International Journal of Scientific Research and Modern Education (IJSRME)
ISSN (Online): 2455 – 5630
(www.rdmodernresearch.com) Volume I, Issue I, 2016

EQUILIRIUM, KINETICS AND THERMODYNAMIC STUDY OF Pb(II) IONS FROM AQUEOUS SOLUTION BYUSING FIRED CERAMIC

Shamim Ahmad*, Anwer Ali* & Ahmad Ashfaq**

* Department of Chemistry, D.S. College, Aligarh, Dr.B. R. Ambedkar University, Agra, Uttar Pradesh

** Civil Engineering Section, Faculty of Engineering & Technology. Aligarh Muslim University, Aligarh

Abstract:

Toxic heavy metals are some of the most common hazardous pollutants found in industrial wastewater. The industrial activities and technological development lead to a discharge of significant amount of heavy metal ions including Pb(II) in their effluent which influence the health of human population and also affect aquatic life. The long term exposure of Pb(II) cause decrease in performance of nervous system, weakness in bone joints, increase in blood pressure, anaemia. High level exposure of lead can severely damage brain, kidneys and may cause miscarriage in pregnant women. Therefore, it is a matter of great concern to remove lead from industrial water before discharging it into the water bodies. The aim of the present study is to explore the feasibility of using Fired Ceramic as adsorbent for the removal of Lead ions from aqueous solutions under different conditions. Batch studies have been conducted to investigate the influence of various parameters of adsorption such as pH, contact time, adsorbent dose and metal ions concentration on the adsorption of lead by fired ceramic. It has been observed that adsorption percentage of Pb(II) increases to 96.320% with increase in pH up to pH 4and decreases with increase of metal ion concentration. Equilibrium time required for the adsorption of lead ions by fired ceramic was found to be 2 hours. The kinetic studies revealed that adsorption of lead by fired ceramic follow both first and second order kinetics. The highest value of $R^2 = 0.997$ *for Langmuir isotherm indicates adsorption of Pb(II) by fired ceramic obey Langmuir isotherm more appropriately than Fruendlich and Temkin model. These results suggested that the fired ceramic can be effectively employed as cost free and environment friendly adsorbent for the removal of heavy metals in aqueous system.*

Key Words: Fired Ceramic, Adsorption, Batch Process, Langmuir, Fruendlich, Temkin Isotherm, Pseudo-First Order, Second Order& Intra-Particle Diffusion.

1. Introduction:

For decades, urban and industrial pollution has led to a gradual environmental degradation of the natural environment (atmosphere, water, soil). This phenomena is serious and requires great efforts to correct the situation and prevent its proliferation. The fast paced development of industries such as metal mining operations, fertilizers and paper industries and pesticides have deliberately discharge various types pollutants into the environments especially in developing countries. Among other issues, water contaminations by heavy metals are more pronounced than other pollutants especially when heavy metals are exposed to the natural ecosystems. Heavy metals refers to any element with the atomic weight between 63.5 and 200.6 and a specific gravity greater than 5.0 [1].Heavy metals are non-biodegradable and tend to accumulate in human body causing various disorders [2].Heavy metals have been expressively released into the environment due to rapid industrialisation and have created a major global concern[3].Although the presence of heavy metals does not cause immediate danger to the population, it can lead to sustained, irreversible or wider contamination of the environment. This is in turn could lead to long term contamination of the surrounding soil and groundwater [4].

Lead (Pb) is considered as one of the priority metals from the point of view of potential health hazards to human, and it is listed by EPA as one of 129 priority pollutants [5]. Lead as a pollutant is a major concern as it has been used as one of the raw materials for battery manufacturing, printing, pigments, fuels, photographic materials and explosive manufacturing. Lead is used to produce batteries, metal products like solder and pipes and X-ray shielding devices. Lead is highly toxic metal and as a result of related health concern, its use in several products like gasoline, paints and pipe solder has been drastically reduced in recent years. Today most common source as lead exposure in the U.S are lead based paint and possibly water pipes in older homes, contaminated soil, house hold dust, drinking water, lead crystals, lead in certain cosmetics and toys and lead glazed pottery. The presence of lead in drinking water even at low concentration may cause disease such as anaemia, encephalopathy, hepatitis and nephritic syndrome. Severe lead poisoning can cause encephalopathy with permanent damage, while moderate lead poisoning result in neurobehavioral and intelligent deficit. Lead poisoning in human causes severe damage to kidneys, nervous system, reproductive system, liver brain. According to the United States Environmental protection Agency (USEPA) the maximum permissible limits in wastewater and potable water are 0.1 mg/L and 0.015 mg/L respectively for lead (II) [6].

EPA has determined that lead is a probable human carcinogen. Permissible limit of lead in drinking water by EPA, SUEPA and WHO is 0.05 mgL^{-1} and that of Bureau of Indian Standards (BIS) is 0.1 mgL^{-1}. Lead can effects every organ and system in the body. Long term exposure of adults can results in decrease performance of nervous system, weakness in fingers and wrists or ankles, increase in blood pressure and anaemia. Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. High level exposure in men can damage the organ responsible for sperm production. Therefore, It becomes necessary to remove these heavy metals from these wastewater by as appropriate treatment before releasing them into the environment [7].

Many conventional techniques have been used to reduce the concentration of heavy metals present in wastewater. Chemical precipitation and filtration, chemical oxidation and reduction, electrochemical treatment, reverse osmosis, solvent extraction and evaporation all shows several disadvantages, such as high cost, incomplete metal removal, low selectivity, high energy requirements and generation of toxic slurries that are difficult to be eliminate [8]. Ion-exchange is a highly popular method and has been widely practiced in industrial wastewater treatment process, but the application such process if often restricted because it cannot guarantee the metal concentration limits required by regulatory standards, especially when the metal concentration in the effluent are below 100 mg/L [9]. Adsorption is one of the physiochemical treatment process found to be effective in removing heavy metals from aqueous solution. The choice of the adsorbent is a key point and the literature review suggested the use of new adsorbents with high adsorption capacity could remove the metal ions effectively. Among them glazed tea mugs [10], saw dust[11], fruit peel of orange[12], rice husk[13], powdered waste sludge (PWS)[14], dried activated sludge biomass[15], flyash [16], gyttja (which has multilayer coal deposits with clay and calcareous gyttja partings) [17], kaolinite supported zero valent iron mono particles [18], Mg oxide coated betonite [19], betonite polyacrylamide composites [20], humic acid immobilised betonite composite

[21], Na-betonite [22], , sepiolite [23], mineral soil [24], perlite [25], sandy soil [26], zeolite prepared from Egyptian kaoline, chitosan coated sand [27], pottery glaze [28]have recently been reported.

In this article the technical feasibility of various clay based and low cost adsorbent for heavy metal removal from contaminated water has been reviewed [29].

Clays have been evaluated for their purifying qualities since they are thought to act as a filter and purifier of pollutants [30], [31], [55]. Given their high permeability, clays are after used as pollutants barrier for water storage sites [32]. In this regard, multiple researchers studied the effectiveness of various type of clay in removing heavy metals from aqueous solutions including natural kaolinite clay [33],natural bentonite [34]**,** montmorillonite, sodium dodecyl sulphate modified iron pillared montmorillonite [35].Adsorption is the most preferred method for the removal of heavy metals from aqueous solution due to its simplicity and its high effectiveness [36, 54].Adsorbent can be considered as cheap or low cost if it is abundant in nature, requires little processing and is a by-product waste of the industry. In the same contest Fired Ceramic is a low cost adsorbent as it is easily available in bulk in local area and is a waste produced by the ceramic industry.

Materials and Methods:

The adsorbent use in the present study is the Fired Ceramic which is obtained as waste when moulded ceramic articles broken down or get deshaped during heating in the furnace. These broken or deshaped articles were collected, grinded into fine particles and sieved through 100 mesh size and used as adsorbent for Pb(II) ions uptake from aqueous solution.

To observed the surface morphology of the adsorbent before and after adsorption of Pb(II), SEM analysis was employed by using Scanning Tunnelling Microscope, JEOL-JSM 6510 LV at USIF (University Sophisticated Instrumentation Facility) Aligarh Muslim University, Aligarh. The types of binding groups present on the adsorbent (RCC) were identified by using Perkin-Elmer Fourier Transformer Spectrophotometer (FTIR) Version 10.03.08 by using KBr pellet technique in the wavelength range 450-4000 cm^{-1} at Instrumentation Lab, Department of Chemistry, AMU, Aligarh.

All chemicals used in the study were of analytical grade purchased from Merck Pvt. Ltd. A stock solution of 500 mg/L of Pb(II) was prepared by dissolving required amount of Lead Nitrate, $Pb(NO_3)_2.3H_2O$ in double distilled water in a 500 ml standard flask. This stock solution was used to prepare the working solutions of desired concentrations for all experiments. pH values of the solutions was adjusted by adding 0.1 mol/L NaOH or 0.1 mol/L HCl. The concentrations of the solution before and after adsorption were analysed by using GBC-902, Atomic Absorption Spectrophotometer (AAS).

Batch Studies:

Batch process were conducted at room temperature $27\pm1^{\circ}C$ to study the adsorption of Pb(II) ions by fired ceramic. An accurately weighed 0.5gm of fired ceramicwas placed in 100ml stoppered conical flask containing 50 ml of Pb(II) ions solution of concentration 50mg/L. This solution was shaken in a rotary shaker for about 15 min and kept for 24 hours to attain equilibrium. All the operations such as effect of pH, adsorbent dose, contact time were conducted at room temperature with 50mlPb(II) ions solutions of 50mg/L except during the study of effect of concentration where 10 to 200 mg/LPb(II) ions concentration solutions were used. After that the mixture was filtered by using whattman filter paper 41 to separate the adsorbent from supernatant liquid. The final concentration of metal ions was analysed by AAS. The amount of metal ion adsorbed was calculated by subtracting final concentration from initial concentration.

The effect of pH on the adsorption of Pb(II) was studied by batch process as follows: 50 ml of 50 mg/L (Initial concentration) metal solution was taken in a 100 ml conical flask. The pH of the solution was adjusted by adding 0.1 M HCl and 0.1 M NaOH solutions by using SYSTRONIC-09 pH meter. This solution was treated with 0.5 gm of adsorbent and left for attaining equilibrium. After attaining equilibrium final concentration of Pb (II) in the solution was determined by AAS.

A series of 100 ml conical flasks, each having 0.5 g fired ceramic and 50 ml solution of 50 mg/L concentration were shaken in a rotary shaker and at the predetermined intervals. The solution of the specified flask was taken out and filtered. The concentration of Pb(II) in the filtrate was determined by AAS.

A series of 100 ml conical flasks, each containing 50 ml solution of 50 mg/L concentration were treated with varying amount adsorbent (0.1 – 1.0g) and shaken in a rotary shaker. After that the solution filtered and the concentration of Pb(II) in the filtrate was determined by Asante amount of lead adsorbed in each case was calculated.

A series of 100 ml conical flasks, having 0.5 g of adsorbent and 50 ml solution each of varying concentration from 10 - 200 mg/L concentration were shaken in a rotary shaker. After predetermined interval the solution was filtered and concentration of Pb(II) in the filtrate was determined by AAS. The amount of lead adsorbed in each case was calculated.

The removal percentage (R%) of Pb(II) ions and Adsorption capacity, q_e(mg/g) adsorbent were calculated for each run by the following expression-

$$R\% = \frac{(Ci-Ce)}{Ci} \text{ x } 100$$

$$q_e = \frac{(Ci-Ce)}{m} \text{ x } V$$

Where,

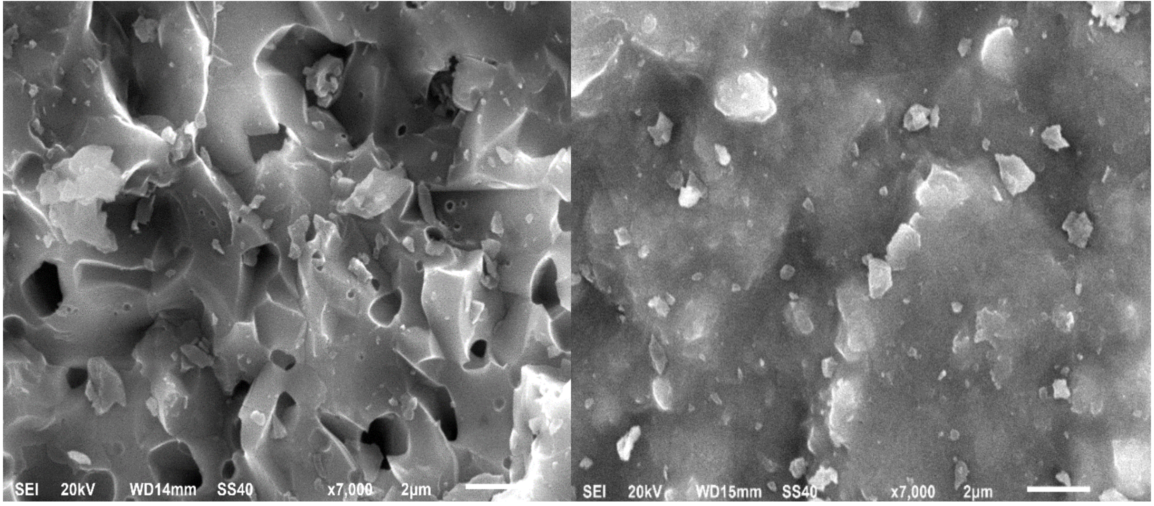
C_i = Initial concentration of metal ions in the solution
C_e= Final concentration of metal ions in the solution
V = Volume of the solution (L)
m = Mass of the adsorbent (in gm)

Results and Discussion:

Characterization of Adsorbent:

SEM Analysis:

Scanning Electron Microscope Analysis was carried out to examine the surface morphology of native and Pb(II) treated fired ceramic which are shown in fig. 1(a) and (b). The surface of fired ceramic in both cases appears to be irregular and porous and thus revealing the presence of suitable adsorbent sites. The morphology of surface is slightly changed after adsorption as before adsorption surface appeared to be less dense with light grey patches but after adsorption surface become slightly regular and denser with dark grey patches showing the adherence of Pb(II) ions on the surface.

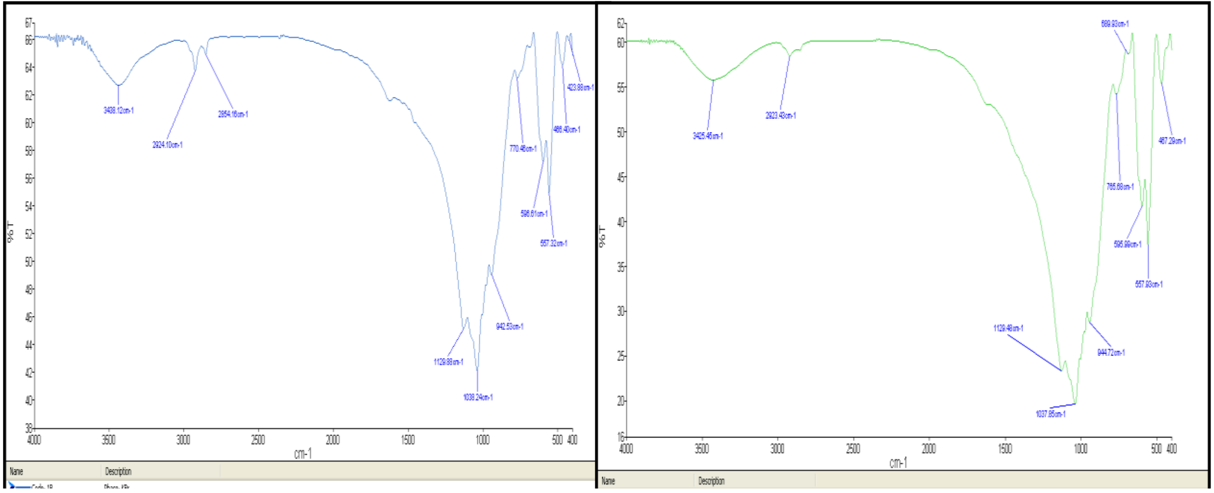


1(a) 1(b)

Figure 1(a) SEM image of native fired ceramic &Figure 1(b) SEM image ofPb(II) treated fired ceramic

FTIR Analysis:

FTIR analysis has been done to find the type and structure of binding groups present on fired ceramic in the wavelength range 400-4000 cm^{-1}. FTIR spectra of untreated and Pb(II) treated fired ceramic is shown in fig. 2(a) & (b). The FTIR spectrum showed a characteristic broad peak at 3438.12 cm^{-1} due to the presence of hydrogen bonded –OH group, while small peak at 2924.10 cm^{-1}and 2854.16 cm^{-1}indicates the presence of C-H stretched bond in alkanes. Sharp and small peak at 1129 cm^{-1} was due to the presence of C-O stretched bond. Peaks between 900 and 1100 cm^{-1} are due to metal oxides bond. The peaks between 500 and 800 cm^{-1} indicates the presence of C-X bonds (X = Halogen). When FTIR spectra of untreated and Pb(II) treated adsorbent were compared, the wave number associated with -OH group was shifted showing the interaction of Pb(II) occurs at -OH groups. All these changes show that this shift is due to metal binding process on the surface of fired ceramic.



2(b) 2(b)

Figure 2 (a): FTIR Image of RCC before adsorption & Figure 2 (b): FTIR Image of RCC after adsorption

Effect of pH:

The pH of the solution has significant effect on the uptake of Pb(II) ions. The amount of Pb(II) adsorbed at different pH values is shown in fig. 3. The amount of

Pb(II) adsorbed on fired ceramic was found to increases from increases from 15.2 % to 98.372% by increasing pH from 1 to 4 and then decrease slightly. The adsorption percentage of Pb(II) was least at pH 1 and increase with increasing pH, reached maximum (98.372%) at pH 4 and then decrease slowly up to pH 10. The variation in the adsorption of Pb(II) with respect to pH can be explained by considering the initial pH (pH_i), final pH or equilibrium pH (pH_f), and speciation of metal ions in the solution[37]. At pH 1 there is competition between H^+ ions and Pb^{2+} ions for binding sites of adsorbent, therefore the adsorption of Pb(II) ions was least (15.2%). When the initial pH of the solution increases to 2 the adsorption percentage increases to 21.5%, possibly due to little less competition of pb^{2+} ions and H^+ ions. However, when initial pH raised to 4 the adsorption of Pb(II) increased up to maximum of 96.320% and will remain almost same when the initial pH adjusted to 6 (96.220%), as a result of maximum adsorption of Pb^{2+} ions along with H^+ ions. Further increase in pH of the solution to 8 results slightly decrease in the adsorption of Pb(II) ions (95.120%). A similar trend was continue when pH increases to 10 (94.113%), 12 (82.99%) and 14 (68.85%) respectively. The decrease in the adsorption of Pb(II) at pH >6 can be explained on the basis of Pb(II) speciation at different pH values. The chemical species of Pb(II) formed at different pH values are Pb^{2+} at pH=2-4, $Pb(OH)^+$ at pH=4-6, $Pb(OH)_2$ at pH=6-10 and $Pb(OH)_3^-$ at pH=10-12 [38, 39]. The speciation suggests that majority of the lead is adsorbed at pH 4 in the form of Pb^{2+} ions and at pH 6 lead is adsorbed in the form of lead hydroxide species due to micro precipitation as shown below

$$Pb^{2+} + H^+ + OH^- \rightarrow Pb(OH)^+ + H^+$$

$$Pb^{2+} + 2H_2O \rightarrow Pb(OH)_2 + 2H^+$$

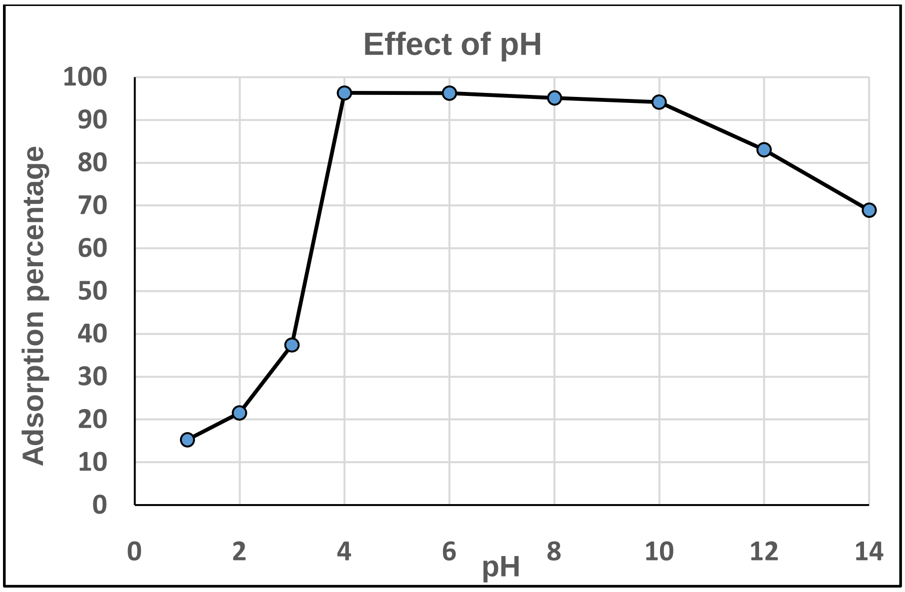


Figure3: Effect of pH on adsorption of Pb(II) on fired ceramic

Effects of Contact Time:

The uptake of lead ions at any particular concentration increases with contact time till the equilibrium attained as shown in fig 4. Initially the adsorption of Pb(II) was found to be fast. It may be due to more number of active sites on the adsorbent surface. After that as active sites becomes less available, the adsorption is likely to become slower and controlled process and attained equilibrium within 2 hours [40, 41].

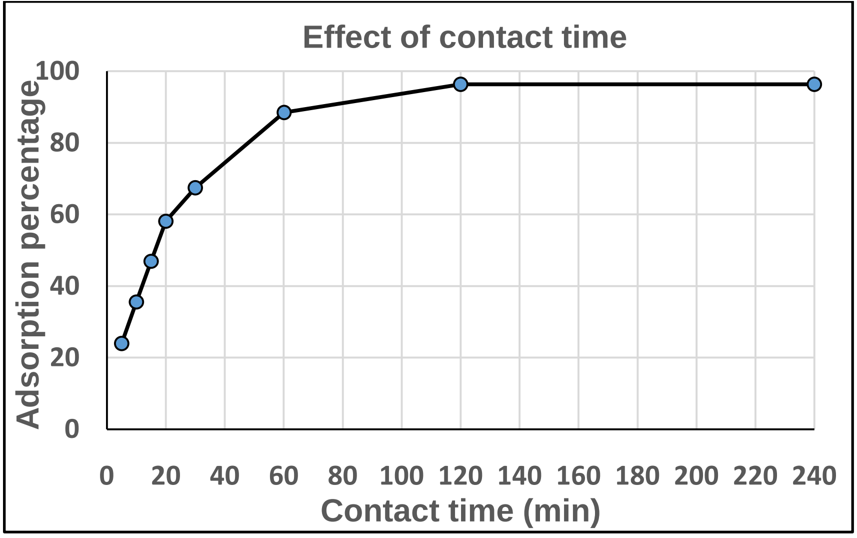


Figure 4: Effect of contact time on adsorption of Pb(II) on fired ceramic

Effects of Adsorbent Dose:

The effect of dose of fired ceramic on adsorption capacity and percentage adsorption of Pb(II) is shown in fig. 5.Percent adsorption increased while adsorption capacity, q_e (mgg^{-1}) decreased when adsorbent dose increased from 0.1 to 1.0 g. the adsorption percentage increases upto 99.45% at 1 g of adsorbent dose. This might be due to the fact that on increasing the adsorption dose, number of sites available for adsorption also increased[42].The adsorption capacity decreases from 11.909 mg/g to 2.486 mg/g on increasing adsorbent dose from 0.1 g to 1.0 g. The decrease in adsorption capacity with an increasing adsorbent dose might be due to the fact that at lower adsorbent dose almost all the adsorption sites are saturated by the Pb(II) uptake but at higher adsorbent dose, the adsorption sites would be excessive for the adsorption reaction since the concentration Pb(II) as well as the volume of the solution are constant. Thus, amount of Pb(II) adsorbed per unit mass of adsorbent was decreased.[43].

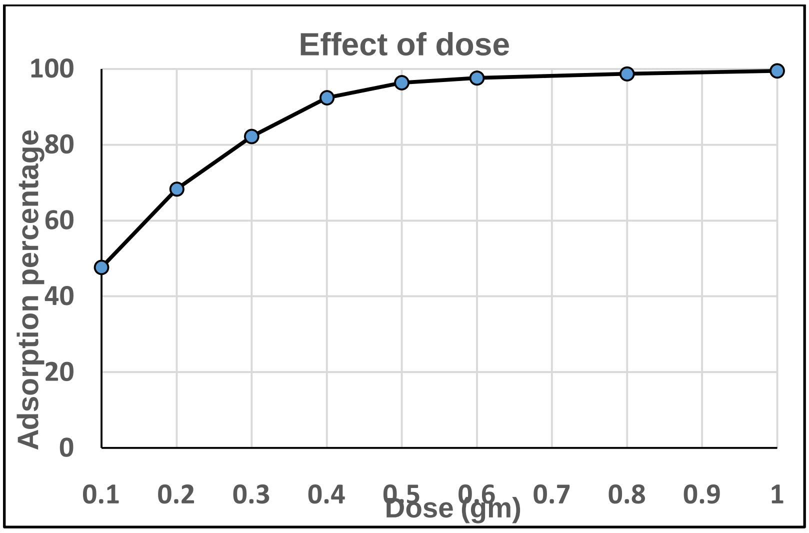


Figure 5: Effect of adsorbent dose on adsorption of Pb(II) on fired ceramic

Effects of Initial Pb(II) ion Concentration:

Adsorption of Pb(II) by any fired ceramic is highly dependent on the initial concentration of metal ions. The adsorption of lead was carried out at different initial Pb(II) ions concentration ranging from 10 mgL^{-1} to 200 mgl^{-1} and was observed that increase of initial lead ions concentration decreases the percentage removal of lead ions from 100 % at 10 mgL^{-1} to 59.195 % at 200 mgL^{-1}as shown in fig. 6. It may be due to the fact that adsorbent has a limited number of active sites, which become saturated at a certain concentration [44].

It is evident from the fig. that adsorption capacity q_e, increases with increase in initial concentration of lead ions from 1 mgg^{-1} at 10 mgL^{-1} to 11.8 mgg^{-1} at 200 mgL^{-1} which may be due to fact that increased concentration gradient between the bulk solution and adsorbent surface lower down the resistance to mass transfer of Pb(II) from aqueous to solid phase[45, 46].

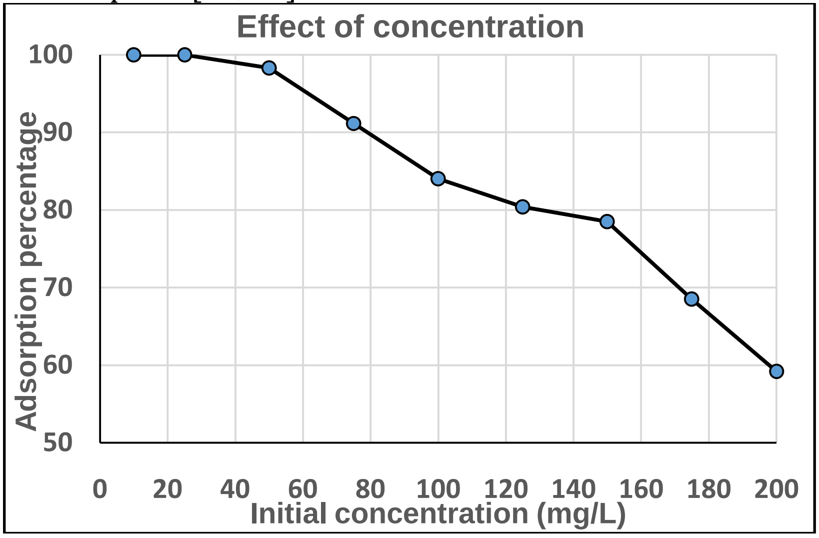


Figure 6: Effect of concentration on adsorption of Pb(II) on fired ceramic

Adsorption Isotherms:

In order to indicate how molecules adsorbate is partitioned between the adsorbent and liquid phase at equilibrium as a function of adsorbate concentration, adsorption isotherms were studied. Adsorption of Pb(II) ions was carried out at concentration ranging from 10 to 200 mg/L at pH 4 for 2 hours of equilibrium time. The obtained data were analysed with the Langmuir [47], Freundlich[48] and Temkin models.

According to Langmuir model the adsorption occurs on a homogeneous surface forming monolayer of adsorbate with constant heat of adsorption for all sites without interaction between adsorbed molecules [50].It is given by equation:

$$\frac{C_e}{q_e} = \frac{1}{b.q_m} + \frac{1}{q_m} \times C_e$$

Where, C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the adsorption capacity (mg/g), b and q_m are the Langmuir constants. q_m is the amount of lead required to form monolayer (mg/g), and b is the constant related to energy of adsorption.

The value of b and q_m can be calculated from the slope and intercept of the linear plot of C_e/q_e Vs C_e as shown in fig. 7.The Freundlich equation has been used for the adsorption of lead(II) on fired ceramic is represented as-

$$\text{Log}q_e = \log K_f + 1/n \log C_e$$

Where, q_e is the amount of lead adsorbed, C_e is the equlibirium concentration of the lead ions in the solution (mg/L), and K_f and n are the constants for adsorption capacity and intensity of adsorption respectively. Plots of $\log q_e$ vs. $\log C_e$ has been shown in fig. 8 and the values of K_f and n was calculated from slopes and intercepts of the plot.

Temkin isotherm assumes that the decrease in the head of adsorption is linear rather logarithmic, as implied in the Freundlich isotherm. It assumes that heat of adsorption on the surface of the adsorbent decrease linearly with coverage due to adsorbent-adsorbate interactions [49]. The linear form of Temkin equation can be represented as

$$q_e = RT/b \times \text{In}A + (RT/b) \times \text{In}C_e$$

or

$$q_e = B\ \text{In}A + B\ \text{In}C_e$$

Where, B=(RT/b), R is universal gas constant, T as absolute temperature and b is a constant. The quantities A (gL^{-1}) and B are Temkin constants related to the adsorption potential and heat of adsorption respectively. The values of A and B can be calculated from slopes and intercepts of the plot of q_e vs. $\text{In}C_e$ as shown in fig. 9.

The obtained from these models and values of correlation coefficients (R^2) 0.9917, 0.8266 and 0.9611 for the Langmuir, Fruendlich and Temkin isotherms respectively indicates that adsorption of Pb(II) on fired ceramic obey best Langmuir isotherm. The obtained data also revealed the better applicability of the Temkin isotherm than Fruendlich isotherm.

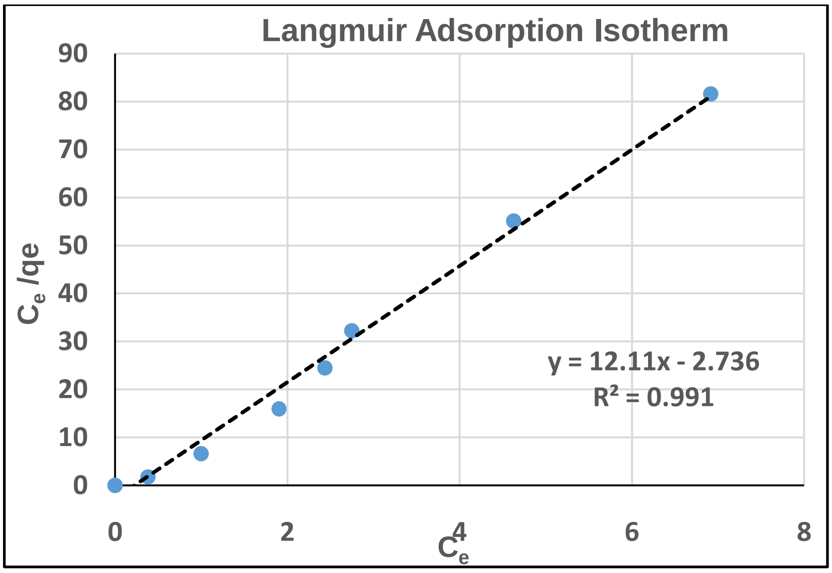


Figure 7: Langmuir adsorption isotherm

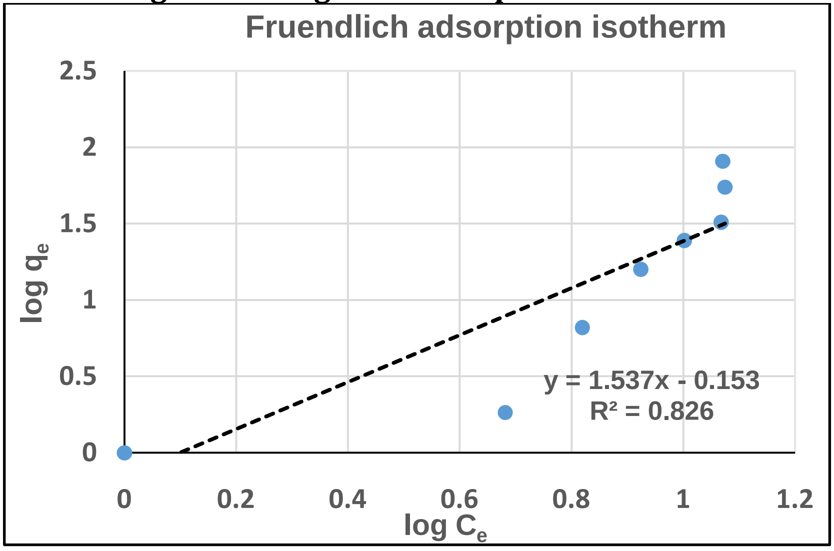


Figure 8: Fruendlich adsorption isotherm

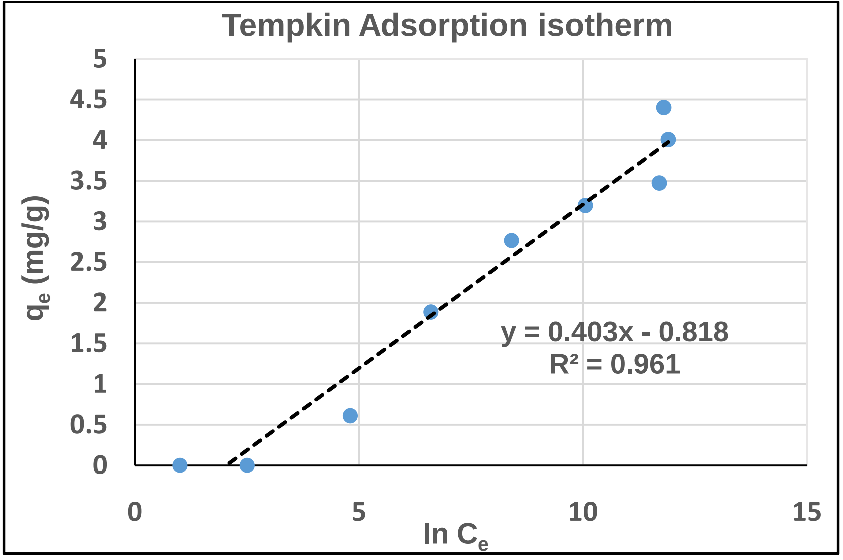


Figure 9: Tempkin adsorption isotherm

Adsorption Kinetic Studies:

In order to investigate the mechanism of adsorption of Pb(II) on fired ceramic, the kinetic data was analysed using the Lagergren first order[50],pseudo second order[51] and Intra-particle diffusion kinetic models[52].

The Lagergren First Order Kinetic Model:

The Lagergren first order rate equation is represented as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Or

$$\log (qe - qt) = \log qe - k_1.t/2.303$$

Where, q_e and $q_t$are the amounts of Pb(II) adsorbed (mgg^{-1}) at equilibrium and at time t , respectively. k_1 is the Lagergren rate constant (min^{-1}). Plots of In(q_e – q_t) versust has been shown in fig.10and values of q_e and k_1 have been calculated from the slope and intercept respectively.

The Pseudo-Second-Order Kinetic Model:

The adsorption data have been applied to pseudo second-order kinetic model also. The equation is represented as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where,K_2(g/mg/min)is the rate constant of second order adsorption and can be obtained from plot of t/q_t against t which has been shown in fig. 11.

The Intra-Particle Diffusion Model:

The kinetic results were analyzed by the Weber and Morris intra-particle diffusion model to explain the diffusion mechanism. The model is expressed as:

$$q_t = K_d. t^{1/2} + I$$

Where, I is the intercept which reflects the boundary layer effect and K_d is the intra-particle diffusion rate constant. Plot of q_t versus $t^{1/2}$ has been shown in fig. 12. The value of K_d and I have been calculated from the slope and intercept of the plot.

All kinetic data and comparative values of correlation coefficient for pseudo first order, pseudo second order and intra particular diffusion model verifies that kinetic data is best fitted for to pseudo second order model as indicated by highest value of correlation coefficient (R^2 = 0.998). Moreover, the high value of correlation coefficient for pseudo first order is also show its validity. Applicability of pseudo first and pseudo second order model implies that adsorption of Pb(II) on fired ceramic is a chemisorption process which involves the formation of one layer of molecules on the surface of adsorbent by chemisorption and may be followed by additional layer of physically adsorbed molecules [53].

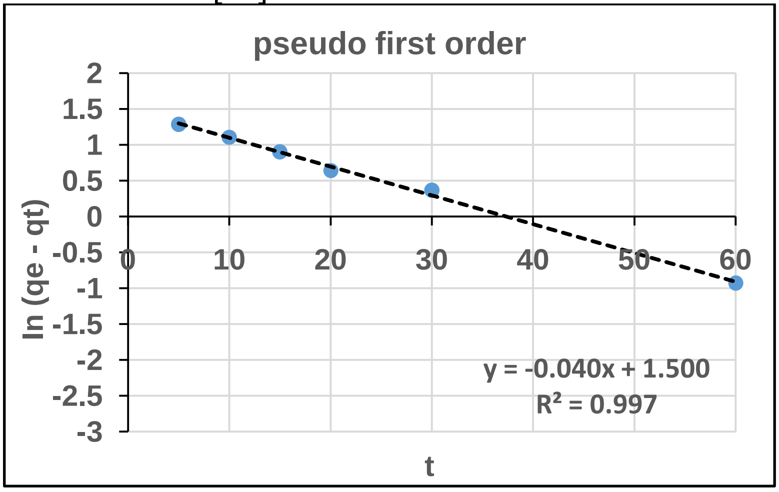


Figure 10: Pseudo first order model

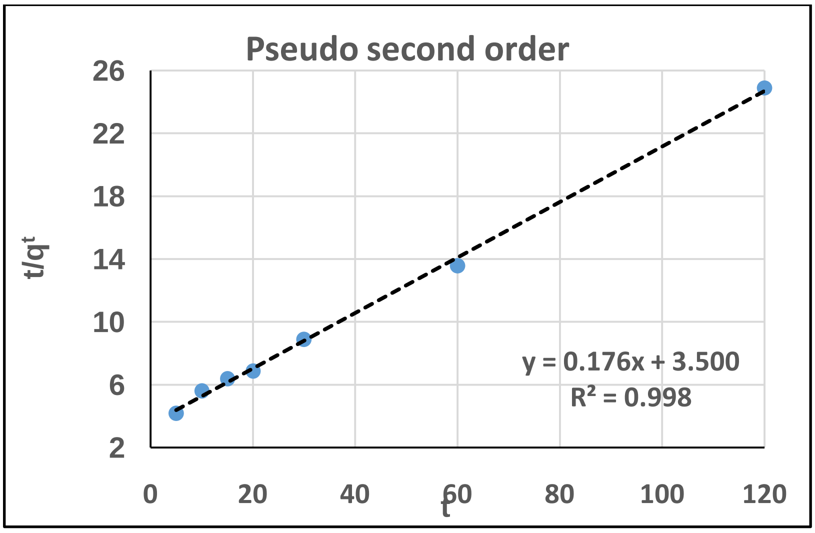


Figure 11: Pseudo second order model

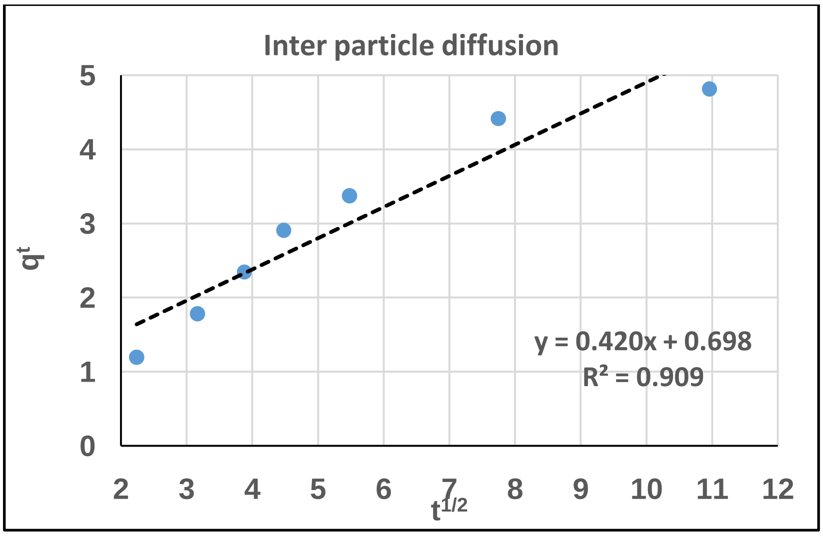


Figure12: Intra particle diffusion model

Conclusion:

The batch studies show that fired ceramic is a potential low cost adsorbent can be used to remove Pb(II) ions from aqueous solution. Adsorption of lead on fired ceramic is a fast process as equilibrium was established within 2 hrs. Adsorption of Pb(II) is a pH dependent and maximum amount of Pb(II) (96.320%) can be removed from aqueous solution at pH ranging 4-6. The experimental data is best fitted to Langmuir isotherm as indicated by the highest value of correlation coefficient (R^2 = 0.9917). Kinetic data also suggest the applicability of both pseudo first and pseudo second order model as indicated by the values of correlation coefficients (R^2 = 0.9974 and 0.9982)which also confirms that adsorption of Pb(II) on fired ceramic involve chemisorption process followed by the physical adsorption of adsorbate molecules. It may be concluded from the above results that fired ceramic can be employed as potential adsorbent for the elimination of Pb(II) ions from aqueous solution since it is cost free adsorbent which is locally available in bulk.

Acknowledgment:

Authors are thankful to the Head, Department of Chemistry, D.S. College, Aligarh for providing research facilities. Support for this work through the Principal, University Polytechnic, Faculty of Engineering & Technology, AMU, Aligarh, India is also greatly acknowledged.

References:

1. Srivastava, N.K. and C.B. Majumder, "Novel biofiltration methods for the treatment of heavy metals from industrial wastewater", Journal of hazardous materials, 151, 1, 1-8, 2008.
2. C. Namasivayam and K. Ranganathan,"Removal of Cd(II) from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide", Water Res., 29, 1737-1744, 1995.
3. Pharr K.E. and Jones B.T. "Extraction of cadmium from urine: a brief review", J. Applied Spectroscopy Review, 432, 563-572, 2007.
4. S. Loutseti, D.B. Denielidis, A. Economouamilli, C. katsaros, R. Santas, P. Santas, "The application of a mico-algal/bacterial biofilter for the detoxification ofcopper and cadmium metal wastes", Bioresources Technology, 100,2099-2105, 2009.
5. A.O Dada, J. O. Ojediran, and A. P. Olalekan, "Sorption of Pb^{+2} form aqueous solution onto modified rice husk: isotherms studies", Journal of Advances in physical chemistry, 1-6, 2013.
6. SulemanQaiser, Anwar R. Saleemi, Muhammad Umar, "Biosorption of lead (II) and chromium (VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study", Electronic journal of biotechnology, 12, 4, 1-17, 2009.
7. Mishra G.K., Meena A. K., Rai, P.K, Chitra R.G, Nagar P.N., "Removal of heavy ions from aqueous solutions using carbon aerogel as an adsorbent", Elsevier B.V, 2005.
8. B. Volesky, "Hydrometallurgy", 59, 2/3, 203-216, 2001.
9. B. Volesky, Z.R. Zholan, "Biosorption of heavy metals", Biotechnology Progress, 11, 3, 235-250, 1995.
10. M. Ajmal,A.U. Khan, A.A Nomaniand ShamimAhmad,"Heavy metals leaching from glazed surfaces of tea mugs", Science of Total Environment, Netherlands. 207,1, 49-54, 1997.
11. M. Ajmal, A.H. Khan, Shamim Ahmad and AneesAhmad,"Role of saw dust in the removal of Cu(II) from industrial waste water", Water Resources U.K. 32, 10, 3085-3091, 1998.

12. M. Ajmal,R.A.K. Rao, Ahmad and R. Ahmad,"Adsorption studies on Citrus Reticulate (Fruit peel of orange): Removaland recovery of Ni(II) from electroplating wastewater", J. Hazardous Material, 79, 117-131, 2000.
13. M. Ajmal,R.A.K. Rao,J.A. Anwar and R. Ahmad,"Adsorption studies on rice husk: Removal and recovery of Cu(II)from waste water", Bioresource Technology, 86, 147-149, 2003.
14. Ahmad Ashfaq, "Removal of Cr(III) by biosorption onto powdered waste sludge (PWS): Effects of operating conditions", Int. J. of Ecology, Environment and Conservation, 17, 3, 593-596, 2011.
15. Ahmad Ashfaq, "Cd(II) removal from aqueous solution by dried activated sludge biomass", Int. J. of Pollution Research, 30, 3, 357-360, 2011.
16. Ahmad Ashfaq, "Evaluation of biosorption characteristics in mixed heavy metal solution by flyash", International Conference on Interface between Chemistry and Environment,Deptt. Of Chemistry, Ramjas College, University of Delhi, India. 13th and 14th march 2012.
17. H. Dikici, K. Saltali, S. Bingolbah,"Equilibrium and kinetics of characteristics of Cu(II) sorption onto Gyttja", J. Bulletin of Environmental Contamination toxicology, 84, 147-151, 2005.
18. C. Uzum, T. Shahwan, A.E. Eroqlu,K.R. Hallam, T.B. Scott, and I. Lieber-wirth, "Synthesis and characterisation of kaolinite-supported zero-valent iron nanoparticles and their application for the removal aqueous Cu^{+2} ion", J. Applied Clay Science, 43, 172-181, 2010.
19. E. Eren,A. Tabak, and B. Eren,"Performance of magnesium oxide –coated betonite in removal process of copper ions from aqueous solution", J. Desalination, 257, 163-169, 2010.
20. Zhao Guixia, Zhang Hongxia, Fan Qiaohui, Ren Xuemei, Li Jiaxing, Chen Yixue, and Wang Xiangke, "Sorption of copper onto super-adsorbent of betonite-polyacrylamide composites", J. of hazardous materials, 173, 661-668, 2010.
21. T.S. Anirudhan and P.S. Suchithra, "Humic acid-immobilized polymer/betonite composite as an adsorbent for the removal of copper(II) ions from solutions and electroplating industry wastewater", J. industrial and engineering chemistry, 16, 130-139, 2010.
22. Liu Zhirong Zhou Scoaqi,"Adsorption of copper and nickel on Na-betonite", Process Safety and Environmental Protection, 88, 62-66, 2010.
23. M. Vidal, M.J. Santos, T. Abrao, J. Rodriguez, and A. Rigol, "Modeling competitive metal sorption in a mineral soil", Geoderma, 149, 189-198, 2009.
24. M. Dogan, a. Turkilmaz, M. Alkam and O. Demarbas,"Adsorption of Cu(II) ions onto sepiolite and electrokinetic properties", Desalination, 238, 257-270, 2009.
25. H. Ghassabzadeha, A. Mohadespourb, M.T. Mostaedic, P. Zaherib, M.G. Maraghehc and H. Taheric, "Adsorption of Ag, Cu and Hg from aqueous solutions using expanded perlite", J. of Hazardous Materials, 177, 178-82, 2010.
26. T.C.M.Yip, D.Y.S. Yan,M.M.T.Yui,D.C.W.Tsang and I.M.C.Lo,"heavy metals extraction from artificially contaminated sandy soil under EDDS deficiency: significance ofhumic acid and chelant mixture", Chemosphere, 80, 416-421, 2010.
27. M.W. Wan, C.C. Kan, B.D. Rogel, and M.L.P.Dalida, "Adsorption of copper(II) and lead(II) ions from aqueous solution on chitosan-caoted sand", Carbohydrate polymer, 80, 891-899, 2010.

28. Rifakat Ali Khan Rao, M. Kashifuddin,"Pottery glaze – An excellent adsorbent for the removal of Cu(II) from aqueous solution", Chin. J. Geochem, 31, 136-146, 2012.
29. V.C. Renge, S.V. Khedkar and V. Pandey Shraddha, "Removal of heavy metals form wastewater using low cost adsorbents: A review", Sci. Revs. Chem. Commun, 2, 4, 580-584, 2012.
30. I.G. Abid, and M.T. Ayadi, "Competitive adsorption of heavy metals on local landfill clay", Arabian journal of chemistry, 8, 25-31, 2015.
31. F. Ayari, E. Srasra, M. Trabelsi-Ayadi, "Characterisation of bentonitic clays and their use adsorbent", Desalination, 185, 391-397, 2005.
32. K. Bellir, Bencheikh-LehocineMossaab, AbdeslamMeniai N. Gherbi, "Study of the retention of heavy metals by natural material used as liners in landfills", Desalination, 185,1, 11-119, 2005.
33. Jiang Mingqin, JinXiaoqiao, and Chen Zuliang,"Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay", J. Desalination, 252, 33-39, 2010.
34. O. Korkut, E. Sayan, O. Lactin, B. Bayrak,"Investigation of adsorption and ultrasound assisted desorption of lead(II) and copper(II) on local bentonite: A modelling study", J. Desalination, 259, 243-248, 2010.
35. Li Shuzen Wu pingxiao,"Characterisation of sodium dodecyl sulaphate modified iron pillard Montmorillonite and its application for the removal of Cu(II) and Co(II)", J. of Hazardous Materials, 173, 62-70, 2010.
36. A. Sdiri, T. Higashi, T. Hatta, F. Jamoussi and N. Tase, "Evaluating the adsorptive capacity of montmorilloniticand calcareous clays on the removal of several heavy metals in aqueous systems", Chem. Eng. J. 172, 1, 37-46, 2011.
37. G.W. Brummer, "Importance of Chemical Speciation in Environmental Process",SpringerVerlag, Berlin, 1986.
38. N. Porreza, T. Nagdhi, "Silicon carbide nanoparticles as an adsorbent for solid phase extraction of lead and determination by flame atomic adsorption spectrometry", J. Ind. Eng. Chem., 20, 3502-3506, 2014.
39. X.L. Tan, P.P. Chang, Q.H. Fan, X.S. Xhou, S.M. Yu, W.S. Wu and X.K. Wang, "Sorption of Pb(II) on Na-rectorite: Efffect of pH, ionic strength and temperature, soil humic acid and fulvic acid, Colloids surface, A 328, 8-14, 2008.
40. V. Sarin and K.K. Pant, "Removal of chromium from industrial waste by suing eucalyptus bark", Bioresources Technology. 97,1, 15-20, 2006.
41. J. Wongjuda and P. Saueprascarsit, "Biosorption of Cr(VI) using rice husk ash and modified husk ash", Environment Research J, 4,3, 244-255, 2010.
42. R. Wang, Q. Li, D.Xie, H. xiao, H. Lu, (2013). Synthesis of NiO using pine template and adsorption performance for Pb(II) from aqueous solution. Appl. Surf. Sci. 279, 129-136.
43. XueYongjie, HouHaobo, and Zhu Shujiing (2009) Competitive adsorption of Cu(ii), Pb(ii) and Zn(II) onto basic oxygen furnace sludge. Journal of Hazardous material. 162, 391-401.
44. Tsai W.T. and Chen H.R. (2010) Removal of malachite green from aqueous solution using low cost chlorella based biomass. J. Hazardous material. 175(1-3), 844-849.
45. R.A.K Rao, M.A. Khan, (2007). Removal and recovery of Cu(II), Cd(II) and Pb(II) ions from single and multimetal systems by batch and column operations on neem oil cake (NOC). Separation, Purification and Technology. 57, 394-402.

46. Z. Aksu, D. Akpinar, (2001) Modelling of simultaneous biosoprtion of phenol and nickel(II) onto dried activated aerobic sludge. Separation, Purification and Technology. 21, 87-99.
47. I. Langmuir,"The sorption of gases on plane surfaces of glass, mica and platinum", Journal of the American Chemical Society, 40, 1361-1403, 1918.
48. H.M.F. Freundlich, "Uber die sorption in losungen", Z. phys. Chem, 57 (A), 387-470, 1906.
49. A.O Dada, A.P. olalekan, A.M. Olatunya, O. Dada, Langmuir, Freundlich. Temkin and Dubinin-Radushkevich isotherms studies of equilibrium sorption of Zn^{2+} onto phosphoric acid modified rice husk, IOSR J. Appl. Chem. 3, 38-45, 2012.
50. S. Lagergren, "About the theory of so-called adsorption of soluble substances", J. Der Sogenannten adsorption gelosterstoffeKungligaSvenskapsalka de Miens Handlingar, 24,1-39, 1898.
51. Y.S. Ho and G. Mckay, "The kinetics of sorption of divalent metal ions onto sphagnum moss peat", Water Res., 34,3, 735-742, 2000.
52. W.J. Weber and J.C. Morris, "Kinetics of adsorption on carbon from solution", J. Saint. Eng. Div. Am. Soc. Eng., 89, 31-60, 1963.
53. E.N. El Qada, S.J. Allen, G.M. Walker, "Adsorption of methylene blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm", Chem. Eng. J., 124, 103-110, 2006.
54. A. Sdiri, T. Higashi, R. Chaabouni, F. Jamoussi, "Competitive removal of heavy metals from aqueous solutions by montmorillonitic and calcareous clays", Water Air Soil Pollution 223, 3, 1194-1204, 2012.
55. F. Ayari, E. Srasra, M. Trabelsi-Ayadi, "Retention of lead from an aqueous solution by use of bentonite as adsorbent for reducing leaching from industrial effluents", Desalination, 206, 391-270, 272, 2007.