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Research Article

ADSORPTION STUDIES OF COPPER (II) IONS USING ACTIVATED CARBON PREPARED FROM *DELONIX REGIA* PODS

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ABSTRACT

The activated carbon produced from *Delonix regia* pods was chemically activated using Potassium hydroxide (PHAC) and utilized as an adsorbent for the removal of Cu(II) from aqueous solution. Adsorption experiments were carried out in a batch process and various experimental parameters such as effect of contact time, initial metal ion concentration, carbon dosage, and pH on percentage removal have been studied. The adsorption process of Cu(II) ions onto PHAC is in good agreement with the Frendlich and Langmuir adsorption isotherm and follows the pseudo-second-order kinetic model. Furthermore, thermodynamics parameters were investigated. The negative ΔG° value reveal the Cu(II) adsorption on PHAC is favourable. The positive value of ΔH° indicates endothermic process and positive value of ΔS° indicate spontaneous nature of adsorption.

Keywords: Activated carbon; Adsorption; Kinetics, Cu(II) removal, Thermodynamics.

1. INTRODUCTION

Heavy metals are non-biodegradable, being easily accumulated in human body. These can cause serious illnesses, such as cancer, damage to the nervous system, respiratory problem, kidney failure, and causing death at high concentrations [1, 2]. For this reason, the pollution of water due to the presence of heavy metals is a major concern today world-wide. Each year large, volumes of wastewater are produced from different industrial sectors, such as mining, metallurgy and smelting, among others. The most common heavy metals present in wastewaters are nickel, zinc, lead, iron, copper, arsenic, cadmium, and uranium [3, 4]. Among these, cooper is considered a harmful metal [5]. There are three forms of copper: Cu^0 metal, Cu^+ cuprous ion, and Cu^{2+} cupric ion, this last form normally appearing in the environment and considered to be the most toxic of the three [6,7]. The main contributors of copper to the environment are mining industries, printing circuits, electroplating industries, paints, fertilizers, plastics and etching, etc. [8-10]. Certain industries that release wastewater into the environment have reported Cu^{2+} concentrations ranging from 2.0 $mg \cdot L^{-1}$ to 900 $mg \cdot L^{-1}$ [11]. Therefore, the recovery of copper, is a subject of great social relevance due to the environmental and economic benefits of eliminating contaminates from industrial effluents. Adsorption is one of the most popular methods for eliminating heavy metals [12]. It is a technology in which the pollutants, particularly in the case of heavy metals, can interact in a physical or chemical way with the active elements of the adsorbent. Adsorption is a technique that is easy to use and design, and it does not produce contaminants [13]. Moreover, another advantage of the adsorption process is the possibility to regenerate the adsorbent by desorption, being therefore a reversible technique, so it is considered a technology that is not aggressive with the environment. These advantages have made adsorption a leading method for wastewater treatment [14]. Different types of adsorbent have been developed, such as active carbon, clay ore, chelating materials, natural chitosan/zeolites, etc. [12, 15, 16].

Delonix regia (Flamboyant) tree plantation is grown around the world for ornamental reasons, preserving the soil and also conserving the environment. Apart from these benefits, the tree produces pods in large quantities, which would be of benefit to the environment as well as the scientific community in the search for cheaper adsorbent materials. There are many factors that influence heavy metal adsorption efficiency, such as initial metal concentration, temperature, sorbate amount, pH, and contact time [13, 16]. Therefore, the objective of this research was to determine the effects of various experimental variables on Cu^{2+}- *Delonix regia* activated carbon adsorption systems. Furthermore, kinetic mechanisms, adsorption isotherms models and thermo-dynamics parameters were investigated.

2. MATERIAL AND METHODS

2.1. Prepartion of activated carbon

The air dried *Delonix regia* pods were cut into small portions and crushed in a pulveriser. About 20 g of the crushed pods was mixed with 75 mL of KOH solution of desired concentration (10, 20 and 30 %). The slurry was retained at room temperature for 24 hours, to ensure the access of the KOH to the *Delonix regia* pods. Then the slurry was exposed to microwave heating of pre-determined power (850 watts) for predetermined duration (12 minutes). Carbon obtained from the above process was washed with 0.5 M HCl followed with warm distilled water and ice cold distilled water until the pH reached 7. Then the carbon was sieved and desiccated at 423 K and kept in desiccators for further studies. The prepared activated designated as Potassium Hydroxide Activated Carbon (PHAC).

2.2. Preparation of adsorbate

A standard solution of Cr (VI) was prepared (1000 mg/L) by dissolving 2.828 g Potassium dichromate salt, $K_2Cr_2O_7$ in one litre of distilled water.

2.3. Batch equilibration method

The effect of functions such as adsorbent dose, solution pH, initial concentration of adsorbate and contact time were investigated by batch technique. A 250 ml iodine flask, 50 ml and a pre-determined concentration of the metal ion solution was transferred into the container. Then the content was rotated in a cycle using a cycle for a prearranged duration of 180 min. The concentration of the centrifuge was measured after proper dilution using the Systronics Dual Beam UV-Visible Spectrometer: 2202. The effect of pH was calculated via bringing the preferred pH of the solutions by adding con. 0.1 N HCl/0.1N NaOH solution. The kinetics investigates were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120, 140, 160 and 180 minutes. Concentration of metal ion before and after adsorption was measured using a double beam UV Visible spectrophotometer. Standards for the establishing of calibration curves were prepared by weakening the stock solutions so as to have 10, 15, 20, 25 and 30 mg/L of the metal ions and the absorbance of the solution at the respective wave lengths were recorded.

2.4. Isotherm studies

The equilibrium between the two phases (liquid and solid state) is rationalized by absorption isotherm.The equilibrium data obtained from the experiments were processed with the following isotherm equations such as Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich adsorption isotherm models. Inference obtained from each isotherm was discussed in detail one by one.

2.4.1. Langmuir isotherm

This is the greatest broadly used model to describe heavy metal ion/dye sorption in adsorbent. The Langmuir reckoning narrates to the coverage of the molecules on a solid surface and the absorption of the contact solution at a relentless temperature. This isotherm is founded on the following expectations, such as limited absorption for monolayer coverage, that all surface bases are the same site with one type of adsorbate and that a molecule is capable of absorbing on a assumed site independently of its neighbouring sites. The Langmuir-isotherm is write down in the subsequent form

$$Q_e = Q_m b\, C_e / 1 + b\, C_e \ldots\ldots\ldots\ldots (1)$$

This equation is often written in linear form as [17]

$$C_e/Q_e = 1/ Q_m b + C_e / Q_m \ldots\ldots\ldots\ldots (2)$$

Qe is the solvent adsorbate in a unit weight of the adsorbent (mg / g), the equipoise attention of the solute in total solute (mg/L), Qm is the maximum monolayer absorption capacity or concentration (mg/g) and b is the absorption energy is the mutual of the concentration reaching half the concentration of the adsorbent. The linear equation is often preferred because of its ease and suitability. The important characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation

$$R_L = 1 / (1+ bC_0) \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

where C_0 is the initial concentration of the adsorbate solution. The separation factor$R_L$indicates the character of the isotherm and the nature of the adsorption process as given below;

R_L value	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The result was attained from Langmuir model for the exclusion of Cu (II) ion onto PHAC was represented in Table.

2.4.2. *Freundlich Isotherm*

The Freundlich equation is an experimental equation. This is the greatest popular model for a single solvent system based on the solvent distribution between the solid state and the aqueous phase in equilibrium.

This equation has the following form [17]:

$$\log q_e = \log K_f + 1/n \log C_e \ldots\ldots (4)$$

where qe is the quantity of adsorbate adsorbed (mg / g) in equilibrium, Ce is the symmetry attention of adsorbate in solution (mg/L), and Kf and n are constants covering all the influences that distress the absorption capacity and intensity of absorption, respectively.

2.4.3. *Tempkin isotherm*

Tempkin isotherm adopts that the temperature of sorption in the film reductions linearly with the attention due to the sorbate/sorbent interactions. Moreover, the drop in heat of absorption is not logarithmic, as stated in the Freundlich expression.

The linear form of Tempkin equation is

$$q_e = RT/b_T \ln a_T + RT/b_T \ln C_e \quad \ldots\ldots\ldots \; (5)$$

Where, b_T is the constant associated to the temperature of sorption (J/mg) and a_T the equilibrium binding constant equivalent to the maximum binding energy (L/g) The constants a_T and b_T were calculated from the slopes and intercepts of q_e versus ln C_e.

2.5. Kinetic study

Several adsorption kinetic models have been conventional to recognize the adsorption kinetics and the rate-limiting step. These include the pseudo-first and second-order rate model, the Weber and Morris sorption kinetic models.

2.5.1. *Pseudo first order kinetics*

The linearised form of the pseudo-first order equation of Lagergren is generally expressed as follows:

$$\log (q_e-q_t)=\log q_e - k_1 /2.303 \times t \; \ldots\ldots\ldots\ldots (6)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at timet respectively (mg/g). k_1 is the rate constant of pseudo first-order adsorption. The plot of log (q_e -q_t) versus t should give a linear relationship; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

2.5.2. *Pseudo second order kinetics*

The pseudo second order kinetic model (Ho equation) is represented by the following linear equation:

$$t/q_t = 1/ k_2.q_e^2 + 1/q_e \, t \; \ldots\ldots\ldots\ldots\ldots (7)$$

where, q_e and q_t are the adsorption capacity at equilibrium and at timet respectively (mg/g).

The initial adsorption rate, h (mg/(g min)), as t⟶0 can be defined as

$$h = k_2 q_e^2 \; \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

The Plot is drawn between of t/q_t and t. Theoretical adsorption capacity (q_e), and the second-order rate constants k_2 (g/(mg min)) can be determined experimentally from the slope and intercept of plots.

2.5.3. *Intra particle diffusion*

According to Weber and Morris, an inner particle distribution is defined by the co-efficient k_p equation:

$$q_t = k_p t^{1/2} + C \ldots\ldots\ldots \; (9)$$

Weber and Morris plot is drawn between q_t and $t^{1/2}$ to understand the intra particle diffusion. Where K_p ($mg/g/min^{1/2}$) is the intra particle diffusion rate constant and C is the thickness of the boundary film. The K_p and C values were obtained from the slope and intercept of the linear portions of the curves drawn between quantity adsorbed in mg/g (q_t) and the square root of time ($t^{1/2}$).

2.5.4. *Test for kinetics models*

Best fitting kinetic model for a system can be determined by using the statistical tool percentage of sum of error squares (SSE). This can be evaluated by the following formula, The sum of error squares is given as follows;

$$SSE\,(\%)= \sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2/ N} \ldots\ldots\ldots\ldots\ldots (10)$$

where N is the number of data points, (q_e)expis the experimental q_e and (q_e)calis the calculated q_e.

2.6. Thermodynamic study

To review the feasibility of the adsorption process, thermodynamic factors such as change in free energy ΔG° (kJ/mol), enthalpy ΔH° (kJ/mol) and entropy ΔS° (J/K/ mol) can be determined using the following equations [19]:

$$k_d = C_{solid} / C_{liquid} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

$$\Delta G^\circ = -RT \ln k_d \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

$$\log k_d = \Delta S^\circ / (2.303RT) - \Delta H^\circ/(2.303R)T \ldots\ldots (13)$$

where k_d is the equilibrium constant, C_{solid} is the solid phase concentration at equilibrium (mg/L), C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in Kelvin and R is the gas constant. The

Vant Hoff plots are drawn between $\ln k_d$ versus 1/T. $\Delta H°$ and $\Delta S°$ values were evaluated from the slope and intercept of the plot respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of adsorbent dosage

The adsorption of Cu (II) ion onto PHAC was studied by varying the dose of the adsorbent from 10 mg/50 mL to 50 mg/50 mL by taking 30 mg/L of the adsorbate. The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose and shown in Fig.1. This is due to the increased carbon surface area and the convenience of more adsorption sites.

3.2. Effect of contact time

The effect of adsorbate - adsorbent interaction time for the % of removal of copper (II) ion from aqueous solution was studied by taking 10 mg/L, 20 mg/L, 30 mg/L and 40 mg/L solutions as initial concentrations for the adsorbent. The effect of contact time on removal of Cu (II) ion is shown in Fig.2. According to results, an increase in contact time led to increase at surface adsorption rate to 60 min thereafter plateau is observed until equilibrium. Maximum adsorption occurred at 60 min with adsorbent dose 10.0 mg/L.

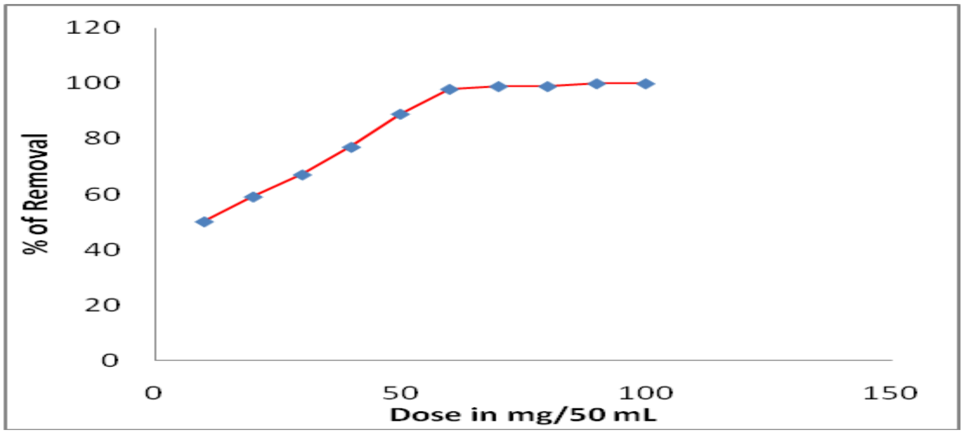

Fig.1: Effect of dose for Cu(II) ion - PHAC

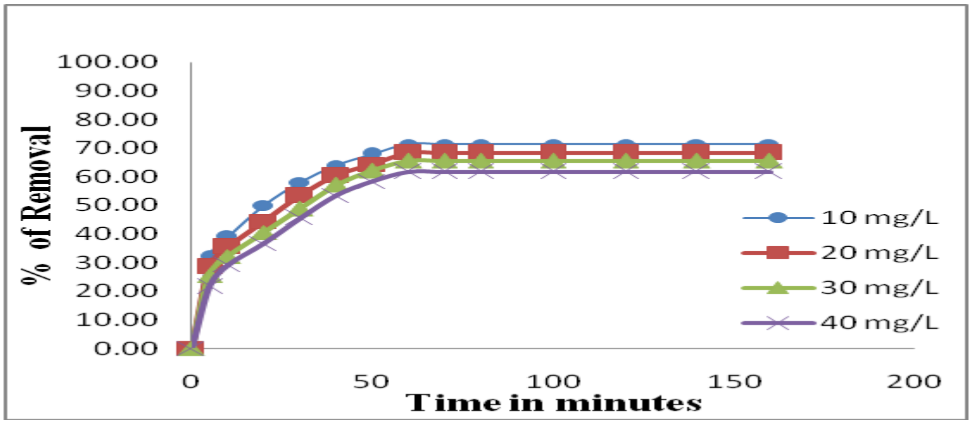

Fig.2: Effect of contact time-Cu(II) ions – PHAC

3.3. Effect of initial concentration

The quantity of Cu (II) ion adsorbed on PHAC was found to increase from 61.75 to 71.40 %, 63.25 to 74.10 %, 66.25 to 76.40 % 70.65% at the temperature 305 K, 315 K, 325 K and 335 K respectively as the initial conc. of Cu (II) ion increased from 10 to 40 mg/L. The percentage of removal and quantity adsorbed with respect to initial concentration is shown in Fig.4.

3.4. Effect of temperature

The percentage of removal improved by an increase of temperature of the solution for all studied initial concentrations of the metal ion. Plots of percentage removal versus temperature were given in Fig.5. The reason may be as follows, at higher temperature, pores may widen up due to increased shaking so that more number of solute may enter into the aperture and get adsorbed in the inner part of the aperture surfaces.

3.5. Effect of pH

The pH of the solution plays important role for determining the quantity of solute adsorbed because the pH of the solution affects the functional groups of the activated carbon and also alters the surface charge of the carbon and governs the speciation of the solute. Here adsorption was studied ranges in between pH 2-10. The highest metal ion removal efficiency was attained at pH 5, as shown in Fig.6. Cu (II) ion generates negative charged metal ions when dissolved in water.

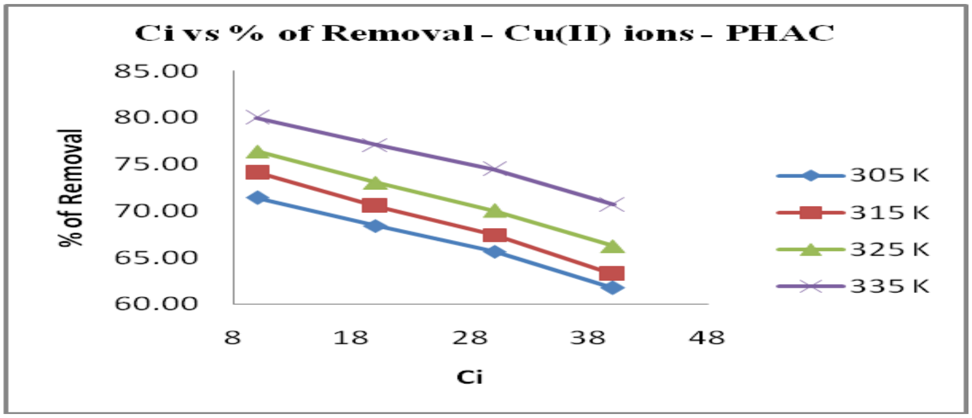

Fig.4: Ci vs % of Removal - Cu(II) ions - PHAC

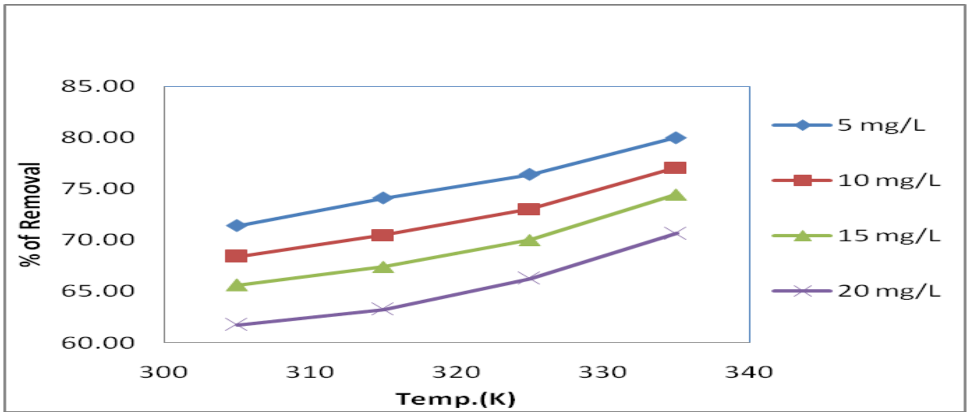

Fig.5: Temp. vs % of Removal-Cu(II) ions-PHAC

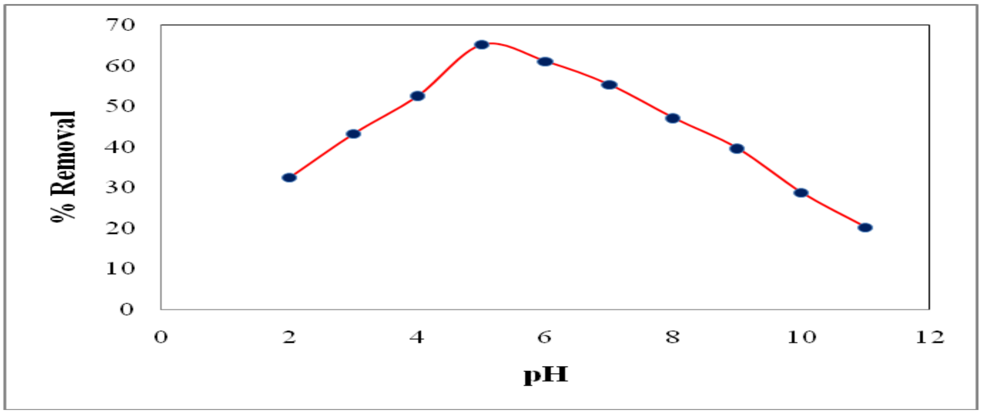

Fig.6: Effect of pH-Cu (II) ion-PHAC

3.6. Adsorption isotherms

3.6.1. Langmuir isotherm

The mono layer adsorption capacity Q_m values (mg/g) for adsorption of Cu (II) ion onto PHAC system the values ranged from 69.93 to 80.64. The adsorption capacity increased with the increase of temperature. Table 1 reveals that adsorption capacity of PHAC was quite reasonable for the adsorption of Cu (II) ion. The values of Langmuir constant 'b', the adsorption energy ranges from 0.050 to 0.077 for all the four systems. These values indicate that the apparent energy of sorption is less and guidelines out the probability of strong interaction between the solute and adsorption site. The dimensionless separation factor R_L values designed for various initial concentrations at different temperatures are lie between 0 and 1 which indicates the favorable adsorption of Cu(II) onto PHAC.

Table 1: Langmuir isotherm results for the adsorption of Cu(II) onto PHAC.

[pH = 4; Dose =30 mg/ 50 mL; Contact time = 180 min]

Temperature (K)	Q_m (mg/g)	b (L/mg)	R_L				R^2
			10 mg/L	20 mg/L	30 mg/L	40 mg/L	
305	142.85	0.050	0.6665	0.4998	0.3998	0.3331	0.9982
315	121.95	0.066	0.6032	0.4319	33639	0.2754	0.9808
325	140.84	0.066	0.6024	0.4310	0.3356	0.2747	0.9990
335	149.25	0.077	0.5646	0.3933	0.3018	0.2448	0.9987

3.6.2. Freundlich Isotherm

The results obtained from Freundlich model for the removal of Cu (II) ion onto PHAC system is given in Table 2.

The square of correlation coefficient (R^2) for Freundlich isotherms are above 0.99 for all the temperatures. It indicates that the experimental data fit well into Freundlich model.

Table 2: Freundlich Isotherm for Cu(II) ions onto PHAC

[pH = 4; Dose=30mg/50mL; Contact time=180 min]

Temperature (K)	N	k_f (mg/g)	R^2
305	1.3358	8.3272	0.9954
315	1.3885	10.5245	0.9962
325	1.3862	12.4423	0.9951
335	1.4529	9.6583	0.9986

3.6.3. Tempkin isotherm

Equilibrium binding constant a_T values (L/g) for adsorption of Cu (II) ion onto PHAC system was ranged from 0.6520 to 0.9434 .The heat of sorption constant b_T values are ranged from 97.1597 J/mg to 108.0364 J/mg. Lower value of a_T and b_T with respect to adsorption of Cu (II) ion is an indication of physisorption rather than chemisorption.

3.7. Kinetic study on Cu (II) ion adsorption

The results obtained from pseudo-first order kinetic model for the removal of Cu (II) ion onto PHAC was represented in Table 4.

Table 3: Tempkin constants for the adsorption of Cu(II) onto PHAC.

[pH =4; Dose=30mg/50 mL; Contact time=180 min]

Temperature (K)	b_T (J/mg)	a_T (L/g)	R^2
305	97.1597	0.6520	0.9877
315	108.0364	0.7614	0.9878
325	100.5040	0.8972	0.9864
335	97.5617	0.9434	0.9872

The linearity of the plot was not so high for PHAC (R^2 = 0.9643 - 0.9840). The first order rate constant, k_1 (min^{-1}) ranged from 0.0046 to 0.0187. The pseudo first order theoretical adsorption capacity (q_e) values, obtained from the intercept of the linear plots were compared with the experimental adsorption capacity q_e values (Table 4). The pseudo first order kinetic model suffered from inadequacies when applied to Cu (II) ion sorption on PHAC at varying Cu (II) ion concentrations. The experimental q_e values differ from the corresponding theoretical values. Discrepancies of this nature have been reported by Ho and McKay.

The pseudo second order parameters, q_e, h, and k_2, obtained from the pseudo second order plot are presented in Table 4. The initial sorption rate, 'h', increases directly with the increase of initial Cu (II) ion concentration at each temperature for PHAC(1.05 – 3.08 mg/g.min^{-1}) while an inverse relationship exists between the overall sorption rate and initial Cu (II) ion concentration for PHAC, (0.0044 - 1.0101). Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity.

Statistically it is tested with the tool sum of error squares (SSE %). The Δq_e and SSE % values were given in Table 4 for both the adsorbents from which it was concluded second order kinetic model was more appropriate than first order kinetic model. The conformance of this plot to the pseudo second order is extremely high.

3.7.1. *Intra-particle diffusion model*

The values of q_t are found to be linearly correlated with values of $t^{1/2}$. The k_p values were calculated by using correlation analysis (Table 4). The values of q_t are found to be linearly correlated with values of $t^{1/2}$. The k_p values were calculated by using correlation analysis (Table 4). The r-values are found to be close to unity, this reveals the presence of intra-particle diffusion process. The values of k_p (mgg^{-1} min.$^{-1/2}$) of the adsorbent indicates that the PHAC is more porous indigenously prepared adsorbent. The values of intercept (Table 4) give an idea about the boundary layer thickness that is, larger the intercept greater is the boundary layer effect. Concerned graph shown in Fig. 7.

3.8. Thermodynamic study

The thermo dynamical parameters calculated are presented in Table. The negative values of ΔG° (Table 5) show that the adsorption is highly favourable and spontaneous for all the studied systems [19]. The ΔH° values were within the range of 1 to 93 kJ/mol which indicates the favourability of physisorption.

Table 4: Kinetics and Intra particle diffusion results for the adsorption o Cu(II) ion onto PHAC

First Order Kinetics – PHAC

Concentration (mg/L)	k_1 (min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	R^2	SSE %
10	0.0555	6.2087	7.14	0.9840	**2.28**
20	0.0530	18.8712	13.68	0.9645	
30	0.0520	12.2687	19.69	0.9831	
40	0.0532	24.6037	24.70	0.9643	

Second Order Kinetics

Concentration (mg/L)	k_2 (g/mg.min)	$q_{e(cal)}$ (mg/g)	h	R^2	SSE %
10	0.0183	7.58	1.05	0.9981	**0.59**
20	1.0101	14.45	2.11	0.9959	
30	0.0061	20.96	2.68	0.9944	
40	0.0044	26.46	3.08	0.9933	

Intra Particle Diffusion

Concentration (mg/L)	k_p (mg/g.min)	R^2
10	0.0123	0.9934
20	0.0231	0.9892
30	0.0354	0.9962
40	0.0452	0.9962

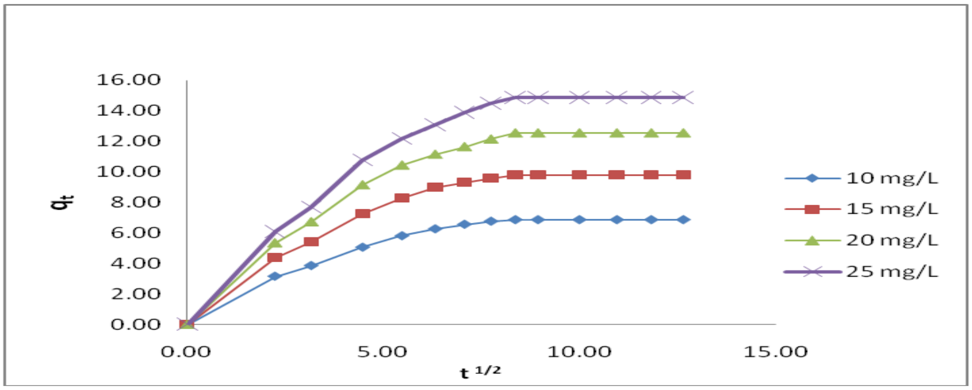

Fig. 7: Intraparticle diffusion for Cu(II) onto PHAC

Table 5: Thermodynamic Parameters results for Cu(II) onto PHAC

Concentration (mg/L)	Temperature (K)	k_d	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° (J/K×mol)
10	305	4.9930	-4.0784	13.018	55.9078
	315	5.7220	-4.5690		
	325	6.4746	-5.0480		
	335	8.0000	-5.7927		
20	305	4.3291	-3.7165	13.047	54.3927
	315	4.7797	-4.0977		
	325	5.4212	-4.5681		
	335	6.7336	-5.3126		
30	305	3.8196	-3.3989	12.334	59.0463
	315	4.1412	-3.7221		
	325	4.6741	-4.1674		
	335	5.8329	-4.9126		
40	305	3.2288	-2.9727	11.694	47.581
	315	3.4422	-3.2378		
	325	3.9259	-3.6960		
	335	4.8143	-4.3780		

4. CONCLUSION

The present study indicates that activated carbon prepared from *Delonix regia* pods is an effective adsorbent for the removal of Cu(II) ions. The extent of adsorption decreases with increase in initial metal ion concentration, increases with increase in adsorbent dosage, adsorption time and pH. The square of correlation coefficient (R^2) for Freundlich and Langmuir isotherms are around 0.99 for all the temperatures. It indicates that the experimental data fit well into Freundlich and Langmuir models. The kinetics fitted a pseudo-second order. Thermodynamic parameters indicating that the adsorption process is spontaneous and endothermic. Hence after carrying out rigorous experiments we finally came to conclusion that activated carbon prepared from *Delonix regia* pods is can be used for the removal of Cu(II) ions effectively.

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