

Poly (furfural-acetone) as New Adsorbent for Removal of Cu(II) from Aqueous Solution: Equilibrium Study

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Abstract: The batch removal of Cu(II) from aqueous solution using poly (furfural-acetone), (PFA) as adsorbent was investigated in this study. The influences of initial Cu(II) ion concentration (10 to 120 ppm), pH (4-8) and contact time have been reported. Adsorption of Cu(II) is highly pH-dependent and the result indicate that the optimum pH for the removal was found to be 6. At this pH a small amount of PFA, 2 g/L, could remove as much as 97% of Cu(II) from a solution of initial concentration 10 ppm. It was observed that an increase in initial concentration of Cu(II) leads to decrease in percent removal of Cu(II) and increase in amount of Cu(II) adsorbed per unit mass of PFA. The adsorption process of Cu(II) is tested with four isotherm models, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R). It was found that all models were applicable and the maximum adsorption capacity was found to be 13.66 mg/g. From the isotherm constants it was confirmed that, the sorption process was physisorption.

Keywords: Poly (furfural -acetone), Adsorption, Isotherm models, Copper(II).

Introduction

The removal of heavy metal ions from aqueous solution, either for pollution control or for raw material recovery, have been taking an increasing importance in recent years. Metal ions are non-biodegradable in nature and therefore, their intake in certain level are toxic¹. For example, copper is both vital and toxic for many biological systems². Recently, several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups which act as chelating groups in binding poly valent metal ions³. The chelate forming polymeric ligands are characterized by reactive functional groups containing O, N, S and P donor atoms and capable of coordinating to different metal ions have been extensively studied⁴⁻¹⁰. The materials most often show preferential selectivity towards certain metal ions from aqueous solutions.

In addition to metal recovery from dilute solutions in waste water treatment, chelating polymers have attracted more interest, due to their application as protective coating on metal surfaces or as priming layers, paper coatings, fibre and fabrics, selective binding of enzymes¹¹⁻¹². Since metals in waste water will not be degraded, accumulation and distribution of these metals to our environment occur, which is of concern to the public. Treatment methods such as chemical precipitation, electrodeposition, ion exchange, membrane separation and adsorption have been applied.

Adsorption techniques, especially those using chelating resin, have been widely demonstrated and promoted as being feasible technology. Biopolymers, such as, chitosan was effectively used for removing some of toxic metals¹³. The aim of the present study was to explore the possibility using of poly(furfural–acetone) for removing of copper from polluted water. The influence of various factors, such as, initial pH, temperature and initial metal ion concentrations on the sorption capacity were studied, also for determination of isotherm constants especially the maximum adsorption capacity.

Experimental

Preparation of poly (furfural–acetone)

The poly (furfural - acetone) was prepared by direct polymerization of furfural and acetone in the presence of aqueous alkali solution¹⁴. Thus, a mixture of furfural (9.6 g, 0.1 mol), acetone (11.6 g, 0.2 mol) and aqueous solution of sodium hydroxide (50% w/v, 50 mL) was kept at room temperature for 1 hour and then at 65 °C for 30 minutes. It was then refluxed at 80 °C for 2 hours, the reaction mixture was poured into 250 mL of distilled water, the yellow precipitate was separated out by filtration. The product was washed with distilled water and aqueous ethanol (50%) many times to get rid off sodium hydroxide. The polymer was dissolved in acetone and was reprecipitated by pouring with rapid stirring into water. Then filtered and dried at 60 °C.

Preparation of copper(II) solution and analysis

A stock solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 500 ppm, was obtained by dissolving 1.9005 g of $\text{Cu}(\text{NO}_3)_2$ in 1 L of deionized water, this solution was used for further experimental solution preparation. The pH values were adjusted with 0.1 M HNO_3 or 0.1 M NaOH. Analytical grade reagents were used through out this study. The pH values of Cu(II) solution were measured by pH meter type HANA, 301 instruments. The residual Cu(II) in the sorption solution was determined by atomic absorption spectrophotometer type (Analyst 200 Perkin Elmer) .

Batch adsorption studies

Effect of pH

The initial pH values were adjusted to 4.0, 5.0, 6.0, 7.0 and 8.0 with 0.1 HNO_3 and 0.1 NaOH. The effect of pH on the adsorption of Cu(II) onto poly (Furfural-acetone) were determined using 0.1 g (2 g/ L) of adsorbent in 50 mL of Cu(II) solution of 10 ppm at 20 °C, shaking was carried using horizontal thermostat shaker model LSB – 015 S, 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 wattman filter paper no. 40, the filtrate was analysed for residual copper concentration.

Effect of initial concentration

The variation of initial concentration of copper were done at solution pH 6.0 by mixing 0.1 g of poly (furfural-acetone) with 50 mL of copper solution, agitated at 20 °C and 140 rpm for 120 minutes.

Adsorption isotherm

Adsorption isotherm experiments were carried out at different temperature (15, 25, 35, 45 °C) by shaking the poly (furfural – acetone) 0.1 g with 50 mL of Cu(II) 20, 30, 40, 50 ppm solution for 120 minutes, at pH 6.0. The amount of Cu(II) adsorbed on to the polymer, q_e mg/g, was calculated using the following equation :

$$q_e = \frac{(C_i - C_e)V}{M} \quad (1)$$

Were C_i and C_e are the initial and equilibrium liquid phase concentration (ppm) 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:

$$R\% = \frac{C_i - C_e}{C_i} \times 100. \quad (2)$$

Results and Discussion*Preparation and characterization of PFA*

The poly (furfural-acetone) PFA was prepared by direct polymerization of furfural with acetone in presence of aqueous alkali. The propagation steps in the poly condensation comprise mostly repeated Michael type reactions¹⁴. The mechanism of poly condensation of furfural with acetone in presence of aqueous alkali can be written as follows¹⁴.

The PFA was a yellow powder, soluble in acetone, dioxane and ethyl methyl ketone, Softening point, 160-173 °C. In the FTIR spectrum of PFA Figure 1, characteristic bands are observed at 3119 and 3125 cm^{-1} are attributed to C-H stretching of the furan ring and the bands at 2926.11 and 28801 cm^{-1} are attributed to C-H stretching vibration of CH_3 and /or $-\text{CH}_2-$. There are two types carbonyl groups in the proposed structure of PFA, one is conjugated which has lower vibration, observed at 1658.841 cm^{-1} and normal C = O band at 1718.77 cm^{-1} . The ethylenic linkage is observed at 1605 cm^{-1} , while the α -olefinic carbon substituted furan are observed at 1556.61, 1504 and 1390 cm^{-1} . Thus the observed spectral characteristics are explicable on the basis of the structure proposed for PFA

Effect of pH on copper(II) adsorption

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution¹⁵. Figure 2 represents the effect of initial pH of the solution on the adsorption of Cu(II) onto poly (furfural-acetone). The optimum pH was found to be pH 6, using 10 ppm initial Cu(II) concentration and 2 g/L polymer concentration. The maximum removal efficiency was 96%. The electrostatic attraction between positive charges of Cu(II) and lone pairs of electrons on the oxygen atoms of carbonyl groups and furan rings could be the main attribution for such process at neutral solution. At pH values higher than 6.0 insoluble copper hydroxide start precipitating from the solutions making true sorption studies impossible¹⁶.

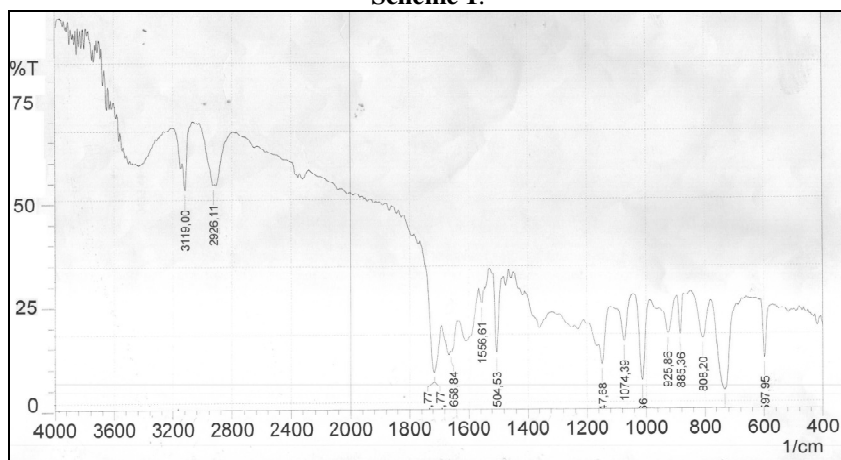
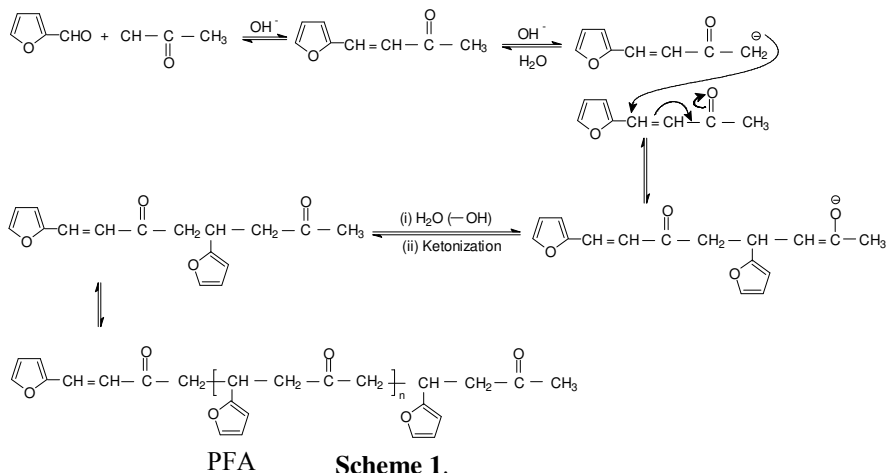


Figure 1. FTIR spectrum of poly (furfural-acetone).

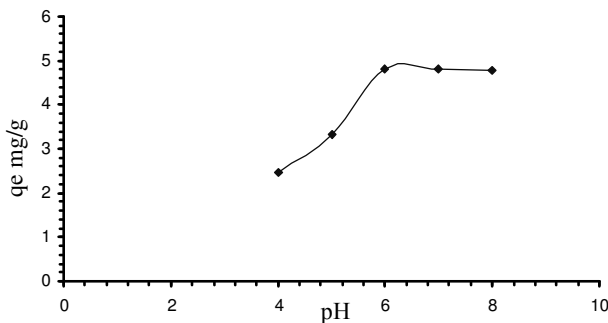


Figure 2. Effect of pH on the adsorption of Cu(II) on to PFA .

Effect of contact time and initial copper(II) concentration

Effect of contact time for the removal of copper(II) by PFA at 2 g / L of PFA is shown in Figure 3. There was a rapid adsorption of copper(II) in the first 5 minutes, Thereafter very little change in the rate of adsorption occurred Figure 4. At the first 5 minutes the R% was 94.48%, the maximum removal was 97.75% at 120 minutes.

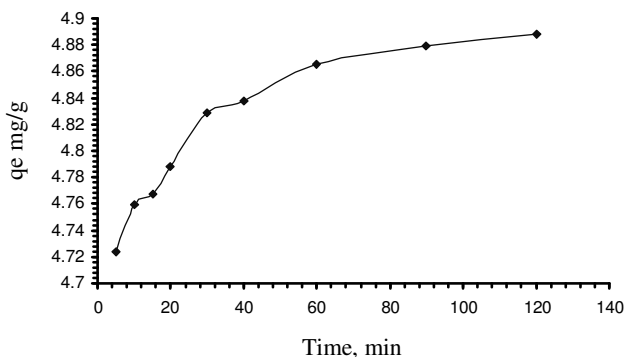


Figure 3. Effect of contact time on the adsorption of Cu(II) onto PFA .

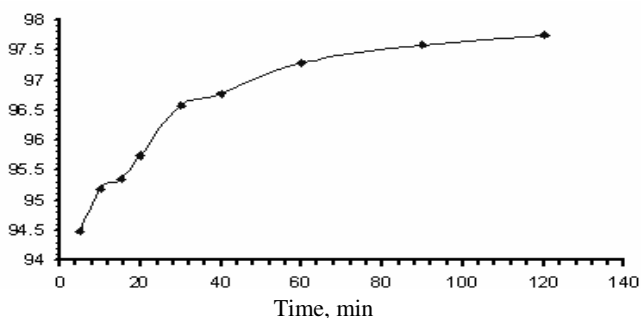


Figure 4. Effect of contact time on the percent removal of Cu(II) onto PFA.

Effect of initial copper(II) concentration on adsorption was investigated at concentration ranging from 10 to 120 ppm as shown in Figure 5. By increasing the initial Cu(II) concentration the percentage of copper removal decreased, that was decreased from 96.9% at 10 ppm of Cu(II) to 42.3% at 120 ppm. Whereas, the actual amount of Cu(II) adsorbed per unit mass of PFA increased with the increase in initial Cu(II) concentration. This increase is due to the decrease in resistance to the uptake of solute from aqueous solution. As the initial concentration provides an important driving force to overcome the mass transfer resistance of copper between the aqueous and solid phases. The same trends was also found by other researcher¹⁷.

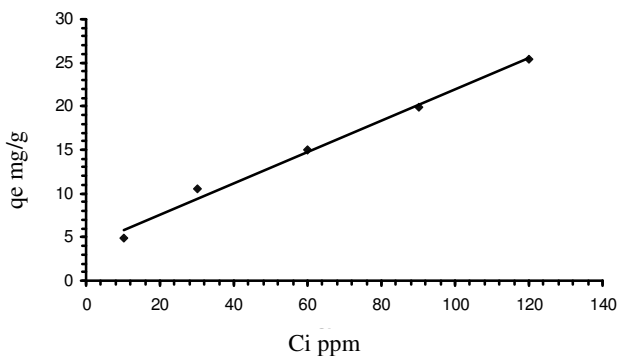


Figure 5. Effect of initial copper concentration on q_e .

Adsorption equilibrium study

Equilibrium data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems. In order to discover capacity of PFA, the experimental data points were fitted to the langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm equations Table 1. The constant parameters of the isotherm equations were calculated. The linear equations of the four isotherm models listed in Table 1.

The langmuir equation, which is valid for monolayer adsorption onto a completely homogenous surface with a finite number of identical sites and with negligible interaction between adsorbed molecules, is shown in the linear from Table 1. K_L is the langmuir adsorption constant ($L\ mg^{-1}$) and Q_m is the theoretical maximum adsorption capacity ($mg\ g^{-1}$). Figure 6 shows a plot of $\frac{1}{q_e} \text{ vs } \frac{1}{C_e}$ for adsorption of Cu(II) on to PFA. The values of

langmuir isotherm constants and correlation coefficient are presented in Table 2. The correlatin coefficients of the isotherm were found to be linear over the whole concentration except at 45 °C where it is some what lower. The values of Q_m increase with temperature increase, thereby confirming that the process is endothermic²². The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of sorption over the surface, the linear form is presented in Table 1. Where K_F ($L\ mg^{-1}$) and n are isotherm constants indicate the capacity and intensity of the adsorption, respectively.

The linear plot of $\log q_e$ versus $\log C_e$ at each temperature indicates that adsorption of Cu(II) also follows Freundlich equation Figure 7. The Freundlich constants and corr. Coefficients are listed in Table

Table 1 . The linear equations of isotherm models.

Isotherm mode	Linear equation	Reference
Langmuir	$\frac{1}{q_e} = \left(\frac{1}{K_L Q_m} \right) \frac{1}{C_e} + \frac{1}{Q_m}$	18
Freundlich	$\text{Log } q_e = \log K_F + \frac{1}{n} \log C_e$	19
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$ $B_T = RT / b_T$	20
Dubinin – Radushkevich (D-R)	$\ln q_e = \ln Q_m - K_{D-R} \varepsilon^2$ $\varepsilon = R T \ln \left(1 + \frac{1}{C_e} \right)$ $E = \frac{1}{\sqrt{2K_{D-R}}}$	21

The values of $\frac{1}{n}$ was found to lie between zero and one, indicating that the Cu(II) is favorably adsorbed by PFA at all studied temperatures²³. On the other hand, all values of n are higher than one indicating a physisorption mechanism²⁴.

The relative adsorption capacity K_F increase with temperature increase confirming that the process in endothermic²². Heat of adsorption and the adsorbent – adsorbate interaction on adsorption isotherm were studied by Tempkin, the linear equation is presented in Table 1. Where T is the absolute temperature (K) and R is the universal gas constant, $8.314\ J\ mol^{-1}\ K^{-1}$.

The constant B_T is related to heat of adsorption ; A_T is the equilibrium binding constant ($l \text{ min}^{-1}$) corresponding to maximum binding energy^{25,26}. A plot of q_e vs. $\ln C_e$ at studied temperatures is given in Figure 8. The constants obtained from Tempkin isotherm are shown in Table 2. The Tempkin constant, B_T , Shows that the heat of adsorption increases with the increase in temperature, except at 45 °C, indicating endothermic adsorption. On the other hand, the maximum binding energy A_T increases with temperature increase, if we exclude it's value at 15 °C, that confirm the process is preferable at higher temperatures .

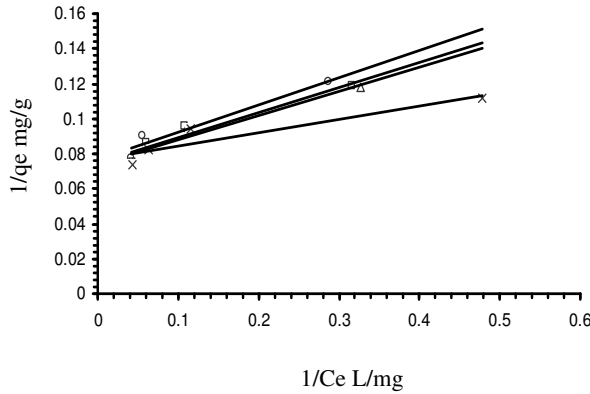


Figure 6. Langmuir plot for the adsorption of Cu(II) onto PFA, 2 g/L, at different temperature pH 6 contact time 2.

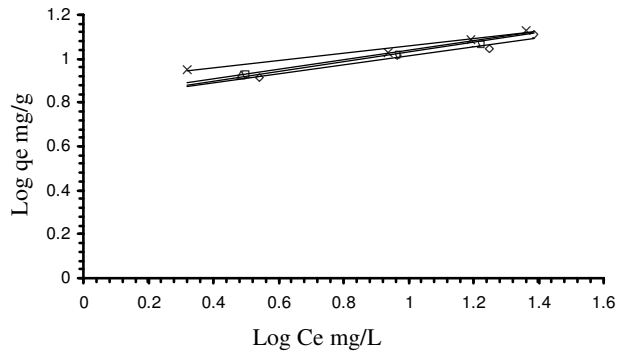


Figure 7. Freundlich plot for the adsorption of Cu(II) onto PFA, 2g/L, at different temperatures

Dubinin-Radushkevich (D-R) isotherm is another isotherm equation, Table 1. they assumed that the characteristics of the sorption curves are related to the porosity of the adsorbent. The final linear form was given in Table 1. Where K_{D-R} is related to the adsorption energy and Q_m the maximum adsorption capacity, ϵ is the polanyi potential and E is the mean energy of sorption . From plot of $\ln q_e$ versus ϵ^2 , the D-R constants and mean energy of adsorption can be calculated Figure 9, and Table 2. The mean adsorption energy values were in the range of physical adsorption reactions. Although the correlation coefficients of D-R plots are a little bit lower than that of Langmuir plots, but the Q_m of both isotherm are almost identical, Table 2. Once again Q_m values are increases with temperature increase, confirming the endothermic process²². From Q_m values it is observed the Langmuir and D-R isotherm are both applicable.

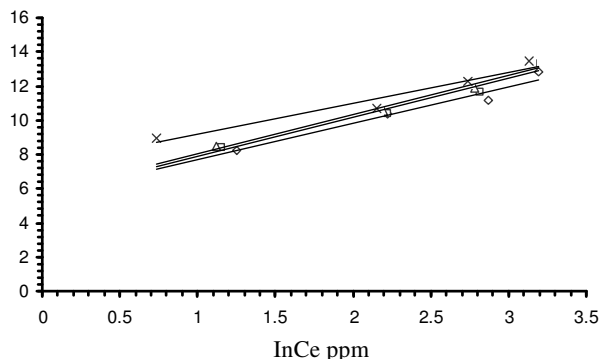


Figure 8. Tempkin plot for the adsorption of Cu(II) on to PFA, 2g/L, at different temperatures.

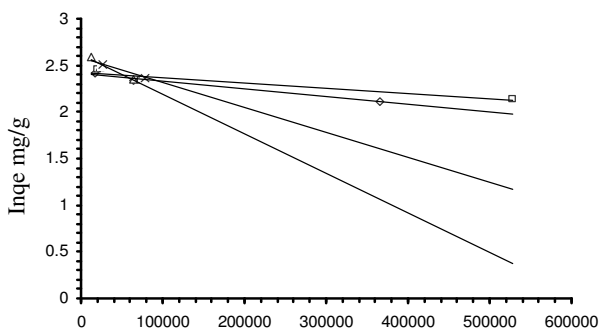


Figure 9. D-R plot for the adsorption of Cu(II) onto PFA 2g/L at different temperatures.

Table 2. Equilibrium parameters and correlation coefficients calculated for various adsorption models at different temperatures for adsorption of Cu(II) on to PFA.

Isotherm model	Temperature, °C			
	15	25	35	45
Langmuir				
Q_m , mg/g	12.97	13.316	13.46	12.94
K_L	0.495	0.524	0.539	1.025
R^2	0.9467	0.928	0.9423	0.8683
Freundlich				
K_F	6.366	6.482	6.583	7.78
n	4.75	4.59	4.58	6.00
R^2	0.9683	0.9832	0.9935	0.9701
Tempkin				
A_T	12.99	11.587	11.728	56.98
B_T	2.1515	2.2842	2.3168	1.8192
R^2	0.9531	0.9617	0.9772	0.9464
D – R				
Q_m , mg/g	11.80	12.053	13.663	13.75
K_{D-R} , $J^{-2} mol^{-2}$	1.00×10^{-6}	0.7×10^{-6}	4×10^{-6}	3×10^{-6}
E_a , $kJmol^{-1}$	0.707	0.845	0.354	0.408
R^2	0.8596	0.8156	0.9175	0.9594

Conclusion

The PFA has been identified as an effective adsorbent for removal of Cu(II) at low concentrations. The adsorption process is pH dependent and the optimum pH was 6.0. The isotherm equilibrium studies confirmed that the four models were Applicable and the highest Q_m was 13.66 mg/g. From the values of isotherm constants it was confirmed that the process was endothermic and the mechanism of the reaction was physisorption.

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