



Adsorption of copper on activated Ganga sand from aqueous solution: kinetics, isotherm, and optimization

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Abstract

In this study, removal of copper from synthetic aqueous solution was done using adsorption process. The batch study was done at room temperature and analyzed using Freundlich and Langmuir isotherms. The Box–Behnken design method of response surface methodology was used to know the interactions between independent variables (pH of aqueous solution, contact time, adsorbent dose, and initial copper concentration) and response variable (copper removal). The activated Ganga sand was used as an adsorbent to make treatment in a cost-effective way. The Ganga sand was activated by using a base solution of 14 N sodium hydroxide. The synthetic aqueous solution was having copper concentration of 100 ppm. The optimum conditions for independent variables to achieve maximum removal of copper from synthetic aqueous solution were also determined. The optimum conditions of aqueous solution for pH, contact time, adsorbent dose, and initial copper concentration were obtained as 8.7, 150 min, 3.5 g/L, and 34 ppm respectively. At this optimum condition, 97.7% of copper removal was achieved. Both isotherms (Freundlich and Langmuir isotherms) were found fitted well with a good correlation coefficient ($R^2 > 0.95$). The kinetic behavior for the responsible adsorption process was analyzed using pseudo-second-order kinetic equations. The results suggested that Ganga sand can be used as a promising economical and conventional adsorbent for copper removal.

Keywords Adsorption · Analysis of variance · Box–Behnken design · Response surface methodology

Introduction

The existence of heavy metals in industrial wastes is of immense distress due to their natural toxicity and hazardous effect. Copper is a type of heavy metal and has various utilization in industries like electroplating, paper, refineries, fertilizers etc. (Karthikeyan et al. 2005). Although copper is a vital element essential for the human body, still it becomes toxic if it is consumed beyond a certain limit. Excessive consumption of copper has short- and long-term influence on humans and may cause serious problems like jaundice, diarrhea, vomiting, nausea, liver and kidney damage, and DNA mutation (Al-Harashseh et al. 2015). The permissible and maximum limit of copper in drinking water is 0.05 mg/L and 1.5 mg/L, respectively, as per the Bureau of Indian Standard

(BIS 2012). EPA (2002) has recommended 1.3 mg/L of copper in drinking water, while WHO recommended 2.0 mg/L. It was also observed that heavy metal has high resistance against biodegradation (Sudha Rani et al. 2018).

There are many active methods used for the dilution of copper from aqueous solution, such as adsorption (Daneshyar et al. 2017), bio-filtration (Majumder et al. 2015), chemical precipitation (Gurmen et al. 2009), electrocoagulation (De Mello Ferreira et al. 2013), ion exchange (Veli and Pekey 2004), reverse osmosis (Sudilovskiy et al. 2008), and ultrafiltration (Molinari et al. 2004). However, these methods remove copper up to some extent but have some limitations like uneconomical, excessive use of reagents, sludge production, incomplete pollutant removal, and high energy requirements to drive the process. The adsorption process has more acceptance among all the other methods as it is more economical, easy to operate, quick and significantly less sludge production or any harmful by-products. These days, low-cost natural materials like silica mud, ash, and agricultural wastes were used for sorbent materials (Al-Harashseh et al. 2015). Adsorption of copper from an aqueous solution can be achieved

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with different adsorbents like chemically activated sawdust (Sciban et al. 2006), anaerobic granular biomass (Hawari and Mulligan 2006), waste iron oxide (Huang et al. 2007), modified activated carbon using sodium acetate (Mugisidi et al. 2007), spent activated clay (Weng et al. 2007), modified coal fly ash (Pizarro et al. 2015; Attari et al. 2017), activated carbon (Daneshyar et al. 2017), carbon foam (Lee et al. 2017), spent-grain (Lee et al. 2017), and laterite soil (Sudha Rani et al. 2018). In many researches, activated carbon was widely accepted adsorbent for the removal of many pollutants along with copper with high removal efficiency, and this is due to its higher surface area. But in many methods, it becomes exceptionally lengthy and uneconomic to synthesize activated carbon. Fly ash emerged as a promising adsorbent, but since it has leaching effect, it requires numerous treatment. Some researchers reported that the fly ash contains high concentration of heavy metals, so there is chances of increasing other heavy metals to the treated water (Sharma and Kalra 2006). It has been found that numerous studies has been done to investigate whether soil and other minerals deposits can remove heavy metals from aqueous solution (Appel et al. 2008; Kul and Koyuncu 2010). Some researcher used laterite soil to remove copper from aqueous solution with 90% efficiency (Sudha Rani et al. 2018). The aforementioned studies suggest and inspire to use soil or mineral deposits to use as base material for adsorbent. The primary material used for the synthesis of adsorbent is Ganga sand, which is easily and abundantly available in the plain region of India and also at a low cost.

Response surface methodology (RSM) was used to get the optimal environments for adsorption parameters for the removal of copper. RSM is a statistical tool created using multivariate nonlinear analysis, which has been acknowledged broadly for the optimization of any adsorption process (Zhao et al. 2011; Xu et al. 2012). RSM is mainly used to signify the effect of individual parameters and to establish the relationship between these independent variables.

The main objective of this study was to remove copper from synthetic aqueous solution using adsorption process. To achieve the main objective, this work was divided into some parts, these are (1) the effects of important variables related to adsorption process on copper removal. (2) The optimum conditions were found for the selected variables in order to achieve the maximum copper removal efficiency. (3) The kinetics and isotherms were plotted to know the responsible mechanism for the removal of copper.

The experimental work of this research has been carried out in the environmental laboratory of National Institute of Technology-Patna (NIT-Patna), India, under the period of February 2019 to January 2020.

Materials and methods

Materials and instrument

The chemicals used in this work were of analytical grade and bought from Merck (India). Milli-Q water was used for the preparation of all kinds of reagents and solutions. The atomic absorption spectrophotometer (AAS) manufactured by Electronic Corporation of India Limited was used to analyze copper concentration in water. Other instruments like digital pH meter (Oakton pH 700), Orbital shaker, and hot air oven were used in this study and calibrated time to time. The base material for the adsorbent was Ganga sand, which was collected from the bank of river Ganga at Gandhi Ghat (Patna, India) with GPS coordinates 25°37'15" N and 85°10'28" S.

Activation of Ganga sand as an adsorbent

Appropriate amount of the Ganga sand was collected from the above-mentioned location and transported immediately to the Environmental Engineering Laboratory of N.I.T. Patna. The sand was washed with tap water to make it free from organic and other impurities. The washed sand was dried in the oven at 60 °C for 2 h to remove moisture. The dried sand was sieved through 125 micron sieve.

The activation of Ganga sand was done by mixing 14 N NaOH solution with dried sand (finer than 125 micron size) in the ratio of 4:3 by volume. The mixing was done continuously for 15 min. The obtained slurry mixture was dried in the oven for 24 h at a temperature of 105 °C. Then the dried mixture was crushed and sieved through 72 micron sieve. The sieved sand was washed with distilled water to remove any residue. Finally, the washed sand was dried in oven at 105 °C until it became free from moisture. The final obtained sand (dried and moisture free) was kept in a container and named as activated Ganga sand.

Preparation of synthetic aqueous solution

Synthetic aqueous solution of 100 ppm of copper was prepared, and determination of copper in aqueous solution was as per the Standard Method for the Examination of Water and Wastewater (APHA 2005). It was prepared by dissolving 0.100 gm of copper-turning in 12 ml of Nitric acid. When copper was dissolved entirely in acid, then it was diluted in a 1000 ml volumetric flask with Milli-Q water. One ml of this solution gives 100 µg of Cu²⁺⁺ concentration. The solution of different concentrations of copper for analysis was prepared by diluting this stock solution. Synthetic aqueous solution was prepared from the stock solution that contains only

Cu^{2+} to avoid the interaction of any other ions or cations. The standards of 0, 0.5, 1.0, 2.0, 5.0, 7.0, and 10 ppm copper concentration were prepared for the calibration curve.

Experimental methodology

The selected independent variables in this study were pH of the solution, dose of adsorbent, initial copper in the aqueous sample, and contact period at a fixed temperature of 25 ± 2 °C. The pH of the solution, contact time, initial copper concentration, and adsorbent dose were varied from 4 to 12, 20 to 180 min, 10 to 150 ppm, and 0.5 to 4 g/L, respectively. The preliminary analysis for each independent variable was investigated to know effect on the response variable (copper removal). A batch study in conical flask was done to perform the preliminary analysis. Three sets of preliminary test was done for each independent variable and reported the average values of results to ensure a minimum error in experimental readings. The obtained results were applied to statistical analysis to find the optimum conditions for independent variables. The experiments were performed at obtained optimum conditions to remove copper from aqueous solution. The Box–Behnken design (BBD) of response surface methodology (RSM) was used for optimization method. The statistical analysis was done with the Design expert 12.0 software. The pH of the solution was fixed using 1 N NaOH and 1 N HCl solution. All the experimental analyses were done at a constant temperature of 25 ± 2 °C. The percentage of copper adsorbed or removed through the adsorption process was calculated through the following equation

$$\text{Copper Removal (Expressed in \%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i represents the initial concentration (ppm) of copper in an aqueous solution, while C_f represents the final residue concentration of copper after the adsorption process.

Experiment design and data analysis

While dealing with RSM problems, the relationships between variables and responses are unidentified, so an appropriate approximation between the factors and response is to be established. The rigorously used approximating functions are polynomials (Nair et al. 2014). The quadratic second-order equation as described below in Eq. 2 with interaction terms was used to establish relation between the variables and response. The pH of the solution, contact time, initial copper concentration, and adsorbent dose were varied from 4–12, 20–180 min, 10–100 ppm, and 0.5–4 g/l, respectively. Design expert 12.0 software (Stat Ease Inc.

Minneapolis, 175, USA) was used to perform statistical analysis with the BBD model.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} X_i X_j \quad (2)$$

where Y , X_i , and X_j represent the predicted response and independent variables, respectively, β_0 , β_i , β_{ii} , and β_{ij} are regression coefficients for intercept, linear, quadratic, and interaction coefficients, respectively, k is the number of variables studied.

Results and discussion

Effect of pH on copper adsorption

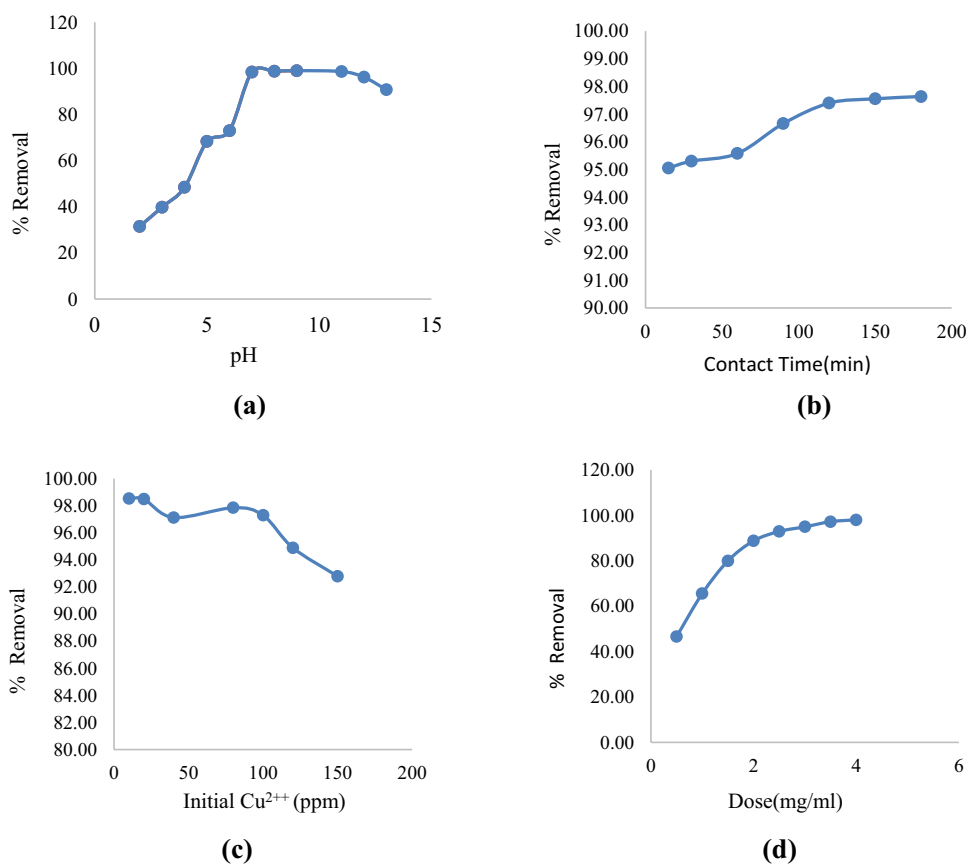
The behavior of pH on the adsorption process was determined under a fixed condition by performing preliminary test. The pH of solution was varied in the range of 2–13 with the help of NaOH and HCl solution, while keeping all other parameters constant. The other parameters like contact time, initial copper concentration and adsorbent dose were fixed to 120 min, 100 ppm, and 1 g/L, respectively. Then it was stirred in a shaker for a time period of 120 min. After it, sample was taken out and filtered on filter paper (Whatman No- 42). Then the filtered solution was analyzed on AAS at a wavelength of 324 nm for residue copper. The variation of pH for adsorbent is shown in Fig. 1a. The optimum pH of 7 was observed at which more than 98% copper was removed from the aqueous solution by this adsorbent. This shows that the neutral region of pH is the most favorable for the adsorption process in this work. It was also observed that the efficiency of the process was more in the basic region compared to the acidic region and this may be due to the reason that in an acidic medium, most of the ions get used in neutralizing themselves and very few sites have remained for the adsorption process.

Effect of contact time on copper adsorption

To determine the effect of contact period on the copper adsorption, the same procedure was followed as in the previous section with the only change being that here contact period was varied, keeping all other parameters constant. From the previous section, it was concluded that at a pH of 7, efficiency was highest, so here pH was fixed to 7. Based on experimental data, the graph is shown in Fig. 1b, and it was observed that a significant copper removal can be achieved at very less contact time of 15 min. But equilibrium time was achieved at 120 min after which only minor changes in the removal efficiency have been noted.



Fig. 1 Effect of individual parameter on adsorption process: **a** effect of pH on the adsorption of copper; **b** effect of contact time; **c** Effect of initial copper concentration; **d** effect of adsorbent's dose



Effect of initial copper concentration on copper adsorption

The same procedure was followed here with Cu²⁺ as a variable. Here pH was fixed to 7 and contact time for 120 min. The effect of initial Cu²⁺ on this adsorbent can be observed from the graph shown in Fig. 1c. Up to a concentration around 100 ppm, it can be seen that good efficiency (up to 98%) was observed after that efficiency dropped to 90% at 150 ppm. So, here it can be noted that up to 100 ppm of Cu²⁺ the adsorption rate was quite high after which it started to fall.

Effect of adsorbent dose on copper adsorption

For this analysis, the adsorbent dose was varied, keeping other parameters constant as per the result of the above section, i.e., pH equals 7, contact time for 120 min and Cu²⁺ as 100 ppm. The adsorbent dose was varied from 0.5 to 4 gm/L. The maximum copper removal (more than 98%) was obtained at an adsorbent dose of 4 gm/L. But at a dose of 2 gm/L, decent (around 92%) efficiency was observed, which indicates that if the adsorbent considered from an economic point of view, we can go with a dose of 2 gm/L, but if we

have to only deal with the efficiency of copper removal, then we would adopt 4 g/L dose of the adsorbent.

Optimization of the adsorption process

During preliminary analysis, the copper removal was optimized by varying only one parameter while keeping all other parameters fixed. For optimizing adsorption process, all the variables should be considered together by varying all the parameters in a single operation. To do so, a software named Design expert 12.0 was used. There was five option (minimum, maximum, within range, none, and target) provided by the mentioned software to set each variable and response for the optimization process. The pH, initial Cu²⁺, contact time, and adsorbent dose were taken as independent variables.

Since the synthesis of an adsorbent is a cost-effective process, it requires to take consideration of the adsorbent dose. The optimization was done based on two criteria. In the first criteria, the adsorbent dose was given priority which means there was a limit for the use of adsorbent. The desired goal (copper removal) was fixed at a maximum, adsorbent dose at a minimum, while pH, contact time, and initial Cu²⁺ were set to within range. The optimum conditions for pH, contact time, initial Cu²⁺, and adsorbent dose were achieved as



9.6, 142 min., 100 ppm and 1.704 g/L, respectively. Copper removal was found 83% at the obtained optimum condition.

While in second criteria, focus was on maximizing the copper removal irrespective of adsorbent dose which means adsorbent dose can go as high to get equilibrium of copper removal. In the first criteria, the only change was the adsorbent dose, which was set to maximum. The optimum values for pH, Contact time, initial Cu²⁺ and adsorbent time were 8.7, 150 min., 34 ppm and 3.5 g/L. The copper removal was found 99% at obtained optimum conditions which is higher than copper removal from first criteria.

In order to ensure the above-predicted result by the software, there were three confirmative experiments done in the laboratory whose average value came 80.3% and 97.7%, respectively, for both the condition.

Isotherm of the adsorption process

At equilibrium, adsorption isotherm established a relationship between adsorbate and adsorbent. The isotherm was carried out by performing Langmuir and Freundlich models. Langmuir model works with the assumption that if there is no interaction between the adsorbed molecules, then the monomolecular layer is formed (Aksu 2002). Equilibrium data were described using the Langmuir constant (K_a), and the maximum monolayer adsorption capacity Q_m (mg/g) associated with the attraction of the binding sites (L/mg) was calculated using the Langmuir adsorption isotherm equation given as:

$$q_e = Q_m K_a C_e / (1 + K_a C_e) \tag{3}$$

The above equation of the Langmuir model can be written in linear form as Eq. 4 given below:

$$C_e/q_e = 1/K_a Q_m + C_e/Q_m \tag{4}$$

where C_e is the equilibrium concentration (mg/L), q_e the amount of solute (Cu²⁺) adsorbed per unit of adsorbent

(mg/g), Q_m monolayer adsorption capacity (mg/g), and k_a is the adsorption intensity. The values of Q_m and k_a can be calculated by the help of slope and intercept of the C_e/q_e Vs C_e plot as shown in Fig. 2a.

The adsorption process which occurs on a heterogeneous surface is explained through the Freundlich isotherm model. It deals with the interaction between the liquid and solid phase capacity at equilibrium, which is based on the multilayer adsorption. This isotherm assumes that the distribution of the adsorption sites is exponential with respect to adsorption's heat (Kalavathy M. et al. 2009). The Freundlich isotherm model is explained through Eq. 5 given as:

$$q_e = K_f (C_e)^{1/n} \tag{5}$$

The above equation can be written in linear form as Eq. 6 given below:

$$\log q_e = 1/n \log C_e + \log K_f \tag{6}$$

where K_f is the empirical constants related to bonding energy or as an indicator of adsorption capacity and $1/n$ measures the adsorption intensity.

Using Eq. 4 and 6, the graph has been drawn to study the Freundlich and Langmuir isotherms, which is shown in Fig. 2. Freundlich isotherm is best fitted with $R^2 = 0.9963$. Langmuir Isotherm with $R^2 = 0.9927$ is also acceptable. The constant of both the model is mentioned in Table 1. The monolayer adsorption capacity (Q_m) derived from Langmuir Isotherm was found to be 80 mg/g, and this validates the acceptance of the adsorbent for the removal of copper.

Kinetic behavior of adsorption process

The kinetic behavior of the process, i.e., the sorption velocity of Cu²⁺ on the activated Ganga sand adsorbent, was analyzed through three different kinetic equations. These three equations have been discussed briefly in this section. The pseudo-first-order equation for the adsorption

Fig. 2 Plot of isotherm: **a** Langmuir isotherm; **b** Freundlich isotherm

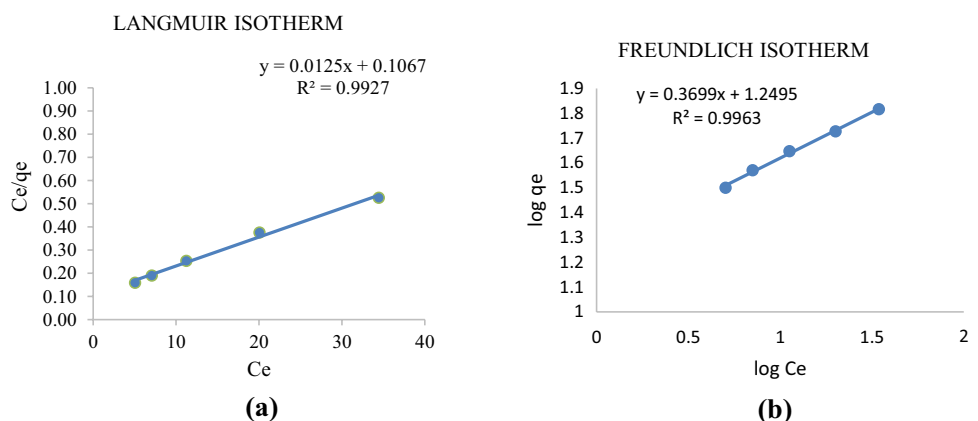


Table 1 Parameters of the Langmuir and Freundlich isotherms for the adsorption process

Temperature (K)	Langmuir constant			Freundlich constants		
	Q_m (mg/g)	K_a (L/mg)	R^2	n (g/L)	K_f (mg/g)	R^2
298 ± 2	80	0.11	0.9927	2.7	17.76	0.9963

of liquid/solid system centered on solid capacity is given as (Balouch et al. 2013).

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \quad (7)$$

When Eq. 7 is integrated for the boundary condition ($t=0$, $q_t=0$ and $t=t$, $q_t=q_t$), we get

$$\log(q_e - q_t) = \log(q_e) - K_1 t \quad (8)$$

where q_e (mg/g) is the sum of adsorbate adsorbed on the adsorbent's surface, q_t (mg/g) is the total of adsorbate on the surface of the adsorbent for time t (min), and K_1 is the equilibrium rate constant (min^{-1}). Equation 8 was used for the analysis of pseudo-first-order kinetics, result of which was plotted and is shown in Fig. 3a. Using the slope of this plot,

K_1 and q_e were determined and compared with the experimental data in Table 2.

A pseudo-second-order equation was also used to test the experimental data. The equation is given as (Ho and Mckaf 2000).

$$dq_t/dt = K_2(q_e - q_t)^2 \quad (9)$$

If Eq. 9 is integrated for the boundary condition ($t=0$, $q_t=0$ and $t=t$, $q_t=q_t$) and rearranged, then this equation forms as

$$t/q_t = 1/h + t/q_e \quad (10)$$

where h is the initial sorption rate, i.e., $h=K_2q_e^2$, and K_2 is termed as rate constant (g/mg/min). Equation 10 was used for the analysis of pseudo-second-order kinetics, result of which was plotted and is shown in Fig. 3b. Using the slope

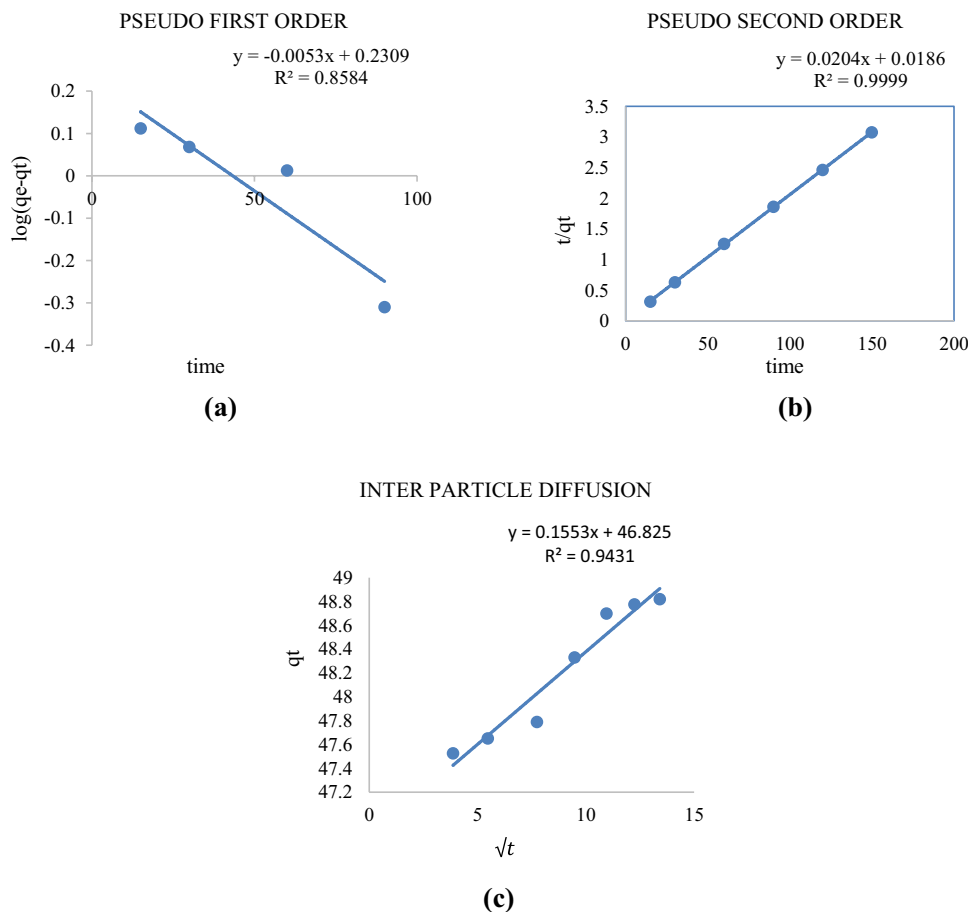
Fig. 3 Kinetics plot: **a** Pseudo-first-order kinetics; **b** Pseudo-second-order kinetics; **c** Plot of intraparticle diffusion

Table 2 Assessment of the pseudo-first-order and pseudo-second-order sorption rate constant at 298 K

Temperature (K)	Pseudo-first-order kinetics			Pseudo-second-order kinetics			q_e (experimental) (mg/g)
	q_e (calculated) (mg/g)	K_1 (min^{-1})	R^2	q_e (calculated) (mg/g)	K_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	R^2	
298 ± 2	1.7	0.0053	0.8584	49	0.02239	0.99	48.82

of this plot, K_2 and q_e were determined and compared with the experimental data in Table 2.

The intraparticle diffusion model was used to identify the mass transfer steps in the Cu^{2+} ions onto the adsorbent (Hu et al. 2013). The intraparticle diffusion model was governed using the following equation (Karthikeyan et al. 2005).

$$q_t = K_p t^{1/2} + C \quad (11)$$

where K_p ($\text{mg/g t}^{1/2}$) is the rate constant for intraparticle diffusion and C is the constant of intercept. The intraparticle diffusion was plotted and is shown in Fig. 3c.

On the analysis of the three mentioned kinetics model, the nonlinear form of the pseudo-second-order model fitted the best for this adsorption process. The value of K_2 and q_e was calculated, and the value of this calculated q_e (49 g/mg/min) was much nearer to the experimental value (48.82 g/mg/min). The coefficient of correlation (R^2) of the pseudo-second-order model is 0.999. This value is very much close to 1, and it indicates that kinetic data followed the pseudo-second-order model, which suggests a chemisorption process (Reddad et al. 2002).

As per literature, if the regression of the intraparticle diffusion plot, i.e., q_t Vs $t^{1/2}$ is linear and passes through the origin, then the intraparticle diffusion will be the rate-controlling step (Svilović et al. 2010). But according to Fig. 3c, the plot was multilinear in this case, which indicates that the adsorption process was being affected by more than one process.

Statistical analysis by design expert 12.0 software

In order to test the model, statistical analysis techniques were used to evaluate the suitability of the model, experimental error, and significance of the terms in the model. In this work, it was done using software named Design Expert 12.0, which evaluates the RSM program. The independent variable which includes pH, contact period, initial Cu^{2+} , and adsorbent dose were nominated as X_1 , X_2 , X_3 , and X_4 , respectively. The experiment range was determined from the result of preliminary analysis and reported in term of low, medium and high level. The low-level, medium- and high-level experimental range for X_1 , X_2 and X_3 was 4, 8, 12; 20, 100, 180; 10, 55, 100, and 0.5, 2.25, 4.0, respectively.

According to the Box–Behnken design (BBD), a total of 29 runs which includes five replicates at the central point, were performed and details of runs with predicted and observed experimental results of responses are presented in Table 3. The observed values fitted by using second-order polynomial, as mentioned in Eq. 2 to satisfy the model. The quadratic equation for copper removal in terms of coded factors is given by Eq. 12 as shown below:

$$\begin{aligned} \text{Cu}^{2+} \text{ removal (\%)} = & 89 + 15X_1 + 183X_2 - 3.25X_3 + 20.75X_4 \\ & - 1.50X_1X_2 + 2.75X_1X_3 + 4.25X_1X_4 + 0.752X_2X_3 + 1.25X_2X_4 \\ & + 2.75X_3X_4 - 18.71X_1^2 - 1.46X_2^2 + 2.17X_3^2 - 17.08X_4^2 \end{aligned} \quad (12)$$

Analysis of variance (ANOVA) was done to ensure the suitability of this second-order polynomial model. Fisher test was also performed to know the consequence of each parameter. Table 4 represents the ANOVA result along with the P value and the F value of each model terms for copper adsorption. If the $P > F$ value becomes greater than 0.05, then the model term is considered as insignificant (Nair et al. 2014). So in Eq. 12, many terms got eliminated except the term to maintain the hierarchical order and reduced to Eq. 13 as given below:

$$\begin{aligned} \text{Cu}^{2+} \text{ removal (\%)} = & 89 + 15X_1 + 183X_2 - 3.25X_3 \\ & + 20.75X_4 - 18.71X_1^2 - 17.08X_4^2 \end{aligned} \quad (13)$$

ANOVA results are generally presented through several parameters such as “ $P > F$ ” value, F value, R^2 value, adjusted R^2 , predicted R^2 , lack of fit (LOF), adequate precision (AP) and coefficient of variance (CV) (Nair et al. 2014). The model behavior can be predicted according to the above-mentioned parameters. The model is considered as significant if the $P > F$ value of the ANOVA test result is found to be less than 0.05 at a 5% confidence interval but if its value is more than 0.05, then the model gets eliminated. A model will be considered a failure if the LOF ($P > F$ value) of the ANOVA test result is less than 0.05, i.e. for a significant model, LOF should be no significant (Kumar and Quaff 2020). The LOF value was found to be 0.0768 (not significant), which is acceptable as it is greater than 0.05.

The values of R^2 , adjusted R^2 and predicted R^2 decide the overall efficiency of the model. The value of R^2 , adjusted R^2 , and predicted R^2 are 0.9455, 0.8910, and 0.7044,



Table 3 BBD design matrix along with actual and predicted response values

Run order	pH	Contact time (min)	Cu ²⁺⁺ concentration (ppm)	Adsorbent dose (gm/l)	Copper removal (%)	
					Actual value	Predicted value
1	8	180	10	2.25	95.00	94.04
2	8	100	55	2.25	94.00	89.00
3	12	100	10	2.25	89.00	87.96
4	4	180	55	2.25	56.00	57.17
5	8	100	10	0.5	57.00	59.33
6	4	100	55	0.5	35.00	21.71
7	8	100	10	4	95.00	95.33
8	12	100	55	0.5	51.00	43.21
9	12	100	100	2.25	82.00	86.96
10	8	100	55	2.25	87.00	89.00
11	8	20	10	2.25	95.00	91.88
12	8	180	100	2.25	94.00	89.04
13	8	180	55	0.5	42.00	50.29
14	12	20	55	2.25	84.00	83.50
15	8	20	55	0.5	39.00	49.13
16	12	180	55	2.25	85.00	84.17
17	8	180	55	4	97.00	94.29
18	12	100	55	4	88.00	93.21
19	8	20	100	2.25	91.00	83.88
20	8	100	55	2.25	90.00	89.00
21	8	100	55	2.25	90.00	89.00
22	8	100	100	4	96.00	94.33
23	4	100	100	2.25	43.00	51.46
24	4	100	10	2.25	61.00	63.46
25	4	20	55	2.25	49.00	50.50
26	8	20	55	4	89.00	88.13
27	4	100	55	4	55.00	54.71
28	8	100	55	2.25	84.00	89.00
29	8	100	100	0.5	47.00	47.33

respectively. The value of R^2 (0.9455) was close to 1, which indicates a good fit. The difference between the two R^2 is 0.1866, which is less than 0.2, which is required for a good fit model. The predicted R^2 is in reasonable agreement with adjusted R^2 .

Adequate precision (AP) is also a deciding term for the adequacy of any model. It is a measurement of the signal-to-noise ratio, and this ratio should be greater than 4, which is necessary for a good fit model (Kumar and Quaff 2020). The AP was found to be 14.54, indicating an adequate signal. The CV tells about the reproducibility of the model, and in this case, its value is 9.51%. Hence, it is acceptable (less than 10% is desirable). On the basis of ANOVA results, it is established that outcomes of the statistical analysis support the acceptance of the model and the model can be considered as a good fit model.

The normal plotting of residuals can also analyze the fitting of the model. A model is said to be well fitted if the said plot has a straight line with very less scattered data (Nair

et al. 2014). The normal plot of the residuals as shown in Fig. 4 has a straight line with a few scattered, which indicates that the quadratic model derived in this model is well accepted. Figure 5 shows the comparisons between the experimental and predicted models for Cu²⁺⁺ removal efficiency. From this plot, it is observed that a straight line with very little difference in the actual and predicted plot which also represent a well-fitted model.

Interaction effects of adsorption parameters

The influence of independent variables and their interaction on the response can be observed as a 3-D response surface plot. The adsorption capacities of the adsorbent at different conditions were shown through a 3-D response surface plot. Figure 6a, b, c and d shows the interaction effect of independent variables on copper removal. The copper removal was found minimum at a low and high level values

Table 4 ANOVA for copper adsorption process

Source	Sum of squares	df	Mean square	F value	p value	
Model	12,184.99	14	870.36	17.35	<0.0001	Significant
X ₁ -pH	2700.00	1	2700.00	53.83	<0.0001	
X ₂ -contact time	40.33	1	40.33	0.8041	0.3850	
X ₃ -initial copper	126.75	1	126.75	2.53	0.1342	
X ₄ -adsorbent dose	5166.75	1	5166.75	103.00	<0.0001	
X ₁ X ₂	9.00	1	9.00	0.1794	0.6783	
X ₁ X ₃	30.25	1	30.25	0.6031	0.4503	
X ₁ X ₄	72.25	1	72.25	1.44	0.2500	
X ₂ X ₃	2.25	1	2.25	0.0449	0.8353	
X ₂ X ₄	6.25	1	6.25	0.1246	0.7294	
X ₃ X ₄	30.25	1	30.25	0.6031	0.4503	
X ₁ ²	2270.28	1	2270.28	45.26	<0.0001	
X ₂ ²	13.80	1	13.80	0.2750	0.6082	
X ₃ ²	30.45	1	30.45	0.6071	0.4489	
X ₄ ²	1893.02	1	1893.02	37.74	<0.0001	
Residual	702.25	14	50.16			
Lack of fit	646.25	10	64.62	4.62	0.0768	Not significant
Pure error	56.00	4	14.00			

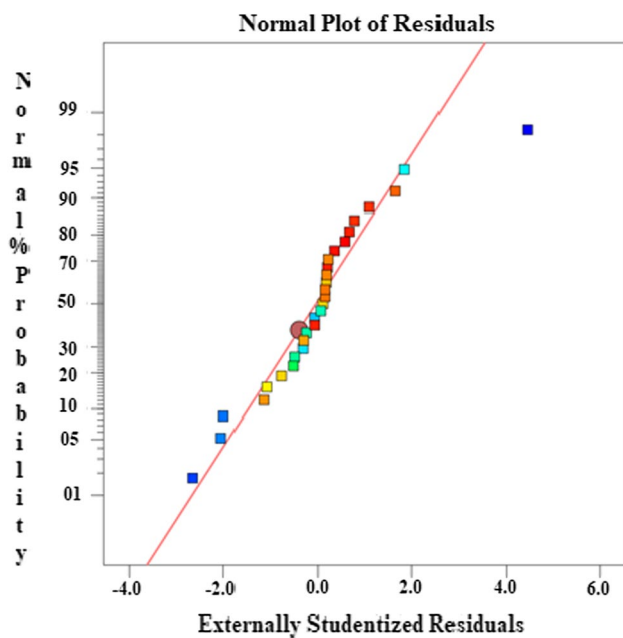


Fig. 4 Normal probability plot of residual for copper removal

of independent variable there was neither increasing nor decreasing trend at some specific points, and this confirms that this was the point of maximum copper removal.

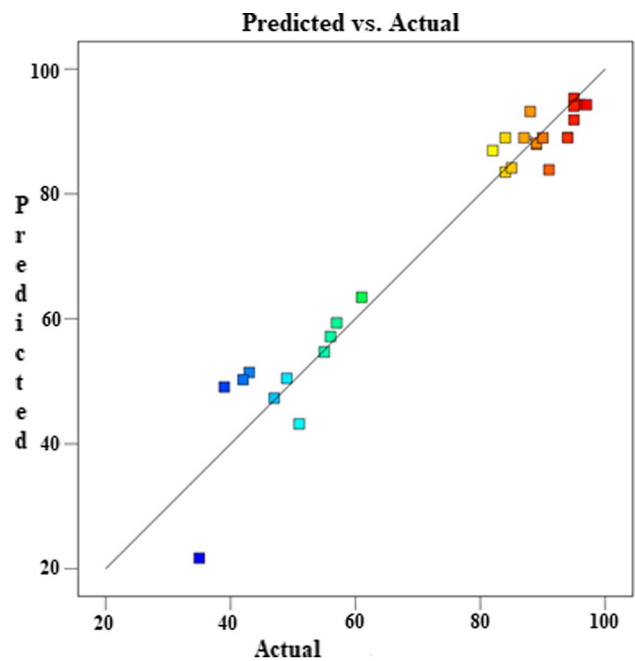


Fig. 5 Plot of predicted versus actual data

Conclusion

The preliminary analysis suggests that the amount of copper removal depends mostly on pH of the solution affect among the all variables. The pH in the neutral region slightly inclined toward the basic region is the most favorable region for the adsorption of the copper from the

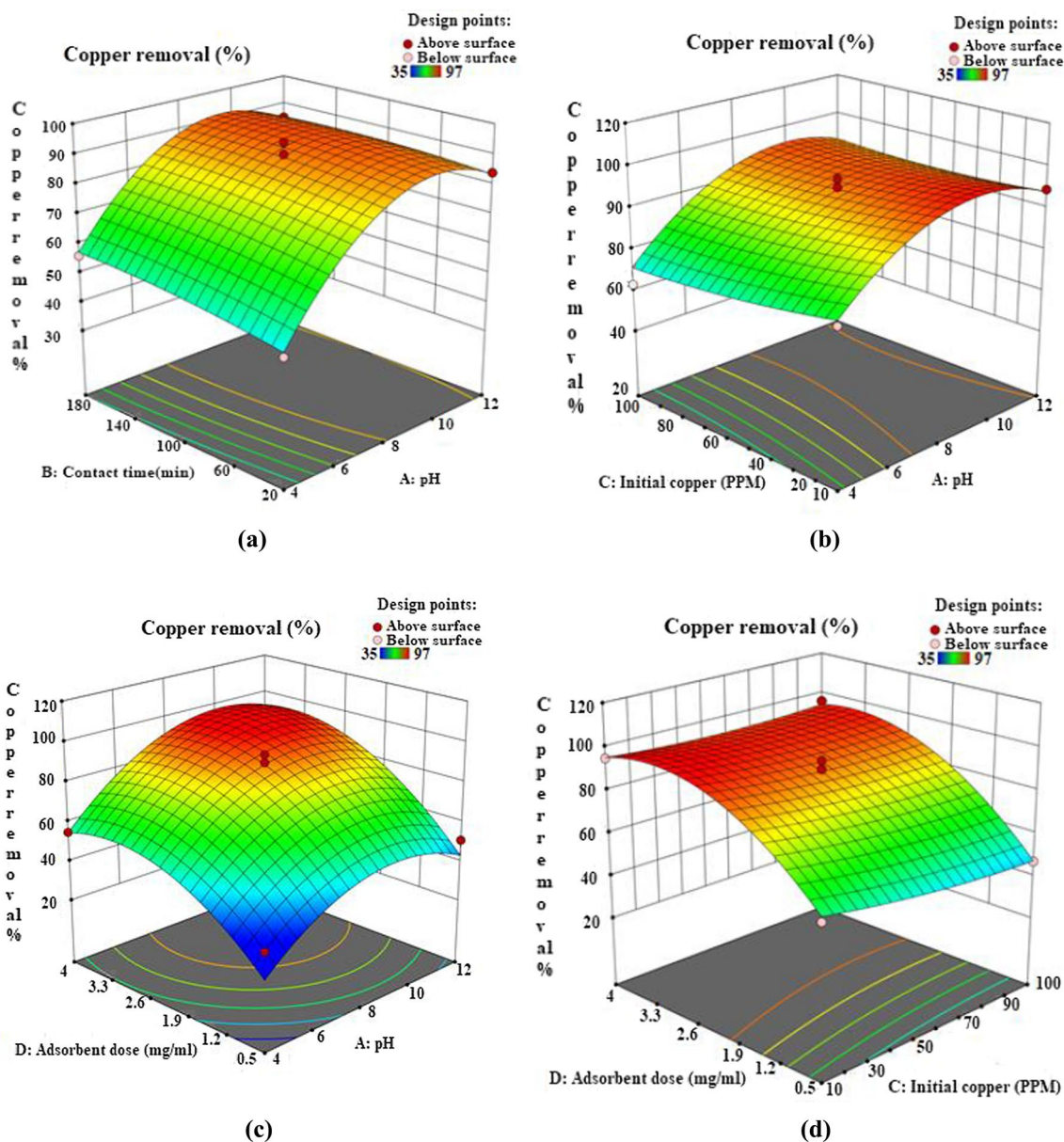


Fig. 6 Three-dimensional response surface: Interaction effect of a contact time and pH with a copper concentration of 55 ppm and the adsorbent dose of 2.25 g/L; **b** copper concentration and pH with contact period of 100 min and the adsorbent dose of 2.25 g/L; **c** adsorbent

dose and pH with contact period of 100 min and initial copper concentration of 55 ppm; **d** adsorbent dose and copper concentration with pH 8 and contact period of 100 min

solution. This may be due to the reason that in an acidic medium, most of the ions get used in neutralizing themselves and very few sites have remained for the adsorption process. The rate of adsorption was found quite high up to 100 ppm concentration Cu^{2++} after which it started to fall due to the high load of the adsorbate. While the contact period was effective only in the initial period afterward, the minimal effect of contact time on copper removal was observed. ANOVA results indicated that the model is significant and well fitted. The variables (pH, copper

concentration, contact period, and adsorbent dose) were successfully optimized using RSM, and the optimum predicted value for copper adsorption was found to be 97.7%. The adsorption capacity at the optimization level of this process was found to be 9.7 mg/g, which a significant figure for the adsorption of copper. Isotherm and kinetic studies of the adsorption process done in this research strongly suggest the use of activated Ganga sand for the adsorption of copper ion from aqueous solution. The adsorption process followed both Freundlich and Langmuir isotherms.



Kinetics of the process was governed by pseudo-second-order kinetics. It can be concluded that the activated Ganga sand may be used as an effective adsorbent and may be successfully applied for the removal of copper from aqueous solution.

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Declarations

Conflict of interest The authors declare that they have no competing interests.

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