Adsorption, kinetic and thermodynamic study of Al, Mn and Fe adsorption with natural attapulgite

FREEMAN NTULI[a], THABO FALAYI[b], CYRIL MABASA[a]

(a) Department of Chemical Engineering, (b)Department of Civil Engineering Sciences,
University of Johannesburg
P.O. Box 17011, Doornfontein 2028, Johannesburg
SOUTH AFRICA
fntuli@uj.ac.za

Abstract: -Natural attapulgite was utilized as an adsorbent for the removal of Al, Fe and Mn from a mixed metal effluent. Adsorption experiments were carried out by agitation of a fixed amount of attapulgite with a fixed volume of effluent waste stream in a thermostatic shaker for varying times. Attapulgite showed that it was capable of neutralising the acidic waste stream effluent as pH after 3 hour rose from 2 to 7.46. 4% solid loading of attapulgite could remove 85% Mn(II), 90% Al(III) and 100% Fe(III) The experimental data best fit Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models and the adsorption mechanism was physisorption. The adsorption process fitted well the pseudo second order kinetics for all metal ions studied. Thermodynamic data showed that Fe(III) and Mn(II) adsorption was thermodynamically spontaneous whilst Al(III) was not thermodynamically spontaneous. The process is endothermic for all metal ions. An increase in temperature resulted in an increase in spontaneity of the adsorption process. An increase in metal concentration resulted in an increase in amount of metal ion adsorbed per unit weight of attapulgite.

Key-Words: - Attapulgite, Adsorption, Isotherm.

1 Introduction

Water is of major importance to all living things, in some organisms, up to 90% of their body weight comes from water and up to 60% of the human body is water [1]. Though metals are essential for human growth, their presence in elevated levels in water has adverse effects on the health of humans [2]. Aluminium is released to the environment by both natural processes and anthropogenic sources. Due to its prominence as a major constituent of the earth's crust, natural processes far exceed the contribution of anthropogenic releases to the environmental distribution of aluminium [3]. The major anthropogenic sources of aluminium-containing particulate matter include coal combustion Aluminium production, and other industrial activities, such as smelting, that process crustal minerals [4]. Iron is usually released into the environment as iron pyrite from coal and gold mining [5]. The sulfide is oxidized to sulfate by bacterial and chemical reactions, releasing hydrogen ions and thus acidifying the water. Manganese compounds may also be released to the environment through their use in batteries, electrical coils, and ceramics. Other important anthropogenic sources of manganese include industrial emissions, combustion of fossil fuels, and landfills [5]. Aluminium can be either beneficial or harmful, depending on the levels of exposure, although acute exposure to high doses of aluminium are well tolerated, aluminium may be a contributing factor in certain neurodegenerative diseases such as Alzheimer's disease (AD), amyotrophic lateral sclerosis (ALS) and Parkinson's Dementia [6]. Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5%. Iron is an essential element in human nutrition. The average lethal dose of iron is 200–250 mg/kg of body weight, but death has been shown to occur following the ingestion of doses as low as 40 mg/kg of body weight [7]. Lethal doses cause haemorrhagic necrosis and sloughing of areas of mucosa in the stomach with extension into the submucosa. Manganese is an essential element for many living organisms, including humans as some enzymes require manganese. High levels of manganese exposure leads to neurological effects [8]. Manganism is caused by exposure to very high levels of manganese dusts or fumes and is characterized by symptoms including weakness, anorexia, muscle pain, apathy, slow speech, monotonous tone of voice. Some motor functions may already be affected following chronic exposure to levels of manganese of ≤ 1 mg/m3 [9, 10]]. Adsorption has been shown to be an effective way to remove metals from water [11]. Clays have been shown to be effective adsorbents [12]. Clays have the advantage of high specific surface area, cation exchange capacity and chemical and mechanical stability[13]. Attapulgite $[(Mg,Al)_4(Si)_8(O,OH,H_2O)_{26}.nH_2O]$ is a hydrated

magnesium aluminium silicate. Adsorption of either Fe(II) or Fe(III) on clays has not been explored much and only a few studies have been reported [14]. Methodologies for aluminium removal that have been developed include cation exchange, reverse osmosis and electro-dialysis, but these methods suffer from high cost and are not viable in developing countries like South Africa [15,16,]. There is therefore need to further study alternative cheap methods for metal removal. This paper seeks to establish the effectiveness of natural attapulgite in the adsorption of aluminium, manganese and iron from mixed metal effluent stream.

2 Materials and Methods

Natural attapulgite was supplied by G&W Base Minerals. Analytical grades of $Fe(NH_4)_2SO_4.6H_2O$, $Al_2(SO_4)_3.18H_2O$, $MnSO_4$, were supplied by Sigma Aldrich and were used to make synthetic mixed metal effluent stream . 98% H_2SO_4 and NaOH were supplied by Sigma Aldrich and were used for pH adjustment.

2.1 Equipment

pH was measured using Metler Toledo dual meter (Sevenduo pH/conductivity meter with a Metler Toledo InLab Pro ISM pH electrode and Metler Toledo InLab738 ISM conductivity probe). Metal analysis was achieved using an Inductively Coupled Plasma spectrometer (GBC Quantima). Adsorption experiments were conducted in a thermostatic shaker (Labotec OrbiShaker).

2.2 Procedure

The adsorption experiments were conducted using synthetic waste stream effluent containing Al, Mn and Fe. Stock solution of 1000 ppm of Al, Mn and Fe were prepared by dissolving appropriate amounts $Fe(NH_4)_2SO_4.6H_2O$, $Al_2(SO_4)_3.18H_2O$ and $MnSO_4$ in reverse osmosis (RO) water. The stock solutions were maintained at a pH of 2 using 98% H_2SO_4.

2.3 Adsorption Experiments

The batch adsorption experiments were carried out in 250 ml conical flasks by mixing natural attapulgite with 200 ml of synthetic waste stream effluent and agitated at various temperatures and times in a thermostatic shaker. After agitation the mixtures were filtered and the filtrate was ready for ICP analysis.

2.3.1 Effect of pH

Three 200 ml of heavy metal effluent (50 ppm of each Fe, Al and Mn) at pH of 2, 5 and 7 respectively were mixed with 8 g of attapulgite. The resulting solutions were agitated at 200 rpm in a thermostatic shaker for 180 min. At the end of 180 min agitation was stopped and the solution was filtered and the solution pH was measured. The filtrate was then taken for ICP metal analysis.

2.3.2 Effect of metal concentration

Three 200 ml of heavy metal effluent with 20, 30 and 50 ppm of each metal (Fe, Al and Mn) respectively were mixed with 8 g of attapulgite. The resulting solutions were agitated at 200 rpm in a thermostatic shaker for 180 min. At the end of 180 min agitation was stopped and the solution was filtered. The filtrates were then taken for ICP metal analysis.
.

2.3.3 Effect of residence time and temperature

8 g of natural attapulgite was added to 200 ml of heavy metal effluent with 50 ppm of each metal in a 250 ml conical flask. The initial pH and conductivity, of the synthetic waste effluent were measured. 7 solutions were used and each solution was agitated at 200 rpm using a thermostatic shaker maintained at 298.15 K. The solutions were run for 15, 30, 45, 60, 90, 120, 150 and 180 min respectively. After each time interval agitation was stopped and the solution pH was measured. The solutions were then subsequently filtered and analysed for heavy metals using the ICP. The amount adsorbed per unit mass of adsorbent at equilibrium q_e is given by

$$q_e = (C_0 - C_e) \times {V}/{M}$$

(1)

Where q_e (mg/g) is the amount of metal adsorbed at equilibrium per unit mass of adsorbent, C_0 (mg/L) is the initial metal concentration in solution, C_e (mg/g) is the equilibrium metal concentration in solution, V (L) is the volume of the solution and M (g) is the mass of adsorbent.
The above procedure was then repeated at 308.15 K and 318.15 K to calculate thermodynamic data.

3 Results and Discussion

3.1 Effect of pH

Fig. 1 shows the variation in metal removal efficiency with pH
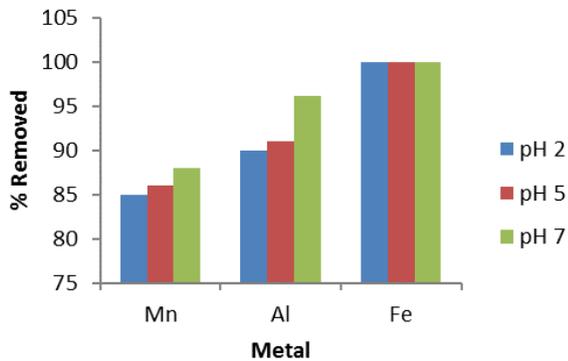
Fig. 1 Variation in metal removal with pH

Fig. 1 shows that the % metal removed increased with an increase in pH for Mn and Al. Fe adsorption was not affected by pH. Mn adsorption at pH 2 was 69% whereas at pH 7 it was 84%. At low pH there are more H^+ ions and the surface of the attapulgite is most likely to be covered with H^+ ions limiting the adsorption of Mn and Al (Gupta and Bhattacharyya, 2008). An increase in pH results in a decrease in H^+ ions concentration, leading to freeing of adsorption sites for Al and Mn resulting in an increase in uptake [17]. Fe^{3+} precipitates in pH above 4 hence the % removal at pH 5 and 7 are the same [18].

3.2 Effect of Adsorbent Concentration

Fig. 2 shows the variation of q_e with adsorbent concentration
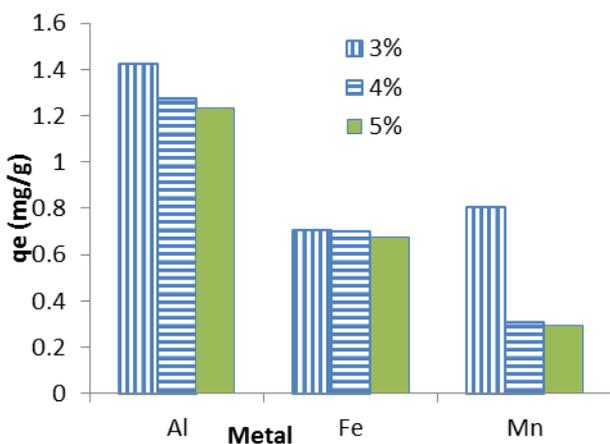
Fig. 2 Variation in q_e with adsorbent weight

The q_e for values Al and Mn decreased with increase with attapulgite concentration because an increase in adsorbent amount reduced unsaturation

of the adsorption sites and high attapulgite amounts have been shown to create aggregates resulting in reduction of total surface area and an increase in diffusional path length [19]. Only the adsorption of Fe^{3+} was significantly unaffected by the increase in metal concentration and this may be because the main mechanism responsible for Fe^{3+} removal from solution has been observed to be precipitation [20].

.

3.3 Effect of metal concentration

Fig. 2 the variation silica yield with solid loading
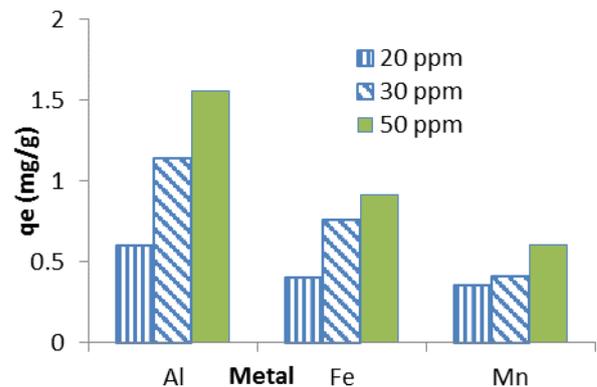
Fig. 3 Variation in q_e with increase in metal concentration

There was an increase in q_e with increase in metal concentration showing that attapulgite has a high affinity for the metal ions as evidenced by positive entropy values [21].

3.4 Effect of residence time

Fig. 4 shows the variation in pH with time (Initial pH 2, 50 ppm metal concentration, 4% m/v attapulgite loading).
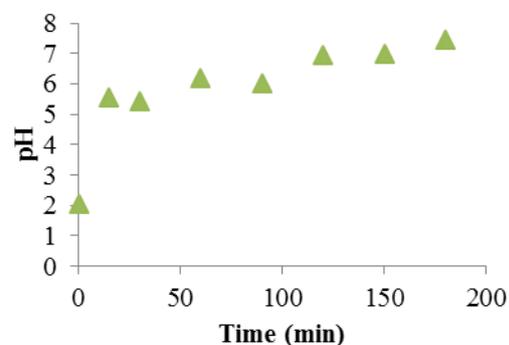
Fig. 4 Variation of pH with agitation time

Attapulgite is able to neutralize synthetic waste stream effluent as pH rises from 2 to 7.26 after 3 h.

Attapulgite has been shown to contain 0.146% Na_2O, 11.43% MgO and 4,19% CaO, these metal oxides have a neutralizing effect on aqueous solution [22].

3.5 Adsorption Isotherm

In order to find the adsorption capacities of the metals adsorbed by attapulgite, the experimental results were analysed using the Langmuir (Eqn.2) and Freundlich (Eqn.3) isotherms. The following linearised equations were used for this purpose

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (3)$$

Where C_e (mg/L) is the metal concentration in solution at equilibrium q_e (mg/g) is the amount of metal adsorbed per unit mass of adsorbent, q_m (mg/g) is the maximum adsorption, b (L/g) is a constant related to enthalpy of adsorption K_F and n are Freundlich equilibrium constants indicative of the adsorption capacity and adsorption intensity. Plots of C_e/q_e vs C_e and log q_e vs log C_e were done to represent the Langmuir and Freundlich isotherms respectively. The experimental data was considered to fit a particular isotherm if the correlation coefficient was greater than 0.99. Table 1 shows the isotherm parameters.

Table 1: Langmuir and Freundlich isotherm parameters.

Langmuir Isotherm	Al	Fe	Mn
q_m (mg/g)	0.031	0.016	0.006
B (L/g)	0.651	1.300	2.105
R_L	0.029806	0.015152	0.009412
R^2	0.999	1.000	0.996
Freundlich			
K_F (mg$^{1-1/n}$L$^{1/n}$g^{-1})	1.585	0.045	0.859
n	5.848	0.122	0.349
R^2	0.997	1.000	0.998

The adsorption process fits both Langmuir and Freundlich isotherms as R^2 values were greater than 0.99. Since $0 < R_L < 1$ (Table 1), for all metals it showed that the adsorption via Langmuir isotherm was favourable [23]. The n values for Fe and Mn

were below unity for Freundlich isotherm indicating that the adsorption was not thermodynamically favourable [24]. Since both Langmuir and Freundlich isotherms fitted the experimental results well, the data was subjected to Temkin and Dubinin–Radushkevich isotherms.

3.5.1 Temkin Isotherm

This isotherm contains a factor that explicitly takes into the account of adsorbent–adsorbate interactions. Excluding extremely low and large value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage [25]. Its derivation is characterized by a uniform distribution of binding. The linearised Temkin Isotherm model is given by equation 4.

$$q_e = B\ln A_T + B\ln C_e \quad (4)$$

Where A_T is the Temkin isotherm equilibrium binding constant (L/g) T is the absolute Temperature (K) and B is the constant related to heat of sorption (J/mol). A plot of q_e vs $ln\ C_e$ should be linear if the model fits the experimental data. Table 2 shows the Temkin model parameters.

.

Table 2: Temkin Isotherm Parameters

Metal	A_T (L/g)	B (J/mol)	R^2
Al	7.89	191	0.9999
Fe	8.26	78	0.9979
Mn	0.66	574	0.9991

The metals data fit the Temkin model well as the R^2 values were greater than 0.99 The low values of the Temkin constants (A_T and B) as shown in Table 2 indicated interactions between the attapulgite and metal ions was consistent with ion-exchange mechanism or physisorption [26].

3.5.2 Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface [27, 28]. The linearised equation is given by equation 5:

$$\ln q_e = \ln q_s - K_{DR}\varepsilon^2 \quad (5)$$

Where q_e, q_s, and K_{DR}, are amount of adsorbate in the adsorbent at equilibrium(mg/g), theoretical isotherm saturation capacity (mg/g), Dubinin–Radushkevich isotherm constant (mol²/kJ²) respectively and ε is another Dubinin–Radushkevich isotherm constant.

Where ε is given by equation 3.

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right)$$

(3)

The values of the sorption energy Es (J/mol) can be correlated to K_{DR} by using equation 4.

$$E_s = \frac{1}{\sqrt{2K_{DR}}}$$

(4)

Table 3 shows the Dubinin-Radushkevich model parameters.

Table 3:
Dubinin-Radushkevich model parameters

Metal	q_s (mg/g)	K_{DR} (mol²/kJ²)	E_s (J/mol)	R^2
Al	1.02	0.000001	707	0.9995
Fe	0.50	0.0000001	2236	0.9718
Mn	0.25	0.000003	408	0.9904

The metals data fit the Dubinin-Radushkevich model well as the R^2 values were greater than 0.99 with the exception of Fe which was 0.97. The mean sorption energy values were below 8kJ/mol (Table 3) indicated that the adsorption process was typical physisorption [29]. This is in agreement with thermodynamics data where ΔG^0 values were below 20kJ/mol (Table 5) indicating that adsorption was through physisorption [30].

3.6 Adsorption kinetics

Plots of log (q_e-q_t) vs t and t/qt vs t were done to represent pseudo first and second order kinetics respectively. The experimental data was considered to fit a particular model if the correlation coefficient was greater than 0.99. Values for pseudo first order kinetics are not shown as the R^2 values were 0.08, 0.65 and 0.16 for Al, Fe and Mn respectively. Table 4 shows the pseudo second order model parameters.

Table 4:
Second Order Kinetic model parameters

Second Order Kinetics	Al	Fe	Mn
q_e (mg/g)	0.316	0.673	1.121
Δq_e (mg/g)	-0.004	-0.016	0.002
K_2 (gmg⁻¹min⁻¹)	7.75	1.41	2.06
R^2	0.9975	0.9997	1.0000

The pseudo second order kinetic model gave the best fit for experimental data as $R^2 \geq 0.99$. The calculated q_e values were very close to experimental values as seen by the Δq_e values further confirming that the model is the best to describe the adsorption kinetics.

3.7 Effect of Temperature
Figure 5 shows the plots of ΔG^0 vs T and Table 5 shows the Lamgmuir Isotherm parameters at different temperatures.
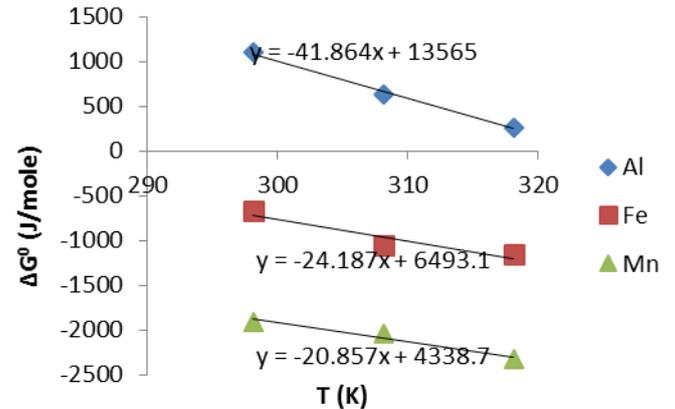
Fig. 5 ΔG^0 vs T plot for Al, Mn and Fe.

Table 5:
Thermodynamic data for adsorption of Al, Fe and Mn.

Metal Temperature K	ΔH^0 (kJ/mol)	ΔS^0 (J/mol)	ΔG^0 (J/mol)		
			298.15	308.15	318.15
Al	13.5	41.8	1101	628	264
Fe	6.49	24.2	-672	-1053	-1156
Mn	4.34	20.9	-1907	-2034	-2324

The positive value for enthalpy show that the adsorption process is endothermic which is supported by the Gibbs free energy values which increase in the negative value as the temperature is increased for Fe and Mn whilst

the positive value for Al decreased (Table 5). The adsorption is endothermic because cations in solution are in hydrated form $M(OH)_n$ and therefore energy is required for the detachment of water molecules from cations (hydration enthalpy). Therefore the more a cation is hydrated the stronger its hydration enthalpy and the less it can interact with the adsorbent [31]. The positive entropy values pointed to a stable configuration during adsorption [19] accompanied by considerable change in surface configuration of the adsorbent due to strong affinity of metal ions for clay surface

4 Conclusion

Attapulgite can be used to immobilise Al, Fe and Mn at 4% solid loading. The adsorption isotherms fitted Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm. Al, Fe and Mn adsorption was endothermic. Mn and Fe adsorption was thermodynamically spontaneous whilst Al adsorption was thermodynamically not spontaneous. Adsorption was via weak electrostatic adsorbent-adsorbate interactions typical of physisorption. An increase in temperature resulted in an increase in spontaneity of the adsorption process.

References:

[1] United States Geological Survey,USA Geological Survey, National Field Manual for the Collection of Water-Quality Data. http://pubs.water.usgs.gov/twri9A/ (2011). Accessed 25 July 2014.

[2] Krewski D, Yokel R.A, Nieboer E, Borchelt D, Cohen J, Harry J, Kacew S, Lindsay J, Mahfouz AM, Rondeau V, Human Health Risk Assessment for Aluminium, Aluminium Oxide, and Aluminium Hydroxide, *Journal of Toxicology and Environmental Health-Part B-Critical Reviews*, Vol.10, 261-269.

[3] Lantzy RJ, MacKenzie FT, Atmospheric trace metals: Global cycles and assessment of man's impact, *Geochim Cosmochim Acta*, Vol.43, 1979, pp.511-525.

[4] Lee RE Jr, Von Lehmden DJ, Trace metal pollution in the environment, *Journal of Air Pollution Control Association*, Vol.23, 1973, pp. 853-857.

[5] Bodek I, Lyman WJ, Reehl WF, Rosenblatt DH, Environmental Inorganic Chemistry: Properties, Processes, and Estimation Methods. In: Walton, B.T., Conway, R.A.(eds). Pergamon Press. New York. SETAC Special Publication Series (1988).

[6] Gidding M, Aluminum. Environmental and Workplace Health Canadian Drinking Water Quality, *Canada*, (1998)

[7] National Research Council. *Iron*. Baltimore, MD, University Park Press, 1979

[8] Canavan MM, Cobb S, Srinke, C, Chronic manganese poisoning, *Archives of Neurology and Psychiatry*, Vol.32, 1934, pp. 501–512.

[9] Roels HA, Ghyselen P, Buchet JP, Ceulemans E, Lauwerys RR, Assessment of the permissible exposure level to manganese in workers exposedto manganese dioxide dust, *British Journal of Industrial Medicine*, Vol.49, 1992, pp. 25–34.

[10] Mergler D, Huel G, Bowler R, Iregren A, Bélanger S, Baldwin M, Tardif R, Smargiassi A, Martin, L, Nervous system dysfunction among workers with long-term exposure to manganese, *Environmental Research*, Vol.64, 1994, pp.151–180.

[11] Tran HH, Roddick FA, O'Donnel JA, Comparison of Chromatography and desiccant silica gels for the adsorption of metal ions-I. Adsorption and kinetics, *Water Research*, Vol.33, 1999, pp. 2992-3000.

[12] Mellah A, Chegrouche S, The removal of Zinc from aqueous solutions by natural bentonites, *Water Research*, Vol.31, 197, pp. 621-629.

[13] Gupta SS, Bhattacharyya KG, Adsorption of heavy metals on kaolinite and montmorillonite: a review. *Phys. Chem. Chem. Phys*, Vol. 14, 2012, pp. 6698–6723.

[14] Pesavento M, Albert G, Bieuz G, Investigation of the speciation of aluminium in drinking waters by sorption on a strong anionic-exchange resin AG1X8, *Analytica Chimica Acta,* Vol.367, 1998, pp.215-222.

[15] Matus P, Kubova J, Complexation of labile aluminum species by chelating resins Iontosorb-a new method for Al environmental risk assessment, *Journal of Inorganic Biochemistry*, Vol. 99, 2005, pp.1769-1778.

[16] Singh TS, Pant KK, Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina, *Separation and Purification Technology*, Vol. 36, 2004, pp. 139-147.

[17] Taty-Costodes VC, Faudue H, Porte C, Delacroix A, Removal of Cd(II) and Pb(II) ions from aqueous solutions, by adsorption onto sawdust of Pinus sylvestris, *Journal of Hazardous Materials B*, Vol.105, 2003, pp. 121-142.

[18] Goldani E, Moro CC, Maia SM, A Study Employing Differents Clays for Fe and Mn Removal in the Treatment of Acid Mine Drainage, *Water Air Soil Pollution*, Vol.224, 2013, pp.1401

[19] Gupta SS, Bhattacharyya KG, Immobilization of Pb(II), Cd(II) and Ni(II) ions on kaolinite and montmorillonite surfaces from aqueous medium, *Journal of Environmental Management*, Vol. 87, 2008, pp. 46-58.

[20] Motsi T, Rowson TA, Simmons MJH, Adsorption of heavy metals from acid mine drainage by natural zeolite, *Interantional Journal of Mineral Processing*, Vol.92, 2009, pp. 42–48.

[21] Gupta VK, Jain CK, Ali I, Sharma M, Saini VK, Removal of Cadmium and nickel from waste water using bagasse fly ash- a sugar industry waste, *Water Research*, Vol. 37, 2003, pp. 4038-4044.

[22] Falayi T, Ntuli F, Removal of heavy metals and neutralization of acid mine drainage with unactivated attapulgite, *Journal of industrial and Engineering Chemistry*, Vol.20, 2014, pp. 1285-1292.

[23] Ho YS, Removal of copper ions from aqueous solution by tree fern, *Water Research*, Vol.34, 2003, pp. 2323-2330.

[24] Tryball, R.E.: Mass Transfers Operations, third ed., McGraw,New York (1980).

[25] Tempkin MI, Pyzhev V, Kinetics of ammonia synthesis on promoted iron catalyst, *Acta Phyics. Chimica USSR*, Vol.12, 1940, pp.327–356.

[26] Horsfall M Jnr. Spiff AI, Equilibrium Sorption Study of Al^{3+}, Co^{2+} and Ag^{2+} in Aqueous Solutions by Fluted Pumpkin (Telfairia Occidentalis Hook F) Waste Biomass, *Acta Chimica Sloveni*, Vol.52, 2005, pp.174-181.

[27] Gunay A, Arslankaya E, Tosun I, Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics, *Journal of Hazardous Material*, Vol.146, 2007, pp. 362–371

[28] Dabrowski A, Adsorption—from theory to practice, *Advanced Colloid Interface Science*, Vol.93, 2001, pp. 135–224.

[29] Riaz A, Tayyab Y, Absari MS, Hasany SM, Sorption Behaviour of Lead(II) Ions from Aqueous Solution onto Haro River Sand, *Adsorpion Science Technology*, Vol.24, 2006, pp.475-486.

[30] Okoye IP, Obi C, Thermodynamic and Kinetic Evaluations of Some Heavy Metal Ions on Aluminum-Pillared and Unpillared Bentonite Clays, *International Archive of Applied Sciences and Technology*, Vol.3, 2012, pp. 58 – 67.

[31] Amarasinghe, BMWPK, Williams RA, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, *Chemical Engineering Journal*, Vol.132, 2007, pp.299–309.