Process Optimization Using Response Surface Methodology for the Removal of Cu(II) and Co(II) from Aqueous Solution Using Gelatin-Cellulose Nanocrystals Hydrogel Membrane

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***Abstract*—The adsorption efficiency of gelatin-cellulose nanocrystals hydrogel membrane (GCHM) for the removal of Cu(II) and Co(II) from aqueous solution was studied in batch experiments. The interactive effect of independent variables such as pH, contact time, temperature, and ratio of gelatin and cellulose nanocrystals on Cu(II) and Co(II) adsorption were investigated. Analysis of variance (ANOVA) showed that the response surface quadratic model is highly impressive and can successfully predict the experimental results. The optimization results of the process variables by response surface methodology- central composition design (RSM-CCD) model was obtained at pH 6, temperature of 52.50 °C, time of 67.50 min. and ration gelatin-CNCs of 3:1. The maximum removal percentage was 86.95% and 89.77% for Cu(II) and Co(II), respectively.**

***Index Terms*—Cellulose, cobalt, copper, gelatin, response surface methodology**

I. Introduction

Heavy metals such as Cu(II) and Co(II) are toxic, not bio-degrade and easily accumulate in living organisms. The presence of these heavy metals in the environment leads to serious illnesses such as low blood pressure, cancer, and damage to the nervous system [1]. So, the effective removal of these metals from the aqueous solution is necessary for environmental protection. Different techniques have been used to remove these heavy metals, including membrane separation, chemical precipitation, electrochemical, ion-exchange, membrane electrolysis, reverse osmosis, and adsorption [2]. Among these techniques, adsorption have been widely used, because it is easy to operate, adaptable and cost-effective. Various adsorbent materials have been developed: clay minerals, activated carbon, zeolites, chelating and cellulose materials [3, 4]. Cellulose nanocrystals (CNCs) and gelatin were found to be the most materials used in adsorption processes [5]. Gelatin is a low-cost protein, available in the market, and is bio-degradable, has film-forming properties, is transparent and presents good processibility [6]. It is obtained by the partial hydrolysis of collagen at controlled pH and temperature conditions [7]. Gelatin shows poor barrier properties, theses drawbacks could be overcome by incorporating reinforcing nanoparticles such as CNCs. Cellulose nanocrystals are one of the most studied polysaccharide-based nanomaterials in polymer nanocomposites [8]. Several reports have described a joint synergistic effect between gelatin and CNCs toward the formation of percolated networks stabilized by hydrogen bonding. The hydrogel membrane films can be used in water treatment as filtration membrane where the solution goes through the hydrogel membrane film as described for gel membrane permeation [9]. Due to the abundance of ion-coordinating sites and their ability to adsorb a large amount of water, hydrogel membrane films have recently found another application in water treatment to remove metal ions using the adsorption process [10]. To the best of our knowledge, no research has been published on the reinforcing effect of CNCs on gelatin films. Furthermore, the necessary to optimize the process parameters for the effective removal of Cu(II) and Co(II) from aqueous solution using Gelatin-CNCs hydrogel membrane (GCHM) has not been reported neither. The response surface methodology (RSM) has been applied to evaluate the significance of process parameters in complex interaction since RSM is more cost-effective [11]. Several works reported that RSM has been used to optimize the process parameters for the removal of heavy metals [12]. Therefore, the objective of this study is to determine the potential of GCHM as adsorbent material and the use of RSM to optimize the factors influencing the removal of Cu(II) and Co(II) from aqueous solution.

II. Materials and Methods

A. Materials

All the chemicals used in this study for the adsorption processes and membrane preparation such as sodium hydroxide sodium, hydrochloric acid, Cellulose nanocrystals (CNCs) gelatin (purity ≥ 98%), Cupric sulfate ($CuSO_4$ $5H_2O$) and Cobalt chloride ($CoCl_2$ $6H_2O$) were of analytical reagent grade (98–99.5%). They were obtained from Sigma Aldrich and LabChem, South Africa. High purity deionised (HPD) water was used to prepare the synthetic solutions.

B. Methods

1) Experimental procedure

The synthetic solutions of metal ions were produced by dissolving $CuSO_4$ $5H_2O$ and $CoCl_2$ $6H_2O$, respectively in high purity deionized (HPD) water. The metal ions concentration in solution (1000 mg/L) were varied to study the effect of the existence of one cation on the other's efficient removal. Atomic adsorption spectroscopy (AAS) (Model Variant Spectra (20/20)) was used to assay the Cu (II)/Co (II)

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mixed synthetic solutions. To minimize errors due to precipitation and container-plating of the ion metals, the sample solutions were used within 48 h after preparation. The CNCs suspension was then homogenized. Certain amount of gelatin was then added into CNCs suspension. The mixture was then stirred at 55 ℃ until a homogeneous viscous mixture was obtained. The cross-linking agent (EDTA 1%) was then added dropwise. After 4 h, the mixture was poured into a petri dish and placed in oven at 45 ℃ until the mixture was dried. Hydrogels as films were removed from the petri dish and washed with the HPD water to remove unreacted chemicals. The unreacted chemicals were removed from hydrogel using acetone [13]. Adequate quantities of CNCs were dispersed in 50 mL of water. Table I presented the ratios composition of GCHM hydrogel.

TABLE I: COMPOSITION OF GCHM HYDROGEL

	Ratio 1:3 A	Ratio 1:1 B	Ratio 3:1 C	Water (mL)
Gelatin	25	50	75	N/A
CNCs	75	50	25	50

2) Batch Adsorption experiment

The adsorption process of Cu(II) and Co(II) ions onto GCHM was tested in batch experiment. A shaker was used to mix the solution. Several process parameters were optimized, and this includes effects of pH, gelatin-CNCs ratios, contact time and temperature. To ensure the validity of the results and repeatability, all experiments were performed in triplicate and the data were reported as average values. The metal ions uptake capacity and the removal efficiency were calculated using Eq. (1) and (2), respectively.

$$q_e = \frac{C_o - C_e}{m} \times V \tag{1}$$

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where q_e (mg/g): amount of metal ions adsorbed per unit mass of adsorbent, Co (mg/L): initial concentration of metal ions, C_e (mg/L): amount of metal ions at equilibrium, V (L): volume of solution used and m (g): mass of GCHM. The experiments were carried out in 250 mL of plastic container, at a constant agitation speed of 250 rpm in 100 mL solution. An amount of 0.25 g of GCHM was added into 100 mL of binary metal ions solution and the mixtures were placed in a rotary shaker between 15 and 120 mins. The effect of various operating temperatures ranging between 30 ℃ and 75 ℃ was investigated using thermo-shaker. The solution of binary metal ions was adjusted in pH solutions between 3 and 7 using 1M of HCl and NaOH. All removal experiments were reproduced three times, and the mean values used. If the standard errors were greater than 0.01, the test was repeated to control the errors.

3) Response surface methodology (RSM)—central composite design (CCD) procedure

RSM is a combination of mathematical and statistical techniques based on fitting empirical models to experimental data. The main advantage of RSM is assessing the primary and interactive effects of variables with the least number of experiments. This methodology is useful when optimizing a response influenced by independent variables [14]. When RSM is employed for fitting mathematical equations to experimental data, it is essential to choose an experimental design. Among several classes of RSM, central composite design (CCD), is the most widely used approach for parameter optimization. This composite design consists of a full factorial design, star points, and a center point. It studies all factors at two levels (low and high, being coded as −1 and +1, respectively). The α value can be calculated by $\alpha = 2k/4$, where k is the number of factors. Central composite design requires N experiments according to $N = 2^k + 2k + C_p$, where C_p is the replicate number of the central point, k is the number of variables [15]. A second-order polynomial regression model is used for predicting responses under certain conditions of process variables as follows [16]:

$$Y = \beta_o + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{1 \le i \le j}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{3}$$

where Y is the predicted response (removal efficiency, %), X_i and X_j are coded values of independent variables, β_o is a constant term, β_i, and β_{ij} are the coefficients of the linear, quadratic, and ε interaction parameters, respectively. ε is the residual associated with the experiments. The validation of the proposed model was tested using analysis of variance (ANOVA). The suitability of the model was evaluated using the values of R^2. The statistical calculation is based on the relationship between the coded value (X_i) and the real value (x_i) as defined in (4) [17]:

$$X_i = \frac{x_i - x_o}{\Delta x} \tag{4}$$

where x_o is the center point value and Δx is the step-change in the real value. In this study, four main variables including the ratio gelatin-CNCs, pH, time and temperature were chosen as independent variables. The adsorption efficiency of Cu(II) and Co(II) removal into GHCN was estimated as the response via central composite design. The levels and symbols of the process variables for CCD are shown in Table II.

TABLE II: FACTORS AND THEIR LEVELS FOR CCD

Factors	Symbol coded	Low −1	High +1
pH	A	3	9
Ratio gelatin-CNCs	B	25	75
Temperature (^{o}C)	C	30	75
Time (min)	D	15	120

Using the Design Expert software 11, the number of experimental runs was calculated to be 21 (k = 4, C_p = 6), which are presented in Table III. Experiments corresponding to the center point are usually repeated to get a good estimate of pure error. Analysis of variance was performed to evaluate the fitted mathematical model to experimental data. The significance and adequacy of this regression model can be evaluated using the *F-value* (Fisher distribution), *p-value* (*Prob* > *F*), and the value of adequate precision. Moreover, the quality of the fitted quadratic model was determined by the coefficient of determination (R^2) values.

III. Results and Discussions

A. Methods

1) Experimental procedure

a) Experimental design and regression model

Response surface methodology (RSM) was employed to evaluate the relations between the response (% removal of Cu(II) and Co(II)) and the four variables. In this study, CCD was selected to evaluate the effect of pH (*A*), ratio of gelatin-CNCs (*B*), temperature (*C*), and time (*D*) as independent variables. Cu(II) removal in % ($Y_{Cu(II)}$) and Co (II) removal in % ($Y_{Co(II)}$) were taken as response variables (Table III). RSM provides a collection of statistical and mathematical techniques for designing experiments and the interaction for the determination of optimum conditions [18]. Eqs. (5) and (6) give the final quadratic polynomial equation regarding coded factors that were used to fit the experimental data.

$$Y_{Cu(II)} = +58.45 - 2.20A + 24.29B - 5.29C + 20.79D - 35.68A^2 - 3.08B^2 + 5.00C^2 - 13.87D^2 + 20.64AB + 0.56AC + 23.96AD - 1.91BC - 0.68BD - 0.59CD \quad (5)$$

$$Y_{Co(II)} = +60.94 + 1.22A + 23.56B - 3.43C + 21.34D - 38.28A^2 - 3.39B^2 + 5.10C^2 - 13.38D^2 + 20.00AB - 1.13AC + 22.47AD - 1.13BC + 0.18BD + 0.62CD \quad (6)$$

where *A*, *B*, *C*, and *D* represent pH, the ratio of gelatin-CNCs, temperature and time, respectively. The positive sign in front of the terms indicates a synergic effect and, the negative sign indicates an antagonist effect in Eqs. (5) and (6). ANOVA analyzed the accuracy, or adequacy fitting, of the regression model for $Y_{Cu(II)}$ and $Y_{Co(II)}$ in Equations 5 and 6 at a 95% significance level and the results are presented in Tables IV and V. High *F* and low *P* (< 0.0500) values of the regression model, as well as each variable term for linear, square and interaction in the model, indicated that they were statistically significant. *F-value* of 29.59 and *p-value* < 0.0500 for $Y_{Cu\,(II)}$ and *F-value* of 25.78 and *p-value* < 0.0500 for $Y_{Co\,(II)}$) show that the model was significant in describing the experimental data. The values of *Prob* > *F* less than 0.0500 indicate that the model terms are significant. In this study, *B*, *C*, *D*, A^2, D^2, *AB*, and *AD* are significant model terms for Cu(II) removal ($Y_{Cu(II)}$) and *B*, *D*, A^2, D^2, *AB*, and *AD* are significant model terms for Co (II) removal ($Y_{Co(II)}$). Values greater than 0.1000 indicate that the model terms are not significant. ANOVA was used to show the impact of each factor and results are shown in Tables IV and V. Considering that most of the factors are statically significant at 95%, among all factors considered, pH (*A*) and the ratio of gelatin-CNCs (*B*) were the most influential in the model with an F-*value* of 105.72 and 38.40 for $Y_{Cu(II)}$ and 98.99 and 29.38 for $Y_{Co(II)}$. The most variables were the interactions between pH/temperature (*AC*) and ratio of gelatin-CNCs/time (*BD*) with *F-value* of 0.082 and 0.024, pH (*A*) and interaction between ratio of gelatin-CNCs/time (*BD*) with *F-value* of 0.078 and 1.430×10^{-3} for $Y_{Co(II)}$.

TABLE III: Central Composite Design Matrix Development with Experimental and Predicted Response for % Removal of Cu(II) and Co(II)

Run	*A*	*B*	*C*	*D*	$Y_{Cu(II)}$	$Y_{Co(II)}$
1	6.00	25.00	52.50	67.50	29.51	33.11
2	6.00	50.00	52.50	67.50	60.33	62.00
3	3.00	50.00	52.50	67.50	23.41	20.57
4	6.00	50.00	52.50	120.0	63.80	66.02
5	6.00	50.00	52.50	67.50	60.33	62.00
6	6.00	50.00	52.50	67.50	74.81	77.86
7	6.00	50.00	52.50	15.00	22.22	25.34
8	6.00	50.00	52.50	67.50	60.33	62.00
9	6.00	50.00	52.50	67.50	60.33	62.00
10	9.00	25.00	30.00	120.0	11.00	13.00
11	9.00	75.00	75.00	15.00	5.740	8.000
12	6.00	50.00	75.00	67.50	48.95	52.47
13	9.00	25.00	75.00	120.0	7.990	12.00
14	3.00	25.00	75.00	15.00	10.81	8.300
15	3.00	25.00	30.00	15.00	13.70	7.230
16	6.00	75.00	52.50	67.50	78.10	80.23
17	9.00	75.00	30.00	15.00	14.00	16.00
18	9.00	50.00	52.00	67.50	19.00	23.00
19	3.00	75.00	30.00	120.0	19.65	12.11
20	3.00	75.00	75.00	120.0	6.770	5.980
21	6.00	50.00	52.50	67.50	60.33	62.00

By studying the main effect and the impact of each factor, the process could be characterized. Therefore, the level of a factor to produce the best results could be predicted. The R^2 values of the models obtained are 0.9857 for $Y_{Cu(II)}$ and 0.9836 for $Y_{Co(II)}$ (Tables IV and V). Besides, adjusted R^2 are obtained as 0.9524 and 0.9455 for $Y_{Cu(II)}$) and $Y_{Co(II)}$, respectively. The high value of R^2 indicates that the quadratic equations can represent the system under the given experimental domain. The predicted $Y_{Cu(II)}$ and $Y_{Co(II)}$ at a 95% confidence level were compared with experimental results in Fig. 1. High values of R^2 show that the quadratic equations are adequate to represent the model under the given experimental area. It was observed that the data points were positioned close together around the line of the best fit.

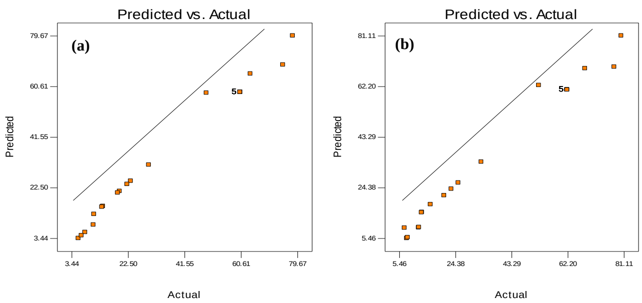

Fig. 1. Relationship between predicted and actual values for $Y_{Cu(II)}$ (a) and $Y_{Co(II)}$ (b).

This shows a proper arrangement between predicted and experimental data and means that this model best describes the relationship between reaction variables. The analysis of variance (ANOVA) was used to evaluate the statistical significance of the quadratic model. It was found that the regression was statistically significant at the *F-value* of 29.59 and *P-value* < 0.0500 and at the *F-value* of 27.78 and *p-value* < 0.0500 for Cu(II) and Co(II), respectively. The determination coefficient (R^2 = 0.986 for Cu(II) and R^2 = 0.984 for Co(II)) demonstrating a good fit of the regression model, only 1.4% for Cu(II) and 1.6% for Co(II) of the total variability was not explained by the model. The adjusted determination coefficient (R^2adj = 0.952 for Cu(II) and R^2adj = 0.946 for Co(II)) is also high, indicating a high significance of the model.

b) Analysis of variance (ANOVA)

ANOVA was used to analyze the accuracy, or adequacy fitting, of the regression model for $Y_{Cu(II)}$ and $Y_{Co(II)}$ in (5) and Eq. (6) at a 95% significance level and the results are presented in Tables IV and V. High *F* and low *p* (< 0.0500) values of the regression model, as well as each variable term for linear, square and interaction in the model, indicated that they were statistically significant. *F-value* of 29.59 and *p-value* < 0.0500 for $Y_{Cu(II)}$ and F-value of 25.78 and *p-value* < 0.0500 for $Y_{Co(II)}$ show that the model was significant in describing the experimental data. The values of *Prob > F* less than 0.0500 indicate that the model terms are significant. In this study, *B*, *C*, *D*, A^2, D^2, *AB*, and *AD* are significant model terms for Cu(II) removal ($Y_{Cu(II)}$) and *B*, *D*, A^2, D^2, *AB*, and *AD* are significant model terms for Co (II) removal ($Y_{Co(II)}$). Values greater than 0.1000 indicate that the model terms are not significant. ANOVA was used to show the impact of each factor and results are shown in Tables IV and V.

TABLE IV: ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL FOR REMOVAL OF CU(II)

Source	Sum of Squares	D_f	Mean Square	*F-value*	*Prof> F*
Model	12735.61	14	909.69	29.59	0.0002
A	9.72	1	9.72	0.32	0.5942
B	1180.49	1	1180.49	38.40	0.0008
C	279.84	1	279..84	9.10	0.0235
D	864.45	1	864.45	28.12	0.0018
A^2	3249.67	1	3249.67	105.71	<0.0001
B^2	24.19	1	24.19	0.79	0.4092
C^2	63.73	1	63.73	2.07	0.2000
D^2	491.36	1	491.36	15.98	0.0071
AB	681.95	1	681.95	22.18	0.0033
AC	2.53	1	2.53	0.082	0.7838
AD	918.72	1	918.72	29.88	0.0016
BC	29.03	1	29.03	0.94	0.3687
BD	0.74	1	0.74	0.024	0.8818
CD	2.81	1	2.81	0.091	0.7727
Res.	184.45	6	30.74		
Lack of Fit	184.45	2	92.23		
Cor Total	12920.06	20			
R^2	0.986				
Adj. R^2	0.952				

Considering that most of the factors are statically significant at 95%, among all factors considered, pH (*A*) and the ratio of gelatin-CNCs (*B*) were the most influential in the model with a *F-value* of 105.72 and 38.40 for $Y_{Cu(II)}$ and 98.99 and 29.38 for $Y_{Co(II)}$. The most ineffective variables were the interactions between pH/temperature (*AC*) and ratio of gelatin-CNCs/time (*BD*) with *F-value* of 0.082 and 0.024, pH (*A*) and interaction between ratio of gelatin-CNCs/time (*BD*) with *F-value* of 0.078 and 1.430×10^{-3} for $Y_{Co(II)}$. By studying the main effect and the impact of each factor, the process could be characterized. Therefore, the level of a factor to produce the best results could be predicted. The R^2 values of the models obtained are 0.9857 for $Y_{Cu(II)}$ and 0.9836 for $Y_{Co(II)}$ (Tables IV and V). Besides, adjusted R^2 are obtained as 0.9524 and 0.9455 for $Y_{Cu(II)}$ and $Y_{Co(II)}$, respectively. The high value of R^2 indicates that the quadratic equations can represent the system under the given experimental domain.

TABLE V: ANOVA FOR RESPONSE SURFACE QUADRATIC MODEL FOR REMOVAL OF CO (II)

Source	Sum of Squares	D_f	Mean Square	*F-value*	*Prof> F*
Model	13637.92	14	974.14	25.78	0.0003
A	2.95	1	2.95	0.078	0.7892
B	1110.15	1	1110.15	29.38	0.0016
C	117.79	1	117.79	3.12	0.1279
D	910.79	1	910.79	24.11	0.0027
A^2	3740.05	1	3740.05	98.99	<0.0001
B^2	29.35	1	29.35	0.78	0.4120
C^2	66.50	1	66.50	1.76	0.2329
D^2	457.09	1	457.09	12.10	0.0132
AB	640.24	1	640.24	16.94	0.0062
AC	10.28	1	10.28	0.27	0.6206
AD	808.11	1	808.11	21.39	0.0036
BC	10.28	1	10.28	0.27	0.6206
BD	0.054	1	0.054	1.430×10^{-3}	0.9711
CD	3.04	1	3.04	0.080	0.7863
Res.	226.70	6	37.78		
Lack of Fit	226.70	2	113.35		
Cor Total	13864.6	20			
R^2	0.984				
Adj. R^2	0.946				

2) Three dimensional (3D), and two dimensional (2D) RSM Plots

To obtain a better understanding of Cu(II) and Co(II) removal in aqueous solution onto GCHM, 2D and 3D response plots were analyzed. As each model had four variables that were kept constant at the centre level, therefore, six total response surfaces were produced.

a) Interaction between pH and ratio of gelatin

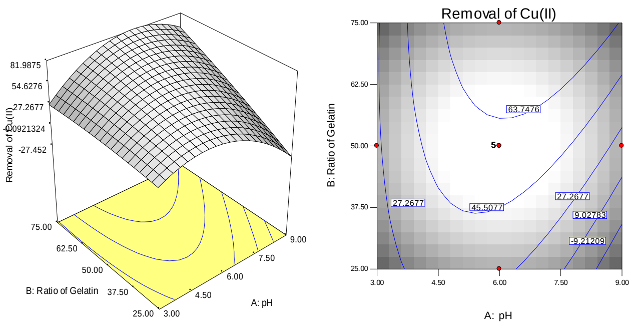

Fig. 2. Effect of pH and ratio of gelatin of Cu(II) removal: (a) response surface method and (b) contour surface plots.

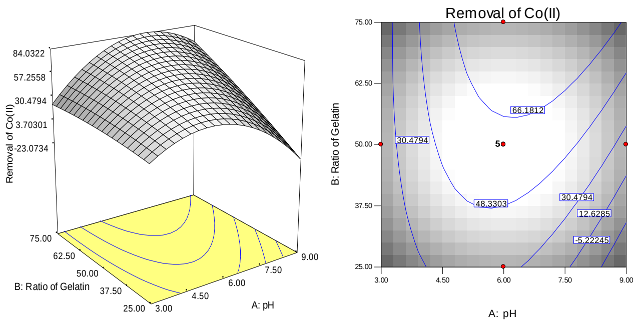

Fig. 3. Effect of pH and ratio of gelatin of Co(II) removal: (a) response surface method and (b) contour surface plots.

The interaction between pH and ratio gelatin is illustrated in Figs. 2 and 3. The circular contour plots revealed that there is a significant interaction between pH and ratio of gelatin on the removal efficiency. The sharp curvature in pH and ratio of gelatin shows that the response metals adsorption efficiency was very sensitive to this process [15]. At a lower range of pH and ratio of gelatin, an increase of percentage removal was observed up to a pH 5 and ratio gelatin ratio of 75.00%. The decrease in the response was observed at a pH greater than 5 and gelatin ratio of less than 75.00%. And at higher pH, Co(II) precipitate as $Co(OH)_2$.

b) Interaction between pH and temperature

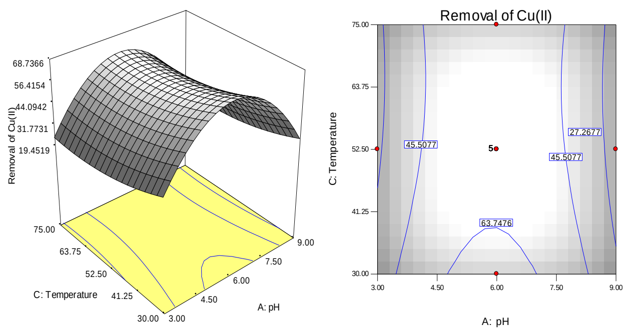

Fig. 4. Effect of pH and temperature of Cu(II) removal: (a) response surface method and (b) contour surface plots.

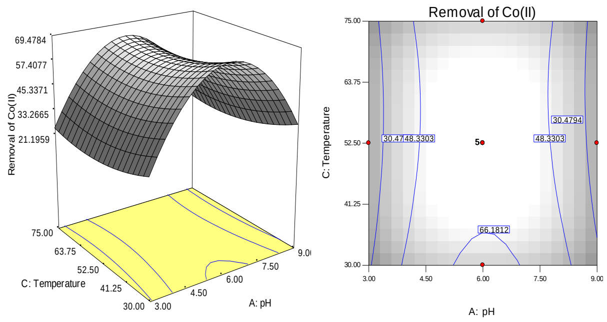

Fig. 5. Effect of pH and temperature of Co(II) removal: (a) response surface method and (b) contour surface plots.

Figs. 4 and 5 illustrate the interaction between pH and temperature with a ratio of gelatin of 50.00% and a time of 67.50 min. The contour indicated that the two variables are significant to the removal of Cu(II) and Co(II) and their interaction decrease the removal of both metal ions. The predicted values from ANOVA were found to be 68.74% and 69.49% for Cu(II) and Co(II), respectively. Under these conditions, adsorption removal decreases with increase in temperature and pH. As the system is exothermic, a high temperature does not favour the adsorption process [19].

3) Interaction between pH and time

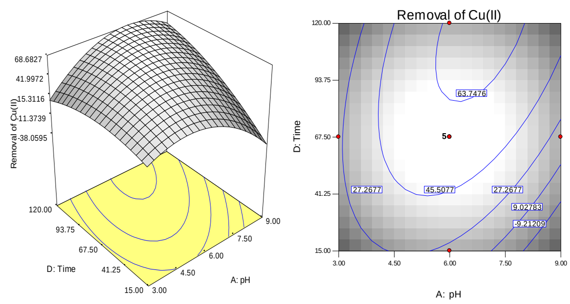

Fig. 6. Effect of pH and time of Cu(II) removal: (a) response surface method and (b) contour surface plots.

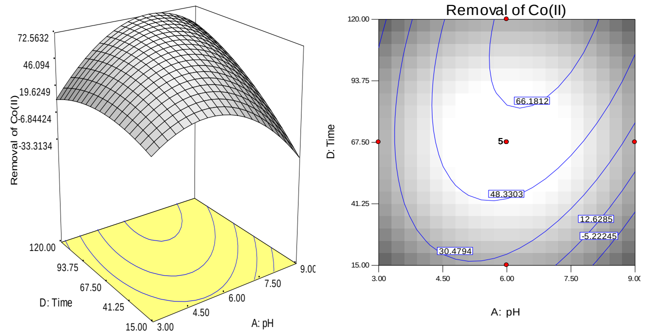

Fig. 7. Effect of pH and time of Co(II) removal: (a) response surface method and (b) contour surface plots.

The RSM plots in Figs. 6 and 7 show the interaction between pH and contact time for a gelatin ratio of 50.00% and a temperature of 52.50 ℃. It can be seen from these figures that initially the percentage removal increases very sharply with increase in time. The predicted values from ANOVA were found to be 68.68% and 72.56% for Cu(II) and Co(II), respectively. This trend is expected because as the gelatin ratio increases the number of binding sites increases and thus more Cu(II) and Co(II) are attached to the surface of GCHM [20].

4) Interaction ratio of gelatin and temperature

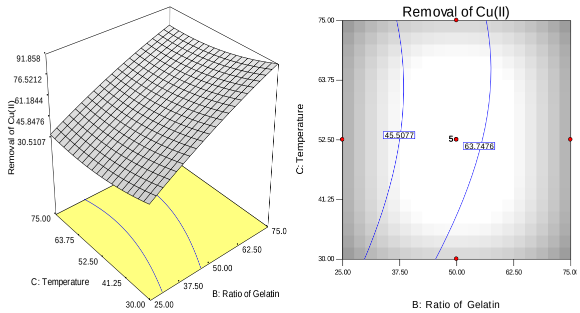

Fig. 8. Effect of ratio of gelatin and temperature of Cu(II) removal: (a) response surface method and (b) contour surface plots.

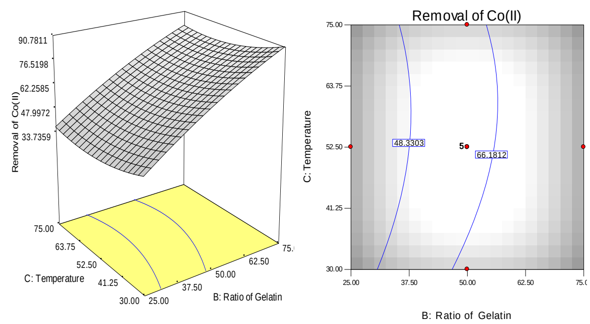

Fig. 9. Effect of of ratio of gelatin and temperature of Co(II) removal: (a) response surface method and (b) contour surface plots.

Figs. 8 and 9 illustrate the interaction between gelatin and temperature for a pH of 6.00 and a time of 67.50 min. With increasing of gelatin ratio, the activity of the functional groups increases which enhances the surface complex formation and reduces the mass transfer resistance. Therefore, system temperature affects synergistically the adsorption of Cu(II) and Co(II). The highest removal efficiency for the combined effect of temperature and the gelatin ratio was found from the optimization study as 91.86% and 90.78%, respectively for Cu(II) and Co(II).

5) Interaction ratio of gelatin and time

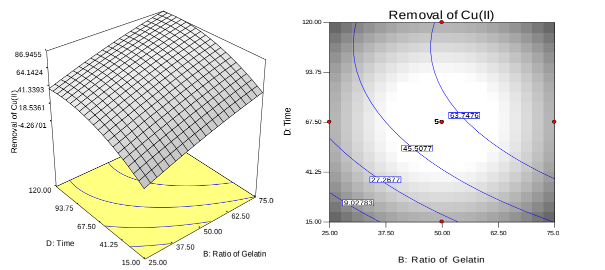

Fig. 10. Effect of ratio of gelatin and time of Cu(II) removal: (a) response surface method and (b) contour surface plots.

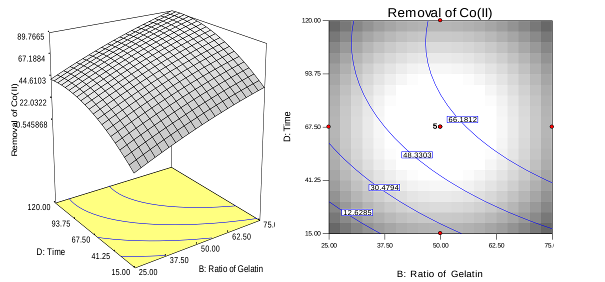

Fig. 11. Effect of ratio of gelatin and time of Co(II) removal: (a) response surface method and (b) contour surface plots.

Figs. 10 and 11 illustrate the interaction between of ratio of gelatin and time on the removal of Cu(II) and Co(II) onto GCHM for a pH of 6.00 and a temperature of 52.50 ℃. Increasing the gelatin ratio provided more metal binding sites; therefore, the rate of Cu(II) and Co(II) adsorption increased even when the pH and temperature were kept constant. The predicted values from ANOVA were found to be 86.95% and 89.77% for Cu(II) and Co(II), respectively [20].

6) Interaction ratio of gelatin and temperature

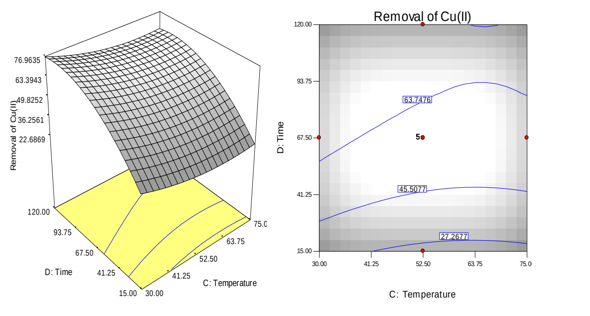

Fig. 12. Effect of temperature and time of Cu(II) removal: (a) response surface method and (b) contour surface plots.

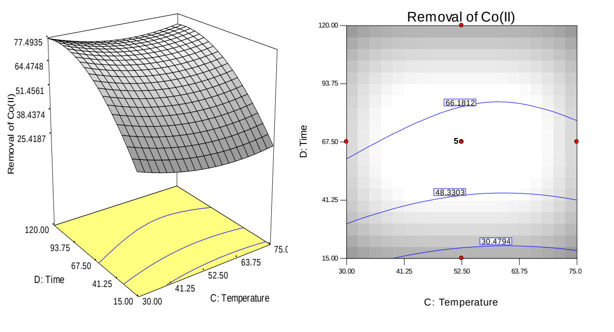

Fig. 13. Effect of temperature and time of Co(II) removal: (a) response surface method and (b) contour surface plots.

The interaction between temperature and time is shown in Figs. 12 and 13 on the removal of Cu(II) and Co(II) onto GCHM where the pH 6 and gelatin ratio (50.00%) have been kept constant. With increasing temperature, the activity of functional groups increases but it has been observed a decrease in the removal for both metals whilst increasing of the temperature. On the other hand, high temperature does not favour the adsorption process of Cu(II) and Co(II) onto GCHM. Therefore, system temperature affects synergistically the adsorption of Cu(II) and Co(II). Maximum removal efficiency for a combination of the effect of time and temperature was found to be 76.96% and 77.49% for Cu(II) and Co(II), respectively [21].

B. Process Optimization

The optimization of Cu(II) and Co(II) adsorption onto GCHM was accomplished using RSM to find the maximum response that collectively meets all process conditions. The optimum conditions were described by three dimensional graphs. Design Expert 11 software was used to determine the predicted response with desirability function. The desired goals are united into desirability function which varies from 0.0 to 1.0. Model optimization analysis implies optimum variable values concordant with maximum metal ions removal with desirability near 0.9 [12].

IV. Conclusion

In this study, GCHM was synthesized to evaluate its effectiveness to remove Cu(II) and Co(II) from aqueous solution. The batch adsorption experiments using RSM-CCD method was successfully used to optimize the influences of experimental variables such as ratio of gelatin/cellulose, contact time, pH, and temperature on Cu(II) and Co(II) removal. The developed quadratic polynomial model equation with independent variables was proved to be reliable. The optimum process parameters for Cu(II) and Co(II) removal were found to be: pH = 6.00, ratio = 3:1 (75% gelatin and 25% cellulose), contact time = 67.50 min and T ° = 67.50 ℃. The adsorption study with 86.95% and 89.77% efficiency of Cu(II) and Co(II) respectively, showed that GCHM was sustainable for removal of Cu(II) and Co(II) from aqueous solution.

Conflict of Interest

We declare that the submitted work was carried out with no conflict of interest.

Author Contributions

J.K analyzed the conceptualization, methodology, validation, formal analysis, investigation, data curation, writing - original draft, writing - review & editing, visualization, resources. T.L performed the methodology, validation, investigation, formal analysis, data curation, writing - original draft.

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