Modelling, analysis and optimization of adsorption parameters for H_3PO_4 activated rubber wood sawdust using response surface methodology (RSM)

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A B S T R A C T

Adsorption capacity of Cu^{2+} from aqueous solution onto H_3PO_4 activated carbon using rubber wood sawdust (RSAC) was investigated in a batch system. Kinetic and isotherm studies were carried out, the thermodynamic parameters like standard Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were evaluated. The pseudo-second-order model was found to explain the kinetics of Cu^{2+} adsorption most effectively. The process optimization was performed through Central Composite Rotary Design using response surface methodology (RSM) by Design Expert Version 5.0.7 (STAT-EASE Inc., Minneapolis, USA). An initial concentration of 35 mg L^{-1}, temperature of 26 °C, carbon loading of 0.45 g $(100 \, mL)^{-1}$, adsorption time 208 min and pH of 6.5 was found to be the optimum conditions for the maximum uptake of copper ions of 5.6 mg g^{-1} in batch mode.

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1. Introduction

Rapid urbanization due to industrial development increased mining and agricultural activities has lead to an increase in the toxic pollutants like heavy metals, dyes, organic substances, etc. being released into the aquatic environment [1]. Further, heavy metals do not undergo biodegradation being predisposed to accumulate into the organisms and enters the food chains [2]. Copper is widely used, and discharged, in many industries such as refineries, electroplating, paper, fertilizer, etc. and it is highly toxic. Copper, even in low concentration affects the aquatic life and food web. For instance, if people are exposed to copper concentrations above 1.3 mg L^{-1} for short periods of time, stomach and intestinal problems occur. While long-term exposure to Cu^{2+} leads to kidney and liver damage, producing DNA mutation, evidence of its oncogenicity [3]. Since copper is harmful to human beings, the removal of copper from process or waste effluents becomes environmentally important. In recent years, considerable attention has been focused on the removal of copper ions from aqueous solution using adsorbents derived from low-cost materials. Various methods for heavy metal removal, including microbial degradation, bioaccumulation, chemical oxidation, membrane separation, electrochemical treatment,

filtration, and reverse osmosis, have been proposed [4]. However, these methods have several disadvantages, which include incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products that require disposal and further treatment. Most of these methods are often ineffective or uneconomical when the heavy metal concentration is in the range of 10–100 mg L^{-1} and the permissible concentration is less than 1 mg L^{-1} [5]. Out of these processes adsorption has been shown to be a simple, quick and an economical viable method for removing trace metals.

A large number of low-cost adsorbents such as coal ash [6], anaerobic granular biomass [7], tea waste [8], spent-grain [9], waste iron oxide [10], walnut, hazelnut, almond, pistachio shell, and apricot stone [11], modification of activated carbon using sodium acetate [12], spent activated clay [13], melamine–formaldehyde–NTA chelating gel resin [14], wood sawdust [15], nonliving lichen biomass of Cladonia rangiformis hoffm [16], seaweeds [17], etc. have been reported in the literature for the removal of heavy metals like lead, cadmium, copper, cobalt, nickel and zinc. Adsorption on activated carbon has long been recognized to be one of the most effective methods for the removal of heavy metals from wastewater. The use of activated carbons to remove Cu^{2+} from water was proposed because of their higher surface areas and active functional groups leading to a search for activated carbons from low-cost adsorbents in recent years.

Adsorption on to rubber wood sawdust activated carbon now offers an attractive and inexpensive option for the removal of copper ions. The abundance and availability of rubber wood sawdust

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Nomenclature

b	Langmuir constant representing adsorption intensity ($L\,mg^{-1}$)
C_{Ae}	equilibrium concentration of Cu^{2+} in the solution ($mg\,L^{-1}$)
C_{Be}	equilibrium concentration of Cu^{2+} on the adsorbent ($mg\,L^{-1}$)
C_e	equilibrium concentration of Cu^{2+} in solution ($mg\,L^{-1}$)
C_0	initial concentration of Cu^{2+} in solution ($mg\,L^{-1}$)
h	initial sorption rate ($mg\,g^{-1}\,min^{-1}$)
K_c	equilibrium constant
K_f	multilayer adsorption capacity ($mg\,g^{-1}$)
K_1	pseudo-first-order rate constant (min^{-1})
K_2	pseudo-second-order rate constant ($g\,mg^{-1}\,min^{-1}$)
M	mass of the adsorbent (g)
n	adsorption intensity ($g\,L^{-1}$)
q_e	adsorption capacity at equilibrium ($mg\,g^{-1}$)
q_t	adsorption capacity at any time t ($mg\,g^{-1}$)
Q_m	adsorption capacity of the adsorbent to form monolayer ($mg\,g^{-1}$)
R	universal gas constant ($kJ\,kg^{-1}\,mol^{-1}\,K^{-1}$)
R^2	regression coefficient
t	contact time (min)
T	temperature (K)
V	volume of adsorbate solution (L)

Greek letters

ΔG°	standard Gibbs free energy change
ΔH°	standard enthalpy change
ΔS°	standard entropy change

makes it economically feasible. The use of adsorbents derived from rubber wood sawdust to adsorb heavy metal and some dyes had been already studied in the previous work by the author [18,19]. The main objective of the present work is to investigate the feasibility of adsorption using activated carbon prepared from rubber wood sawdust for the removal of copper ions from wastewater and to estimate the maximum adsorption capacity and kinetic parameters of the adsorbent. The important parameters that affect the adsorption, such as contact time, initial copper ion concentration, carbon dosage, temperature and pH of metal ion solution have also been explored using the response surface methodology (RSM) approach. The central composite rotatable design (CCRD) was used to obtain the experimental design matrix. This approach has limited number of actual experiments performed while allowing probing into possible interaction between these parameters studied and their effect on adsorption capacity of Cu^{2+} on to H_3PO_4 activated rubber wood sawdust.

2. Experimental procedure

2.1. Materials and methods

2.1.1. Reagents

Copper sulphate penta hydrate was purchased from Ranbaxy Ltd. Copper stock solution of $1000\,mg\,L^{-1}$ was prepared by dissolving copper sulphate penta hydrate in deionized water. Working solutions of the desired concentration were then prepared by successive dilution. The other chemicals such as sodium diethyl dithiocarbamate, ammonia, citric acid, EDTA, chloroform, sulphuric acid used for the analysis of copper were of analytical grade.

2.1.2. Preparation of adsorbent

Rubber wood sawdust was procured from Coimbatore (Tamilnadu, India). The sawdust of average particle size 0.074 mm was mixed with 200% by weight of phosphoric acid and soaked for 24 h so that the reagents are fully adsorbed into the raw material. After impregnation, the mixture was transferred to a pyrex glass plate and placed in the hot air oven for drying at 110 °C for 1.5 h. After drying, the sawdust was activated in a self-generated atmosphere at 400 °C in a muffle furnace for an hour. The carbon thus produced was then repeatedly washed with distilled water to recover all the excess acid and the material attained neutral pH. Activated carbon thus obtained was dried in a hot air oven at a temperature of 105 ± 5 °C until a constant weight of activated carbon was reached. The activated carbon thus produced was used to carry out the adsorption experiments.

2.2. Adsorption experiments

Adsorption experiments were carried out by agitating the carbon in 100 mL of copper ion solution of desired concentration and pH in a rotary shaker at 180 rpm. The experiments were carried out varying carbon loading, initial Cu^{2+} concentration, retention times, temperature and pH. The samples were withdrawn from the flasks at predetermined time intervals and analyzed for their Cu^{2+} content spectrophotometrically at 435 nm using a UV spectrophotometer (HITACHI U 2002). The effect of pH was studied by adjusting the pH of the copper ion solutions using HCl and NaOH. Studies on the effect of temperature on adsorption were carried out using a thermostatic orbital shaker (Scigenics, ORBITEK, Chennai, India).

2.3. Response surface methodology

Process engineers need to determine the values of the design parameters at which the response reaches its optimum. The optimum could be either a maximum or a minimum of a function of the design parameters. One of the methodologies for obtaining the optimum results is response surface methodology. It is essential that an experimental design methodology be economical for extracting the maximum amount of complex information, a significant reduction in experimental time, saving both material and personnel cost [20]. RSM is a statistical method based on the multivariate non-linear model that has been widely used for optimization of the process variables of adsorption [5,21,22]. Further, RSM consists of designing experiments to provide adequate and reliable measurements of the response, developing a mathematical model having the best fit to the data obtained from the experimental design, and determining the optimal value of the independent variables that produces a maximum or minimum response [23–26]. It is also useful in studying the interactions of the various parameters affecting the process. RSM examines the responses of several factors by varying them simultaneously with limited number of experiments. It is worthy to quote that the response surface methodology does not elucidate the mechanism of the processes studied but only ascertains the effects of factors upon response and the interactions between the factors. Nevertheless, the RSM is a powerful tool for statistical modelling and optimization of the separation processes using lesser number of experimental runs planned according to experimental design [27].

2.4. Design of experiment using central composite design

A central composite rotatable design for five independent variables was employed to design experiments in which the variance of the predicted response, Y, at some points of independent variables, X, is only a function of the distance from the point to the design center [23–26]. The design of experiments is intended to

reduce the number of experiments and to arrange the experiments with various combinations of independent variables. In the rotatable design, the standard error, which depends on the coordinates of the point on the response surface at which Y is evaluated and on the coefficients β, is the same for all points that are the same distance from the central point. The value of α for rotatability depends on the number of points in the factorial portion of the design, which is given in Eq. (1)

$$\alpha = (F)^{1/5} \tag{1}$$

where F is the number of points in the cube portion of the design ($F = 2^k$, k is the number of factors). Since there are five factors, the F number is equal to 2^5 (=32) points, while α is equal to $(32)^{1/5}$ (=2) according to Eq. (1). Process parameters like, carbon dosage, adsorption temperature, contact time, pH and initial concentration of the solution were selected as the independent variables. The range of the independent variables is based on the conditions screened prior to optimization and is often used in the literature [14,18]. In this article, the design of experiment and the response surface methodology were employed using Design Expert Software Version 7.1.1 (STAT-EASE Inc., Minneapolis, USA).

The range and levels used in the experiments are given in Table 1 in which X_1 denotes carbon dosage, X_2 initial concentration of the solution, X_3 pH of the solution, X_4 adsorption temperature and X_5 contact time of solution with adsorbent, respectively. In the experimental design, all variables are coded for statistical calculation according to Eq. (2) [23–26].

$$x_i = \frac{\alpha[2X_i - (X_{\max} + X_{\min})]}{X_{\max} - X_{\min}} \tag{2}$$

where x_i is the dimensionless coded value of the ith variable, X_i the natural value of the ith variable, $X_{\max}$ and $X_{\min}$ the highest and the lowest limits of the ith variable, respectively. Once the desired range of values for the variables are defined, they are coded to lie at ± 1 for the factorial points, 0 for the center points and $\pm\alpha$ for the axial points.

The experimental design matrix resulted by the CCRD shown in Table 2 consists of 50 sets of coded conditions expressed in natural values. The design consists of a two-level full factorial design 32 Fact points (25 = 32), 8 center points, and 10 axial points. Based on this table, the experiments were conducted for obtaining the response, i.e., capacity of Cu^{2+} adsorption is carried out at the corresponding independent variables addressed in the experimental design matrix. These experimental data are used for validating the single-response model of the adsorption process. The sequence of experiment was randomized in order to minimize the effects of uncontrolled factors.

2.5. Mathematical modelling

The single-response modeled using the RSM corresponded to independent variables. By the RSM, a quadratic polynomial equation was developed to predict the response as a function of independent variables involving their interactions [23–26]. In general, the response for the quadratic polynomial is described in Eq.

(3).

$$Y_i = \beta_o + \sum_i \beta_i x_i + \sum_{ii} \beta_{ii} x_i^2 + \sum_{ij} \beta_{ij} x_i x_j \tag{3}$$

where Y is the predicted response, β_0 the intercept coefficient, β_i the linear terms, β_{ii} the squared terms, β_{ij} the interaction terms, and x_i and x_j represent the coded independent variables. In this study, a second-order polynomial equation was obtained using the uncoded independent variables as such

$$
\begin{aligned}
Y = {} & \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_5 X_5 + \beta_{11} X_1{}^2 + \beta_{22} X_2{}^2 \\
& + \beta_{33} X_3{}^2 + \beta_{44} X_4{}^2 + \beta_{55} X_5{}^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 \\
& + \beta_{15} X_1 X_5 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{25} X_2 X_5 + \beta_{34} X_3 X_4 \\
& + \beta_{35} X_3 X_5 + \beta_{45} X_4 X_5
\end{aligned}
\tag{4}
$$

The coefficient of the model for the response was estimated using multiple regression analysis technique included in the RSM. Fit quality of the models was judged from their coefficients of correlation and determination.

2.6. RSM evaluation

When fitting the model, various statistical analysis techniques were employed to judge the experimental error, the suitability of the model, and the statistical significance of the terms in the model. This is usually done with the help of a computer, using either a statistics package or a dedicated RSM program. In the present work the adequacy of the model was justified through analysis of variance (ANOVA). Some model terms may turn out not to be significant for a good representation of the experimental data, so usually a subset of the model with fewer terms is selected. There are often several subsets that lead to similar results, so care must be taken when trying to interpret single model terms. The final model can be used to create graphical representations of the parameter dependencies, e.g., as contour plots, to see the relative influence of the parameters, to find an optimum parameter combination, and to predict experimental results for other parameter combinations [28].

3. Results and discussion

3.1. Adsorption studies

The adsorption capacity of the activated carbon was evaluated by the following equation [29].

$$q_t = (C_0 - C_t)\frac{V}{M} \tag{5}$$

where C_0 is the initial copper ion concentration in the solution ($mg\,L^{-1}$), C_t the concentration of copper ion in the solution at any time t ($mg\,L^{-1}$), V the volume of solution (L) and M the mass of the adsorbent (g).

The effects of contact time and initial concentration of metal ion on the adsorption capacity were studied and shown in Fig. 1.

Table 1
Level of variables consider for the adsorption of Cu(II) by Central Composite Rotary Design (CCRD).

S. No.	Variable	Name	Variable level				
			−2 (−α)	−1	0	+1	2 (+α)
1	X_1	Adsorbent concentration (g (100 mL)$^{-1}$)	0.3	0.45	0.6	0.75	0.9
2	X_2	Initial adsorbate concentration (mg L^{-1})	5	15	25	35	45
3	X_3	pH	2	3.5	5	6.5	8
4	X_4	Time (min)	30	90	150	210	270
5	X_5	Temperature (°C)	20	25	30	35	40

Table 2
Independent variables and result for the adsorption of Cu(II) by Central Composite Rotary Design (CCRD).

| Run order	Standard order	Coded variable					Actual variable					Response	
		X_1	X_2	X_3	X_4	X_5	X_1	X_2	X_3	X_4	X_5	Experimental	Predicted
1	47	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
2	41	0	0	0	0	−2	0.6	25	5	150	20	3.852	3.6610
3	25	−1	−1	−1	1	1	0.45	15	3.5	210	35	2.048	1.8984
4	49	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
5	20	1	1	−1	−1	1	0.75	35	3.5	90	35	1.235	1.1417
6	11	−1	1	−1	1	−1	0.45	35	3.5	210	25	2.245	2.2741
7	21	−1	−1	1	−1	1	0.45	15	6.5	90	35	2.831	2.8522
8	32	1	1	1	1	1	0.75	35	6.5	210	35	4.12	4.0786
9	23	−1	1	1	−1	1	0.45	35	6.5	90	35	4.681	4.7708
10	28	1	1	−1	1	1	0.75	35	3.5	210	35	1.494	1.4690
11	27	−1	1	−1	1	1	0.45	35	3.5	210	35	1.45	1.7355
12	37	0	0	−2	0	0	0.6	25	2	150	30	0.014	0.0053
13	15	−1	1	1	1	−1	0.45	35	6.5	210	25	5.591	5.6368
14	10	1	−1	−1	1	−1	0.75	15	3.5	210	25	1.66	1.7148
15	39	0	0	0	−2	0	0.6	25	5	30	30	3.271	3.0667
16	24	1	1	1	−1	1	0.75	35	6.5	90	35	3.578	3.7512
17	5	−1	−1	1	−1	−1	0.45	15	6.5	90	25	3.017	3.1682
18	9	−1	−1	−1	1	−1	0.45	15	3.5	210	25	2.397	2.2144
19	2	1	−1	−1	−1	−1	0.75	15	3.5	90	25	1.593	1.6451
20	48	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
21	6	1	−1	1	−1	−1	0.75	15	6.5	90	25	1.981	1.9155
22	19	−1	1	−1	−1	1	0.45	35	3.5	90	35	1.272	1.4081
23	17	−1	−1	−1	−1	1	0.45	15	3.5	90	35	1.921	1.8286
24	13	−1	−1	1	1	−1	0.45	15	6.5	210	25	3.123	3.2379
25	40	0	0	0	2	0	0.6	25	5	270	30	3.54	3.4638
26	14	1	−1	1	1	−1	0.75	15	6.5	210	25	1.999	1.9853
27	43	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
28	3	−1	1	−1	−1	−1	0.45	35	3.5	90	25	1.602	1.9467
29	31	−1	1	1	1	1	0.45	35	6.5	210	35	5.071	5.0981
30	42	0	0	0	0	2	0.6	25	5	150	40	3.129	3.0395
31	34	2	0	0	0	0	0.9	25	5	150	30	2.643	2.6117
32	22	1	−1	1	−1	1	0.75	15	6.5	90	35	1.914	1.8326
33	44	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
34	8	1	1	1	−1	−1	0.75	35	6.5	90	25	3.906	4.0567
35	50	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
36	46	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
37	1	−1	−1	−1	−1	−1	0.45	15	3.5	90	25	2.247	2.1446
38	4	1	1	−1	−1	−1	0.75	35	3.5	90	25	1.621	1.4472
39	29	−1	−1	1	1	1	0.45	15	6.5	210	35	2.901	2.9219
40	12	1	1	−1	1	−1	0.75	35	3.5	210	25	1.796	1.7745
41	45	0	0	0	0	0	0.6	25	5	150	30	3.596	3.6311
42	33	−2	0	0	0	0	0.3	25	5	150	30	4.38	4.1308
43	38	0	0	2	0	0	0.6	25	8	150	30	3.889	3.6278
44	18	1	−1	−1	−1	1	0.75	15	3.5	90	35	1.423	1.5622
45	35	0	−2	0	0	0	0.6	5	5	150	30	1.254	1.4361
46	7	−1	1	1	−1	−1	0.45	35	6.5	90	25	5.27	5.3094
47	30	1	−1	1	1	1	0.75	15	6.5	210	35	1.971	1.9024
48	26	1	−1	−1	1	1	0.75	15	3.5	210	35	1.514	1.6320
49	16	1	1	1	1	−1	0.75	35	6.5	210	25	4.145	4.3841
50	36	0	2	0	0	0	0.6	45	5	150	30	3.877	3.4144
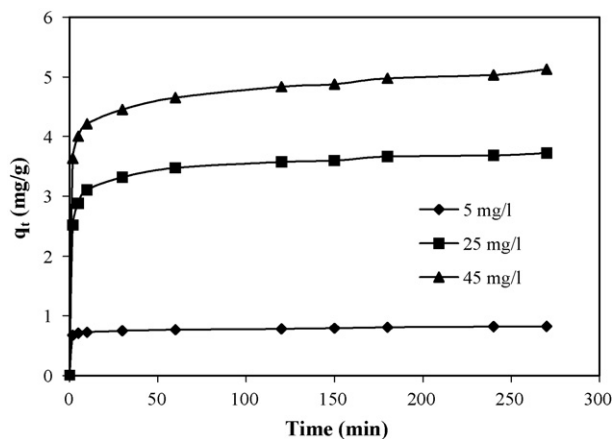
Fig. 1. Effect of Initial Cu^{2+} ion concentration on adsorption capacity. (Carbon dosage concentration = 0.6 g (100 mL)$^{-1}$, adsorption temperature = 30 °C, pH = 5.)

Contact time studies were carried out at 30 °C, and pH 5 with 0.6 g (100 mL)$^{-1}$ of adsorbent dosage for three different adsorbate concentrations. The adsorption capacity of activated carbon increased with contact time and attained maximum value at 270 min. Further, increase in the contact time did not show a significant change in adsorption capacity. The equilibrium time was hence taken as 270 min. Therefore, for further studies, the time for attaining equilibrium was set at 270 min.

The influence of the initial metal ion concentration in the solutions on the adsorption capacity of carbon was studied. The experiments were carried out for different initial metal ion concentration at fixed adsorbent dosage of 0.6 g (100 mL)$^{-1}$, pH 5 and temperature 30 °C. The adsorption capacity increased with increase in initial metal ion concentration (Fig. 1). The adsorption capacity increased from 0.8267 mg g^{-1} to 5.127 mg g^{-1} when the metal ion concentration was increased from 5 mg L^{-1} to 45 mg L^{-1}.

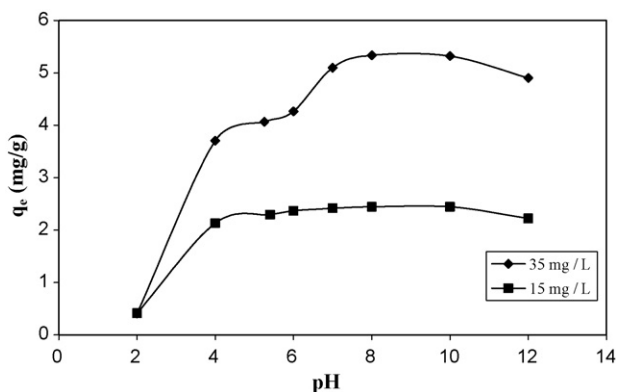To determine the necessary activated carbon quantity required for the maximum removal of Cu^{2+} ions, the effect of activated
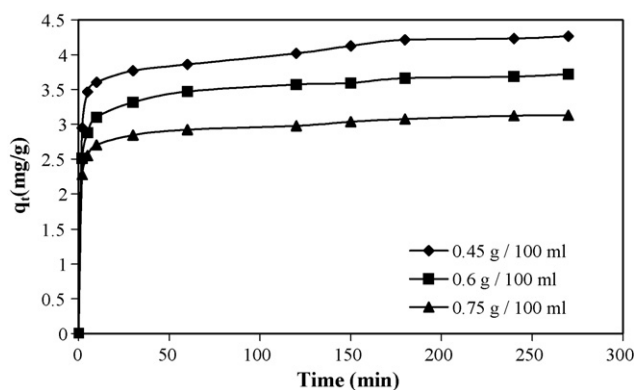
Fig. 2. Effect of initial adsorbent concentration on adsorption capacity. (Initial copper ion concentration = 25 mg L^{-1}, adsorption temperature = 30 °C, pH = 5.)

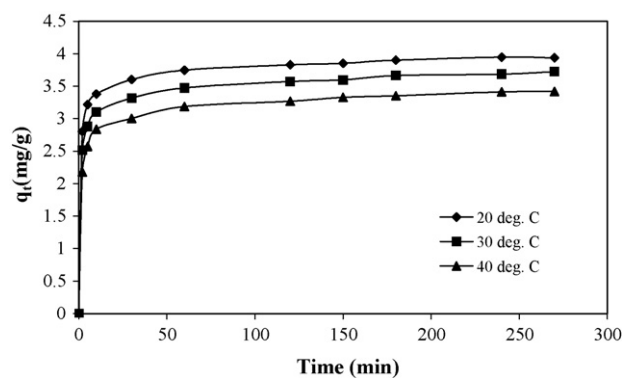**Fig. 4.** Effect of temperature on adsorption capacity. (Initial copper ion concentration = 25 mg L^{-1}, initial adsorbate concentration = 0.6 g (100 mL)$^{-1}$, pH = 5.)

carbon dosage on adsorption capacity was studied (Fig. 2). The adsorption studies were carried out at pH 5, temperature 30 °C for different retention period, taking 100 mL of 25 mg L^{-1} of CuSO$_4$ solution for various activated carbon dosages. It can be easily inferred that the adsorption capacity of activated carbon decreases with increasing weight of the activated carbon. The adsorption capacity decreased from 4.2677 mg g^{-1} to 3.1296 mg g^{-1} when the weight of carbon was increased from 0.45 g (100 mL)$^{-1}$ to 0.75 g (100 mL)$^{-1}$. This is due to the fact that more the activated carbon, greater will be the availability of the exchangeable sites or surface offered to the adsorption of Cu^{2+} ions [18].

The effect of pH on adsorption of copper ion is shown in Fig. 3. The pH experiments were studied for two different initial metal ion concentrations at a temperature of 35 °C by varying the initial pH of Cu^{2+} solution from 2 to 12 for a constant carbon dosage of 0.6 g (100 mL)$^{-1}$ of solution. The adsorption experiments were conducted for equilibration time previously determined. The percentage removal of Cu^{2+} was found to increase with increasing pH till pH 6.0 for 15 mg L^{-1} and till pH 7 for 35 mg L^{-1}. The optimum initial pH was however chosen to be natural pH because precipitation of copper hydroxide was observed at pH greater than 6.5. Similar observations had been reported by others [30,31]. It was suggested that the increase in adsorption depended on the properties of the adsorbent surface and metal ion. The increase in adsorption capacity with increasing pH is due to the increase in the negative charge on the carbon surface; thus, the electrostatic attraction forces between carbon surface and the metal ion were increased.

Fig. 4 shows the relationship between temperature and adsorption capacity. The experiments were carried out for a concentration

of 25 mg L^{-1} for different retention times at pH 5 with constant carbon loading of 0.6 g (100 mL)$^{-1}$ of copper solution. The results obtained indicate that the amount of copper ion adsorbed decreased gradually with increasing temperature from 20 °C to 40 °C. The reduction in the percent removal of copper ions shows that the adsorption by activated carbon is exothermic and reversible in nature. Temperature dependence of adsorption is associated with various thermodynamic parameters.

Thermodynamic parameters such as standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy ($\Delta S°$) change of adsorption can be evaluated from the following Eqs. (6) and (7) [14].

$$\Delta G° = -RT \ln K_c \tag{6}$$
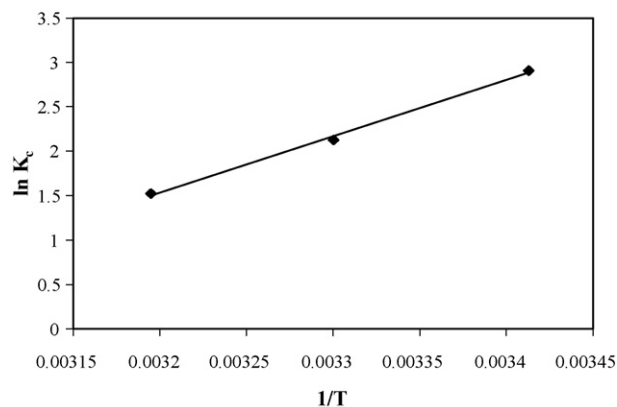
where, K_C is the equilibrium constant.

$$K_c = \frac{C_{Be}}{C_{Ae}} \tag{7}$$

where C_{Ae} and C_{Be} are the equilibrium concentration of Cu^{2+} in the solution and on the adsorbent. Standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were determined from the Van't Hoff equation,

$$\ln K_c = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{8}$$

$\Delta H°$ and $\Delta S°$ were obtained from the slope and intercept of the plot of $\ln K_c$ vs T^{-1} as shown in Fig. 5. The values of the parameters thus calculated are recorded in Table 3. Negative values of $\Delta G°$ indicate the spontaneous nature of the adsorption process. The value of $\Delta G°$ becomes less negative with increasing temperature. This shows that a decrease in temperature favors the removal process. The negative value of $\Delta H°$ indicates that the adsorption process is exothermic in nature. The negative values of $\Delta S°$ suggest the probability of

Fig. 3. Effect of pH on adsorption capacity. (Carbon dosage = 0.6 g (100 mL)$^{-1}$, time = 270 min, temperature = 35 °C.)

Fig. 5. Van't Hoff plot for the adsorption of copper ion. (Initial adsorbate concentration = 25 mg L^{-1}, pH = 5, time = 270 min, carbon dosage = 0.6 g (100 mL)$^{-1}$.)

Table 3
Thermodynamic parameters for the adsorption of Copper ion.

T (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ mol^{-1} K^{-1})
293	−7.0812	−52.8754	−0.1565
303	−5.3529		
313	−3.9591		

favorable adsorption and also the disorderliness of the adsorption at solid–liquid interface.

3.2. Isotherm studies

Adsorption isotherms describe how the adsorbates interact with the adsorbents and are critical in optimizing the use of the adsorbents. The Langmuir and Freundlich isotherm model equations are in common use for describing adsorption isotherm [32,33].

The Langmuir isotherm is based on monolayer adsorption (constant heat of adsorption for all sites) on the active sites of the adsorbent. The data on the uptake of copper ion has been processed in accordance with the Langmuir isotherm equation

$$q_e = \frac{Q_{max}bC_e}{1 + bC_e} \qquad (9)$$

The linear form of the Langmuir isotherm is represented by the equation

$$\frac{C_e}{q_e} = \frac{C_e}{Q_{max}} + \frac{1}{bQ_{max}} \qquad (10)$$

where C_e is the equilibrium concentration of copper ion in the solution (mg L^{-1}), q_e the amount of the copper ion adsorbed at equilibrium (mg g^{-1}), Q_{max} the amount of copper ion required to form a monolayer, i.e., adsorption capacity of the adsorbent (mg g^{-1}), and b is the equilibrium constant representing adsorption intensity (L mg^{-1}). The values of Q_{max} and b can be calculated from the slope and intercept of the plot of C_e/q_e vs C_e.

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption (heterogeneous surface). This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by

$$q_e = K_f(C_e)^{1/n} \qquad (11)$$

The linear form of Freundlich isotherm is represented by the equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad (12)$$

where K_f (mg g^{-1}) and n (g L^{-1}) are Freundlich isotherm constants relating multilayer adsorption capacity and adsorption intensity. The values of n and K_f can be calculated from the slope and intercept of log q_e vs log C_e plot. The Langmuir and Freundlich isotherms are shown in Figs. 6 and 7. The isotherm constants along with the regression coefficients are listed in Table 4. The value of R^2 was higher for the Langmuir isotherm than the Freundlich isotherm; this means the Langmuir equation represented the adsorption process very well. This may be due to the homogeneous distribution of active sites on activated carbon surface.

3.3. Kinetic studies

To analyze the adsorption rates of metal ions on to activated carbon from rubber wood saw dust, two simple kinetic equations were tested.
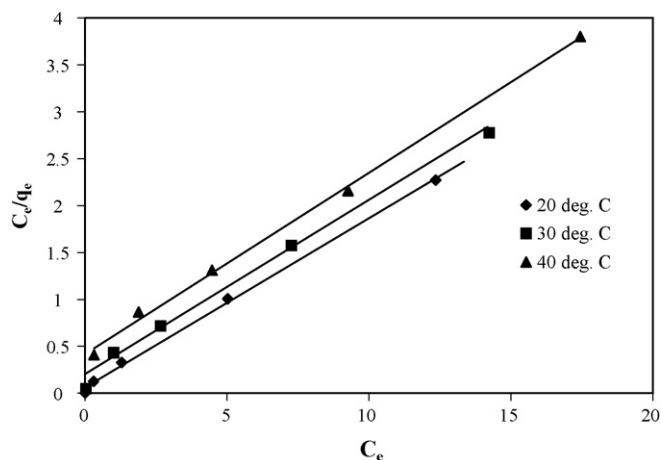
Fig. 6. Langmuir adsorption isotherm at different temperature. (Initial adsorbate concentration = 25 mg L^{-1}, pH = 5, time = 270 min, carbon dosage = 0.6 g (100 mL)$^{-1}$.)

3.3.1. Pseudo-first-order equation

This was the first equation for the sorption of liquid/solid system based on solid capacity. The Lagergren's pseudo-first-order equation [34] is given as

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (13)$$

Eq. (13) can be integrated for the boundary conditions $t = 0$, $q_t = 0$, and $t = t$, $q_t = q_t$, to obtain

$$\log (q_e - q_t) = \log (q_e) - K_1 t \qquad (14)$$

where q_t (mg g^{-1} of dry weight) is the amount of adsorbate on the surface of the adsorbent at any time t (min), q_e is the amount of adsorbate on the surface of adsorbent at equilibrium and K_1 is the equilibrium rate constant of pseudo-first-order adsorption (min^{-1}). K_1 and q_e is calculated from the slope of log $(q_e - q_t)$ against time (min) plots and is shown in Fig. 8.
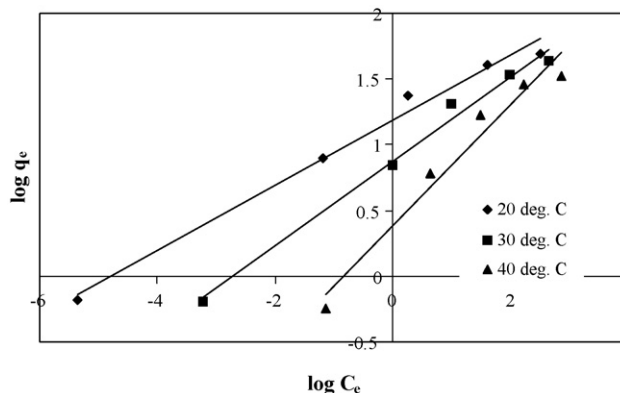
3.3.2. Pseudo-second-order equation

The experimental data are tested with pseudo-second-order equation [35]. The kinetic rate equation is,

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (15)$$

On integration of Eq. (15) for the boundary conditions, $t = 0$, $q_t = 0$ and $t = t$, $q_t = q_t$ and rearranging it to obtain the linearized form as,

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (16)$$

Fig. 7. Freundlich adsorption isotherm at different temperature. (Initial adsorbate concentration = 25 mg L^{-1}, pH = 5, time = 270 min, carbon dosage = 0.6 g (100 mL)$^{-1}$.)

Table 4
Langmuir and Freundlich parameters for the adsorption of Copper ion.

Temperature (K)	Langmuir constants			Freundlich constants		
	X_m (mg g^{-1})	b (L mg^{-1})	R^2	K (mg g^{-1})	n (g L^{-1})	R^2
293	5.5494	2.874	0.9982	3.2700	4.0437	0.9871
303	5.3850	1.0784	0.9939	2.3948	3.1124	0.9882
313	5.1760	0.4622	0.9979	1.4774	2.1763	0.9627

Table 5
Comparison of the pseudo-first-order and pseudo-second-order adsorption rate constants for different Temperature.

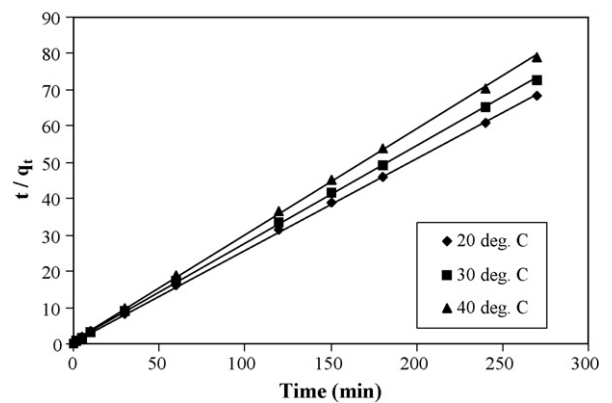| Temperature (K)	Pseudo-first-order kinetics			Pseudo-second-order kinetics			q_e (experimental) (mg g^{-1})
	q_e (calculated) (mg g^{-1})	K_1 (min^{-1})	R^2	K_2 (g mg^{-1} min^{-1})	q_e (calculated) (mg g^{-1})	R^2	
293	1.17069	0.0208	0.8847	0.12992	3.9557	0.9998	3.9508
303	1.063	0.0153	0.8653	0.11338	3.7161	0.9997	3.7221
313	1.1788	0.0189	0.9041	0.11104	3.4247	0.9996	3.4198
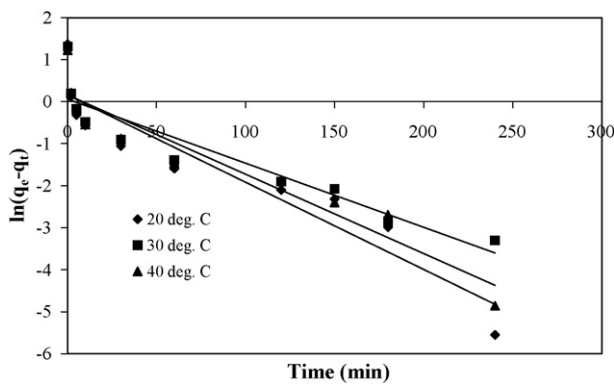
Fig. 8. Pseudo-first-order kinetics for copper ion adsorption. (Initial adsorbate concentration = 25 mg L^{-1}, pH = 5, time = 270 min, carbon dosage = 0.6 g (100 mL)$^{-1}$.)

Fig. 9. Pseudo-second-order kinetics for copper ion adsorption. (Initial adsorbate concentration = 25 mg L^{-1}, pH = 5, time = 270 min, carbon dosage = 0.6 g (100 mL)$^{-1}$.)

where, $h = K_2 q_e^2$, K_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}) and h the initial sorption rate (mg g^{-1} min^{-1}). The equation constants can be determined by plotting t/q_t against t. The experimental and calculated values of the adsorption capacity are compared and given in Table 5. Based on the regression coefficient and calculated values of adsorption capacity, the adsorption process was found to obey the pseudo-second-order kinetic model, as shown in Fig. 9.

3.4. Development of regression model equation

In the present study, CCRD for five variables (activated carbon loading, initial concentration of copper, pH, adsorption time and temperature), each with five levels (±1 for the factorial points, 0 for the center points and ±α for the axial points), was used as the experimental design model. The model has the advantage that it permits the use of relatively few combinations of variables for determining the complex response function [36]. A total of 50 experiments were required to be performed to calculate 21 coefficients of the second-order polynomial equation. The adsorption of copper ion estimated as adsorption capacity of saw dust was taken as the response of the

system. The experimental design matrix derived from CCRD and the adsorption capacities are shown in Table 2. According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased. For percentage adsorption of Cu^{2+} ions, the quadratic model was suggested by the software, which was selected in this case due to the higher order polynomial (Table 6).

The coefficient of the model for the response was estimated using multiple regression analysis technique included in the RSM. The quadratic model thus obtained was given as follows:

$$\text{Adsorption capacity } (Y) = -5.4519 + 2.4689\,X_1 + 0.0083 X_2$$
$$+ 2.0473 X_3 + 0.0076 X_4 + 0.1012 X_5 + 0.0238 X_1 X_2 - 0.8368 X_1 X_3$$
$$- 0.0019 X_1 X_4 + 0.0777 X_1 X_5 + 0.0390 X_2 X_3 + 0.0001 X_2 X_4$$
$$- 0.0011 X_2 X_5 + 1.84 \times 10^{-05} X_3 X_4 + 0.0035 X_3 X_5$$
$$- 5.2 \times 10^{-07} X_4 X_5 - 2.8864 X_1^2 - 0.003 X_2^2 - 0.2022 X_3^2$$
$$- 2.5 \times 10^{-05} X_4^2 - 0.0028 X_5^2 \tag{17}$$

Table 6
Model summary statistics.

| Source	Standard deviation	R^2	Adjusted R^2	Predicted R^2	PRESS	Comments
Linear	0.7314	0.6795	0.6430	0.5862	30.3906	
2FI	0.5700	0.8495	0.7831	0.7592	17.6819	
Quadratic	0.1818	0.9869	0.9779	0.9493	3.71951	Suggested
Cubic	0.1448	0.9960	0.9860	0.5495	33.0828	Aliased

Table 7
Analysis of variance (ANOVA) for response surface quadratic model for adsorption capacity (Eq. (17)).

Source	Sum of squares	Degrees of freedom	Mean square	F value	P value Prob >F
Model	72.4928	20	3.6246	109.6116	<0.0001
X_1-carbon dosage	5.7692	1	5.7692	174.4633	<0.0001
X_2-initial concentration	9.7847	1	9.7842	295.8801	<0.0001
X_3-Ph	32.9985	1	32.9985	997.8981	<0.0001
X_4-Time	0.3942	1	0.3942	11.9215	0.0017
X_5-Temp	0.9657	1	0.9657	29.2021	<0.0001
X_1X_2	0.0408	1	0.0408	1.2346	0.2756
X_1X_3	1.1344	1	1.1344	34.3048	<0.0001
X_1X_4	0.0090	1	0.0090	0.2725	0.6056
X_1X_5	0.1087	1	0.1087	3.2870	0.0802
X_2X_3	10.9430	1	10.9430	330.924	<0.0001
X_2X_4	0.1327	1	0.1327	4.0142	0.0545
X_2X_5	0.0991	1	0.0991	2.9976	0.0940
X_3X_4	8.78×10^{-05}	1	8.78×10^{-05}	0.0027	0.9593
X_3X_5	0.0220	1	0.0220	0.6652	0.4214
X_4X_5	7.81×10^{-07}	1	7.81×10^{-07}	2.36×10^{-05}	0.9962
X_1^2	0.1350	1	0.1350	4.0815	0.0527
X_2^2	2.9078	1	2.9076	87.9334	<0.0001
X_3^2	6.6232	1	6.6232	200.2889	<0.0001
X_4^2	0.2676	1	0.2676	8.0919	0.0081
X_5^2	0.1577	1	0.1577	4.7680	0.0372

Table 8
Standard deviation and R^2 for the model Eq. (18).

Standard deviation	0.1741	R^2	0.9859
Mean	2.8447	Adjusted R^2	0.9798
C.V.%	6.1212	Predicted R^2	0.9564
PRESS	3.2035	Adequate precision	57.2786

Apart from the linear effects of the adsorption variables on adsorption capacity, an analysis using RSM also gives an insight into the quadratic and interaction effects of the parameters. The result of this in the form of analysis of variance for Eq. (17) is given in Table 7. In general, the Fischer's '$F_{statistics}$' value with a low probability 'P' value indicates high significance of the regression model. The significance of the regression coefficient of the parameter can be verified by the Student's t-test as a tool, while 'P' values signify the pattern of interaction among the factors. The larger the value of t and smaller the value of P, the more significant is the corresponding coefficient term [37]. By analyzing the '$F_{statistics}$' and 'P' values from Table 7; it was found that the X_1, X_2, X_3, X_4, X_5, X_1X_3, X_2X_3, X_2X_4, X_1^2, X_2^2, X_3^2, X_4^2, X_5^2 had high significance and X_1X_5, X_2X_5 terms had moderate significance to explain the individual and interaction
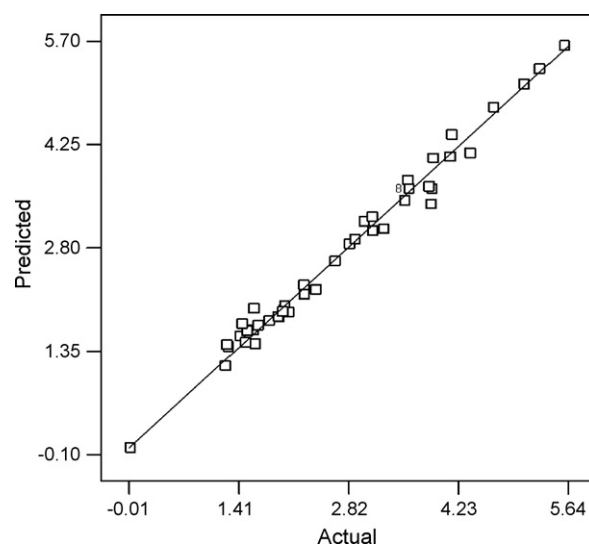

Fig. 10. Comparison plot between the experimental and model predicted Cu^{2+} adsorption capacity.

Table 9
Analysis of variance (ANOVA) for response surface quadratic model for adsorption capacity (Eq. (18)).

Source	Sum of squares	Degrees of freedom	Mean square	F value	P value Prob >F
Model	72.4209	15	4.8281	159.2341	<0.0001
X_1-carbon Dosage	5.7696	1	5.7692	190.2726	<0.0001
X_2-initial concentration	9.7847	1	9.7842	322.6917	<0.0001
X_3-pH	32.9985	1	32.9985	1088.324	<0.0001
X_4-time	0.3942	1	0.3942	13.0018	0.0010
X_5-temperature	0.9657	1	0.9656	31.8483	<0.0001
X_1X_3	1.1344	1	1.1344	37.4134	<0.0001
X_1X_5	0.1087	1	0.1087	3.5848	0.0668
X_2X_3	10.9430	1	10.9430	360.911	<0.0001
X_2X_4	0.1327	1	0.1327	4.3779	0.0439
X_2X_5	0.0991	1	0.0991	3.2692	0.0794
X_1^2	0.1350	1	0.1350	4.4513	0.0423
X_2^2	2.9078	1	2.9078	95.9016	<0.0001
X_3^2	6.6232	1	6.6232	218.4383	<0.0001
X_4^2	0.2676	1	0.2676	8.82514	0.0054
X_5^2	0.1577	1	0.1577	5.2001	0.0290
Residual	1.0309	34	0.0303		
Lack of Fit	1.0309	27	0.0382		
Pure error	0	7	0		
Cor total	73.452	49			
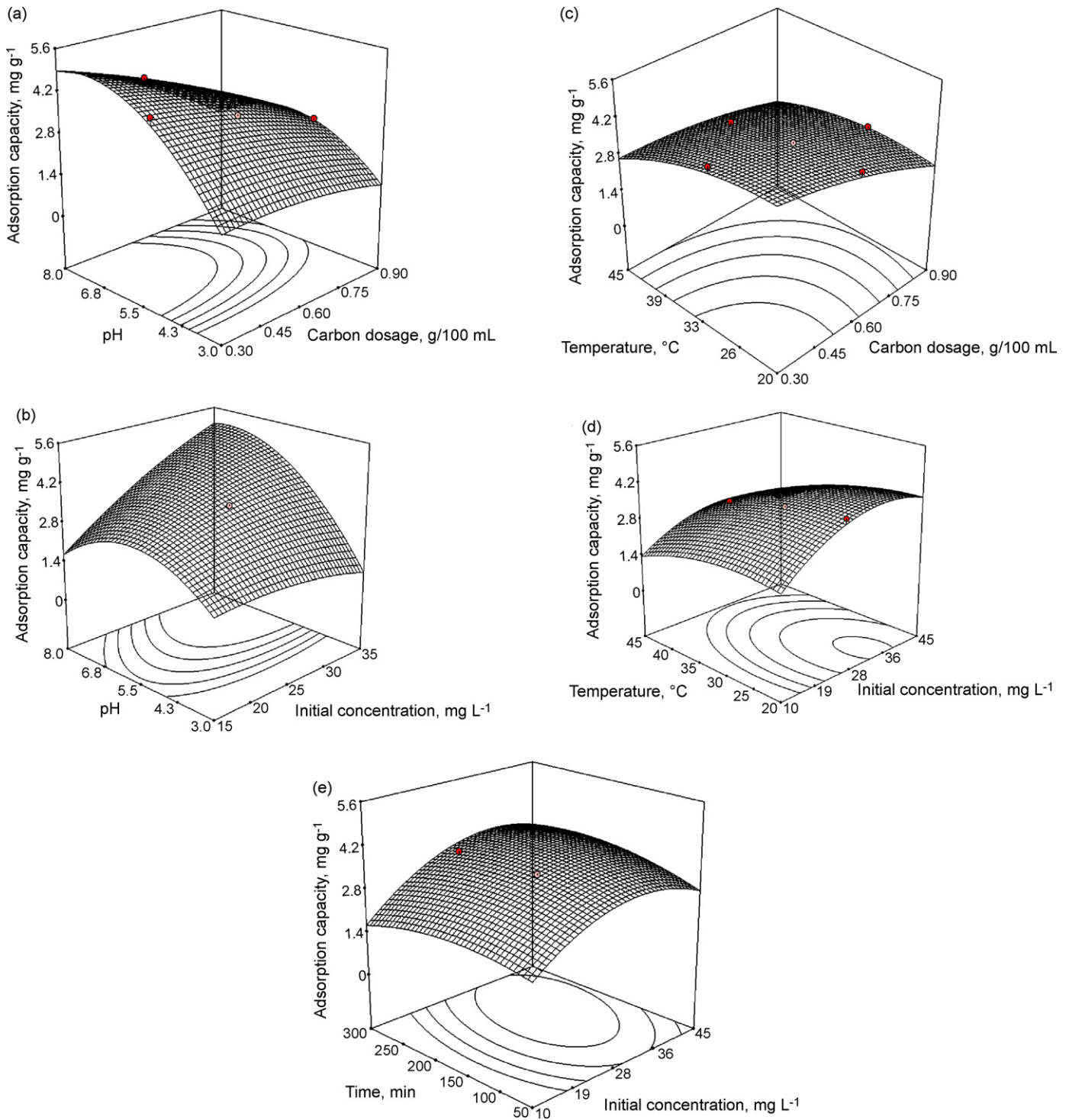
Fig. 11. (a) 3D response surface: Interactive effects of varied initial adsorbent concentration and pH at adsorption time 150 min, initial adsorbate concentration 25 mg L^{-1} and adsorption temperature 30 °C on adsorption capacity. (b) 3D response surface: Interactive effects of initial adsorbate concentration and pH at initial adsorbent concentration 0.6 g (100 mL)$^{-1}$, adsorption temperature 30 °C and adsorption time 150 min on adsorption capacity. (c) 3D response surface: Interactive effects of varied initial adsorbent concentration and adsorption temperature at initial adsorbate concentration 25 mg L^{-1}, adsorption time 150 min and pH 5 on adsorption capacity. (d) 3D response surface: Interactive effects of initial adsorbate concentration and adsorption temperature at initial adsorbent concentration 0.6 g (100 mL)$^{-1}$, pH 5 and adsorption time 150 min on adsorption capacity. (e) 3D response surface: Interactive effects of adsorption time and initial adsorbate concentration at initial adsorbent concentration 0.6 g (100 mL)$^{-1}$, pH 5 and adsorption temperature 30 °C on adsorption capacity.

Table 10
Optimized process variable values for adsorption process through point prediction method.

Adsorbent concentration ($g (100 \, mL)^{-1}$)	Initial adsorbate concentration ($mg \, L^{-1}$)	pH	Adsorption time (min)	Temperature (°C)	Adsorption capacity ($mg \, g^{-1}$)	
					Predicted	Experimental
0.45	35	6.5	208	26	5.60	5.58

effect of adsorption variables on the adsorption of Cu^{2+} to predict the response. All the other terms (X_1X_4, X_3X_4, X_3X_5, and X_4X_5) are insignificant in the equation and are not required to explain the adsorption process. Hence, the model was reduced to the following form by neglecting insignificant terms (Eq. (18)).

$$Y = -6.17715 + 2.784611X_1 + 0.022544X_2 + 2.154937X_3$$
$$+ 0.006591X_4 + 0.118593X_5 - 0.83681X_1X_3 + 0.077708X_1X_5$$
$$+ 0.038985X_2X_3 + 0.000107X_2X_4 - 0.00111X_2X_5 - 2.88639X_1^2$$
$$- 0.00301X_2^2 - 0.2022X_3^2 - 2.5 \times 10^{-05}X_4^2 - 0.00281X_5^2 \quad (18)$$

The predicted adsorption capacity values from this equation are given in Table 2. Fig. 10 shows the comparison between the adsorption capacities obtained through experiments and that predicted by Eq. (18).

The value of the determination coefficient ($R^2 = 98.59$) for Eq. (18) indicates that about 1.41% of the total variations were not satisfactorily explained by the model (Table 8). The ANOVA Table 9 can be used to test the statistical significance of the ratio of mean square due to regression and mean square due to residual error. From this table it is evident that, the $F_{statistics}$ values of linear and squared regression were higher. These large values imply, that the adsorption capacity can be adequately explained by the model equation. Generally P values lower than 0.001 indicates that the model is considered to be statistically significant at the 99% confidence level [38]. The adsorption capacity prediction from the model is shown in Table 2. The unexplained part of the model (1.03%) is represented as residual error in the ANOVA table. From Table 9, it was observed that the linear effects of all the variables were significant ($P < 0.001$) and the coefficient of X_2^2 and X_3^2 were highly significant ($P < 0.001$), when compared to the squared terms X_1^2 ($P = 0.0423$), X_4^2 ($P = 0.0054$) and X_5^2 ($P = 0.0290$). Among the interaction terms, the interactions between X_1–X_3 and X_2–X_3 ($P < 0.001$) were highly significant on the adsorption capacity.

3.5. Interaction effects of adsorption variables

The adsorption capacities of the present adsorbent over different combinations of independent variables were visualized through three-dimensional view of response surface plots (Fig. 11a–e). The plots (Fig. 11a and e) were represented as a function of two factors at a time, holding other factors at a fixed level. All the response surface plots revealed that at low and high levels of the variables the capacity of the adsorbent was minimal, however, it was noted that there existed a region where neither an increasing nor a decreasing trend in the adsorption capacity was observed. This phenomenon conforms that there was an existence of optimum for the adsorption variables in order to maximize the adsorption capacity. Also there existed a direct proportional relationship between the amount of adsorbent loading and pH (X_1 and X_3) on the copper ion uptake. These interactions were also substantiated by the fact that the interaction between adsorbent loading and pH was very significant ($P < 0.001$) and was found to be solely responsible for achieving a relatively high copper ion uptake as predicted by the model and the response contour plot (Fig. 11a). The curved contour lines showed that there was an interaction between adsor-

bent loading and pH. Further, the initial concentration also played an important role in copper ion uptake as was evident from the equation and plot (Fig. 11b). A relatively strong interaction existed between initial concentration and pH, which was reflected by the corresponding P value ($P < 0.001$) and it was deduced from the curvature of the contour. It was also observed that the temperature of the adsorption process had appreciable amount of interaction effect with the adsorbent loading ($P = 0.0668$) and initial concentration ($P = 0.0794$) (Fig. 11c and d). Furthermore, a moderate interaction was found between initial adsorbate concentration and adsorption time as shown in Fig. 11e.

The maximum predicted adsorption capacity for optimum adsorption variables was obtained through point prediction method and surface response plots and given in Table 10. The adsorption experiment was then performed at the optimized process conditions and it was found that the experimental data obtained was well represented by the present model Eq. (18).

4. Conclusion

Kinetic and isotherm studies revealed that rubber wood sawdust activated carbon prepared using phosphoric acid as the activating agent can be effectively employed for the adsorption of copper ions. Copper adsorption was found to be pH-dependent, follows the Langmuir isotherm and obeys a pseudo-second-order model. Thermodynamic analysis of the adsorption suggests the process to be exothermic as well as spontaneous. The development of a mathematical model for Cu^{2+} adsorption process simulation and optimization on the basis of statistical design of experiments appears to be a useful tool for prediction and understanding of the interaction effects between experimental parameters. Response surface methodology and the central composite rotatable design were appropriate for determining the optimal conditions for copper ions adsorption onto H_3PO_4 activated rubber wood sawdust. The optimal conditions of adsorption established by RSM are as follows: adsorbent concentration $0.45 \, g (100 \, mL)^{-1}$, initial adsorbate concentration $35 \, mg \, L^{-1}$, pH of the solution 6.5, adsorption temperature 26 °C and adsorption time 208 min; in these conditions the adsorption capacity was $5.60 \, mg \, g^{-1}$.

References

[1] A.H. Hawari, C.N. Mulligan, Heavy metals uptake mechanisms in a fixed bed column by calcium-treated anaerobic biomass, Process Biochemistry 41 (2006) 187.

[2] F. Qin, B. Wen, X.-Q. Shan, Y.-N. Xie, T. Liu, S.-Z. Zhang, S.U. Khan, Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat, Environmental Pollution 144 (2006) 669.

[3] R. Molinari, P. Argurio, T. Poerio, Comparison of polyethylenimine, polyacrylic acid and poly(dimethylamine-co-epichlorohydrin-co-ethylenediamme) in Cu^{2+} removal from wastewaters by polymer-assisted ultrafiltration, Desalination 162 (2004) 217.

[4] K. Kadirvelu, K. Thamaraiselvi, C. Namasivayam, Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste, Bioresource Technology 76 (2001) 63.

[5] Z.R. Holan, B. Volesky, Biosorption of Pb and Ni by biomass of marine algae, Biotechnology and Bioengineering 43 (1994) 1001.

[6] S. Wang, M. Soudi, L. Li, Z.H. Zhu, Coal ash conversion into effective adsorbents for removal of heavy metals and dyes from wastewater, Journal of Hazardous Materials B 133 (1–3) (2006) 243.

[7] A.H. Hawari, C.N. Mulligan, Biosorption of lead(II), cadmium(II), copper(II) and nickel(II) by anaerobic granular biomass, Bioresource Technology 97 (2006) 692.

[8] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, Chemical Engineering Journal 132 (2007) 299.

[9] S. Lu, S.W. Gibb, Copper removal from wastewater using spent-grain as biosorbent, Bioresource Technology 99 (2008) 1509.

[10] Y.H. Huang, C.L. Hsueh, H.P. Cheng, L.C. Su, C.Y. Chen, Thermodynamics and kinetics of adsorption of Cu(II) onto waste iron oxide, Journal of Hazardous Materials 144 (1–2) (2007) 406.

[11] M. Kazemipour, M. Ansari, S. Tajrobehkar, M. Majdzadeh, H.R. Kermani, Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone, Journal of Hazardous Materials 150 (2007) 322.

[12] D. Mugisidi, A. Ranaldo, J.W. Soedarsono, M. Hikam, Modification of activated carbon using sodium acetate and its regeneration using sodium hydroxide for the adsorption of copper from aqueous solution, Carbon 45 (2007) 1081.

[13] C.-H. Weng, C.-Z. Tsai, S.-H. Chu, Y.C. Sharma, Adsorption characteristics of copper(II) onto spent activated clay, Separation and Purification Technology 54 (2007) 187.

[14] A. Baraka, P.J. Hall, M.J. Heslop, Melamine–formaldehyde–NTA chelating gel resin: synthesis, characterization and application for copper (II) ion removal from synthetic wastewater, Journal of Hazardous Materials 140 (2007) 86.

[15] M. Sciban, B. Radetic, Z. Kevresan, M. Klasnja, Adsorption of heavy metals from electroplating wastewater by wood sawdust, Bioresource Technology 98 (2007) 402.

[16] F. Ekmekyapar, A. Aslan, Y. Kemal Bayhan, A. Cakici, Biosorption of copper(II) by nonliving lichen biomass of Cladonia rangiformis hoffm, Journal of Hazardous Materials B137 (2006) 293.

[17] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of cobalt(II) and nickel(II) by seaweeds: batch and column studies, Separation and Purification Technology 44 (2005) 53.

[18] M.H. Kalavathy, T. Karthikeyan, S. Rajgopal, L.R. Miranda, Miranda, Kinetic and isotherm studies of Cu(II) adsorption onto H_3PO_4-activated rubber wood sawdust, Journal of Colloid and Interface Science 292 (2005) 354.

[19] T. Karthikeyan, S. Rajgopal, L.R. Miranda, Chromium(VI) adsorption from aqueous solution by Hevea Brasilienesis sawdust activated carbon, Journal of Hazardous Materials B124 (2005) 192.

[20] M. Kincl, S. Turk, F. Vrecer, Application of experimental design methodology in development and optimization of drug release method, International Journal of Pharmaceutics 291 (2005) 39.

[21] M.M.D. Zulkali, A.L. Ahmad, N.H. Norulakmal, Oryza sativa L. husk as heavy metal adsorbent: optimization with lead as model solution, Bioresource Technology 97 (2006) 21.

[22] J. Goel, K. Kadirvelu, C. Rajagopal, V.K. Garg, Cadmium(II) uptake from aqueous solution by adsorption onto carbon aerogel using a response surface methodological approach, Industrial and Engineering Chemistry Research 45 (2006) 6531.

[23] D.C. Montgomery, Design and Analysis of Experiments, fifth ed., John Wiley & Sons, New York, 2001.

[24] G.M. Clarke, R.E. Kempson, Introduction to the Design and Analysis of Experiments, Arnold, London, 1997.

[25] J.A. Cornell, How to Apply Response Surface Methodology, second ed., American Society for Quality Control, Wisconsin, 1990.

[26] G. Box, N. Draper, Empirical Model Building and Response Surfaces, John Wiley & Sons, New York, 1987.

[27] C. Cojocaru, G. Zakrzewska-Trznadel, Response surface modeling and optimization of copper removal from aqua solutions using polymer assisted ultrafiltration, Journal of Membrane Science 298 (2007) 56.

[28] R. Wachter, A. Cordery, Response surface methodology modelling of diamond-like carbon film deposition, Carbon 37 (1999) 1529.

[29] D.E. Egirani, A.R. Baker, J.E. Andrews, Copper and zinc removal from aqueous solution, by mixed mineral systems I. Reactivity and removal kinetics, Journal of Colloid and Interface Science 291 (2005) 319.

[30] M. Goyal, V.K. Rattan, D. Aggarwal, R.C. Bansal, Removal of copper from aqueous solutions by adsorption on activated carbons, Colloids and Surfaces A: Physicochemical and Engineering Aspects 190 (2001) 229.

[31] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, Role of sawdust in the removal of Cu(II) from industrial waste, Water Research 32 (1998) 3085.

[32] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, Journal of American Chemical Society 40 (1918) 1361.

[33] H. Freundlich, Uber die. adsorption. in. losungen, Zeitschrift fur Physical Chemistry 57 (1906) 385.

[34] S. Lagergren, Zur theorie der sogenannten adsorption gelöster stoffe, Kungliga Svenska Vetenskapsakademiens, Handlingar 24 (4) (1898) 1.

[35] Y.S. Ho, G. McKay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Canadian Journal of Chemical Engineering 76 (1998) 822.

[36] C.A. Toles, W.E. Marshall, M.M. Johns, Granular activated carbon from nutshells for the uptake of metal ions and organic compounds, Carbon 35 (1997) 1407.

[37] A.I. Khuri, J.A. Cornell, Response Surfaces: Design and Analysis, fifth ed., Marcel Dekker, New York, 1987.

[38] K. Ravikumar, K. Pakshirajan, T. Swaminathan, K. Balu, Optimization of batch process parameters using response surface methodology for dye removal by a novel adsorbent, Chemical Engineering Journal 105 (2005) 131.