite-based composite, Microporous and Mesoporous Materials, 195, 2014, p. 67.

Manuscript received: 25.11.2015