Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2015, 7(3):51-58
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Adsorption of Zinc(II) ions from aqueous solution onto Kaolinite and Metakaolinite

G. Ndongo Kounou[1], J. Ndi Nsami[1*], D. P. Belibi Belibi[1], D. Kouotou[1], G. M. Tagne[1], D. D. Dina Joh[2] and J. Ketcha Mbadcam[1]

[1]*Physical and Theoretical Chemistry Laboratory, Department of Inorganic Chemistry, Faculty of Science, University of Yaoundé I, Yaoundé – Cameroon*
[2]*Department of Chemistry, University of Douala, Douala – Cameroon*

ABSTRACT

Kaolinite and metakaolinite obtained from clay soils from the South Western Region of Cameroon were used as adsorbents to study their adsorptive capacities on the removal of zinc(II) ions. The effects of pH (2.0 - 8.5), agitation time (5 - 120 min), adsorbent dose (0.05 - 1.10 g), initial concentration (0.1 - 1.8 mmol/L) were investigated. The experiments showed that the removal of zinc(II) ions depends on the pH, the initial concentration and the mass of the adsorbents. The maximum adsorption took place at pH = 8.5 for the two adsorbents. With the adsorbent mass of 0.05 g, the quantities adsorbed of 7.196 and 12.375 mg/g were recorded for kaolinite and metakaolinite respectively. According to the Dubinin-Radushkevich isotherm model, the adsorption isotherm of zinc(II) ions on the kaolinite was a physisorption process, whereas on the metakaolinite, the process was chemisorption. The kinetic studies showed that the adsorption of zinc(II) ions on the kaolinite and metakaolinite followed the pseudo-second order equation. The average energies of adsorption were of 12.90 KJ/mol and 707.11 KJ/mol which confirmed that physical and chemical adsorption processes controlled the zinc(II) ions uptake on the two adsorbents respectively.

Keys words: Adsorption, Kaolinite, Metakaolinite, Isotherm, Kinetic

---

INTRODUCTION

The discharge of heavy metals into aquatic ecosystem has become a matter of concern over the last few decades. The pollutants of serious concern include mercury, uranium, lead, chromium, arsenic, cadmium, gold, copper, nickel and zinc [1]. The presence of heavy metals in the environment is a major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentration [2]. The presence of these heavy metals in aquatic environments is know to cause severe damage to aquatic life because they kill microorganisms during biological treatment of waste water which leads to a consequent delay in the process of water purication.

Most heavy metals salts are soluble in water and consequently cannot be eliminated by ordinary physical techniques of separation . Elevated environmental levels of zinc(II) ions comes from variety of sources such as mining, metal cleaning, plating baths, pulp, paper board mills, fertilizer industries etc…, which are the potential sources of zinc(II) ions in industrial effluents [3]. Zinc(II) ions, are widely used as metal in industry where they play an important role and participate in a good number of cellular processes where they act as enzyme cofactor and they also influence the transcription factor of gene expression [4]. According to WHO the maximum acceptable concentration of zinc(II) ions in drinking water is 5 mg /L [5]. If an excessive amount of zinc(II) is allowed to enter into the environment it can cause serious health issues such as aneamia, massive gastrointestinal, vomiting, skin dermatitis and nausea [6]. The removal of metal ions from wastewaters becomes an important issue for the treatment of contaminated wastewaters . The efficient methods for the removal of metals has resulted in the development of new separation techniques such as, the electro-chemical processes, electrodialysis, nano-filtration, reverse omosis ,precipitation, ion-exchange, floculation, and membrane separation [7,8]. For instance, these methods seems to be inefficient or expensive when the heavy metal ions exist in low concentrations [9]. Thus, the adsorption process is an alternative technology in which many studies focused because of its cost effectiveness, local availability and technical feasibility for the removal of heavy metal ions from the wastewater [10].

The main aim of this study is to evaluate the effective removal of zinc(II) ions from aqueous solution using kaolinite and metakaolinite . These clay materials which are in large quantities in Cameroon, being economic and eco-friendly due to their unique chemical composition, ready availability, renewability and low cost, seems to be a viable option for heavy metal remadiation.

METERIALS AND METHODS

Chemical reagents

Laboratory grade reagents supplied in powder form by Merck was used without further purification for the preparation of synthetic aqueous solution.

Treatment of adsorbents

The clay material was obtained from the South West region of Cameroon. The clay was extensively washed with tap water to remove dirt and other particles, followed by washing with distilled water. The principle of sedimentation was used to obtain particles of sizes less or equal to 2 µm. The metakaolinite was obtained from kaolinite by heating a 20 g of kaolinite at a heating rate of 5 °C /min. When the temperature of 700 °C was reached, the heating was stopped and the sample was allowed to cool to room temperature .The dried adsorbent was ground in a laboratory blender and stored using standard test sieves. Before usage for adsorption process, the adsorbents were primarily heated in an oven for dryness at 110 °C for 24 hours and cooled in a dessicator.

Preparation of Zinc solution

The solution of zinc(II) ions of 0.1 mol/L was prepared by dissolving 2.7 g of zinc chloride, $ZnCl_2$, in a volumetric flask of 1000 mL and filled with distilled water. Then it was finally diluted to obtain standard solutions of the desired concentrations (0.1- 1.8 mmol/L). The pH of the solution was adjusted by using 0.1 M HCl or 0.1 M NaOH.

Adsorption studies

Batch adsorption test were carried out by mechanical agitation at room temperature. For each run, 50 mL of zinc(II) ions of initial concentration (0.1- 1.8 mmol/L) was mixed with a known weight (0.05 g) of kaolinite or metakaolinite. After agitation at the required time, the solution was filtered and the filtrate was analyzed using a UV/Vis spectrophotometer, F.A 05005 to determine the residual concentration of zinc(II) ions.

RESULTS AND DISCUSSION

Characterization of the Adsorbent

The physico-chemical properties of the metakaolinite are listed in Table 1.

Table 1: Physico-chemical properties of metakaolinite

Sample	Metakaolinite	Kaolinite
Specific surface area (m^2/g)	33.8331	20.1819
Average width of the pores (nm)	11.0548	/
Diameter average of the pores (nm)	9.9178	/
Total volume of the pores (cm^3/g)	0.0935	/
Type of hysteresis	Type III	Type II

Table 2. Chemical composition of the adsorbents

Oxides (%)	Kaolinite	Metakaolinite
SiO_2	49.52	46.99
Al_2O_3	32.04	34.66
Na_2O	0.05	10.55
TiO_2	0.99	0.94
Fe_2O_3	0.75	0.79
K_2O	0.69	0.67
MgO	0.13	0.16
CaO	0.04	0.06
Loss on ignition	15.73	5.05
Total	99.94	99.91

The chemical analysis of Kaolinte and Metakaolinite is presented in Table 2. This shows that the major elements in these two adsorbents materials are SiO_2 and Al_2O_3.

Effect of agitation time

The agitation time was evaluated as one of the most important factors affecting the adsorption efficiency. The quantity adsorbed with respect to contact time was plotted and presented in Figure 1. According to the graph, the quantity of zinc(II) ions adsorbed increase quickly in the first ten minutes and reaches equilibrium at 20 minutes where no further adsorption took place. The increasing adsorption rate at the beginning was due to the fact that most of the adsorption sites were still free for which thereafter saturation occurred which led to equilibrium [11]. These results are similar to those obtained by Ketcha et al. 2011 during the Kinetic and Equilibrium Studies of Adsorption of Lead(II) Ions from Aqueous Solution onto Two Cameroon Clays: Kaolinite and Smectite

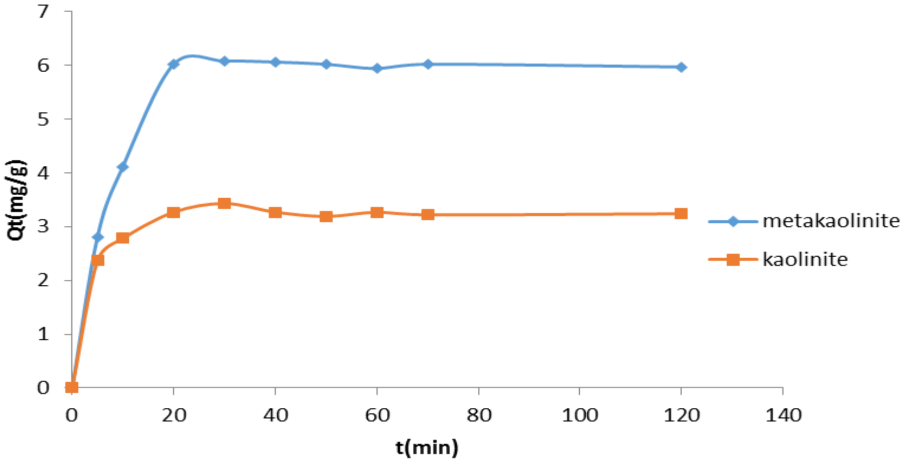

Figure 1. Effect of contact time on zinc(II) ions adsorbed.

Effect of adsorbent dose

Adsorption experiments were performed at different adsorbent doses (0.05, 0.3, 0.5, 0.7, 0.9 and 1.1 g) of kaolinite and metakaolinite. Figure 2 bellow shows that the quantity adsorbed decreases with an increasing adsorbent dose. The reduction of quantity adsorbed with the increase in mass is due to the fact that; interactions between the materials' particles increases with mass. The decrease in adsorption capacity may be due to the overlapping of the adsorption sites as a result of overcrowding adsorbent particles [12,13]. Similar results were also obtained by Gaston et al. 2014.

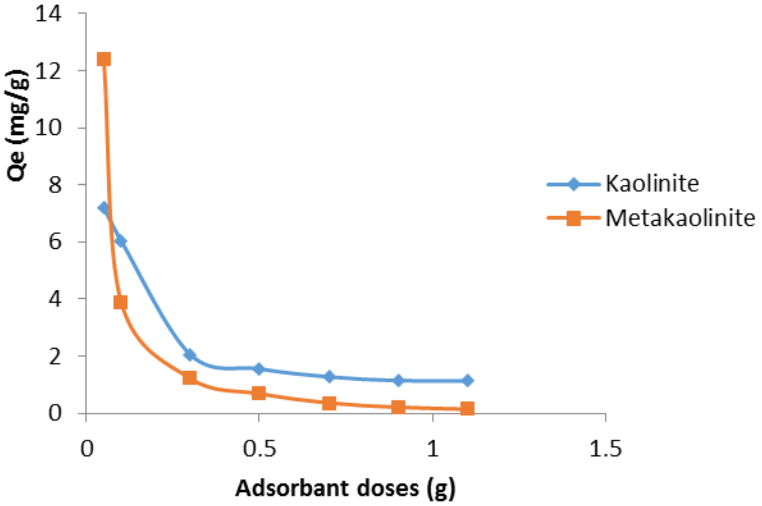

Figure 2. Effect of adsorbent dose on quantity of Zinc(II) ions

Effect of pH

The pH of the solution is an important parameter in the adsorption process. It is well known that the pH of the medium affects the solubility of metal ion and the concentration of the counter ion on the functional groups of the clay. The batch adsorption studies at different pH values were carried out in the range of 2.04 - 8.50 as presented in Figure 3. These results revealed that the maximum adsorption of zinc(II) ions occurred at pH equal 8.5. At a lower pH value, the zinc(II) ions removal seems to be inhibited. This may be due to adsorption competition between hydrogen ions and zinc(II) ions on the available adsorption sites, because at low pH , the medium contains a high concentration of hydrogen ions rather than at pH greater or equals to 8.5 [14]. Throughout this experiment, it is observed that metakaolinte is an excellent adsorbent as compared to kaolinite. This might be due to it high specific surface area of 33.83 m^2/g as 20.18 m^2/g in kaolinite.

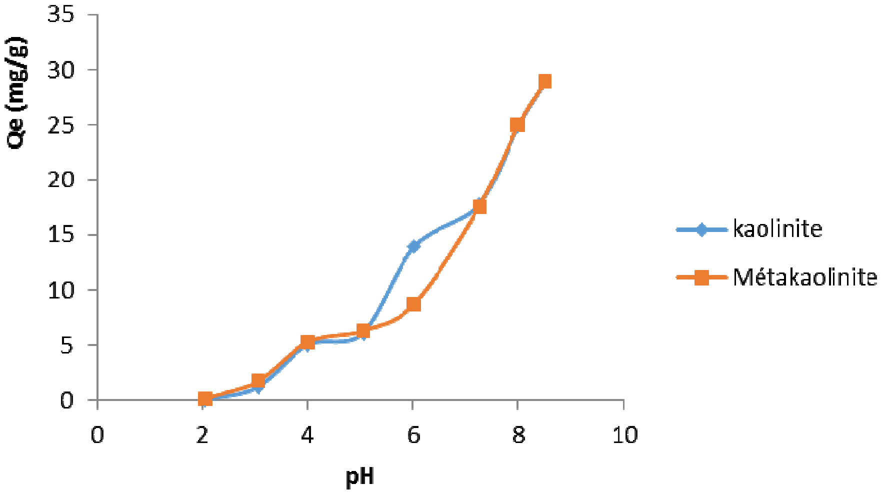

Figure 3: Effect of pH on quantity Zinc(II) ion adsorbed

KINETICS OF ADSORPTION

The pseudo-first order rate expression, popularly known as the Largergren equation, is generally described by the following equation [15].

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \qquad (1)$$

Where, Q_e *and* Q_t in (mg/g) are the adsorption capacities at equilibrium and at time t, respectively while K_1 is the rate constant for the pseudo-first order adsorption (L/min).

The adsorption data was also analyzed in terms of the pseud-second order mechanism [16].

$$\frac{T}{Qt} = \frac{1}{ho} + \frac{T}{Qe} \qquad (2)$$

Where, $h_o = k_2 Qe$ is the initial adsorption rate, when t tend to 0, k_2 is the rate constant of pseudo-second order adsorption ($g.mg^{-1}min^{-1}$) [17]. Parameters of kinetic models for Zn^{2+} ions adsorption on kaolinite and metakaolinite are given in Table 2

Table 2: Kinetic parameters of zinc(II) ions adsorption onto kaolinite and metakaolinite at ambient temperature and $C_O = 10^{-3}M$; m = 0.05 g .

Adsorbents		Kaolinite	Metakaolinite
Pseudo-first order	K_1 (min^{-1})	0.147	0.2334
	Q_e($mg.g^{-1}$)	2.84	9.53
	R^2	0.9788	9.927
Pseudo-second order	K($g.min^{-1}.g^{-1}$)	0.1236	6.211
	Q_e($mg.g^{-1}$)	2.32	5.15
	R^2	0.999	0.996

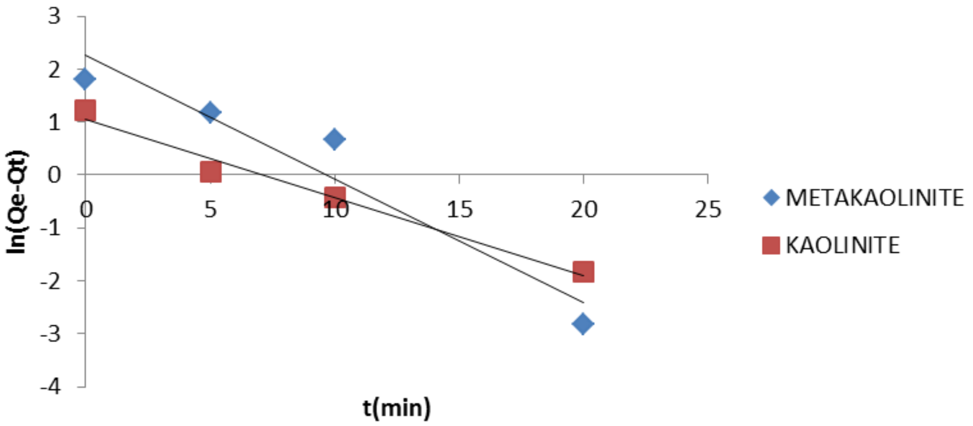

Figure 4: Linear plot of pseudo-first order for the adsorption of zinc(II) ions on kaolinite and metakaolinite with same legends as for Figure 4

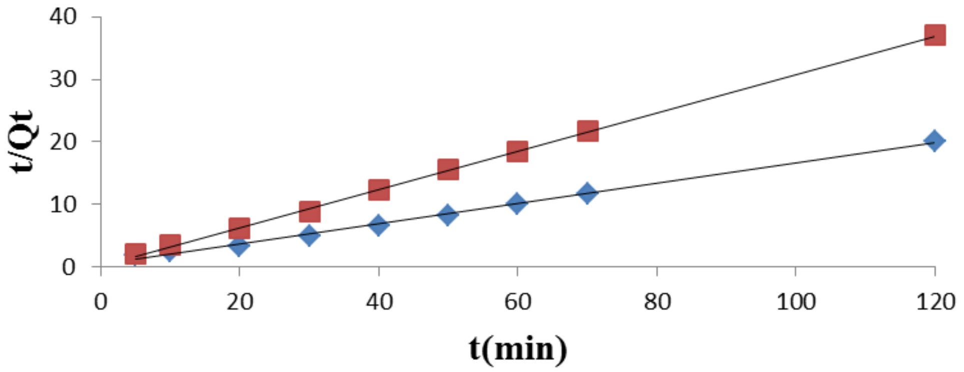

Figure 5: Linear plot of second-first order for adsorption of zinc(II) ions on kaolinite and metakaolinite

ADSORPTION ISOTHERMS

Tree types of adsorption isotherm models namely, Langmuir, Freundlich and Dubinin-Radushkevich isotherms were confronted to the experimental data. The Langmuir isotherm model is given as follow:

$$\frac{Ce}{Qe}=\frac{1}{Qm}b+\frac{Ce}{Qm} \qquad (3)$$

Where,

C_e is the concentration of zinc(II) ions (mol/L); Q_e, the quantity of zinc(II) ions adsorbed at equilibrium (mg/g); Q_m and b are the Langmuir constants; adsorption capacity and adsorption energy respectively. The Linear plots of $\frac{Ce}{Qe}$ versus Ce suggest the applicability of Langmuir isotherm (Figure 6). The value of Qm, K_L, r^2 and R_L were determined from the slopes and intercepts of the plots (Table 3)

Table 3: Statistical parameters of the Langmuir isotherm

	r^2	Q_m	K_L	R_L
Kaolinite	0. 9595	0.31	1.349	0.8
Metakaolinite	0.978	0.67	1.456	0.906

According to the value of R_L, adsorption process is unfavorable for both the two adsorbents (kaolinite and metakaolinite) for the removal of zinc(II) ions.

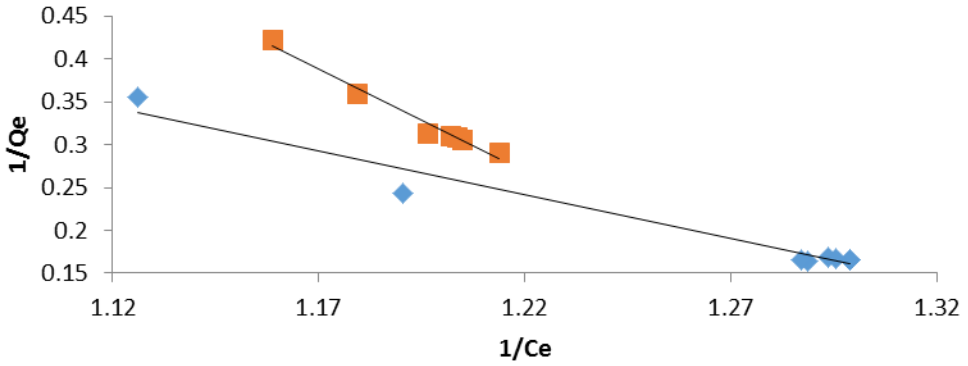

Figure 6: Linear transformation of the Langmuir isotherm for the adsorption of zinc(II) ions by kaolinite and metakaolinite

Freundlich isotherm model

The logarithmic form of Freundlich isotherm model is given as follows,

$$\log Qe = \log K_F + \frac{1}{n}\log Ce \qquad (4)$$

Where,

Qe is the quantity of zinc(II) ions adsorbed at equilibrium (mg/g); Ce is the concentration of zinc(II) ions at equilibrium (mol/L); K_F (L/g) is the Freundlich constant and n the intensity of adsorption process.

The values of K_F and $\frac{1}{n}$ obtained from the plots are given in Table 4. The value of $\frac{1}{n}$ is greater than 1 for the two adsorbents. This implies that we have Van der Waals attractions bonding the adsorbent and adsorbate particles.

Table 4: Values of the Freundlich constants

sample	K_F	$\frac{1}{n}$	r^2
kaolinite	0.734	8.038	0.9878
metakaolinite	1.569	5.208	0.986

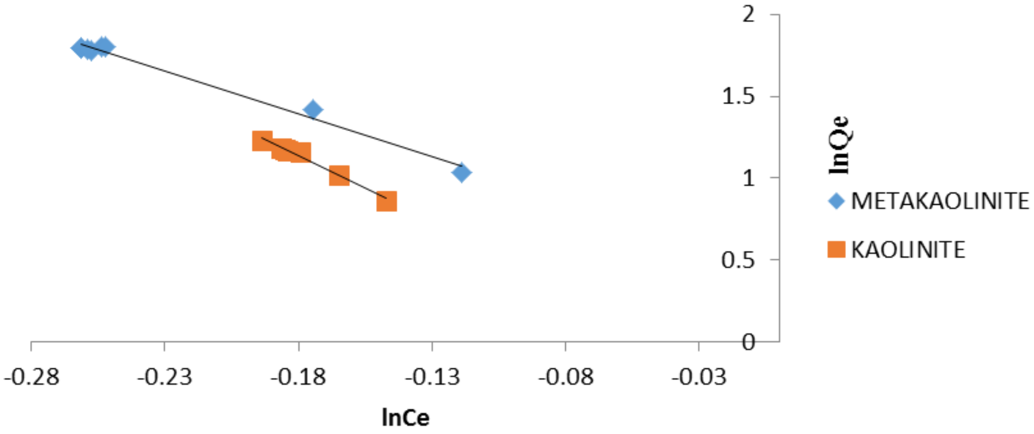

Figure 7: Linear transformation of the Freundlich isotherm for zinc(II) ions adsorption on kaolinite and metakaolinite

Dubinin-Radushkevich model

The Dubinin-Radushkevich model was developed for the adsorption of substances in traces in the aqueous phase onto porous solids. This model is more general than that of Langmuir because it is applicable even to non-homogeneous adsorption sites. It is expressed as [18].

$$Q_e=Q_m \exp(-k'\varepsilon^2) \qquad (5)$$

$$lnQ_e = lnQ_m - k^{'}\varepsilon^2 \qquad (6)$$

$k^{'}$ is obtained from the linear plot of lnQ_e against ε^2, and the average energy of adsorption E ($kJ.mol^{-1}$) can be obtained starting from the value of $K^{'}$ by employing the following equation [19]:

$$E= (2k^{'})^{-1/2} \qquad (7)$$

This model was applied to equilibrium data to determine which adsorption (physical or chemical) occurred. The plot of lnQ_e against ε^2 is stated (Figure 8).The values of Q_m, R^2

and E (kj/mol) are presented in Table 5. The energy of adsorption for the kaolinite is 12.9 kJ/mol and metakaolinite is 707.106 kJ/mol, which suggested that the physical and chemical adsorption dominate the process of adsorption over a uniform surface respectively for both the kaolinite and metakaolinite.

Table 5: Dubinin-Radushkevich constants and statistical parameter

sample	Q_m (mg/g)	E(kj/mol)	R^2
kaolinite	10^{-8}	12.9	0.9873
metakaolinite	0.099	707.106	0.9824

CONCLUSION

Adsorption is a potentially attractive technique for the treatment of heavy metals such as zinc(II) ions from wastewater. This work was carried out using the kaolinite and metakaolinite as adsorbents. The adsorption capacity strongly depends on the contact time, adsorbent doses and the pH. The kinetic of zinc(II) ions adsorption followed the pseudo-first and second order equations. The experimental data well fitted the Freundlich equation, with the correlation coefficients close to unity. Resulting tests on the zinc(II) ions removal from aqueous solution using metakaolinite could serve as potential applicability of this adsorbent in industrial wastewater treatment.

Acknowledgement
The authors acknowledged Dr. Isaac NONGWE BEAS, Department of Civil and Chemical Engineering UNISA, RSA for recording the BET of the adsorbents and also the Research Unit: Adsorption and Surface.

REFERENCES

[1]-P.E. Aikpokpodion, R.R. Ipinmoroti and S.M. Omotoso, *American-Eurasian Journal of Toxicological Sciences*, **2010**, 2(2), pp 72-82.
[2]-M. Bansal, D. Singh, V. K. Garg and R. Pawan, *International Journal of Civil and Environmental Engineering*, **2009**, 1(2), pp 108-114.
[3]-B. Amarasinghe and R. A. William, *Chemical Engineering Journal*, **2007**, 132, pp 299- 309.
[4]-R. S. MacDonald, *Journal Nutriment*, **2000**, pp 1500 -1508
[5]-M. Helen Kalavathy, L. R. Miranda, *Chemical Engineering Journal*, **2010**, pp 188- 199.
[6]-K. S. Rao, S. Anand and P. Venkateswarlu, *Bioresource* , **2010**, 5, pp 438- 454 .
[7]-M. Rio, A.V. Parwate and A. G. Bhole, *Waste Management*, **2002**, 22, pp 812- 830.
[8]-T. I. Anirudhan and P. G. Radhakrishnan, *Journal of Chemical Thermodynamics*, **2008**, 40, pp702- 709.
[9]-H. Duygu, H. Kumbur, B. Saha and J. Hans Van Leeuwen, *Bioresource Technology*, **2008**, 99, pp 4943- 4948.
[10]-xiaomin li, yanru tang, xiuju cao, dandan lu, fang luo, wenjing shao, *colloids and surfaces*, **2008**, 317, PP 512-521.
[11]- R. Soug , D. Touaiba , B. Bonayada and A. Boucenna, *European Journal of Research* , **2009**, 35, pp 416-425.
[12]-M. R. Ajimal, A. K. Rao, J. Ahmed and R. Ahmad, *Journal of Environmental Science and Engineering* ,**2006** ,48(3), pp 221- 224.
[13]- Garg V. K. , Gupta R., Yadav A. B., and R. Kumar, *Bioresource Technology*, **2003**, 89, pp 121-124.
[14]-D. Chauhan and N. Sankararamakrishnan, *Bioresource Technology*, **2008**. 99(8), pp 9021 - 9024.
[15]-J. M. Ketcha, S. G. Anagho, J. N. Ndi and A. M. Kammegne, *Journal of Environmental Chemistry and Ecotoxicology* ,**2011**, 3(11), pp 290- 297.
[16]-A. Abdellah, I. Abdelkader, and S.O. Mohand, *Water Quality Research Journal of Canada*, **2007**, 42(1), pp41-45.
[17]-J. C. Igwé, A. A. Abia and C. A. Ibeh, *International Journal of Environmental Science and Technology*, **2008**, 5(1), pp 83 -92.
[18]-A. Benhammou, A. Yaacoubi, and B. Tanouti, *Journal of Hazardous Materials*, **2005**, 117, pp 243 - 249.
[19]-O. Hamdaoui and E. Naffrechoux, *Journal of Hazardous Materials*, **2007**, 147, pp 381- 394.

[20]- G. Fumba, J. S. Essomba, G. M. Tagne, J. Ndi Nsami, P. D. Bélibi Bélibi and J. Ketcha Mbadcam, *Journal of Academia and Industrial Research (JAIR)*, **2014**, 3(4), pp 156-163.