JBLD, SPECIAL ISSUE, NOVEMBER 2014, pp.120-135
©ARDHI UNIVERSITY, DAR ES SALAAM, TANZANIA

ASSESSMENT OF THE POTENTIAL EFFECTIVENESS OF POULTRY EGG SHELLS IN THE REMOVAL OF LEAD IONS FROM CONTAMINATED WATER

W.J.S. MWEGOHA* AND C. KIHAMPA**

ABSTRACT

The influence of pH, initial concentration of Pb^{2+} ions, sorbent (poultry egg shells) dose, and contact time on the adsorption of Pb^{2+} from contaminated water to egg shells was studied. Results indicate that adsorption capacity increases with the increase of Pb^{2+} ion concentration and dose of egg shells, and varied with change of pH. Egg shell was mainly composed of $CaCO_3$ and other few elements as, S, Al, Mg, Si, Cl, K and Zn. The optimum pH for lead removal was at pH 7 with highest efficiency of 96.65 %, this was also revealed by Freundlich adsorption isotherm that displayed the highest value of K of 3.18419 for wastewater of concentration 0.884 mg/l Pb. The optimum dose of egg shells was 25g with contact time of 90 min and residue lead of 0.027 mg/l which is lower than the Limits for Municipal and Industrial Wastewater discharge (0.1 mg/l). The adsorption isotherms also showed that the lead removal efficiency was descending from pH 7, 12.3 to 3.4. These results suggest that poultry egg shells can be a potential candidate adsorbent material for removal of lead ions from contaminated water.

Keywords: Adsorption, Lead, Egg shells, Sorbent, Poultry, Water

INTRODUCTION

During the past two decades, extensive attention has been paid to the management of the environmental pollution caused by hazardous materials such as heavy metals (Eamsiri et. al., 2005). Heavy metals are a group of pollutants which occur as natural constituents of the earth's crust. Serious consequences of biological hazards caused by metal toxicity cannot be ruled out. A high degree of industrialization and urbanization has substantially enhanced the degradation of aquatic environments through the discharge of industrial wastewater that contain toxic pollutants including heavy metals. This has resulted into significant amounts of heavy metals being deposited into natural aquatic and terrestrial ecosystems (Nilanjana et.al. 2007. Removal of heavy metals from polluted water has often been achieved by the application of *inter alia*, processes as adsorption. (Sari et al., 2007; Song et al., 2000; Brooks, 1991; Fahim et al., 2006; Tiravanti et al., 1997; Kapoor et al., 1999; Filibeli et al., 2000; Song et al., 2004; Fabianil et al., 1996; Macchi et al., 1991).

Biosorption represents a biotechnological innovation as well as a cost effective excellent tool for removing heavy metals from aqueous solutions (Nilanjana et al., 2007), including lead. Previously it has been established that poultry egg shell membrane (Goto and Suyama 2000) and egg shells can adsorb a wide variety of dissolved metals from water and as such, these materials could be used to remove metal contaminants from heavy metal-ladden water. This study reports the potential use of egg shells as biosorbents for the removal of lead ions from contaminated water.

*W.J.S. Mwegoha is a Senior Lecturer, Department of Environmental Science and Management, Ardhi University, Dar es Salaam, Tanzania. His contact address is P.O. Box 35176, E-mail: mwegoha@hotmail.com

**C. Kihampa is a Senior Lecturer, Department of Environmental Science and Management, Ardhi University, Dar es Salaam, Tanzania. His contact address is P.O. Box 35176, E-mail: kihampa@aru.ac.tz

MATERIALS AND METHODS

Poultry Egg Shells Preparation

The poultry egg shells were collected separately from the rest of the solid waste in restaurants in Ardhi University Campus, Dar es Salaam, Tanzania. The shells were then washed with tap water and dried for 2 hours using hot air oven at 125°C and allowed to cool at room temperature. The dried egg shells were then ground by mortar and pestle. Particles with 0.8 mm were used in the performance of the experiments were obtained through manual sieving for 10 minutes. The sieved material was stored in foil papers and stored in desiccators for subsequent experiments. The chemical composition of egg shells were examined by X-ray Fluorescence Spectrometer at Southern Africa Mineralogical Centre (SEAMIC) laboratory and the results are shown in Table 1.

Batch Experiments

100 ml solution of initial concentration 1 mg/l Pb was prepared from a standard solution of 1000 mg/L (1000 ppm) were placed in 250 ml beaker. Different samples of adsorbent material of masses (1, 3, 5, 10, 15 20 and 25 g) with size of 0.8mm were added in solutions (Figure 1). NaOH and HNO_3 acid solutions were used to alter the pH from 3.4 to 12.3. Solutions were stirred by magnetic stirrer on for 1 hour at 500 rpm. Treated water samples were filtered by using the Whatman filter papers (grade 181, size 9.0 cm) before measurement for lead ions in Atomic Absorption Spectrophotometer. Optimum masses of adsorbent and the pH obtained from previous experiments were placed in magnetic stirrer and rotated at 500 rpm. 5 g dose of ground egg shell and the initial pollutant concentration of 0.67 mg/l Pb were used. 75 ml of the treated wastewater was taken at 30 min, 60 min, 90 min, 240 min, 300 min, and 390 min (Figure 2). All adsorption experiments were carried out at the at room temperature and pH of 12.3. The obtained results were analyzed using adsorption isotherms.

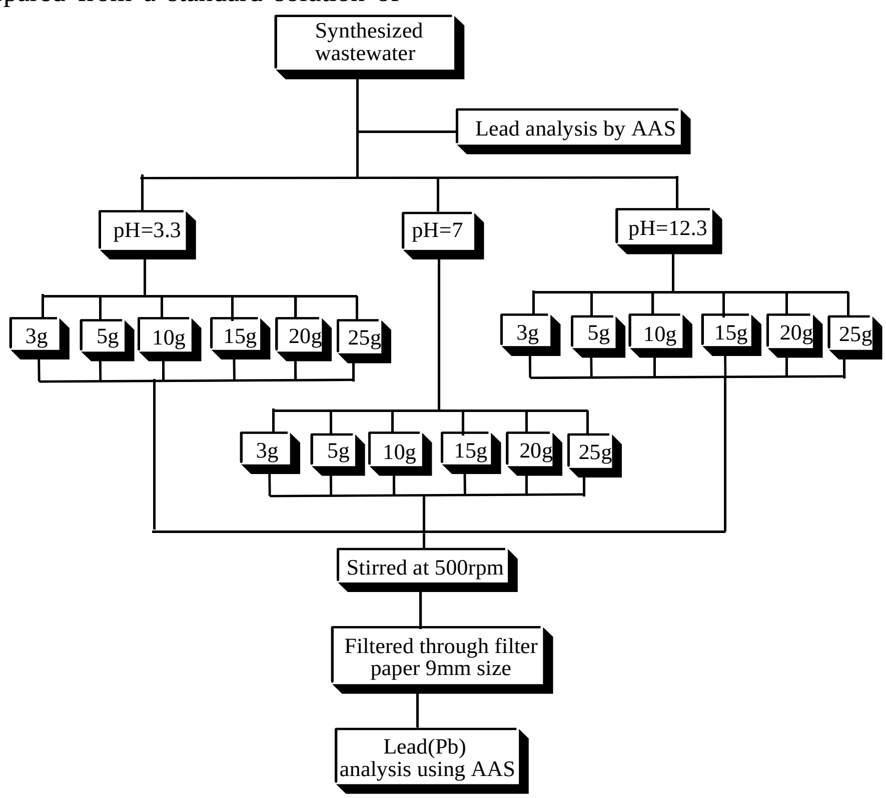

Figure 1 Batch experiment layout, effect of dose and pH on the removal of lead.

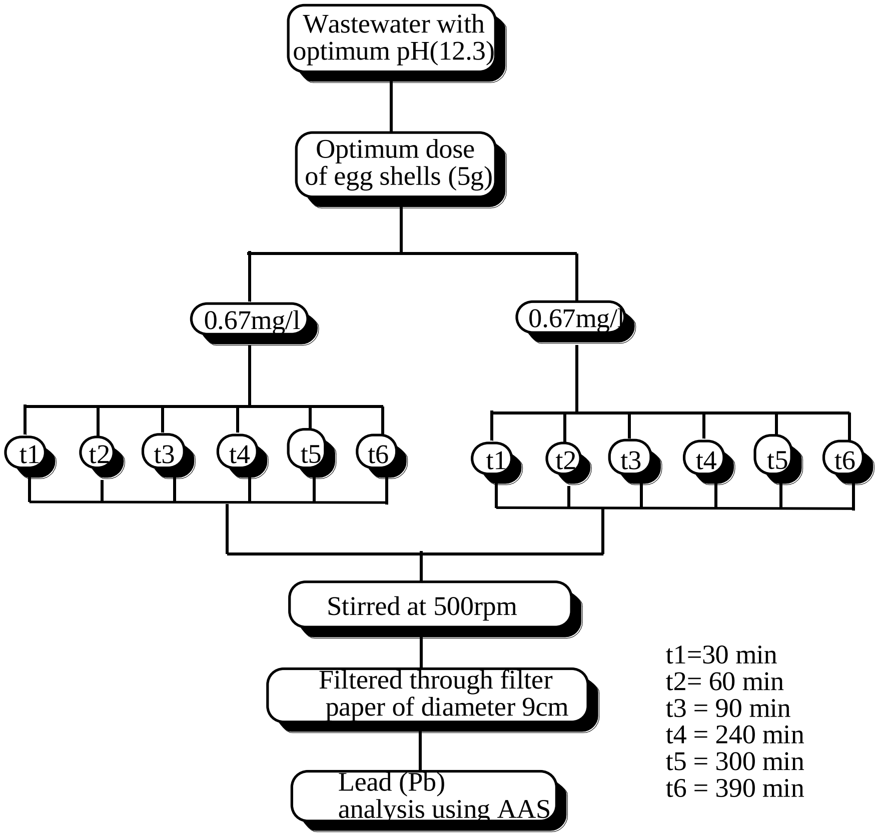

Figure 2 Batch Experiment layout, Effects of Contact time

Column Experiments

Two columns of internal diameter of 2 cm, with adsorbent heights of 20 cm each were filled with adsorbents. 1.5 L container was used for storage of contaminated water with concentrations of 0.133 and 0.181 mg/l Pb eluted through the column at 5 ml/min. 0.5 L capacity bottles were used as collecting containers for the treated water every after 60 min for six hours (Figure 3), i.e. 6 samples. 150 ml of treated water was collected from the columns for analysis of lead ion concentrations using AAS.

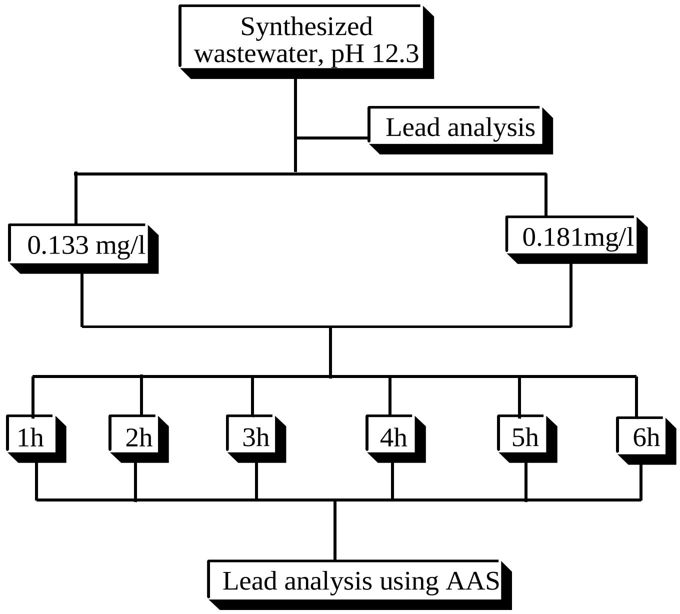

Figure 3 ***Column experiment layout, Effect of contact time and initial concentration***

ANALYTICAL METHODS

Lead Concentrations

Lead analysis was done by using a Perking AAnalyst 100 atomic Absorption Spectrophotometer, with Perking Elmer HGA 850 Flame absorption, Perkin-Elmer, (1996) and Perking 800 Auto-sampler with a computer interface for operation and reading display, Varian SpectrAA AAS with SpectrAA_{55} analyzer. X ray fluorescence was used to determine the chemical composition of egg shell at (Southern and Eastern Africa Mineralogical) SEAMIC Laboratory.

Organic Matter Content

Organic matter content of egg shells was determined by Vecstar furnace. The egg shells sample was oven dried for 2 hours at 105°C. Then a small dry sample was combusted in furnace at 600°C for 4 hours and left to cool under ambient temperature, after which the sample was weighed again. Weight loss was recorded to be the percent attributed to organic matter content.

Bulk Density

The bulk density of egg shells was determined by wetting the egg shells followed by measuring the mass of the beaker with wet egg shells as M_1 and the volume of the sample in the beaker as V_1. The content was left for 24 hrs; the mass was taken as M_2 and volume as V_2. Then bulk density was calculated as follows:

$$D = \frac{M_2 - M_1}{V_2 - V_1}$$

Loss on Ignition

The chemical composition of the eggshell waste powder sample was determined by X-ray fluorescence. The loss on ignition (Loi) of the calcined sample at 1000°C was determined according with % Loi = $(A_i - A_f)/A_i \times 100$, in which A_i is the weight of the dry sample at 110°C and A_f is the weight of the calcined sample at 1000°C, during 1h.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Adsorbent Materials

The bulk density of the egg shells was found to be 2 g/cm^3, this value was within the range to calcium carbonate materials and comparable to the reported value by Heloisa (2006) which was 2.47 g/cm^3. Some important chemical characteristics of eggshells are presented in Table 1. The table shows that the egg shell contents are mainly CaO and few other elements of S, Al, Mg, Si, Cl, K and Zn. In reality CaO represent the composition of $CaCO_3$ which is the main component of the chicken egg shells. The presence of CaO observed during XRF measurements is due to the decomposition of $CaCO_3$ into CaO and CO_2, as also reported by Kaewsomboon (2006) and Heloisa (2006) who reported that egg shell consist of several mutual layers of $CaCO_3$. High loss of ignition (LOI) is caused by decomposition of calcite ($CaCO_3$) and organic matter as reported by Tacon (1982). The low value of $CaCO_3$ detected (45.5%) could be due the different kinds of foods that poultry is fed during growth. Porosity was found to be 55.37%. The organic content of the egg shell was 6.84 %, this was slightly higher than 5.36%. reported by Tacon (1982).

Table 1: Composition of Poultry Egg shells

Compound	CaO	SiO_2	Al_2O_3	MgO	K_2O	SO_3	Cl	ZnO	LOI
Composition [%]	45.5	0.15	0.13	1.04	0.06	2.72	0.08	0.87	47.52

BATCH EXPERIMENTS

Batch experiments were used to determine the influence of different parameters on adsorption of lead by chicken egg shells. These include pH, adsorbent dose and contact time.

Effect of pH

The pH of the aqueous solution is an important controlling parameter that affects the adsorption of metals on the surface of eggshell. It is responsible for protonation of metal binding sites, calcium carbonate solubility (the main constituent of eggshell) and metal speciation in the solution, Figure 4 describes the effect of pH variations at different concentrations of adsorbent (egg shells).

From the table the highest and the lowest removal efficiencies at pH 3.3, 7, and 12.3 were 94.68, 96.95 and 94.90 and 82.46, 88.68 and 80.76% respectively. This shows that the highest removal was at pH 7 with percentage removal efficiency of 96.95 and concentration of 0.027 mg/l. This concentration is within the acceptable industrial wastewater standard effluent as per TBS standard which is 0.1 mg/l (Limits for Municipal and Industrial Wastewater, 2005). The removal of lead by egg shells is envisaged to be adsorption process whereby the egg shells act as adsorbent. On the other hand the adsorption could be taking place in two ways: physiosorption and chemisorption in which chemisorption is influenced by pH variation.

Chemical precipitation (Chemisorption) was the main process in neutral pH, and it is an indication of the displacement reaction where by lead ions (Pb^{2+}) displace calcium carbonate ions from $CaCO_3$ salts to form insoluble lead carbonate ($PbCO_3$). During the experiment solubility of lead continuously decreased from pH 3.4 to pH 7, an indication that almost all lead was completely precipitated into $Pb(OH)_2$, $PbCO_3$ (Cerussite) and $Pb_3(CO_3)_2(OH)_2$ (Kaewsomboon, 2006).

$$\text{Egg shell } (CaCO_3) + Pb^{2+} + 2H_2O \longrightarrow \text{Egg shell \_ } (PbCO_3.2H_2O) + Ca^{2+}$$

This is because the main composition of egg shell is $CaCO_3$ and Ksp of $CaCO_3$ is higher than Ksp of $PbCO_3$ (K_{sp} of $CaCO_3$= $4.8x10^{-9}$, Ksp of $PbCO_3$ = $1.5x10^{-13}$) (Kaewsomboon, 2006). Also at low pH the H^+ ions are much larger than ions of metal ions of metal on the egg shell which limits the access of metal ions on the adsorbent surface. When the pH increases, the effect of competition from H^+ ions decreases and the positively charged ions attach on the adsorbent surface. Functional groups in the egg shell powder appear as target sites for the fixation of heavy metals. This condition decrease as pH increases to basic condition.(Rafika et. al., 2009).

These results are also similar to Naksawas, (2004) on removal of Lead from Battery Wastewater by ground fish scales, at pH 8, 9, 10, in which the removal was concluded to be chemical precipitation process. The study reports that at pH 7 lead ions were completely precipitated in form of $Pb(OH)_2$.Similar results was also obtained by Kaewsomboon (2006) in which lead from battery wastewater was removed by egg shells through chemical precipitation and concluded to be optimum at pH 7.

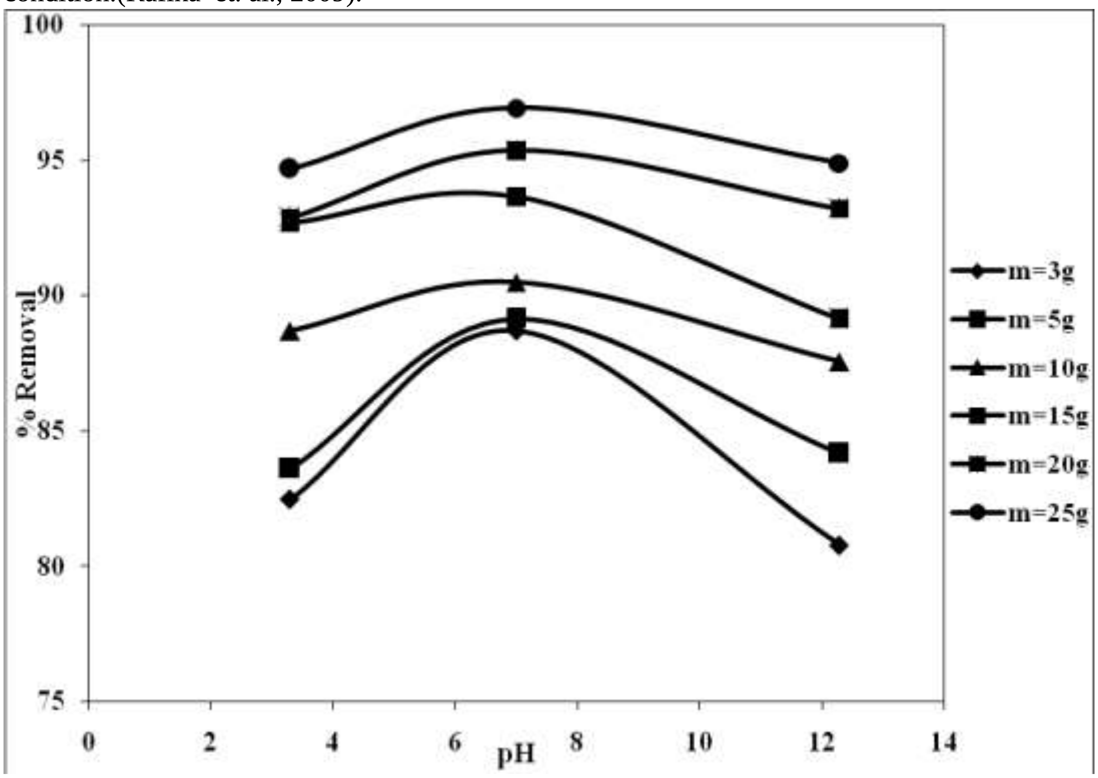

Figure 4 Effect of pH on Lead removal with different egg shell doses

Figure 5 shows the effect of dose of egg shells on removal of lead. As the dose increase, the removal increase The highest removal efficiency, 96.95 % was observed at 25 g dose of egg shells and neutral pH. Major alkaline contributors in egg shell is $CaCO_3$ so it is expected that any aqueous solution equilibrated with egg shell become more basic so heavy metal can precipitate and deposit on egg shell particles that confirmed with the following mechanisms;

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$$HCO_3^- + Pb^{2+} + 2OH^- \longrightarrow 2\ PbCO_3 + 2H_2O$$

Hydrolysis reaction of $CaCO_3$ occurred; basic solution was formed because Ca^{2+} and OH^- increased pH of solution (Brown, 1985). Basic property of egg shells which increased pH was advantageous to decrease the use of expensive chemical reagents for adjusting pH of wastewater (Decreasing in operational cost) and reduced chemical residues in the environment, especially at optimum condition 25 g of egg shell. Other possible reason for reaction of egg shells and Lead is caused by protein acid mucopolysaccharide complex that bind heavy metal to form complex (Polamesanaporn, 2001) Numerous studies have reported that the pore structure (physisorption) of adsorbent particularly affected the adsorption capacity and egg shells have numerous pores 55.37 %, thus the increase of dose of egg shell increases the removal of lead (Polamesanaporn, 2001). As stated earlier, the percentage of removal increased with increase of dose of egg shells, this is by physisorption (increase of active sites) and Chemisorption (increase of amount of $CaCO_3$). And the results showed that dose of egg shell affected the removal of lead directly (Eamsiri et. al., 2005).

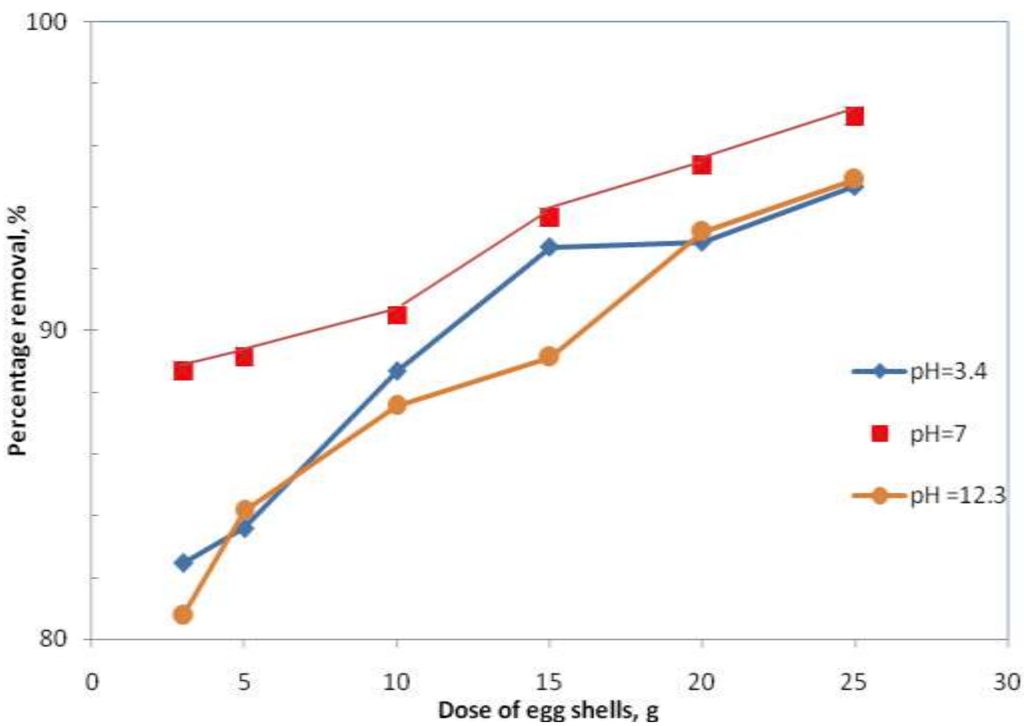

Figure 5 Effect of Dose of egg shell at different pH

Effect of Contact Time

Figure 6, shows the effect of contact time on removal of lead with highest removals of 98.656 and 92.0895% at pH 12.3 and 3.3 respectively at dose of egg shell 25 g, 90 minutes. As the contact time increased, the removal of lead increased rapidly but after time adsorption rate decreased as time passed by. The mechanism can be explained that heavy metal ion binds to active sites as time passes (physisorption); and after the equilibrium contact time passes active sites for adsorbing ion are reduced, decreasing the adsorption rate, because active sites were getting saturated/ exhausted. The increase was reversed when optimum time passed while stirring of the solution continued. The present active sites were exhausted and there was no more adsorption. The equilibrium contact time for lead removal by egg shells was reached at approximately period of 90-150 mins. This indicated that the contact time is related to the removal efficiency. These results are similar to that of Pawebang and Sukcharoen (1992) who reported that the equilibrium time to remove lead in synthetic wastewater by egg shells could be reached at about 80 min. Kaewsomboon, 2006 reported that optimum contact time was 90 min. As well as the study of Lee et. al (1998) who studied on the equilibrium time of lead removal by crab shell particle, and the results showed that the necessary contact time to reach equilibrium was about 90-120 min.

$CaCO_3$ in the adsorbent material cause precipitation of Pb (Chemisorption), which increases as the time of the chemical reaction is prolonged. Physical adsorption took place due to presence of pore structures of egg shells. But after the saturation of the adsorbent's active sites there were no more Lead uptake, continuation of stirring possibly causes de-attachment of lead or chemical reaction which causes the increase of lead in the solution (Figure 6).

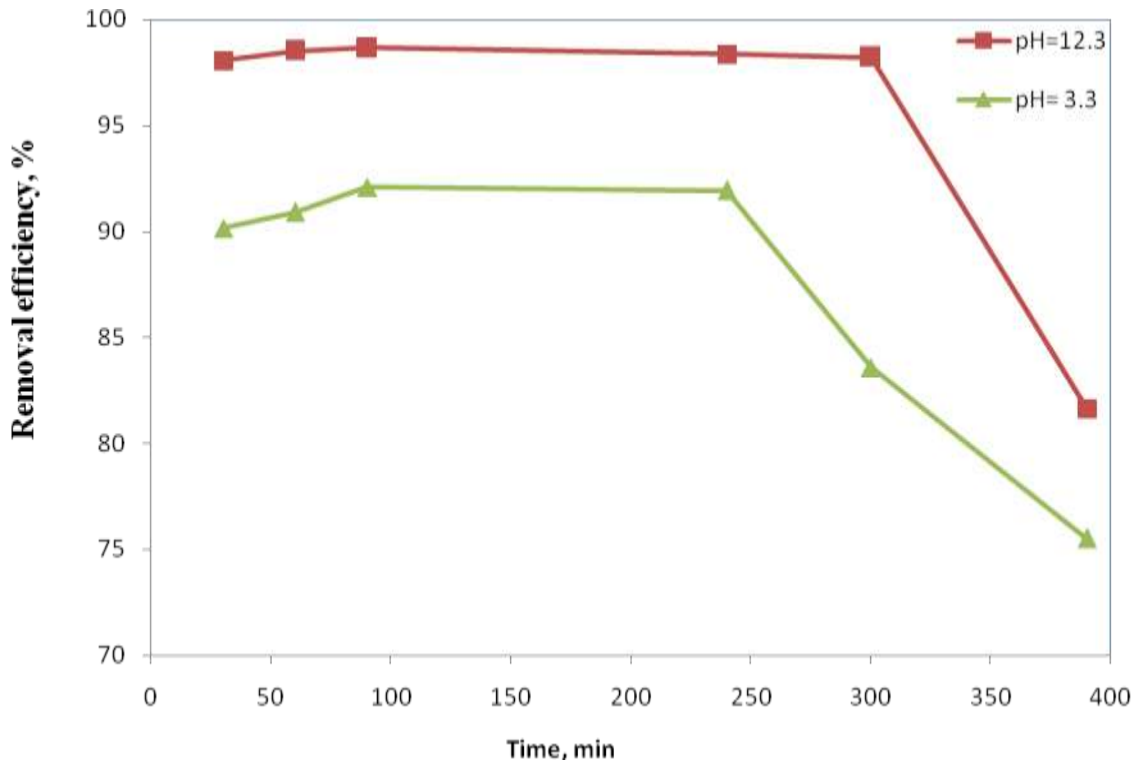

Figure 6 Effect of contact time on lead removal

The removal efficiency of egg shell increased from 30 min to 90 min i.e. 90.14, 90.89 and 92.08% at pH 3.3 and 98.05, 98.50 and 98.65% at pH 12.3. And after the highest removal efficiencies 92.08% and 98.65% at 90 min time passed, the removal decreased towards 390 minutes i.e. 91.94, 83.58 and 75.52% at pH of 3.3 and 98.358, 98.208 and 81.64% at pH 12.3.

The equilibrium time for all types of egg shells were reached at 90 minutes. This indicated that the removal efficiency increases as contact time increases till when the adsorbent's active sites are saturated.

Adsorption Isotherms

Experiments were conducted to determine the adsorption isotherm of lead using egg shells at 3, 5,10,15,20 and 25 g in 100 ml of synthesized wastewater with pH 3.3, 7, and 12.3. Initial Lead concentration was 0.884 mg/l. The experimental data were calculated to determine the adsorption isotherm using the Freundlich model, which assumes the heterogeneous surface energies because the effects of different egg shell dosages on the adsorption of Lead were found to correspond to the Freundlich adsorption isotherm since the plot of log (X/m) versus log Ce yields a straight line, which implies that the adsorption process conforms to Freundlich equation:

log (X/m) = log k + (1/n) log Ce

In this equation, X/m is the mass of lead adsorbed per mass of egg shells, Ce is the equilibrium concentration of lead in solution, K and 1/n are empirical constants (Freundlich parameters), the values of which are equal to the intercept and slope of the plot of log X/m versus log Ce. Log X/m versus log Ce, was plot as shown in Figures 7 to 9. The values of the constants for each pH were determined, after linearizing the equations through linear regression analysis. From the intercept, the parameter K is obtained, while the slope is equal to (1/n). The Freundlich constants (K and 1/n) and correlation coefficients R^2 for Lead by the egg shells are given in Tables 4 and 5.

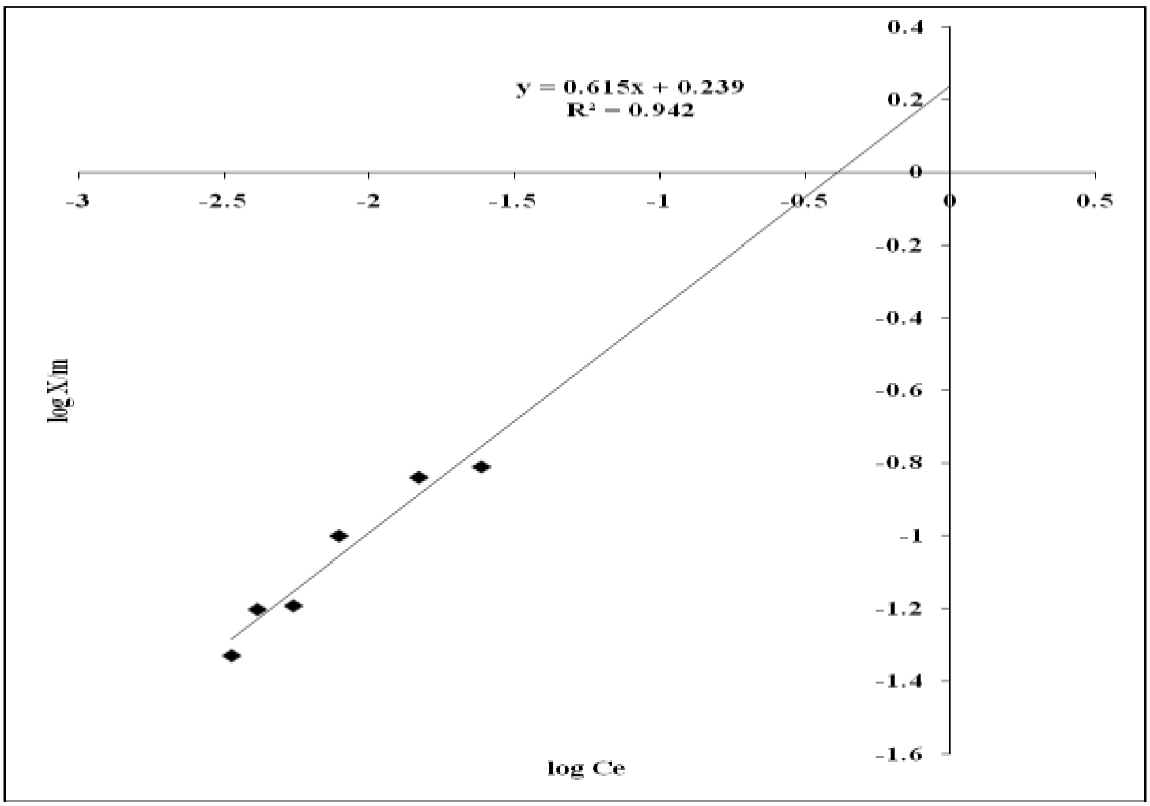

Figure 7 **Freundlich adsorption isotherm for removal of Lead at pH= 3.3**

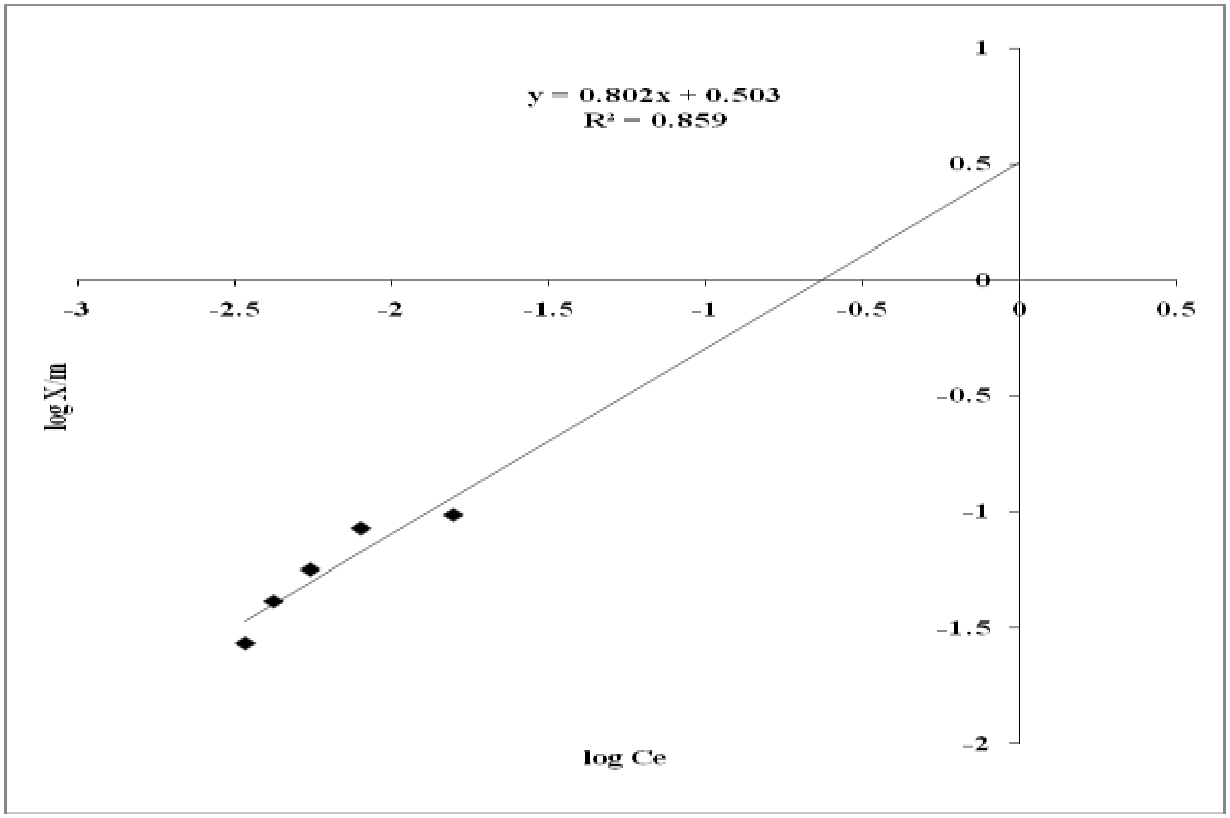

Figure 8 Freundlich adsorption isotherm for removal of Lead at pH= 7

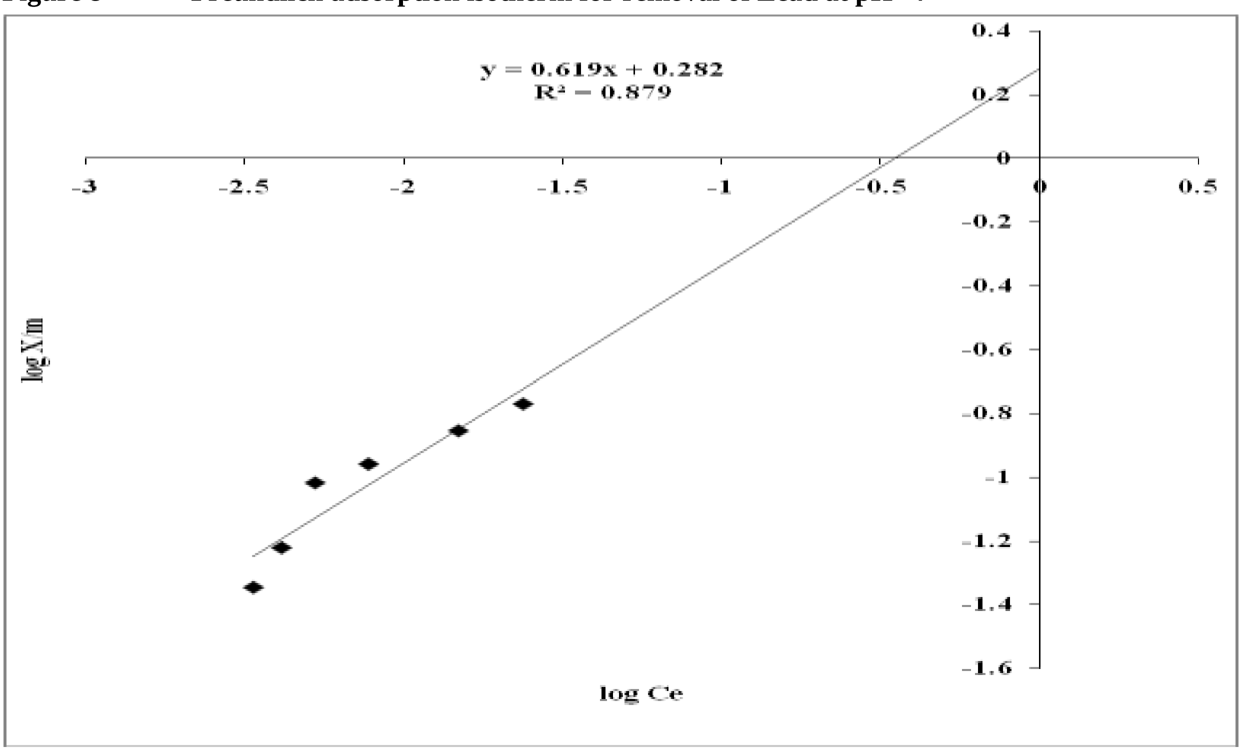

Figure 9 Freundlich adsorption isotherm for removal of Lead at pH=12.3

Table 4 **Freundlich Models' Constants and correlation coefficients for Lead removal on deferent pH**

pH	K	1/n	R^2
3.3	1.7338	0.615	0.942
7	3.18419	0.802	0.859
12.3	1.9142	0.619	0.879

Table 5 **Freundlich Constants and correlation coefficients for different adsorbents from the literatures**

Parameters	Adsorbent		
	Algerian Hoof	*Gallus domesticus*	Egg Shell
1/n	0.625	0.7136	0.615
K	3.33	2.61	1.7338
R^2	0.99	0.9981	0.942

From the results in Tables 4 and 5, the values of which express the selective uptake of lead and affinity of adsorbent, K values can be used to compare the removal efficiency of each adsorbent for different component and the capacity of adsorbent A larger value of K indicates good adsorption capacity/ higher removal efficiency for the dose of egg shell at a particular pH.

The highest K value is observed at pH 7 with value of 3.18419 showing it has higher removal capacity than others, followed with pH 12.3 with 1.9425 values and lastly with pH 3.3 of value 1.7338, this was also shown in the statistical analysis done to the data. The egg shell have protein fiber when observed by SEM, the protein fiber which comprising of carboxyl and amine groups that may promote the egg shell to bind lead ions tightly. Moreover acid condition i.e. pH 3.4 of wastewater may caused protein fiber to contract and slightly captured that blocked reaction H^+ and $CaCO_3$ causing less removal. From this study removal of lead might go through more than one type of mechanism i.e., adsorption and precipitation, especially at high doses of egg shells which increased final pH so precipitation might take place in the adsorption process. Formation of $Pb(OH)_2$ on the surface of ash was presumably mechanism followed by adsorption. Precipitation of some $Pb(OH)_2$ could deposit on fly ash particles.

The value of n is differently discussed according to different literatures, as its magnitude is related to distribution of bonded ions on the sorbent surface, an indication of the favorability, rate/ change in effectiveness over different equilibrium concentrations (sensitivity of the adsorbent to the change of initial concentration of the solute). Normally the value of 1/n ranges from 0.2 to 0.7, (Martines M et. al., 2005) in this research the value of 1/n ranges from 0.615-0.802. This shows that sensitivity of adsorption of lead at neutral pH is very high since the n value is 0.802. The value of n is also anticipated by Alhalya et. al. 2005 that for good adsorbent n ranges from 1-10, as beneficial adsorption showing that egg shell is a good for lead ions since the values of n are all greater than 1 i.e. 1.626, 1.675, and 1.2468. The higher values of correlation coefficients (>0.7) recorded for the three pH is an indication that the Freundlich adsorption isotherm applied is valid for the egg shell removal of lead.

COLUMN EXPERIMENTS

Determination of Adsorption Capacity

In the field, the breakthrough adsorption capacity, $(X/m)_b$ of the egg shells is some percentage of the theoretical adsorption capacity (Table 6) found from isotherm $(X/m)_o$. It is usually assumed to be 25-50 % of the theoretical capacity $(X/m)_o$ (Metcalf and Eddy, 1991).

Table 6 Theoretical & Actual field adsorption capacity of egg shells.

pH	Theoretical Adsorption capacity, $(X/m)_o$ (mg/g)	Actual field adsorption capacity, $(X/m)_b$ mg/g [25% $(X/m)_o$], (mg/g)
3.3	0.142	0.0355
7	0.21	0.0525
12.3	0.132	0.033

The theoretical adsorption capacities (Figure 10, 11 and 12) ($(X/m)_o$ at pH 3.3, 7, 12.3 are 0.142, 0.21, and 0.132 respectively. The actual adsorption at the field is 25-50 % of the theoretical capacity. Assume 25 % is the minimum theoretical adsorption capacity, thus adsorption capacities at pH 3.3, 7 and 12.3 are 0.0355, 0.0525 and 0.033 respectively. Thus the adsorption capacity is highest at pH 7 followed by 3.3 and lastly 12.3.This trend is also seen at discussion in section 4.3 where pH 7 had highest K value thus highest adsorption capacity in comparison to others.

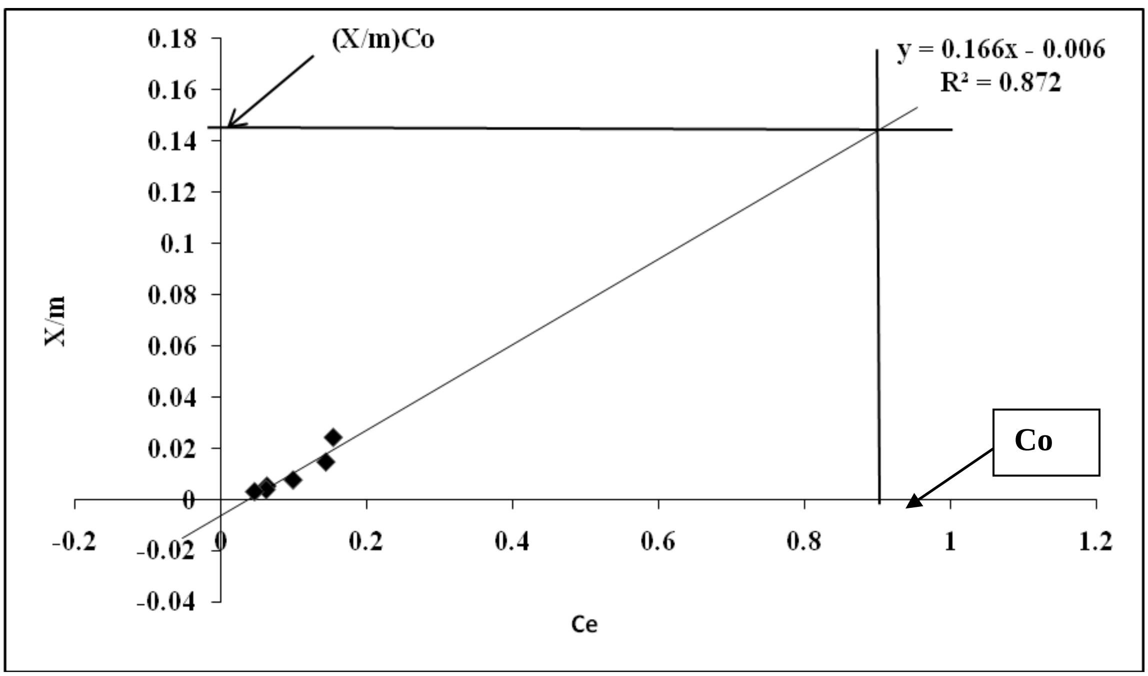

Figure 10 Adsorption capacity of Lead removal at pH 3.4

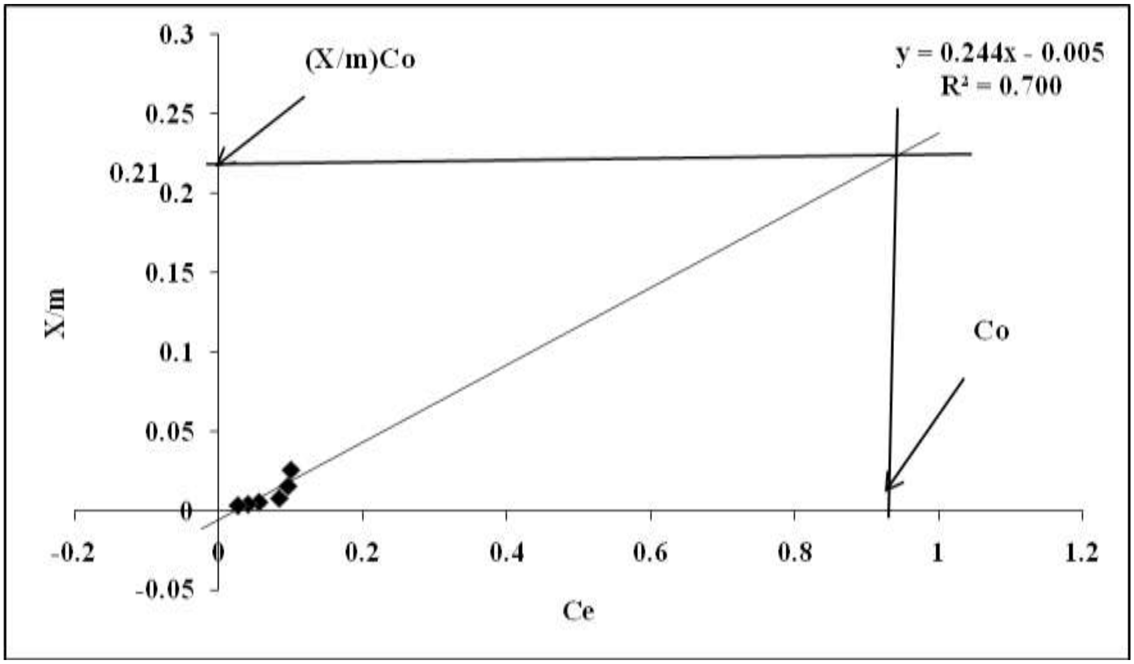

Figure 11 Adsorption capacity of Lead removal at pH 7

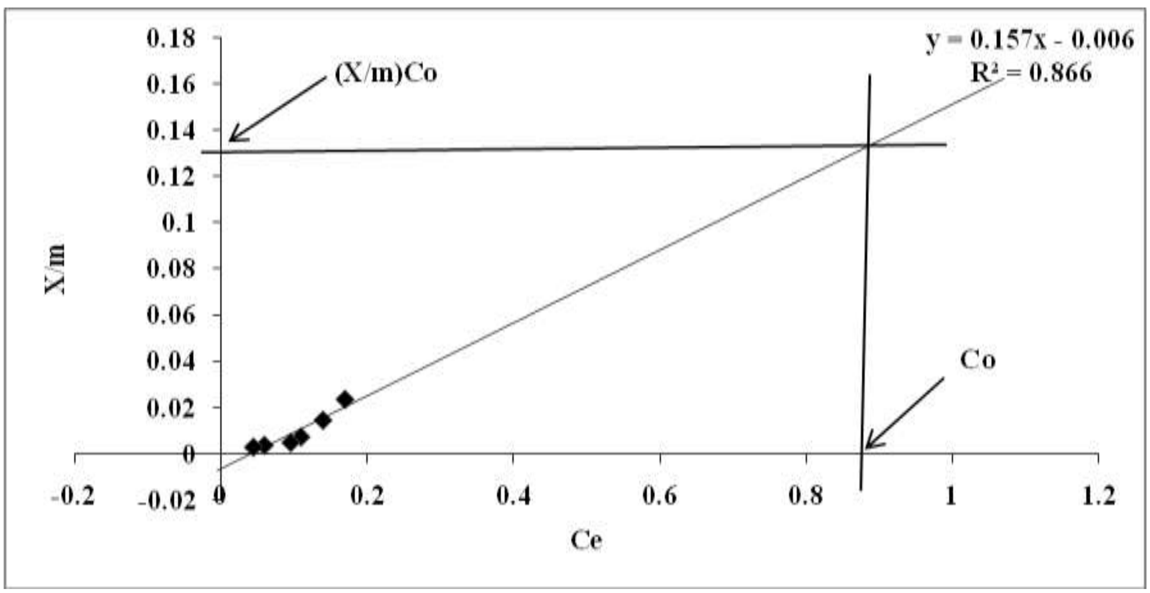

Figure 12 Adsorption capacity of Lead removal at pH 12.3

Breakthrough Time

Break through time is the time that the active sites for adsorbents start to become exhausted, the effluents concentration stats to contain some influent ions of lead. Initial concentration has effect on the breakthrough time. This effect was determined (Figure 13) so as to obtain breakthrough times (Table 7).

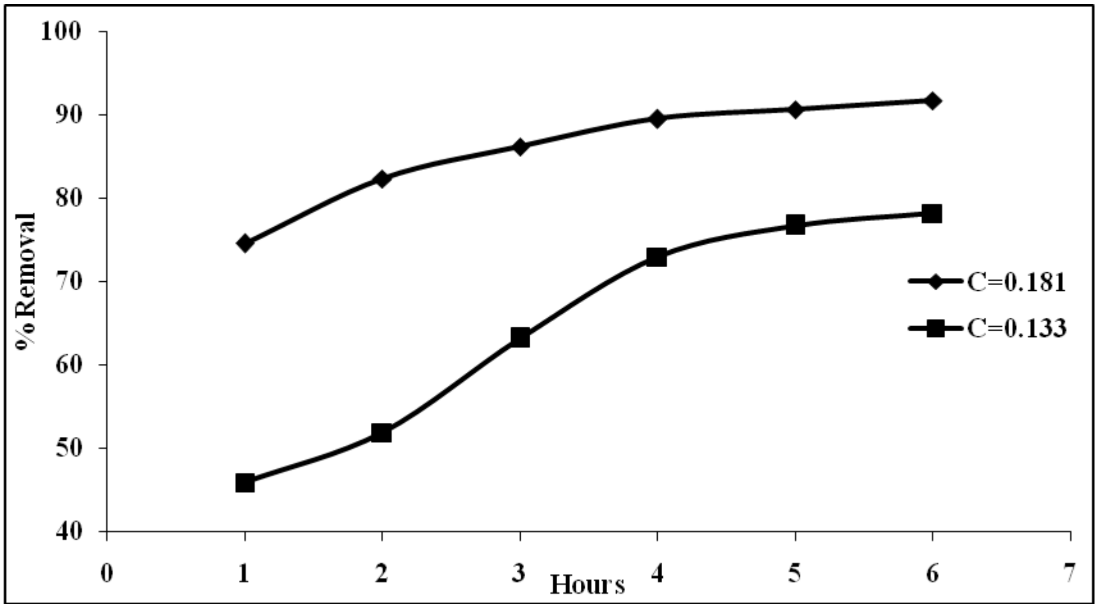

Figure 13 Effect of initial concentration on time for removal of Lead

The egg shell break through time experiment was not done to its end point so the breakthrough was calculated. Egg shell break through time can be determined after obtaining theoretical breakthrough capacity $(X/m)_o$ (Metcalf and Eddy, 1991), by using the following formula;

$$t_b = \frac{(X/m)_b Mc}{Q\left(C_{i-}\left(C_b/2\right)\left(8.34\,lb/Mgal.(mg/l)\right)\right)}$$

Given flow rate of the waste water into the column 5 ml/min = 1.0998 x 10^{-9} Mgal/min.

Surface area of the column $A = \pi r^2$ = π X $(0.01)^2$= 0.000314m^2=0.00103 ft^2
Depth of the filter column = 0.2 m= 0.656 ft
The influent concentration =0.056 mg/l
The breakthrough Lead concentration had been set at C_b =0.01 mg/l
The density of the egg shells to be used was 2 g/cm^3 =1343.954 lb/ft^3

Table 7 Breakthrough time for egg shell at different initial concentrations

Initial Conc. mg/l	Break through time, t_b
0.181	1.3945days=33.46hrs
0.133	6.08 day = 146.03hrs

It is seen from results that break through time of the egg shell varied according to initial concentration rapidly showing that egg shell is sensitive to the change of initial concentration of lead ions. When the initial concentration of lead ions increased, the break through time appeared to be early (decreased) compared to less initial concentration, i.e. at 0.181mg/l BTC was 33.4 hrs and at 0.133mg/l Break through Time (BTC) was 146.03 hours. Thus initial concentration of lead ions is inversely proportional to break through time.

CONCLUSIONS

From the experimental results, it is demonstrated that egg shells are able to be an alternative raw material/ adsorbent for lead removal. The chemical composition of the egg shells were mainly $CaCO_3$, 45.5 % and few other elements i.e. S, Mg, K, Al, Cl, and Zn. This amount of $CaCO_3$ shows that there is possibility of chemical reaction between Lead ions and Carbonate ions (chemisorption), raise of pH on treated wastewater due to the presence of carbonates which enhances removal of Pb ions. The results from this work showed that the optimum pH was at 7, dose of egg shell 25 g/100 ml with lead concentration of 0.884 mg/l and the contact time of approximately 90 minutes was required to reach the maximum removal. Final concentration of lead at optimum conditions was 0.027 mg/l (which is lower than the wastewater quality standard i.e. 0.1 mg/l. (Limits for Municipal and Industrial Wastewater, 2005). The data fitted well in Freundlich adsorption model which was used in the isotherm plotting. This is observed from the values of correlation coefficient R^2 which were >0.7.

From this research, precipitation might take place in the adsorption process, especially at high doses of egg shells which increased the pH of the solution. The results of the adsorption isotherm demonstrated that the adsorption was affected by the change of pH, due to variation of K value where it decreased from pH 7, 12.3, to 3.3. Thus, highest removal was found in the neutral condition of the wastewater since precipitation and deposition was favored at this condition. In summary, the egg shell could remove lead from synthetic wastewater due to its chemical and physical characteristics/ properties. Chemical factor of egg shells that affected removal of lead is presence of $CaCO_3$, pore structures protein matrix and functional group such as carboxyl, amine and sulfate group. Moreover, egg shell is acid-neutralizing agent, any aqueous solution equilibrated with egg shell become more basic so heavy metal can precipitate and deposit on egg shell particles. The egg shell was good for Pb removal. In addition it could reduce chemical residues, decrease operational cost and possibly reuse of solid waste produced by egg shells disposal.

REFERENCES

Alhalya N, Kanamadi R.D, Ramachandra TV. (2005). “Biosorption of chromium (VI) from aqueous solution by the husk of Bengal gram (*Cicer arintinum*), *Electronic J Biotechnol. 56*, 107-103.

Eamsiri A, Arunletaree C and Datchaneekul K (2005). “Removal of Heavy metals in Synthetic wastewater by adsorption on Bentonite”, Environmental and Natural Resource.2005(3): 21-30.

Fabianil C, Rusciol F, Spadonil M and Pizzichini M (1996). “Chromium(III) salts recovery process from tannery wastewaters”. *Desalination. 108*, 183.

Fahim NF, Barsoum BN and Eid AE (2006). “Removal of chromium(III) from tannery wastewater using activated carbon from sugar industrial waste”. *J. Hazard. Mat. 136*, 303-337.

Filibeli A, Buyukkamaci N and Senol H (2000). “Solidification of tannery wastes”. *Resource. Conservation. Recy. 29*, 251- 261.

Goto, M., and Suyama, K. (2000). "Occlusion of Transition Metal Ions by New Adsorbents Synthesized from Plant Polyphenols and Animal Fibrous Proteins." *Appl Biochem Biotechnol, 84*-6, 1021-1038.

Heloisa Andrade de Paula Tudury. (2006). “The use of hatchery residual biosorbents for removal of heavy metals from wastewater” *MSc of Science*, University of Maryland

Kapoor A and Viraraghavana T. (1998). ‘Biosorption of heavy metals on Aspergillus” Niger. *J. Bioresour. Technol. 63*, 109-113.

Lee Moo-Yeal, Lee Sung-Ho, Shin Hyun-Jae, Kajiuchi Toshio and Yang Ji-Won. (1998). “Characteristics of lead removal by crab shell particles”, *Process Biochem., 33*: 749-753.”

Macchi G, Pagano M, Pettine M, Santrori M and Tiravanti G (1991). “A bench study on chromium recovery from tannery sludge”. *Water Res. 25,* 1019-1026.

Martines M., Miralles N., Hildago S., Fiol N., Villacscusa I. and Poch J (2005). “Removal of Lead and Cadimium from aqueous solutions using grape stalk waste, *Journal of Hazardous Material*. 28:1-9.

Nilanjana Das, R Vimala, V. Vinondhini and P Karthika,(2007). “Use of Natural products as Biosorbent of heavy metals”-an overview

Pawebang P. and Sukcharoen. (1992). “Comparative studies on adsorption of Lead by egg shell and fish scale”, *Science and Technology.1999(2)*:51-57. (In Thai)

Polamesanaporn Y, (2001). “Development of an adsorbing material from egg shell for the removal of Cadmium” [*MSc. Thesis in Natural Resource Management*] Bankok: Faculty of Graduated Studies, King Mongkut University of Technology Thonburi(in Thai)

Rafika Souang, Djilali Touabia, Benchreit Benayada, Ali Boucenna, (2009). ‘Adsorption of Heavy metal (Cd, Zn and Pb) from Water using Keratin Powder Preared from Algerian Sheep Hoofs”.

Sari A, Tuzen M and Soylak M (2007). “Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtic clay”. J. *Hazard. Mater. 144*, 41- 46.

Song Z, Williams CJ and Edyvean RGJ (2000). “Sedimentation of tannery wastewater. *Water” Res. 34*, 2171-2176.

Song Z, Williams CJ, Edyvean RGJ (2004). “Treatment of tannery wastewater by chemical coagulation”. *Desalination. 164,* 249-259.

Tiravanti G, Petruzzelli D and Passino R (1997). “Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery”. *Water Sci. Technol. 36,* 197–207.