Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2014, 3 (5): 2138-2146

(International Peer Reviewed Journal)

Adsorption-Kinetics of Lead in Water

D. Prabhakara Chary[1]*, I.V. Kasiviswanath[2] and T. Mallikarjun[2]

1. Department of physical Sciences, Kakatiya Institute of Technology & Science Warangal-506 015, Telangana State., **INDIA**
2. Department of Chemistry, K L University, Vaddeswaram, Guntur – 522 502, A.P, **INDIA**

Email: dpcnkd@gmail.com

Accepted on 17th September 2014

ABSTRACT

Water quality is of utmost importance for mankind since it is directly linked with human welfare. Millions of people, all over the globe, particularly in developing countries, are losing their lives due to water-borne diseases. Polluted water is culprit in all these cases. Water pollution may be caused due to domestic waste, waste from different industries, fungicides and pesticides used in agriculture, etc. Therefore, assessing the quality of water samples collected from various habitats affected by municipal and industrial activities is most warranted. In developing countries the high cost of activated carbon, inhibits its large scale use as an adsorbent. Hence, we present the use of low-cost residential waste ash and market waste ash from Warangal Municipal Corporation (WMC) as heavy metal ion sorbents. These ashes were soaked in doubled distilled water and dried in the oven at above 500^0C for 24 h. This was done by several times. These dried ashes were found to be good adsorbents for the removal of lead. The kinetics of adsorption of lead was studied using Legergren's plots.

Keywords: Contents of lead, Adsorption, Isotherm, Kinetics, Solid waste ashes.

INTRODUCTION

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, aquifers and groundwater. Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. Water pollution affects plants and organisms living in these bodies of water. In almost all cases the effect is damaging not only to individuals species and populations, but also to the natural biological communities. Heavy metals (elements with an atomic density greater than 6 g $cm^{3\ -1}$) are one of the most persistent pollutants in water. Unlike other pollutants, they are difficult to degrade, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances[1-3]. It is well known fact that potable safe water is absolutely essential for healthy living. The problem of drinking water contamination, water conservation and water quality management has assumed a very complex shape [4]. Rapid industrialization has led to increased disposal of heavy metals and radio nuclides into the environment [5-7]. Adsorption has been shown to be commonly used adsorbent for adsorption due to effectiveness and versatility[8-9].

The low-cost WMC residential waste ash and market waste ash were used as heavy metal ions sorbents.

These ashes were soaked in double distilled water and dried in the oven at above 500°C for 24 h. This was done by several times. These dried ashes were found to be good adsorbents for the heavy metal water pollution. These studies are discussed in the following sections. Buffers of varied pH's were prepared for the purpose of our studies. A series of stock solutions was prepared by combination of the members of which, set of desired pH's was obtained.

MATERIALS AND METHODS

The Orion Cat. No.810007(3M KCl) was used as internal filling solution and Orion Cat. No.810007 (1g KCl in 200 ml distilled water which pH is 7) was used as storage solution for pH electrode. Always used fresh buffers (pH=4.02 and pH=9.40) were used for calibration. Orion model 9482BN electrode and along with this Orion model 90-02 double junction reference electrode were used for the determination of lead ion(Pb^{+2}). The reference electrode of lead inner chamber was filled with Orion Cat. No.900002 and outer chamber was filled with Orion Cat. No.900003 solutions. The Orion Cat. No. 90062 solution was used for filling of lead electrode. The contents of lead were measured by ion-selective electrodes. It is accurate even up to $1X10^{-6}$ M level. The lead electrode measures the ion activity of lead in solution rather than concentration. A 5M sodium per chlorate solution was used as Ionic Strength Adjuster (ISA) [10].

The adsorption of heavy metal ion on the selected adsorbents (waste ash) were multi-step work–up and the study of kinetics could not be carried out on a single reaction pot. As many as 15 or 20 stoppered 20 mL test tubes were pasted with labels 0,1,2,3,4,5,8,12,15,20,30,40,50,and 60 denoting the time in minutes elapsed after the adsorbate and adsorbent were mixed. Whenever needed, a few more timings were inserted in some more tubes. The thermostat was used for the maintaining the temperature.

In each of all the test tubes but that labeled '0', a carefully weighed out adsorbent (30mg of ash powder by a microbalance) was transferred to which 9 mL of the desired buffer was added. The contents were thoroughly shaken and their pH's measured by dipping the combined glass electrode of the Orion Ion Meter. It was observed that all the tubes measured near similar pH and the same was recorded. Into each of these test tubes, but one after the other, 1ml of the stock solution of the desired metal ion was added and again the contents were immediately filtered through a G4 sintered Buchner funnel by suction. The metal ion was analyzed in the filtrate by using electro-analytical technique. The pH of the buffer varies with the adsorption. In the control tube labeled'0', only 9 ml buffer of the measured pH and 1ml of the metal ion solution were mixed with no adsorbent. The data of the measured concentrations and the times of contact between the adsorbate and adsorbent were appropriately processed.

RESULTS AND DISCUSSIONS

Effect of Sorbent Dosage and Time: We studied the effect of mass of adsorbent on the extent of adsorption to check the reversibility of adsorption, shown in figure 1

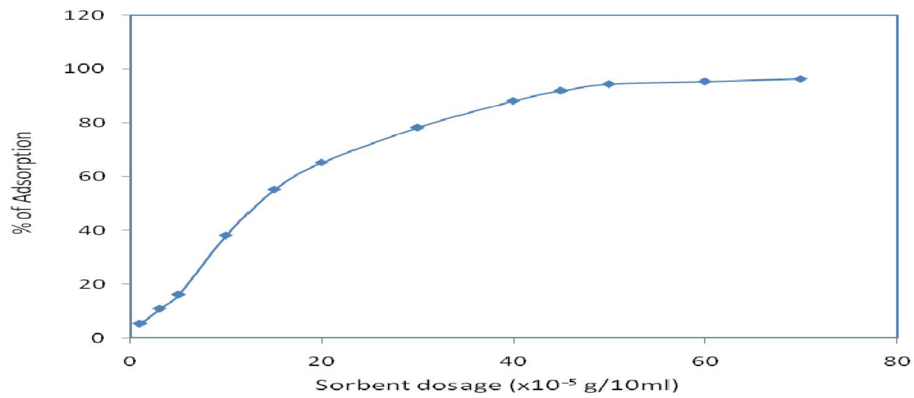

Figure 1: Effect of sorbent dosage on the adsorption of lead at (1.048 mg L^{-1}) pH = 5.018 and at 30 ºC.

It is evident that for the quantitative removal of 1.048 mg L^{-1} of lead in 10 mL at pH = 5.018, a minimum sorbent dosage of 30 mg of waste ash is required. The studies clearly show that the optimum weight of sorbent is 30 mg. Since 100 % adsorption mark was not approached by the curve for any concentration of metal ion at less than 1 mg L^{-1} and for sorbent dosage at more than 30 mg 10 mL^{-1} of the solution, the quantitative studies of adsorption of heavy metal ions on the ashes were undertaken within these analytical limits.

From figure 2, It is investigated that optimum time for maximum adsorption i.e. one hour.

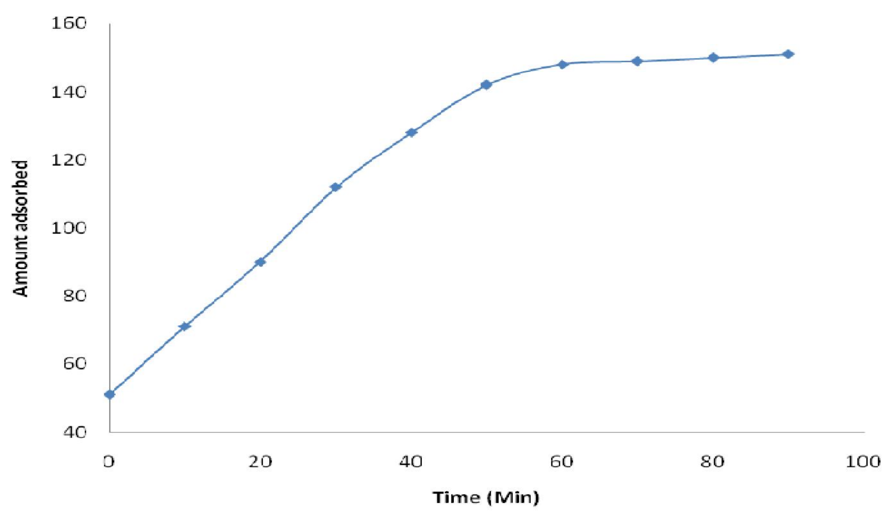

Figure 2: Effect of time on the adsorption of lead (1.048 mg L^{-1} at pH = 5.018 with residential waste ash (30 mg)

The kinetics of adsorption of lead on residential waste ash was studied by using Legergren's' s equation

$$\log(q_e - q) = \log q_e - \frac{k_r t}{2.303} \qquad (1)$$

where q_e =Amount in mg/g of lead adsorbed per 30 mg of the sorbent at equilibrium time

q = Amount in mg/g of lead adsorbed per 30 mg of the sorbent at time t,

k_r = Adsorption constant and t is the time in minutes.

In figure 3, the linearity of the plot indicates the validity of the Legergren's equation for the present system

and suggests that the process follows first order kinetics.
The value of k_r, was calculated from the slope of the plot and found to be $7.599x10^{-2}$ per minute for lead at pH=5.018.

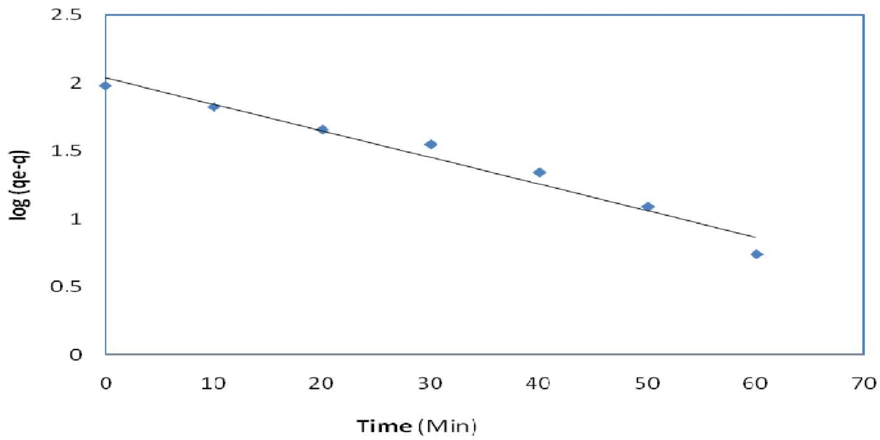

Figure 3: Legergren's plot for the adsorption of lead (1.048 mg L^{-1}) on residential waste ash at 30 ºC.

Effect of pH on the Kinetics of Adsorption : The effect of pH on the kinetics of adsorption of lead is shown in figure 4. At pH=8 to 10 the rate of adsorption increases slightly because the metal forms hydroxy complexes that are specifically sorbed to a considerable extent.

$$M^{+2} + H_20 \leftrightarrow MOH^+ + H^+$$

The presence of OH^- group around the metal ions and the preferential adsorption of OH^- ions on the sorbent sites enhances the adsorptivity due to the possibility of hydrogen bonds. In order Pb^{+2} to be sorbed on sorbent surfaces, the metal can also diffuse into the adsorbent.

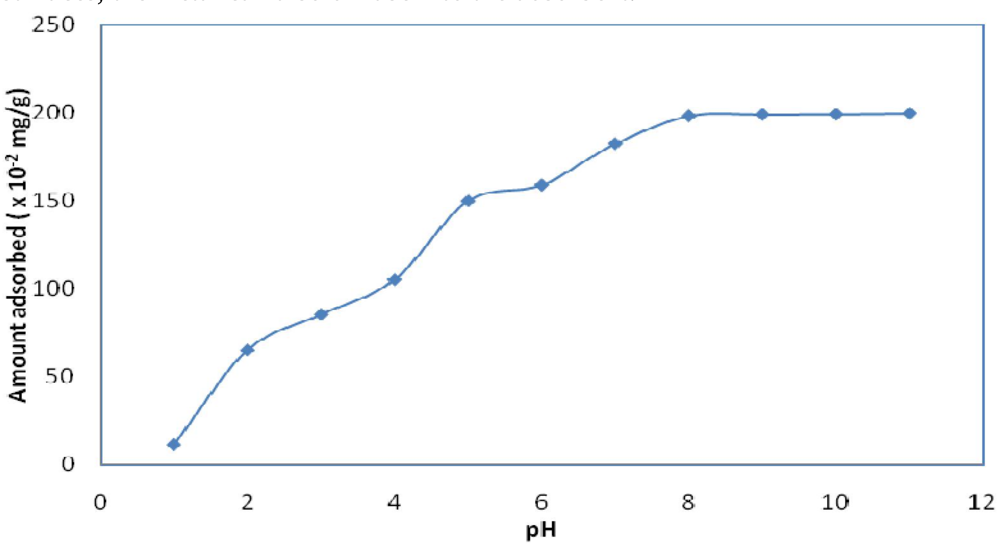

Figure 4: Effect of pH on the adsorption of lead (1.048 mg L^{-1}) on residential waste ash at 30 ºC.

Effect of Temperature on Adsorption: In figure 5 the intactness of the linearity of these plots at different temperatures reveals that the kinetics comply with first order kinetics at all these temperatures.

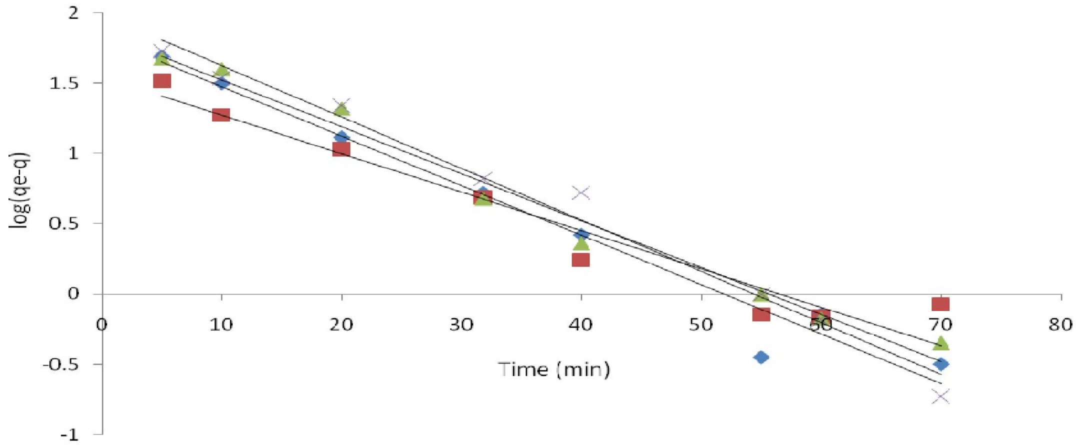

Figure 5: Freundlich adsorption isotherm for lead (1.048 mg L^{-1}) on residential waste ash (30 mg) at (—◆—) 20 ºC, (—■—) 30 ºC, (—▲—) 40 ºC, (—×—)50 ºC, at pH = 5.018.

The mechanism of adsorption was found to be rather the temperature - independent. The values of k_r are collected in table 1.

Using Arrhenius equation

$$\log(k_r) = \log(z) - \frac{Ea}{2.303RT} \qquad (2)$$

where z is a frequency factor, R is the gas constant and T the absolute temperature, k_r the adsorption rate constant (time-I) and E_a the activation energy. From this equation, the thermodynamic activation energy could be evaluated. A plot of log k_r versus l/T was found to be linear for lead as shown in figure 6. The activation energy (E_a) value, calculated from the slope of the plot is found to be 1.22254 J mol^{-1} for lead.

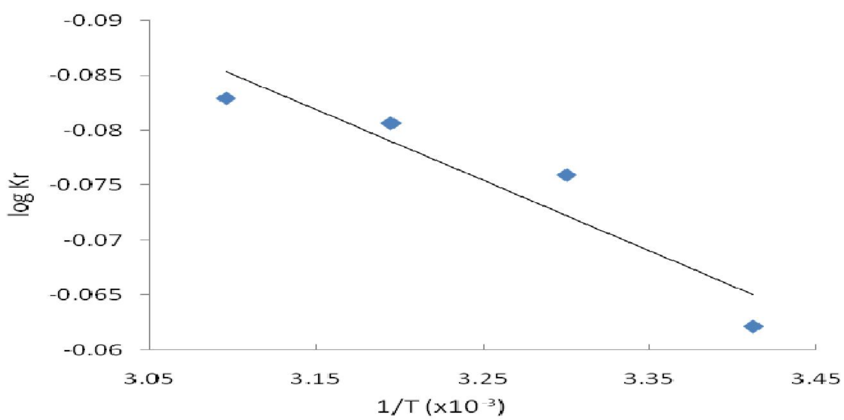

Figure 6: Plot of log (Kr) Vs 1/T for adsorption of lead (1.048 mg L^{-1}) on residential waste ash (30 mg) at pH = 5.018.

Table 1: Rate constants of the adsorption of lead on waste ash at different temperatures.

Temperature (ºC)	k_r X 10^{-2} per minute
20	6.2181
30	7.5999
40	8.0605
50	8.2908

ADSORPTION ISOTHERMS: The residential and market waste ashes are potential adsorbents of lead ions[6,7]. From the plot of adsorption versus time (Figure 3), it is also clear that the adsorption of lead on ashes, reaches equilibrium. Hence, it is felt appropriate to study the adsorption isotherms in the light of well-known isotherms.

Freundlich Isotherm: The adsorption data were fit for the Freundlich equation,

$$\log(q_e) = \log(k_f) - \frac{1}{n}\log(C_e) \quad (3)$$

where q_e is the amount of lead adsorbed per unit mass of the sorbent after the equilibrium time, k_f is a measure of adsorption capacity and 1/n indicates the adsorption intensity. Figure **7** reveals that the straight lines are parallel to one another the relevant data pertaining to these plots are given in table 2. Thus indicate that the Freundlich constants are temperature-dependent.

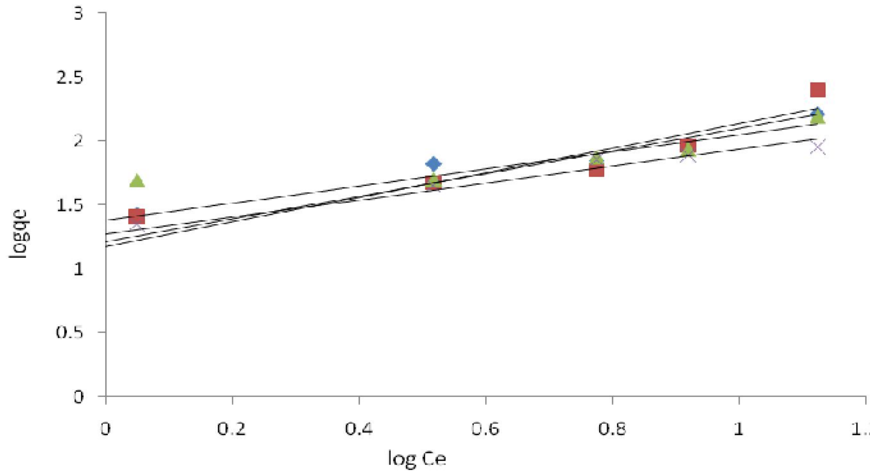

Figure 7: Freundlich adsorption isotherm for lead (1.048 mg L^{-1}) on residential waste ash (30 mg) at (—◆—) 20 ºC, (—■—) 30 ºC, (—▲—) 40 ºC, (—×—)50 ºC, at pH = 5.018.

Table 2: Freundlich constants for the adsorption of lead on waste ash at different temperatures

Temperature (ºC)	K_f	1/n
20	1.178	0.957
30	1.216	0.883
40	1.278	0.670
50	1.385	0.668

Hence, correlation of these data to the temperature in the light of Van't Hoff's reaction isochoric, given by

$$\log(k_f) = \log(k_f^{\,0}) - \frac{\Delta H^0}{2.303RT} \quad (4)$$

can be done to find the thermodynamic parameters of the adsorption equilibrium. The plot of log (K_f) versus l/T is shown in figure 8. The ΔH^0 value obtained from this slope of the plot is found to be 11.6989 J mol^{-1} for lead.

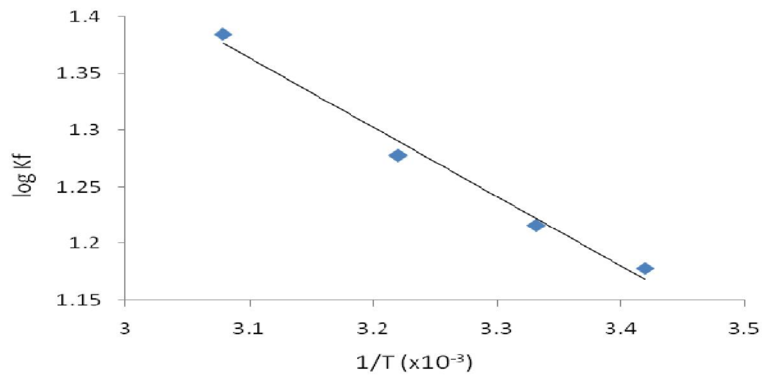

Figure 8: Plot of log (K_f) Vs 1/T for adsorption of lead (1.048 mg L^{-1}) on residential waste ash (30 mg)

Langmuir Adsorption Isotherm: The equilibrium data for removal of lead by adsorption on residential waste ash at several temperatures were also fit into the Langmuir isotherm,

$$\frac{C_e}{q_e} = \frac{1}{K_L}b + \frac{C_e}{b} \qquad (5)$$

where C_e is the equilibrium concentration in mg L^{-1}, q_e is the amount adsorbed at equilibrium in mg g-1, K_L is Langmuir equilibrium constant and b is Langmuir adsorption capacity respectively.
Figures **9-12** show that the plots of C_e versus C_e/qe at different temperatures follow linear relationship and these indicate that the applicability of Langmuir adsorption isotherm for the present adsorption process. The values of Langmuir adsorption rate constant (K_L) and Langmuir adsorption capacity are given in table 3.

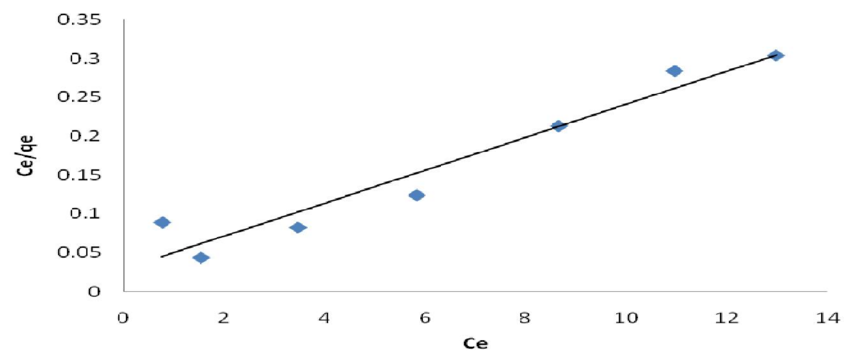

Figure 9: Langmuir adsorption isotherm for lead (1.048 mg L^{-1}) on residential waste ash (30 mg) at 20 ºC.

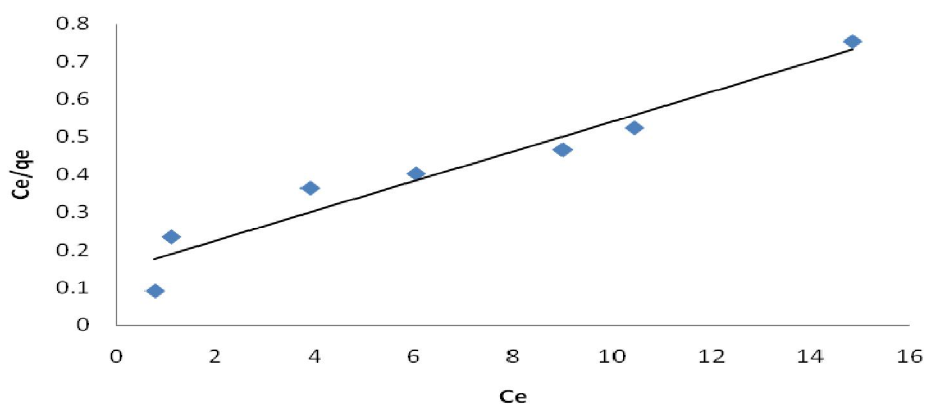

Figure 10: Langmuir adsorption isotherm for lead (1.048 mg L^{-1}) on residential waste ash (30 mg) at 30 ºC.

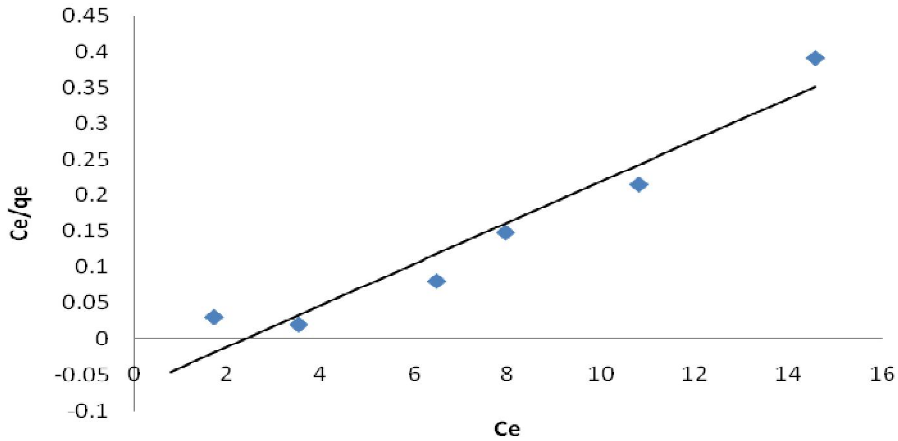

Figure 11: Langmuir adsorption isotherm for lead (1.048 mg L^{-1}) on residential waste ash (30 mg) at 40 ºC.

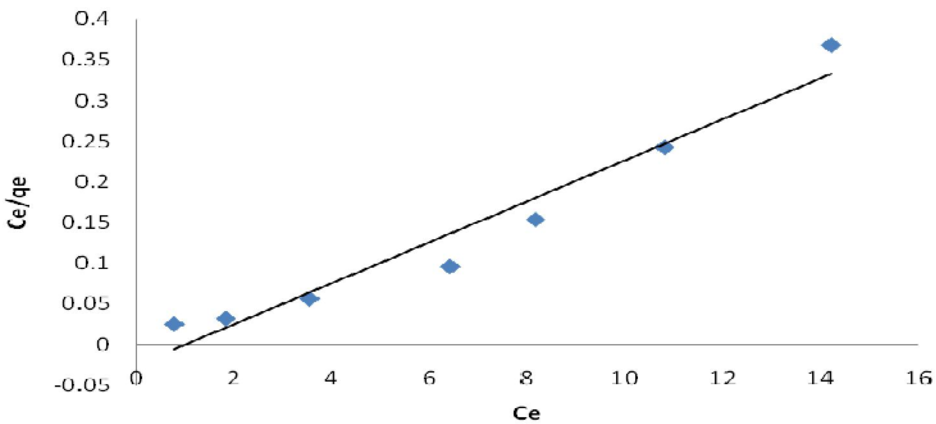

Figure 12: Langmuir adsorption isotherm for lead (1.048 mg L^{-1}) on residential waste ash (30 mg) at 50 ºC.

Table 3: Langmuir constants for the adsorption of lead on residential waste ash at different temperatures.

Temperature (°C)	Langmuir constants	
	K_L (mg/g)	b (mg/l)
20	4.7843	0.4542
30	5.3246	0.4453
40	6.5718	0.4345
50	7.2805	0.4296

APPLICATIONS

As the results indicate the Warangal Municipal Corporation market waste and residential waste ashes usage may be promoted as good adsorbents of heavy metal ions like lead in water bodies. These ashes are no-cost and eco-friendly materials.

CONCLUSIONS

Warangal Municipal Corporation market waste ash is good adsorbent when compare to the residential waste ash. It is also clear that the adsorption of lead on the waste ashes attains equilibrium. It is evident that from the studies carried out that the market waste and residential waste ashes are potential adsorbents of lead ions (Pb^{+2}).

REFERENCES

[1] Akpor O. B. and Muchie M., *International Journal Physical Sciences*, **2010, 5**, 12.
[2] D. Prabhakara Chary, *Journal of Applicable Chemistry*, **2013,** 2, 6.
[3] E.Aksorm, P. Visoottiviseth, *Science Asia*, **2004,** 30.
[4] APHA, AWWA, WPCF, Standard methods for Examination of Water and waste water, Washington, D.C. USA, 19th Ed., **1995.**
[5] F. Chigondo, B. C. Nyamunda, S.C. Sithole and L.Gwatidzo, *Journal of Applied Chemistry*, **2013**, 5, 1.
[6] N. A. Babarinde, J. O. Babalola and A. R. A. Sanni, *International Journal Physical Sciences*, **2006,** 1, 1.
[7] S. D. Kim, K. S. Park and M.B. Gu, *Journal of Hazardous Materials*, **2002**, 93, 2.
[8] Z.Asku, *Process Biochemistry*, **2009**, 40.
[9] Z. Lotfy and N. Adhoum, *Separation and Purification Technology*, **2002**, 26, 3.
[10] Model EA 940 Expandable Ion Analyser Instruction Manual, Orion Company, U.S.A, **1991.**