Poly(Furfural-Acetone) as New Adsorbent for Removal of Cu(II) from Aqueous Solution: Thermodynamic and Kinetic Studies

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Abstract

Poly(furfural-acetone) was prepared and used for the removal of Cu(II) from aqueous solution. The optimum pH for the removal was found to be 6. The adsorption kinetic of Cu(II) was studied, and the rates of sorption were found to conform to Pseudo–Second-order kinetic with a correlation coefficient (R^2=1), results indicate that the pH 6 of the system supported the adsorption of Cu(II) on PFA, which involve higher negative value of ΔG^o. On the other hand, the degree of spontaneity of the reaction increases with increasing temperature for all concentrations of Cu(II). The positive values of $\Delta H°$ reveals, the endothermic nature of the process and its value lie in the range of physisorption. It was also observed that the randomness increases at the solid-solution interface from the positive values of $\Delta S°$. Estimation of sticking probability $S*$ values reveal that the process is favorable due to low value of $S*(S*<1)$. Activation energy Ea values were consistent with values of $\Delta H°$ both are positive and their values lie in the range of physisorption.

Keywords: Poly(furfural-acetone), Adsorption, Copper, Thermodynamic Parameters, Sticking Probability

1. Introduction

Pollution from heavy metals is a major concern in developing countries. The discharge of heavy metals into water-courses is a serious pollution problem which may affect the quality of water supply. Increasing concentrations of these metals in the water constitute a severe health hazard mainly due to their non-degradability and toxicity. Numerous metals such as chromium Cr(III) and Cr(VI), Copper (Cu), Lead (pb), Manganese (Mn), Mercury (Hg), Cadmium (Cd), etc. are known to be significantly toxic (Nordberg, 2007). Copper, the metal considered in this project, is a widely used material. Copper metal contamination exists in aqueous waste streams from many industries such as electronic and electrical, metal plating, mining, manufacture of complex heat sinks, Cu plumbing, as a component in ceramic glazing and glass coloring. Unfortunately, Cu is a persistent, bioaccumulative and toxic chemical that does not readily break down in the environment and is not easily metabolized (Irelond, 1991; Vernet, 1992). It may accumulate in the human or ecological food chain through consumption or uptake and may be hazardous to human health or the environment. Drinking water that contains higher than normal levels of Cu may cause vomiting, diarrhea, stomach cramp and nausea. The chronic effects of consumption of high levels of copper are liver and kidney damage (Najua, 2008). The safe level of Cu in drinking water for human is between 1.5 to 2.0 mg∕L. hence, removal of copper form water and waste water assumes important (Najua, 2008). Chelating resin provide a dramatic improvement in ion selectivity relative to traditional ion exchange resin but still suffer from two distinct drawbacks: slow metal uptake kinetics and limited operating pH range (Rivas, 2001; Rivas, 1995), on the otherhand, chelating polymer resins are found to be more selective by nature (Rivas, 2001; Rivas, 1995) as compared to other conventional techniques in the removal of metal ion (Huang, 1971; Wing, 1975; Netzer, 1974; Sundersen, 1978; Patterson,

1977; Lindstdt, 1971; Shukla, 1994). In the light of the above, poly (furfural-acetone) was prepared and the kinetic models and thermodynamic parameter of the adsorption of Cu on the polymer were investigated.

2. Experimental

2.1 Preparation of poly (furfural-acetone)

The poly(furfural-acetone), PFA was prepared by direct polymerization of furfural and acetone in the presence of aqueous alkali solution according to literature (Patel, 1983) the FTIR spectrum of PFA was done using FTIR spectrophotometer Type Shimadzu 8000.

2.2 Preparation of Copper(II) solutions and analysis

A stock solution of $Cu(NO_3)_2 \cdot 3H_2O$, 500 mg/L was obtained by dissolving 1.9005g Of $Cu(NO_3)_2$ in 1L of deionized water, this solution was used for further experimental solution preparation. The pH values were adjusted with 0.1M HNO_3 or 0.1M NaOH. Analytical grade reagents were used throughout this study. The pH values of Cu(II) solutions were measured by pH meter Type HANA,301 instruments. The residual Cu(II) in the sorption solutions was determined by atomic absorption spectrophotometer Type AAnalyst 200 Perkin Elmer.

2.3 Effect of pH

The pH effect on adsorption were done using batch process. The initial pH values were adjusted to 4.0, 5.0, 6.0, 7.0 and 8.0 with 0.1M HNO_3 and 0.1M NaOH. The effect of pH on the adsorption of Cu(II) onto poly(furfural-acetone) were determined using 0.1g of PFA in 50 ml of Cu(II) solution of 10 ppm at 20 °C, shaking was carried out using horizontal thermostat shaker model LSB-015S, at 140 rpm, for 100 minutes time. In all batch experiments and after completion of adsorption time, samples were collected from duplicate flasks, filtered by whattman filter paper no.40, the filtrate was analyzed for residual copper concentration. The amount of Cu(II) adsorbed onto the polymer, q_e mg/g, was calculated using the following equation:

$$q_e=(C_i - C_e)V/M \tag{1}$$

Where C_i and C_e are the initial and equilibrium liquid phase concentration of Cu(II) respectively, V is the volume of the solution (L) and M is the weight of the polymer used (g). the copper percent removal (R%) was calculated using the following equation:

$$R\%= (C_i - C_e /C_i) \ 100 \tag{2}$$

3. Results and Discussion

3.1 Characterization of PFA

Poly(furfural-acetone) was prepared according to literature (Patel, 1983). The final Structure of the polymer is formed through the following mechanism (Patel, 1983):

PFA
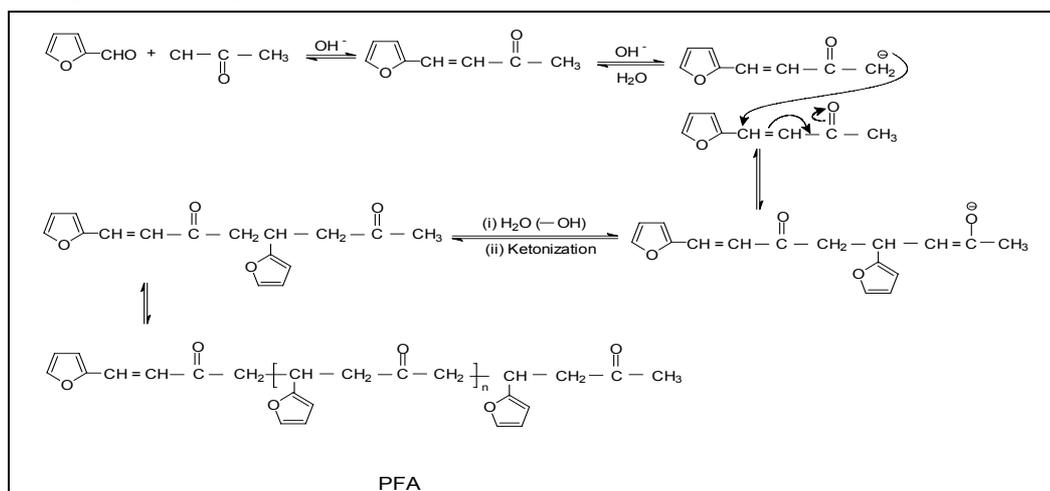
PFA was a yellow powder, soluble in acetone, dioxane and ethyl methyl ketone, softening point 160-173°C.The intrinsic viscosity of PFA in acetone was $3.6*10^{-2}$ dl.g^{-1}. The number average molecular weight was determined by conductometric titration in nonaqueous medium and was 1500 . Figure1 represent the FTIR spectrum of PFA, The characteristic bands observed at 3116 and 3125 cm^{-1} are attributed to C-H streching vibration of furan ring.

The band of 2923.88 cm^{-1} are attributed to C-H stretching vibration of CH$_3$ and /or-CH$_2$-. There are two types of carbonyl groups in the proposed structured of PFA, one is conjugated which has lower vibration, observed at 1666.38 cm^{-1} and normal C=O band at 1712.67 cm^{-1}. The ethylenic linkage is observed at 1604.66 cm^{-1}, while the α-olefinic carbon of substituted furan are observed at 1504.37 and 1357.79 cm^{-1}. Thus the observed spectral characteristics are explicable on the basis of the structure proposed by PFA.

3.2 Effect of pH

The effect of pH (4.0 to 8.0) on removal of Cu(II) was studied. It was observed that maximum percentage of Cu(II) removal was at pH 6 by using 2 g/L of PFA and

10 ppm of Cu(II) concentration at 20 °C, the maximum removal efficiency was 96%. Figure 2 represent the effect of pH of the solution on the adsorption of Cu(II) onto PFA. The electrostatic attraction between positive charges of Cu(II) and lone pair of electrons on the oxygen atoms of carbonyl groups and furan rings could be the main attribution for such process at neutral solution.

3.3 Adsorption kinetic study

Four kinetics models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process. Table1 shows the final kinetic equations used in this study. Where, q_e and q_t refer to the amount of Cu adsorbed (mg.g^{-1}) at equilibrium and at any time, t(min), respectively, k_1, and k_2 are the first and second order equilibrium rate constants respectively, h is initial adsorption rate in the pseudo-second order kinetic, α is the initial adsorption rate(mg.g^{-1}) in the Elovich kinetic model, and β is the desorption constant (g.mg^{-1}) related to the extent of surface coverage and activation energy for chemisorption, K_{dif} (mg.g^{-1} min^{-1}) is the intraparticle diffution rate constant and B_L is related to the thickness of the boundary layer, the layer separate between the liquid phase and the solid phase (adsorbent). From application of the **first-order** kinetic equation for the adsorption of Cu(II) onto PFA, a straight line was obtained, with correlation coefficient of 0.9951, nevertheless, the rate of removal of copper onto PFA does not follow the pseudo-first order equation due to the big difference between experimental q_e (q_{exp}) and calculated q_e (q_{cal}), Table 2.

When the experimental data were applied to the **pseudo-second-order** rate equation, a straight line was obtained with correlation coefficient of 1.00 figure 3, and the value of q_e(cal) in well agreement with the $q_e(_{exp})$ table 2, indicating that the rate of removal of copper onto PFA follow the pseudo-second-order equation. The high value of the initial adsorption rate, h=14.168 mg.g^{-1} min^{-1} table 2 indicate that the most of Cu(II) adsorbed at the beginning of the process, where more than 94% adsorbed at the first 5 minutes. When, the **Elovich** kinetic model was applied to the experimental data, where, the q_t was plot versus ln(t) a straight line was obtained with correlation coefficient of 0.97971, fig.4, confirms that the Elovich model also applicable, the kinetic parameter are listed in table 2. The **intraparticle** diffusion is another kinetic model to study the rate-determining step for Cu(II) removal by PFA . If intraparticle diffusion occurs, then plot of q_t vs. $t^{1/2}$ will be linear and the line will pass through the origin, if the intra-particle diffusion was the only rate limiting parameter controlling the process. Otherwise, some other mechanism is also involved. Fig.5 present intraparticle plot for Cu(II) removal by PFA the correlation coefficient was, 0.9475, indicates the applicable of intraparticle diffusion, but the large value of B_L 4.688 indicates a large thickness of boundary layer, which mean, a decrease in the chance of external mass transfer and the chance of internal mass transfer, this attribution is confirmed by low value of K_{diff}, 0.022 mg.g^{-1} min-$^{1/2}$. So, the second order kinetic mainly controls the sorption rate.

4. Adsorprion thermodynamics

The change in Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for the adsorption process was obtained using the following equation (Arivoli, 2008; Edwin, 2008; Arivoli, 2008; Edwin, 2008; El Nemr, 2007):

$$[Cu]_{liquid} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [Cu]_{solid}$$
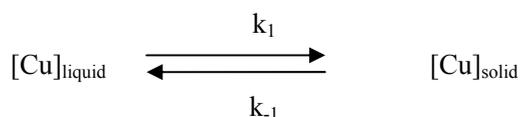
$$K_o = \frac{[Cu]_{solid}}{[Cu]_{liquid}} \tag{3}$$

$$\Delta G^o = -RTLnK_o \tag{4}$$

$$LogK_o = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \tag{5}$$

Where K_o is the equilibrium constant, $[Cu]_{solid}$ is the concentration of Cu, ppm, at the solid phase at equilibrium, $[Cu]_{liquid}$ is the liquid phase concentration of copper, ppm, T is the temperature(K) and R is the ideal gas constant (8.314 J mol^{-1} K^{-1}). The enthalpy change ($\Delta H°$) and the entropy change ($\Delta S°$) are calculated from plot of logK$_o$ versus 1/T Fig. 6. The results of these thermodynamic calculation are shown in Table 3.

The Gibbs free energy indicate the spontaneity of the adsorption process, where higher negative values a more energetically favorable adsorption process. The calculation of $\Delta G°$ values at different pH, Table 4 gave an indication that at pH 6, the adsorption of Cu(II) onto PFA is more preferable due to the highest negative value of $\Delta G°$. The positive $\Delta G°$ value obtained at pH 4, table 4, indicate a decrease in adsorption process at pH 4. The study confirm that as the pH of the system increase, the adsorption of Cu(II) increases and reach the optimum at pH 6, which involve higher negative value of $\Delta G°$. The negative values of the Gibbs free energy show the removal process of copper by PFA is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature for all concentrations of Cu(II)table3.The overall process seems to be endothermic (ΔH^o =12.48, 2.425, 4.6 and 2.27 KJ mol^{-1}), moreover, the $\Delta H°$ values lie in the range of physisorption process, table 3. Table 3 also shows that the ΔS^o values were positive (i.e that entropy increases as a result of the removal process of copper). This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of ΔS^o and randomness will increase at the solid-solution interface during the process of adsorption (Argun, 2007). Adsorption is thus likely to occur spontaneously at normal and high temperatures because $\Delta H>0$ and $\Delta S>0$.

The other parameters which can be estimated from the experimental data are, the activation energy Ea and sticking probability S*, which they can give further support for the assertion of physical adsorption in the studied case. They were calculated using modified Arrhenius type equation related to surface coverage (θ) as follows (Amin, 2009; Najim, 2009).

$$\theta = \left[1 - \frac{C_e}{C_i}\right] \qquad or \frac{C_e}{C_i} = 1 - \theta \qquad \text{.......(6)}$$

$$S* = (1 - \theta)e^{\frac{-Ea}{RT}} \qquad \text{.......(7)}$$

$$\ln S* = \ln(1 - \theta) - \frac{E_a}{RT} \qquad \text{.........(8)}$$

$$\ln(1 - \theta) = \ln S* + \frac{E_a}{RT} \qquad \text{.........(9)}$$

The sticking probability S*, is a function of the adsorbate/adsorbent system under investigation, its value lies in the range $0<S*<1$ for preferable process, and is dependent on the temperature of the system (Amin,2009; Najim, 2009). The values of Ea and S* can be calculated from slope and intercept of the plot of ln(1-θ) versus 1/T respectively, figure 7 and table 5. The values of Ea, table5, found to be 10.796, 1.7, 2.694 and 1.193 KJ mol^{-1} were consistent with the values of $\Delta H°$,table3, both are positive, indicate the endothermic nature of the adsorption process and the values lie in the range of physical adsorption. Ea values almost decreases with increasing temperature, that indicate the preferable process at higher temperature, which is in agreement with the values of $\Delta G°$ Table3. The values of sticking probability are less than one, table 5, which indicate that the probability of Cu(II) ions to stick on surface of PFA is high as S*<1 these values confirm that, the sorption process is physisorption.

5. Conclusion

The present study indicates that the new adsorbent is effective for the removal of copper from aqueous solution. The lone pair of electrons on the oxygen atoms of carbonyl groups and furan rings may be the main chelating positions for removal of copper from aqueous solution. The adsorption process is highly dependent on pH, the maximum removal of copper was obtained at pH 6. The experimental data fit well with the second-order kinetic. The values of $\Delta H°$ and E_a were both positive and lie in the range of physisorption.

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Table 1. Kinetic equations used in this study

Kinetic models	Kinetic equation	Reference
Pseudo first- order	$Log\,(q_e - q_t) = Log\,q_e - \dfrac{k_1}{2.303}(t)$	(Lagergren, 1898)
Pseudo-second- order	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^2} + \dfrac{1}{q_e}(t)$ $h = k_2 q_e^2$	(Mckay, 1999)
Elovich kinetic model	$q_t = \dfrac{1}{\beta}\ln(\alpha\beta) + \dfrac{1}{\beta}\ln(t)$	(Chien, 1980)
Intra.Particle diffusion	$q_t = K_{dif}\, t^{\frac{1}{2}} + B_L$	(Weber, 1963)

Table 2. Parameter obtained from Pseudo-first-order, Pseudo-second-order, Elovich and Intraparticle diffusion kinetic models for the adsorption of Cu(II) onto PFA, 2g/L at pH 6 and 20°C

Pseudo-first-order				Pseudo-second-order				Elovich		
k_1	$q_{(exp)}$	$q_{(cal)}$	R^2	k_2	$q_{e(cal)}$	h	R^2	α	β	R^2
0.034	4.888	0.1842	0.9951	0.592	4.892	14.168	1.00	1.003	17.54	0.9797

Intraparticle diffusion		
K_{diff}	B_L	R^2
0.022	4.688	0.9475

Table 3. Thermodynamic parameter for the removal of Cu(II) by PFA, 2g /L

Cu(II) Conc ppm	$\Delta H°$ KJ mol^{-1}	$\Delta S°$ Jmol^{-1}K^{-1}	$\Delta G°$ KJ mol^{-1}				R^2
			15 °C	25 °C	35 °C	45 °C	
20	12.48	56.51	-3.729	-4.145	-4.382	-5.679	0.9963
30	2.425	14.96	-2.398	-2.178	-1.931	-2.013	0.9165
40	4.6	18.07	-0.551	-0.823	-0.988	-1.208	0.9952
50	2.27	8.38	-0.123	-0.306	-0.349	-0.421	0.9982

Table 4. Thermodynamic parameter for the adsorption of Cu(II),10 ppm, by PFA 2g/L temperature 20 °C, at different pH

pH	Ce	Ca	Ca/Ce	Ln K_o	$\Delta G°$ KJmol^{-1}
4	5.135	4.865	0.9474	-0.054	0.1315
5	3.292	6.708	2.0377	0.7118	-1.734
6	0.382	9.618	25.178	3.226	-7.858
7	0.402	9.598	23.876	3.173	-7.729
8	0.462	9.538	20.775	3.034	-7.391

Table 5. Sticking probability and activation energy for the adsorption of Cu(II) onto PFA

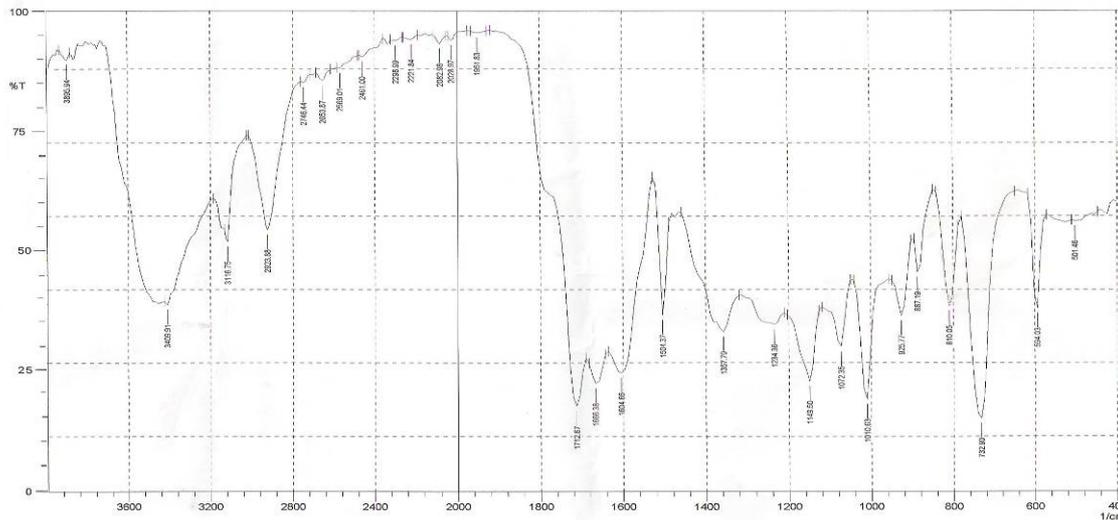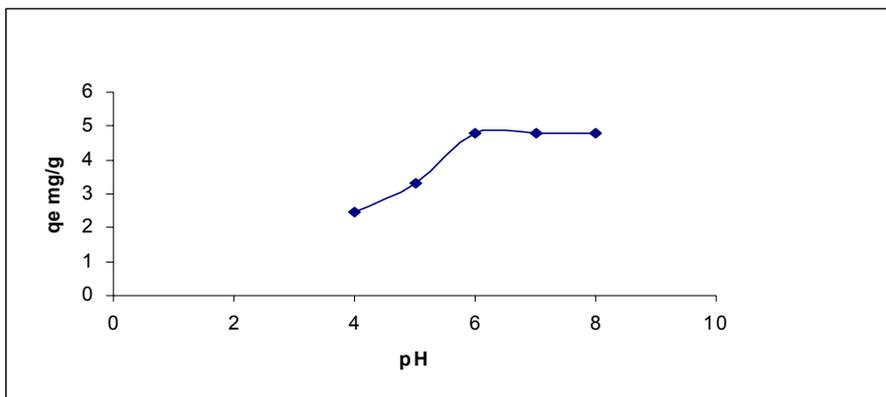| Cu(II) conc.ppm	Ea KJ mol^{-1}	S*	R^2
20	10.796	0.0019	0.996
30	1.700	0.154	0.9138
40	2.694	0.143	0.9936
50	1.193	0.295	0.9988

Figure 1. FTIR spectrum of PFA

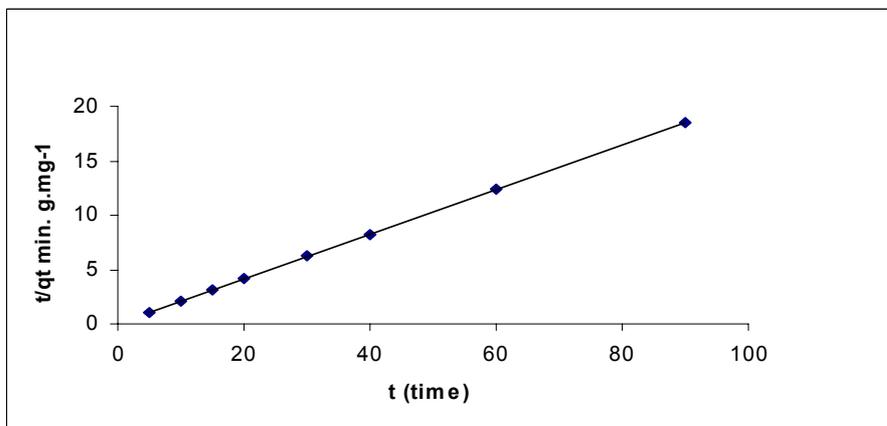Figure 2. Effect of pH on the adsorption of Cu(II) on to PFA

Figure 3. Pseudo-Second-order kinetic for removal of Cu(II) onto PFA at 20 ºC
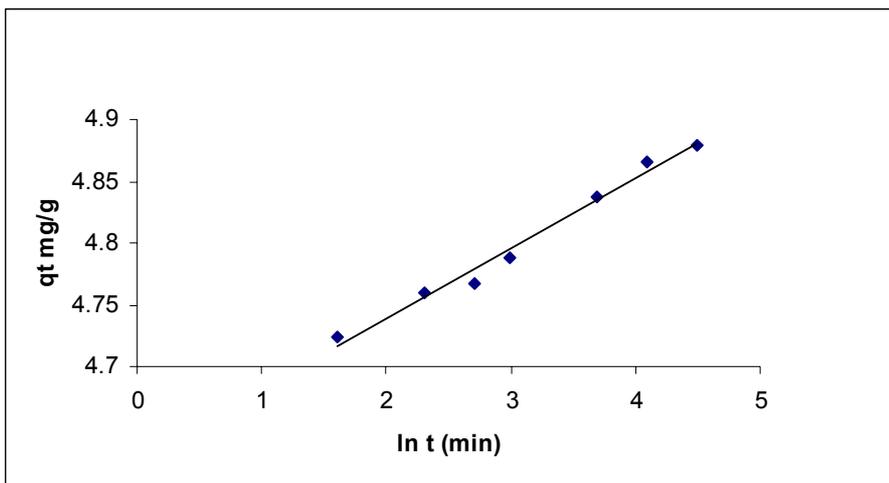
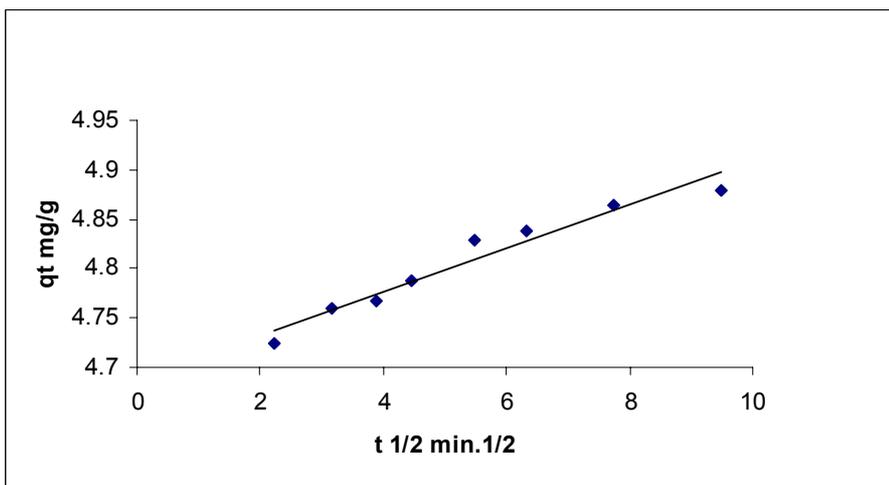Figure 4. Elovich model plot for removal of Cu(II) onto PFA at 20 ºC

Figure 5. Intraparticle diffusion plot for the removal of Cu(II), 10 ppm, at 20 °C, pH 6.0 by PFA 2 g/L
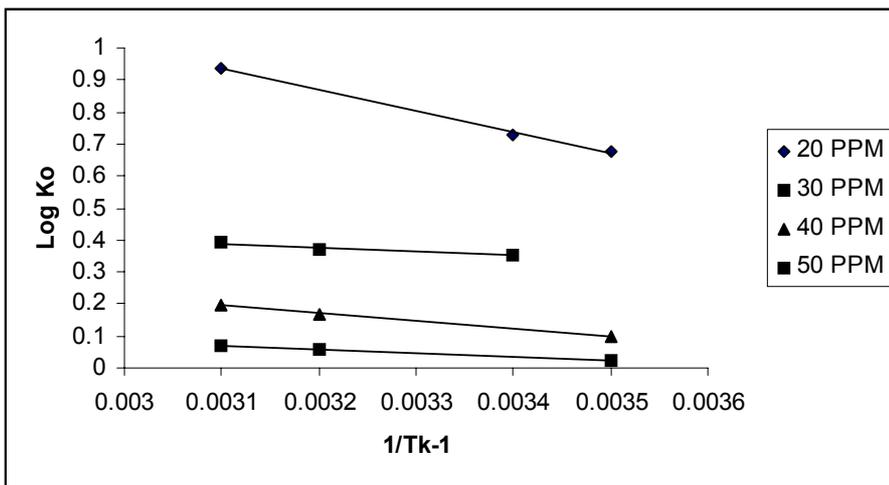

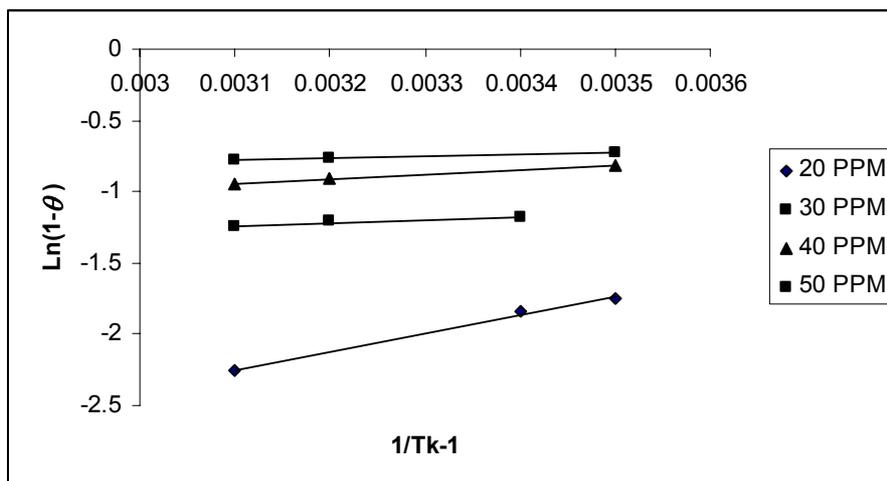Figure 6. Plot of log K_o vs 1/T for the removal of Cu(II) by PFA, 2g/L

Figure 7. Plot of ln (1-θ) vs. reciprocal of temperature for the adsorption of Cu (II) onto PFA