IV International Conference
„ECOLOGY OF URBAN AREAS“ 2014

ADSORPTION OF FE^{2+} AND ZN^{2+} IONS FROM LANDFILL LEACHATE BY NATURAL BENTONITE FROM KRIVA PALANKA(B - KP), REPUBLIC OF MACEDONIA

Blagica Bliznakovska[1], Katerina Atkovska[1], Gordana Ruseska[1], Slobodan Bogoevski[1], Bosko Boskovski[1], Petre Makreski[2], Anita Grozdanov[1]
[1]University “SS Cyril and Methodius”, Faculty of Technology and Metallurgy, Skopje, Republic of Macedonia
[2]University “SS Cyril and Methodius”, Faculty of Natural Sciences, Skopje, Republic of Macedonia
blagica@tmf.ukim.edu.mk*; kburevska@tmf.ukim.edu.mk; gruseska@tmf.ukim.edu.mk

ABSTRACT

Due to its typical layered silicate structure, large specific surface area, chemical and mechanical stability, high cation exchange capacity, bentonite has been widely applied as heavy metals adsorbent from aqueous solutions. In this paper the adsorptive properties of natural bentonite from Kriva Palanka, Republic of Macedonia, for the removal of Fe^{2+} *and* Zn^{2+} *ions from landfill leachate were studied. The raw material (B-KP) was characterized in terms of chemical composition (conventional silicate analysis), structural morphology (XRD, FT- IR, TGA-DTA), specific surface area, particle sixe distribution (wet - sieve analysis). It was considered that montmorillonite is dominant phase in B-KP. For adsorption experiments the batch method has been employed using volume of 25* cm^3*, 50* cm^3*, 75* cm^3*, 100* cm^3 *and 125* cm^3 *of leachate with 2 g of bentonite, at 298 K. The initial metal ion concentration in the leachate was 9,25* mg/dm^3 *for* Fe^{2+} *and 0,22* mg/dm^3 *for* Zn^{2+} *and these concentrations as well as the concentrations after adsorption were determined by atomic absorption spectrophotometer (AAS). Applied Freundlich and Langmuir adsorption isotherms showed good fits to the experimental data. The monolayer capacities of bentonite for* Fe^{2+} *and* Zn^{2+} *were determined by Langmuir equation and are 0,4371 mg/g and* $4,1\cdot10^{-3}$ *mg/g, respectively. The removal efficiency for zinc was above 98%.*

Key words: *municipal solid waste leachate,* Fe^{2+}*,* Zn^{2+}*, adsorption isotherms, bentonite.*

INTRODUCTION

Due to the irregular management, municipal solid waste landfills (MSWL’s) are major threat to the quality of the environment in Macedonia as in many other developing countries. Produced and freely released leachate is a source of groundwater and soil pollution. Leachate is highly polluted liquid composed of many inorganic (sulfates, chlorides, heavy metals) and organic (acids, alcohols) pollutants. The MSWL Drisla, does not contain any drainage system for the underground waters protection nor any receiving reservoir for primary treatment. The leachate is freely released into the stream of Meckin Dol. Therefore the presence of heavy metals in leachate is a serious threat for groundwater and nearby fields and accordingly for the health of the population. .

The methods used for removal of heavy metals include chemical precipitation, ion exchange, solvent extraction, membrane processes, adsorption and others. Among all the approaches proposed, adsorption is one of the most popular method and it is considered as an effective, efficient and economic method for wastewater purification. Various materials such as activated carbon (Kouakou et al., 2013; Bernard and Jimoh 2013) natural and synthetic zeolites (Erdem et al., 2004; Shaheen et al., 2012), bentonite (Ghormi et al., 2013; Kaya and Oren 2005) have been used as adsorbents for the removal of heavy metals from water and wastewater.

Among the natural clays of high surface area and eminent cation exchange capacity as well as the adsorption affinity for organic and inorganic ions and a low cost, bentonite is marked as the most promising adsorbent for the removal of heavy metals (arsenic, cadmium, chromium, iron, lead, zinc) from aqueous solutions. Bentonite has a typical layered silicate structure consisting of two silica tetrahedral sheets with a central octahedral sheet. The interlayer space is easily accessible to water and another polar liquids. Bentonite has a good cation exchange capacity due to the presence of hydrated cations as Ca^{2+}, Na^{+}, K^{+}, etc., in their interlayer surfaces, and these cations can be easily exchanged by heavy metals compensating the negative charge.

There are many studies on the adsorption of iron and zinc (Sheta et al., 2003; Bhattacharyya and Gupta 2006; Mishra and Patel 2009) The aim of this work is to study the Macedonian natural bentonite as potential adsorbent for iron and zinc removal from wastewater.

EXPERIMENTAL

The bentonite samples in this study, originate from Kriva Palanka, (Ginevci district) Republic of Macedonia. Bentonite was used in its natural form without any treatment. For bentonite characterization, specific surface, sieve, chemical, XRD, FT- IR and TGA- DTA analysis were performed.

The initial metal ion concentration in the leachate taken from MSWL Drisla was determined by atomic absorption spectrophotometer (AAS) and it was 9,25 mg/dm^3 and 0,22 mg/dm^3 for Fe^{2+} and Zn^{2+}, respectively. The pH value of the leachate was 7,8. The batch method was used for adsorption processes. Volume of 25 cm^3, 50 cm^3, 75 cm^3, 100 cm^3 and 125 cm^3 of leachate with 2 g of bentonite were placed in 5 Erlenmeyer flasks to commence the experiment. Flasks were set in the shaker (CERTOMAT R, B. Braun supplied by Biotech International) at constant temperature of 298 K. 100 rpm shaking was applied in the shaker for 5h and the last 1h at 140 rpm until equilibrium was attained. The solutions were filtered and the filtrates were analyzed for Fe^{2+} and Zn^{2+} by atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

In this work specific surface of bentonite was evaluated from data of equilibrium adsorption of water vapor at 298K. The adsorption isotherm at 298K is interpreted by linear form of BET equation:

$$\frac{x}{n^a(1-x)} = \frac{1}{n_m^a C} + \frac{C-1}{n_m^a C} x \qquad (1)$$

where, x is relative pressure ($x = P/P_0$), n^a [mol/g] is amount of adsorbed water vapour, n_m^a [mol/g] is monolayer capacity of adsorbent and C is a constant. The diagram of the linear form of the equation is given in Figure 1. The good fit of the experimental isotherm to the equation is evidenced by the linearity of the plot. The value of regression coefficient is higher than 0,98.

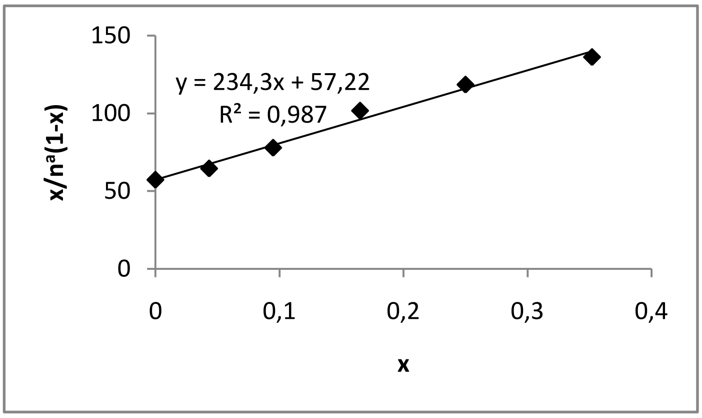


Figure 1. Diagram of linear form of BET equation of adsorption of water vapour on bentonite

The value of monolayer capacity is used to calculate the specific surface area of bentonite by the equation:

$$a_s = n_m^a N_A a_m 10^{-18} \tag{2}$$

where a_s is the specific surface area, a_m is surface of adsorbent occupied by one molecule of adsorbate, which for water is 0,106 nm^2.

The values of the parameters of the equation, monolayer capacity, n_m^a and constant C, and the specific surface area, a_s, are $3{,}43\cdot10^{-3}$ mol/g, 5,10 and 219 m^2/g, respectively.

It was proved by XRD analysis on this bentonite, Figure 2, that the dominant component is montmorillonite and the remaining components are muscovite, quartz, feldspar and kaolinite.

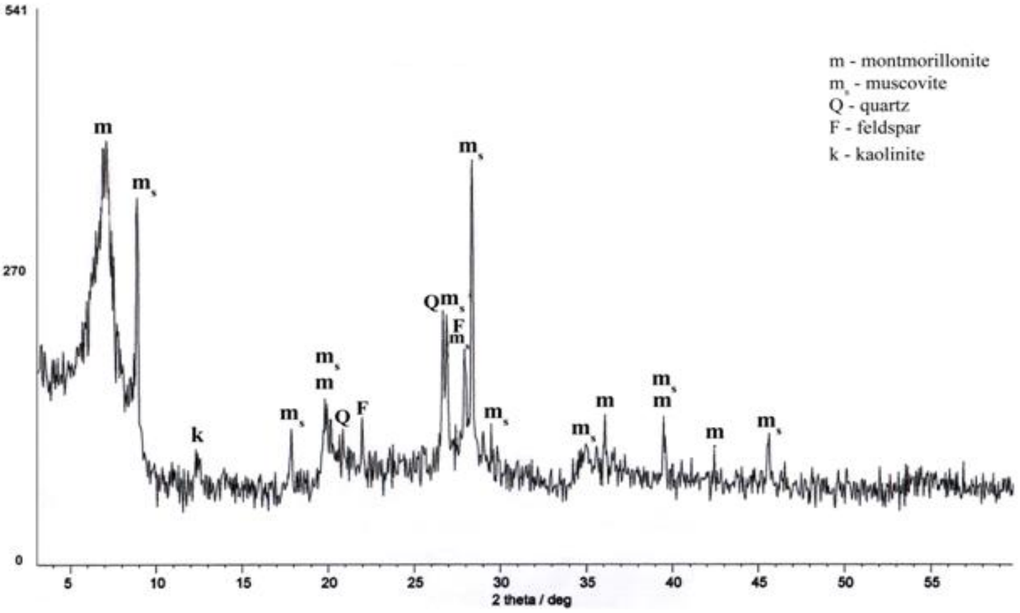


Figure 2. XRD patterns of the bentonite

Structural composition of B-KP revealed by XRD analysis was confirmed by FT-IR results, Figure 3. Namely, the adsorption bands at 467, 517, 783 and 1120 cm^{-1} point to the presence of quartz (Si-O-Si) while the bands at 1034 and 1634 cm^{-1} reveal the presence of SiO$_2$ amorphous. The bands appearing at 617 and 675 cm^{-1} outline the Al-O-Si-O bond (feldspar presence) and at 917 cm^{-1} the Al-Al-OH bond. The presence of adsorbed water is manifested by appearance of bands at 1634, 3442 and 3617 cm^{-1}. OH$^-$ groups considered with bands at 917, 3442 and 3692 cm^{-1} were additionally confirmed by TGA-DTA analysis, Figure 4, that point to the different nature of OH$^-$ groups present in B-KP.

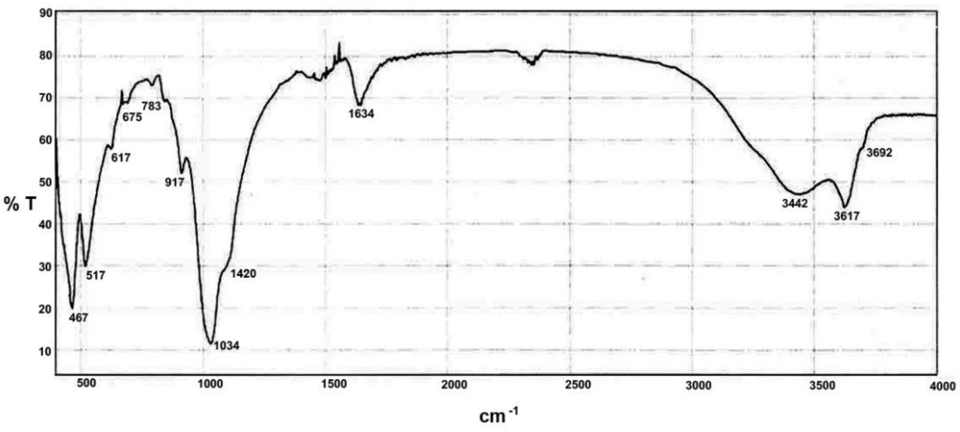


Figure 3. FT-IR spectrum of bentonite

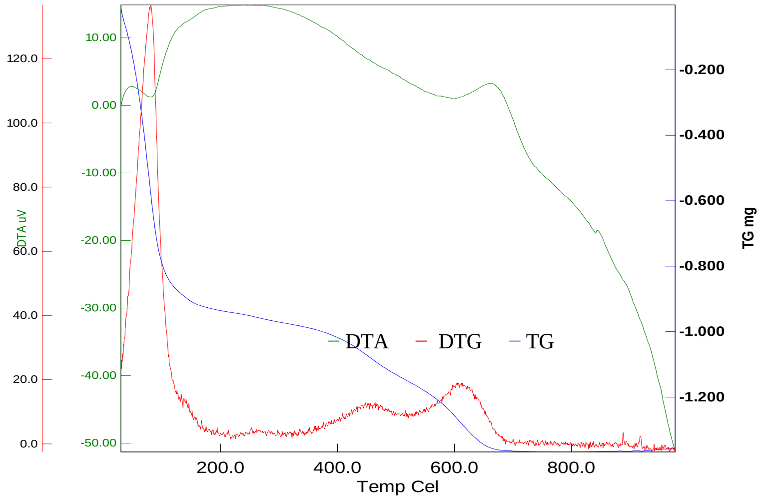


Figure 4. TGA-DTA diagram of bentonite

The results of granulometric sieve analysis and chemical composition of the bentonite determined by conventional silicate chemical analysis are presented in Table 1 and Table 2, respectively.

Table 1: Granulometric sieve analysis of bentonite

Fraction [mm]	Mass [%]
+0,071	3,82
-0,071+0,063	0,55
-0,063+0,040	5,26
-0,040+0,032	1,79
-0,032	88,58
$\sum$	100

Table 2: Chemical composition of bentonite

Composition	Mass [%]
SiO_2	60,82
Al_2O_3	21,32
Fe_2O_3	3,21
MgO	4,15
CaO	2,03
Na_2O	0,40
K_2O	0,40
$H_2O + CO_2$	8,06

Adsorption studies

The adsorbed amount of metal ion per unit adsorbent mass, m^a [mg/g], was calculated as follows:

$$m^a = \frac{(C_0 - C_e)V}{m} \tag{3}$$

where C_0 [mg/dm^3] is the initial heavy metal concentration, C_e [mg/dm^3] is equilibrium heavy metal concentration, m is the amount of the bentonite [g] and V is the leachete volume [dm^3]. Initial concentrations of Fe^{2+} and Zn^{2+} metal ions in leachate were 9,25 mg/dm^3 and 0,22 mg/dm^3, respectively.

Adsorption isotherms are important for adsorption processes research. Langmuir and Freundlich isotherms are the most widely used for practical applications. The Langmuir adsorption isotherm is valid for monolayer sorption onto a surface with a finite number of identical sites (Melichova and Hromada 2013; Al Dwairi and Al Rawajfeh 2012), and it can be defined according to the following linear form:

$$\frac{C_e}{m^a} = \frac{1}{m_m^a b} + \frac{C_e}{m_m^a} \qquad (4)$$

where m_m^a [mg/g] is the monolayer capacity and b is the equilibrium constant.

The dependence of C_e/m^a from C_e, obtained by using experimental results, is shown in Figure 5 for Fe^{2+}, and in Figure 6 for Zn^{2+}.

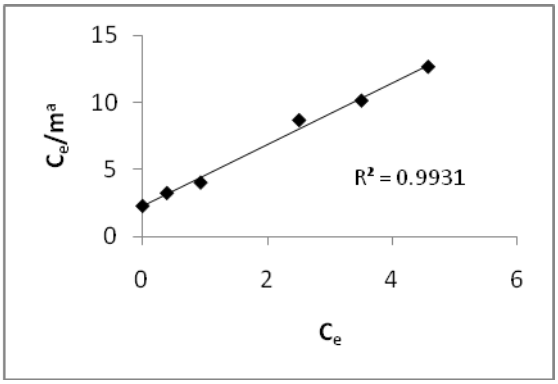


Figure 5. Langmuir adsorption model for Fe^{2+}

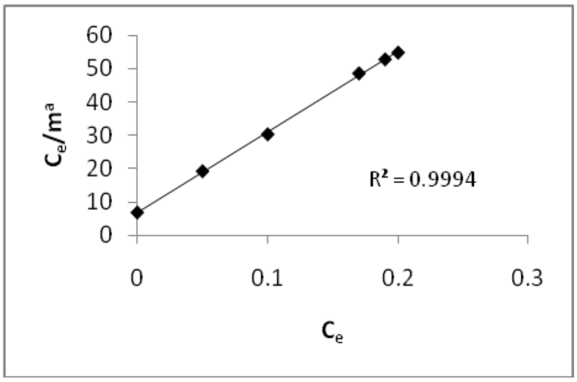


Figure 6. Langmuir adsorption model for Zn^{2+}

The values of m_m^a and b were determined from the linear form of the Langmuir equation and the Langmuir plot. The calculated results and correlation coefficients R^2 are listed in Table 3.

Langmuir isotherm determines the adsorption favorable or unfavorable. To determine the characteristic behavior of adsorption, dimensionless equilibrium parameter, R_L (known as the separation factor) is used (Al Dwairi and Al Rawajfeh 2012; Budsaereechai et al., 2012). This parameter is given by:

$$R_L = \frac{1}{1 + bC_0} \qquad (5)$$

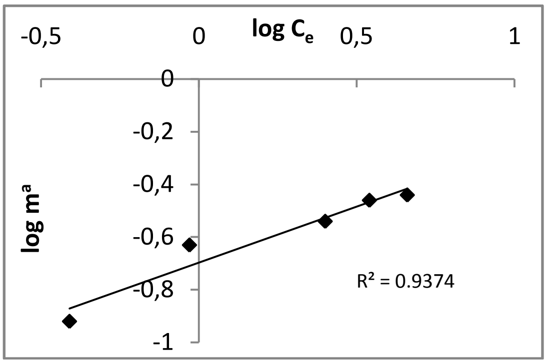
For favorable adsorption R_L value must take place $0 < R_L < 1$. In our results R_L values were found 0,10 and 0,11 for Fe^{2+} and Zn^{2+} respectively, and that confirms that the adsorption process is favorable.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained by the linear form:

$$\log m^a = \log K_F + \frac{1}{n} \log C_e \qquad (6)$$

where K_F is the Freundlich constant [mg/g] and n is an empirical parameter related to the intensity of adsorption. The linear Freundlich plots for iron and zinc are given in Figure 7 and Figure 8.

The parameters of Freundlich equation as well as the correlation coefficients for both metal ions are listed in Table 3.



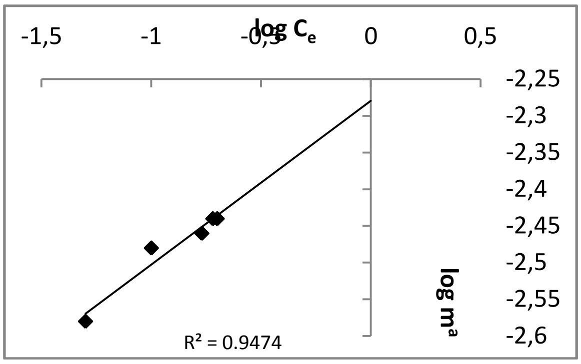


Figure 7. Freundlich adsorption model for Fe^{2+}

Figure 8. Freundlich adsorption model for Zn^{2+}

Table 3:Parameters of the Langmuir and Freundlich isotherms

Metal	Langmuir			Freundlich		
	m_m^a [mg/g]	*b*	R^2	K_F [mg/g]	*N*	R^2
Fe	0,4371	1,01	0,993	0,20	2,35	0,937
Zn	$4{,}1\cdot10^{-3}$	35,7	0,999	$5{,}25\cdot10^{-3}$	4,49	0,947

The linearity of the plots, Figures 5, 6, 7 and 8 and higher values of correlation coefficients show that Langmuir isotherms correspond better than Freundlich isotherms for both metals.

Langmuir monolayer capacity m_m^a and Freundlich constant K_F, that could be considered as the amount of metal adsorbed by solid phase at the equilibrium concentration of unity (Ghasemi-Fasae et al., 2012) do indicate and compare adsorption performance. According to the results for monolayer capacity, m_m^a and Freundlich constant K_F, bentonite shows greater sorption capacity for Fe^{2+} than for Zn^{2+}. According to many literature data (Budsaereechai et al., 2012; Ghormi et al., 2013; Melichova and Hromada 2013) it was expected the bentonite to have higher values for monolayer capacity. In our case, because of the complexity of investigated system (leachate) which is highly polluted with many inorganic and organic pollutants and there is an increase of the competitiveness for bentonite adsorption sites, we have much lower results for sorption capacity.

The adsorption parameter *n* in the Freundlich isotherm which measures preferential adsorption of one adsorbate to other and the intensity of adsorption, compared directly with Langmuir constant *b* a factor which relate to heat of adsorption and affinity to the binding site (Okeola and Odebunmi 2010). As it can be seen from the Table 3 the two constants *b* and *n* are proportionally related for both metals and the higher values of *b* and *n* for Zn^{2+} indicate a stronger bond between bentonite and Zn^{2+} ions than bentonite and Fe^{2+} ions. Using mathematical calculations *n* values between 1 and 10 indicate effective adsorption (Al-Shahrani 2012) Our results show effective adsorption for Fe^{2+} and Zn^{2+} according to the *n* values which are 2,35 and 4,49 respectively.

From economic point of view it is necessary to define the optimal ratio between amount of used bentonite and dose of leachate. For that purpose the removal efficiency of Fe^{2+} and Zn^{2+} metal ions adsorption on bentonite was calculated by the following equation and the results are listed in Table 4.

$$\text{Removal }\% = \frac{C_0 - C_e}{C_0}\cdot 100 \tag{7}$$

Table 4: Removal efficiency of bentonite for Fe^{2+} and Zn^{2+}

Amounts of leachate/bentonite	Removal [%]	
	Fe	Zn
25 cm^3 / 2g	95,78	98,82
50 cm^3 / 2g	89,95	98,50
75 cm^3 / 2g	72,86	98,41
100 cm^3 / 2g	62,05	98,36
125 cm^3 / 2g	50,49	98,34

The results show that to keep removal percentage above 90% for Fe metal ions the ratio between amount of leachate and bentonite should be 25 cm^3 / 2g because using the bigger volume of leachate drastically decreases the removal percentage. But, as it can be seen from the table, for Zn ions by increasing the leachate volume, percentage of removal, almost, do not change at all, and it is 98%.

CONCLUSION

The natural bentonite from Kriva Palanka, Republic of Macedonia (B-KP), belongs to the group of clay minerals with montmorillonite as main constituent. Bentonite has high specific surface area of 219 m^2/g.

The linear form of Langmuir and Freundlich equations were used to describe the adsorption isotherms. The experimental results were well fitted with both isotherms, but the values of the correlation coefficients show that Langmuir model correspond better. The monolayer capacities of bentonite for iron and zinc were determined by Langmuir equation and are 0,4371 mg/g and $4{,}1\cdot10^{-3}$ mg/g, respectively. This values are very low because we investigated a real system which is highly polluted and there is an increase of competitivety for superficial sites in bentonite.

The results for removal percentage indicate that in that conditions bentonite is more effective as adsorbent for zinc and the removal efficiency above 98% is economically reasonable.

The further investigations would be conducted to examine adsorption characteristics of Macedonian bentonite under various operating variables like initial metal concentration, solution pH, contact time, clay dosage and temperature. Further studies would be dedicated to the investigations under which conditions the bentonite is no longer reusable as well as to determine the expected lifetime of the bentonite.

REFERENCES

Al Dwairi, R. A. & Al Rawajfeh, A. E. (2012). Removal of cobalt and nickel from wastewater by using Jordan low – cost zeolite and bentonite. *Journal of the University of Chemical Technology and Metallurgy*, 47(1), 69 – 76

Al – Shahrani, S. S. (2012). Treatment of wastewater contaminated with nickel using Khulays activated carbon. *International Journal of Engineering & Technology*, 12(4), 14 – 18

Bernard, E. & Jimoh, A. (2013). Adsorption of Pb, Fe, Cu and Zn from industrial electroplating wastewater by orange peel activated carbon. *International Journal of Engineering and Applied Sciences*, 4, 95 – 103

Bhattacharyya, K. G. & Gupta, S. S. (2006). Adsorption of Fe(III) from water by natural and acid activated clays: studies on equilibrium isotherm, kinetics and thermodynamics of interactions. *Adsorption*, 12(3), 185 - 204

Budsaereechai, S., Kamwialisak, K. & Ngernyen, Y. (2012). Adsorption of lead, cadmium and copper on natural and acid activated bentonite clay. *KKU Res. J.*, 17(5), 800 – 810

Erdeme, E., Karapinar, N. & Donat, R. (2004). The removal of heavy metal cations by natural zeolites. *Journal of Colloid and Interface Science*, 309 – 314

Ghasemi – Fasae, R. Gafari – Haghigh, M., Mousavi, S. M. & Dehghan, M. (2012). Sorption characteristics of heavy metals onto natural zeolite of clinoptilolite type. *International Research Journal of Applied and Basic Sciences*, 3(10), 2079 – 2084

Ghormi, F., Lahsini, A., Laajeb, A. & Addaou, A. (2013). The removal of heavy metal ions (copper, zinc, nickel and cobalt) by natural bentonite. *Larhyss Journal*, 37 – 54

Kaya, A. & Oren, A. H. (2005). Adsorption of zinc from aqueous solutions to bentonite. *Journal of Hazardous Materials*, 183 – 189

Kouakau, U., Ello, A. S., yapo, J. A. & Trokourey, A (2013). Adsorption of iron and zinc on commercial activated carbon. *Journal of Environmental Chemistry and Ecotoxicology*, 5(6), 168 - 171

Melichova, Z. & Hromada, L. (2013). Adsorption of Pb^{2+} and Cu^{2+} ions from aqueous solutions on natural bentonite. *Pol. J. Eniron. Stud.*, 22(2), 457 – 464

Mishara, P. C. & Patel, R. K. (2009). Removal of lead and zinc ions from water by low cost adsorbents. *Journal of Hazardous Materials*, 168(1), 319 - 325

Okeola, F. O. & Odebunmi, E. O. (2010). Freundlich and Langmuir isotherms parameters for adsorption of methylene blue by activated carbon derived from agrowastes. *Advances in Natural and Applied sciences*, 4(3), 281 – 288

Shaheen, S. M., Derbalah, A. S. & Moghanm, F. S. (2012). Removal of heavy metals from aqueous solution by zeolite in competitive sorption system. *International Journal of Environmental Science and Developmen*, 3, 362 – 367

Sheta, A. S., Falatah, A. M. Al – Sewailem, M. S., Khaled, E. M. & Sallam, A. S. (2003). Sorption characteristics of zinc and iron by natural zeolite and bentonite. *Microporous and Mesoporous Materials* 61, 127 - 136