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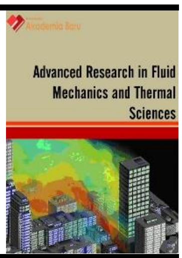

Optimization of Cu(II) Removal Using Aceh Natural Bentonite, Intercalated Bentonite and Pillared Bentonite Using Box–Behnken Design In Response Surface Methodology

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Jakfar[1], Husni Husin[2], Abrar Muslim[2,*], Darmadi[2]

[1] Doctoral Program of Engineering, Faculty of Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh, Indonesia
[2] Department of Chemical Engineering, Faculty of Engineering, Universitas Syiah Kuala, Darussalam, Banda Aceh, Indonesia

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ABSTRACT

Optimization of the Cu(II) removal by natural bentonite from Aceh through modification with NaCl intercalation and pillarization with $AlCl_3$ in aqueous solution was conducted using Response surface methodology (RSM). Batch mode experiments were conducted based on a Box-Behnken Design in the RSM. Adsorption results were investigated as a function of two independent factors i.e. initial Cu(II) ions concentration (100-500 mg/L) and agitation time (30-120 min), bentonite mass of (2 g). The results of analysis of variance were obtained viz. the influence of the two independent variables viz. initial copper concentration and agitation time are very significant. Optimization equation were obtained for natural bentonite (NB), intercalated bentonite (IB) and pillared bentoned (PB). The optimization conditions for copper removal were obtained at 300 mg/L initial copper concentrations and 75.901 min of agitation times. The maximum Cu(II) adsorption capacity of the NB, IB and PB were 27.101, 27.568 and 28.969 mg/g respectively.

Keywords:
Adsorption; Bentonite; Optimization; Response surface Methodology

1. Introduction

Heavy metal which is not easy biodegradable pollutant might release from industrial practices [1-2]. Among heavy metal, copper can threat human health in excessive amount causing tissues and organs malfunction such as stomach distress and kidney damage. It can cause anemia and death [3-5]. Copper may be found in many industrial waste such as mining practices, smelting and electroplating, steel and fertilizer industries, circuit wires and chemical reagents production [6-9].

There are several methods developed for removing heavy metal ions from wastewater before disposal, which are bioremediation [10], neutralization using chemicals [11], nano hollow sphere-

* *Corresponding author.*
E-mail address: abrar.muslim@che.unsyiah.ac.id

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based separation [12] and photocatalytic oxidation [13]. Adsorption is the better one because it is an inexpensive and simple process and less energy use [14-15].

Natural bentonite has different adsorption according to its composition and mineral content of the impurities, therefore it needs to be purified and modified so as to increase its adsorption [16-17]. Likes natural zeolite, natural bentonite was chosen as a raw material of adsorbent because it has several advantages, among others, namely as excellent material, chemically stable, heat resistant [18], and easily intercalated and pillared with other elements or chemical compounds [19-20]. This modification method of natural bentonite was applied tartrazine removal [21], adsorption of bisphenol [22] and cobalt(II) [23] and phosphate from aqueous solution [24]. Unfortunately, there is limited number of studies proposing intercalated and pillared bentonite using Indonesian and even Acehnese natural bentonite for copper removal. Meanwhile, intercalated and pillared bentonite have high surface area for surfactants and phenol adsorption [25-26]. Interestingly, Indonesia has an abundant natural bentonite which is approximately 380 million tons, and Aceh is expected to have approximately 2.6 million tons [27]. The use of intercalated and pillared Acehnese bentonite would be an innovative adsorbent for copper removal.

Wastewater treatment process is not suitable with the classical method because it requires a lot of time, unreliable and inflexible. Response surface methodology (RSM) is very efficient design and widely used technique, can be adapted for parameters optimization of various wastewater treatment processes [28-29]. RSM is better alternative is used because it includes the influences of individual factors as well as the influences of their interaction. Box–Behnken design in the RSM is a technique for designing experiments, evaluating the effects of several factors, and achieving the optimum conditions for desirable responses with a limited number of planned experiments [30-32]. Therefore, optimization of Cu(II) removal using intercalated and pillared Acehnese bentonite based Box–Behnken design in the RSM would be the novel of current study.

Current study proposed preparation of intercalated and pillared Aceh natural bentonite for the removal of Cu(II) from aqueous solution. Natural bentonite was modified through intercalate Na ions using NaCl and pillared Al ions using $AlCl_3$. The objective of this research was to study the effect of initial Cu(II) ions concentration and agitation time on adsorption of Cu(II) using Aceh natural bentonite and intercalated and pillared Aceh natural bentonite. The optimum conditions of Cu(II) removal was determined using Box–Behnken design in the RSM under Design Expert software.

2. Materials and Experimental Procedure

2.1 Natural Bentonite (NB)

Natural bentonite was obtained from Cot Mambo Village, Nisam Sub-district, North Aceh District, Aceh Province, Indonesia. In the first utilization step of natural bentonite, natural bentonite of 25 g was grinded using ball mill and sieved to get a size of 180-200 mesh. Then the mixed solution is separated by decantation, afterwards the bentonite was heated at 105^{o}C for two hours and saved in desiccator. Bentonite after sifting and heating was spread in a solution 500 ml buffer acetate at pH 4,8 and stirred for 5 hours until no $CO_{2(g)}$ was formed. Then, mixture was separated using centrifuge tub. Bentonite deposits was dried at 105 ^{o}C using an oven. After drying, it was leaved in the oven until reaching at 27 ^{o}C and then it were stored in a bottle for Cu(II) adsorption experiments.

2.2 Intercalated Bentonite (IB)

Purified natural bentonite of 25 g was mashed to get a size of 180-200 and then it was inserted into 500 ml M NaCl. The mixture was stirred using a magnetic stirrer for 24 hours at 70°C. The mixture was separated by decantation, and the precipitate was washed with aqubides to remove residual chloride ions. The filtrate from leaching sludge was tested with 1 M $AgNO_3$ solution until there was no AgCl white precipitate was formed. Bentonite deposits that free from Cl^- ions was dried at 105 °C.

2.3 Pillared Bentonite (IB)

Aluminium polication solution was prepared by adding 660 ml of 0.2 M NaOH solution slowly to 300 ml $AlCl_3$ 0,1 M solution with the OH/Al volume ratio of 2.2 and it was stirred for up to 48 hours. Preparation of intercalated bentonite suspension was carry out by weighing 3.333 g of intercalated bentonite, dissolved it in 166.7 ml of water to obtain 2 % suspension, and it was stirred for 1 hour. The result obtained in the preparation of Al polycation solution were taken as much as 960 ml and added simultaneously slowly into 2 % intercalated bentonite suspension and stirred for 24 hours at room temperature. Then, the precipitate was washed with aqubides to remove chloride ions and tested with $AgNO_3$ until no precipitate was formed. The precipitate was dried at 40°C for 3 days. Then, it was heated to 300°C for 5 hours. The results were analyzed by testing adsorption of Cu(II) ions by AAS.

2.4 Experimental Design

The statistical design of experiments is an efficient procedure for planning experiment so that the data obtained was analyzed to yield valid and objective conclusions. The two main applications of experimental design were screened, in which the factors that influence the experiment were identified and optimized, in which the optimal setting or conditions for an experiment can be found [21, 22]. Design Expert 12 (Stat-Ease Inc., Minneapolis, MN, USA) software used for regression and graphical analysis of obtained data. Box-Behnken design was used under the RSM design. In order to achieve optimum Cu(II) removal, the RSM experimental was used to study response pattern and to determine the best combination of variables which gave the optimum condition for the experiment. In this research, two variables X_1 (initial copper concentration) and X_2 (agitation time) were used. An experimental design for Aceh natural bentonite, intercalated bentonite and pillared bentonite as adsorbents are shown in Table 1. Batch mode of Cu(II) adsorption experiments were carried out with adsorption systems consisting 2 g of adsorbent, 200 mL Cu(II) ions in solution and stirred at 100-rpm, 27 °C (± 1 °C) and 1 atm.

Table 1
Design and analysis experiment

Run	Factor 1 X_1 (mg/L)	Factor 2 X_2 (min)	Response 1 Y_1 (mg/L)	Response 2 Y_2 (mg/L)	Response 3 Y_3 (mg/L)
1	300	75	275.532	280.351	290.211
2	300	130	296.234	298.234	299.511
3	300	75	275.532	280.351	290.211
4	100	30	40.322	40.322	40.500
5	500	75	300.321	304.234	310.211
6	500	30	60.231	61.547	65.212
7	300	75	275.532	280.351	290.211
8	100	120	95.251	96.131	98.430
9	300	75	275.532	280.351	290.211
10	100	75	60.431	61.671	63.912
11	300	75	275.532	280.351	290.211
12	300	30	50.673	52.120	53.0321
13	500	120	300.573	303.211	97.202

Information: X_1 = initial Cu(II) ions concentration; X_2 = stirring time; Y_1: the NB adsorption response, Y_2: the IB adsorption response, Y_3: the PB adsorption response

For statistical analysis, relationship between the coded and the actual variables can be expressed as Eq. (1).

$$x_i = \left(\frac{X_1 - X_2}{\Delta X} \right) \tag{1}$$

where x_i is independent variable or the dimensionless value of the i^th independent variable, X_1 is independent real value, X_2 is independent real value on the centre point and ΔX is the step change value. The removal of copper is taken as the dependent variable or response. The behaviour of system is explained by the following of system is explained by the following second-order polynomial model Eq. (2).

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

where Y is predicted response of copper removal in solution, x_i, x_j, ..., x_k are the input variables, which affect the response Y, x_i^2, x_j^2, ..., x_k^2 are the square effects, $x_i x_j$, $x_i x_k$ and $x_j x_k$ are the interaction effects, β_o is the intercept term, β_i (i=1, 2, ..., k) is the linier effect, β_{ii} (i=1, 2, ..., k) is the square effect, β_{ij} (i=1, 2, ..., k; j = 1, 2, ...,k) is the interaction effect and is random error [17, 21, 22]. For this research, Eq. (2) can be written as Eq. (3).

$$Y_i = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \tag{3}$$

3. Results and discussion

3.1 ANOVA in the regression model

The data in Table 1 was taken into account for ANOVA and multiple regression analysis in Box-Behnken design using polynomial model Eq. (3). The results are shown in Tables 2, 3 and 4.

Table 2
The NB Analysis of variance

Source	SS	DF	MS	F-value	Prob > F
Model	1.45E+005	5	2.90E+004	19.0	0.000609
X_1	3.61E+004	1	3.61E+004	23.6	0.00184
X_2	5.53E+004	1	5.53E+004	36.2	0.000534
X_1^2	1.81E+004	1	1.81E+004	11.9	0.0108
X_2^2	1.89E+004	1	1.89E+004	12.4	0.00976
$X_1 X_2$	8.59E+003	1	8.59E+003	5.62	0.0495
Residual	1.07E+004	7	1.53E+003	-	-

Table 3
The IB Analysis of variance

Source	SS	DF	MS	F-value	Prob > F
Model	1.49E+005	5	2.98E+004	19.1	0.000594
X_1	3.70E+004	1	3.70E+004	23.7	0.00182
X_2	5,61E+004	1	5,61E+004	36.0	0.000542
X_1^2	1.89E+004	1	1.89E+004	12.1	0.0102
X_2^2	1.99E+004	1	1.99E+004	12.8	0.00904
$X_1 X_2$	8,64E+003	1	8,64E+003	5.54	0.0508
Residual	1.09E+004	7	1.56+003	-	-

Table 4
The PB Analysis of variance

Source	SS	DF	MS	F-value	Prob > F
Model	1.57+005	5	3.13E+004	19.9	0.000519
X_1	3.89E+005	1	3.89E+005	24.7	0.00161
X_2	5.71E+004	1	5.71E+004	36.4	0.000526
X_1^2	2.03E+004	1	2.03E+004	12.9	0.00883
X_2^2	2.23E+004	1	2.23E+004	14.2	0.00702
$X_1 X_2$	8.76E+003	1	8.76E+003	5.58	0.0502
Residual	1.10E+004	7	1.57E+003	-	-

Note: X_1 = initial Cu(II) ions concentration; X_2 = stirring time; SS = sum of squares; DF = degree of freedom; MS = mean square

Analysis of variance (ANOVA) for responses (NB), (IB), and (PB) indicate that effect of individual factors, interaction factors for degree of confidence ≥ 95 %. The RSM model is selected quadratic model, R^2= 0.93, CV = 19.1, and the model is very significant.

3.2 Fitting model

Analysis of variance (ANOVA) were used to evaluate effect of individual factors, interaction factors, and multiple regression analysis in Design Expert 12. Box-Behnken Design in the RSM was used. The model equation which are used to predict the optimum degree of Cu(II) removal were determined by multiple regression analysis using following equations.

The NB final equation in terms of actual factors is shown by Eq. (4).

$$Y_1 = -263 + 1.17X_1 + 5.89X_2 - 0.00195X_1^2 - 0.0357X_2^2 + 0.00515X_1X_2 \quad (4)$$

The IB final equation in terms of actual factors is shown by Eq. (5).

$$Y_2 = -270 + 1.20X_1 + 6.04X_2 - 0.00200X_1^2 - 0.0367X_2^2 + 0.00516X_1X_2 \quad (5)$$

The PB final equation in terms of actual factors is shown by Eq. (6).

$$Y_3 = -270 + 1.20X_1 + 6.04X_2 - 0.002X_1^2 - 0.0367X_2^2 + 0.00516X_1X_2 \quad (6)$$

where Y_1 is the NB predicted response for Cu(II) ions removal, Y_2 is the IB response for Cu(II) ions removal, and Y_3 is the PB response for Cu(II) ions removal. Meanwhile X_1, and X_2 are independent variables for initial Cu(II) ions concentration and agitation time respectively.

Based on the equations it showed that the influence of initial Cu(II) ions concentrations (X_1) and stirring time (X_2) affected the Cu(II) adsorption by bentonite third for natural bentonite (NB), bentonite intercalation results(IB) and bentonite result of pillarization (PB). These effects can be observed from the intercept and coefficients of the three optimization equations respectively. The level of influence of PB > IB> NB [19-20]. The relationship between the bentonite mass and agitation time on Cu(II) removal are shown in Figures 1, 2 and 3. The optimization response surface contour and 3-D for desirability ramp plots for the effect initial Cu(II) ions concentration and agitation time on Cu(II) removal is clearly shown in Figure 4. The optimum condition found was a removal system with initial copper concentration of 300 mg/L and agitation time of 75.901 min shown by the desirability value of 0.935.

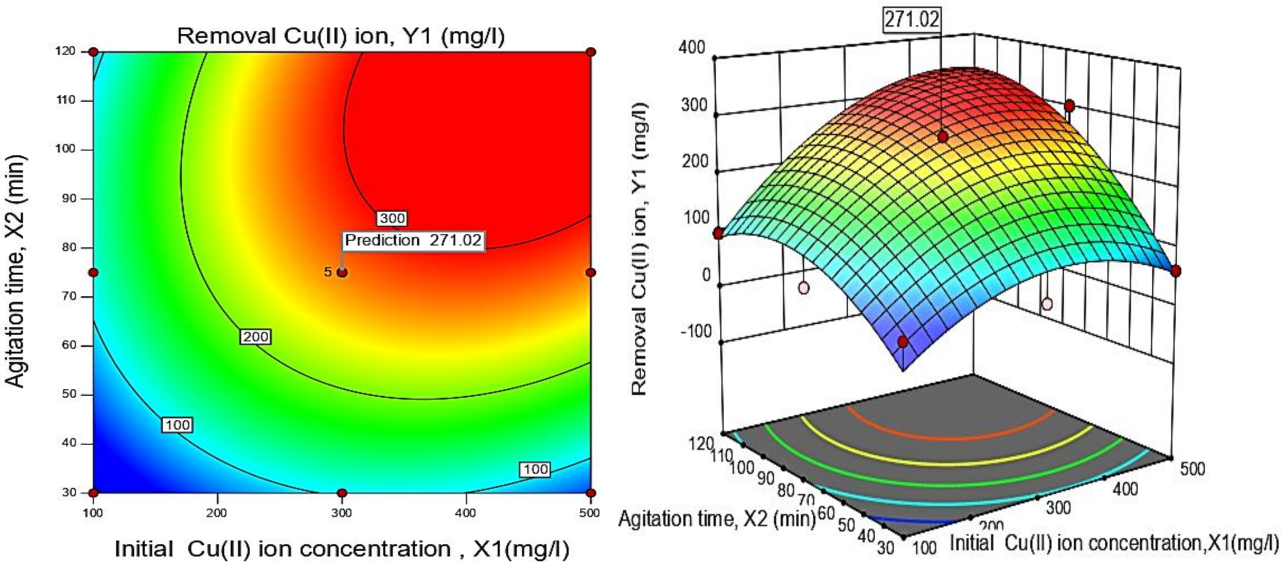

Fig. 1. The NB response surface contour and 3-D plots for the effect of initial Cu(II) ions concentration and agitation time (min) on Cu(II) removal (mg/L)

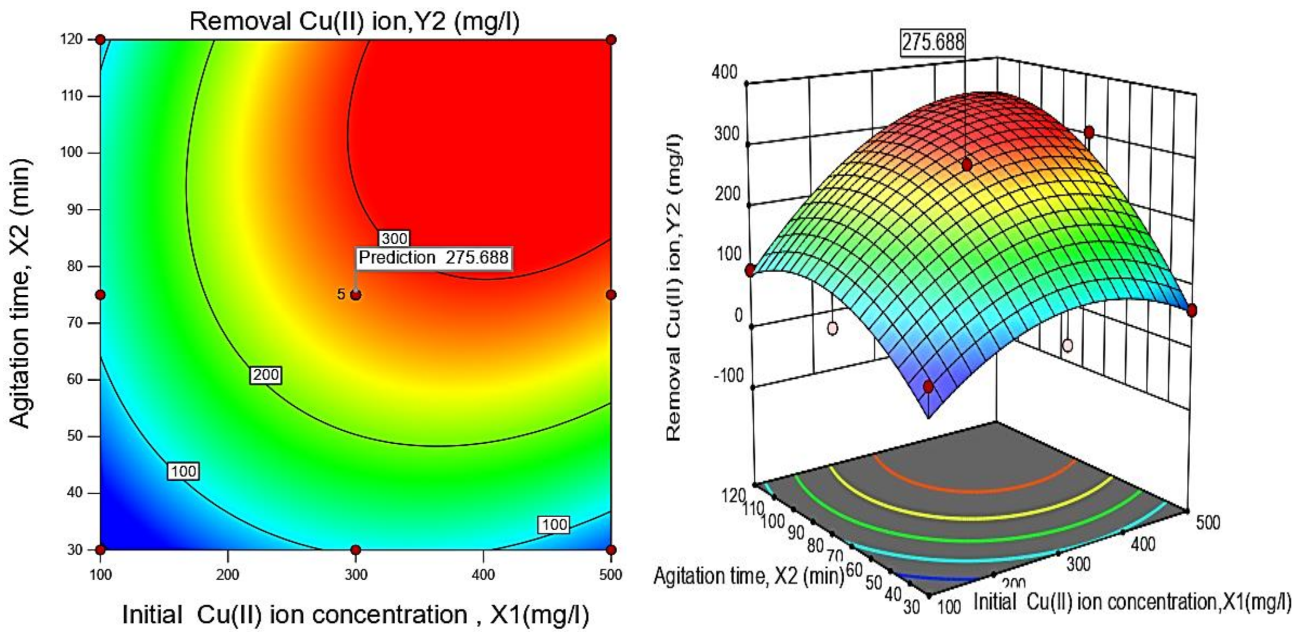

Fig. 2. The IB response surface contour and 3-D plots for the effect initial Cu(II) ions concentration and agitation time (min) on Cu(II) removal (mg/L)

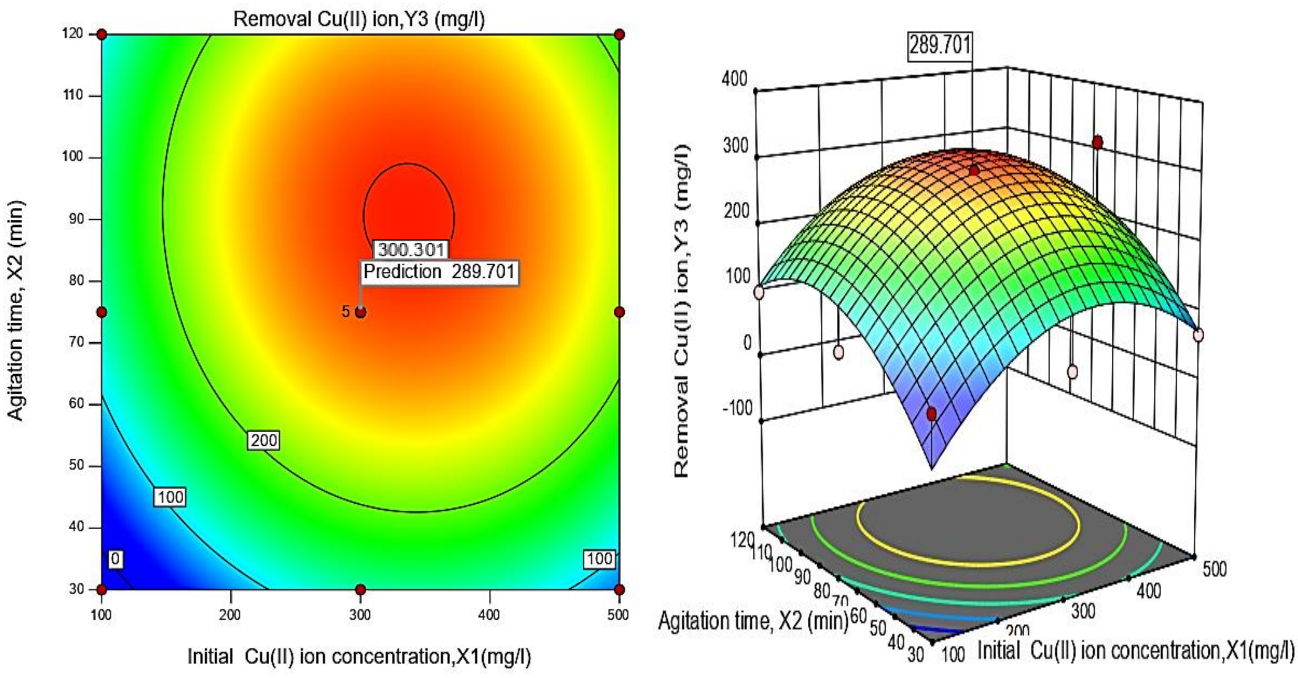

Fig. 3. The PB response surface contour and 3-D plots for the effect of initial Cu(II) ions concentration and agitation time (min) on Cu(II) removal (mg/L)

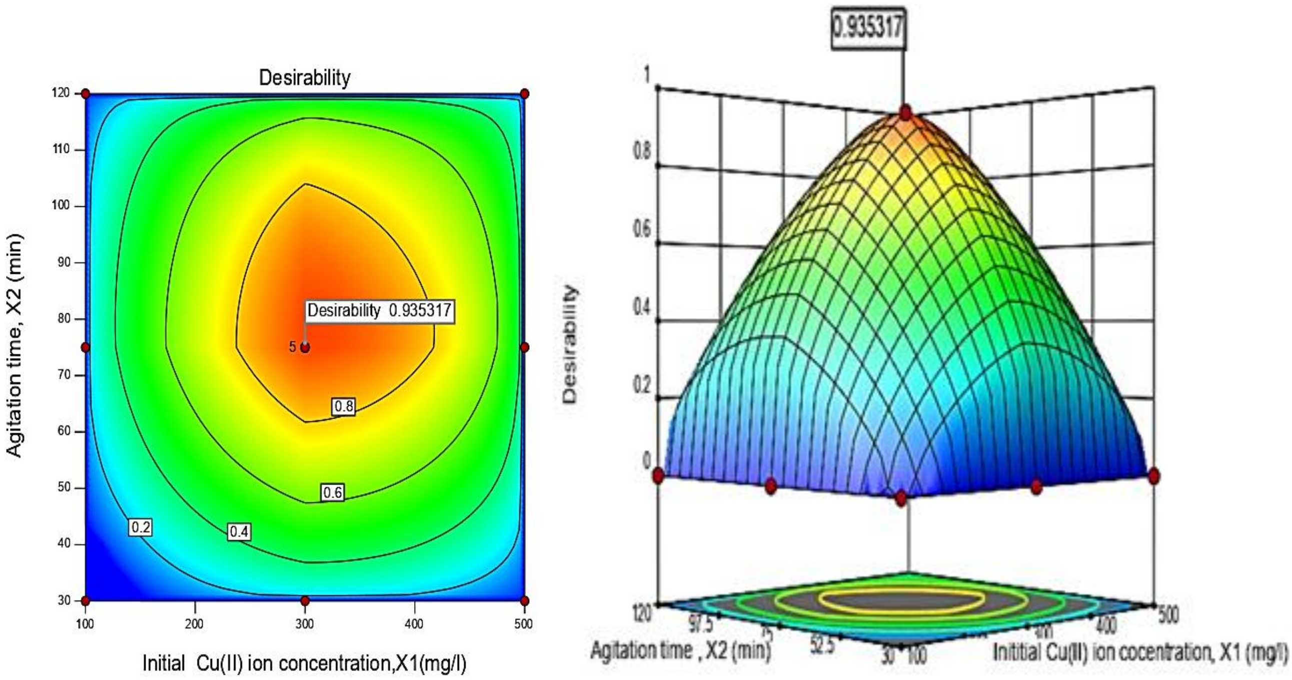

Fig. 4. Optimization Response surface contour and 3-D for desirability ramp plots for the effect initial Cu(II) ions concentration and agitation time (min) on Cu(II) removal (mg/L)

The interactive effect of any two of three independent factors on dependent factor were showed graphically by contour and 3-D response surface. Optimization using the desirability function was shown in Figure 5.

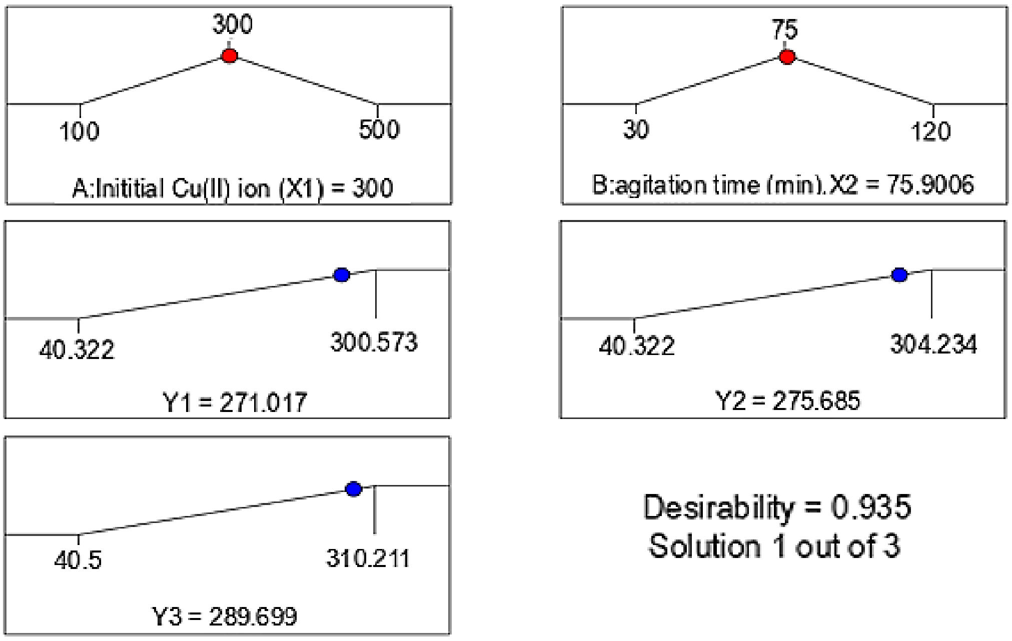

Fig. 5. Desirability ramp for numerical optimization of two goals of independent variable i.e. the initial copper ion concentration and agitation time and copper removal as response variable

Based on the numerical optimization, it was obtained that the maximum copper removal by the NB, IB and PB were 271.017, 275.685 and 289.699 mg/L respectively with initial copper concentration of 300 mg/L and agitation time of 75.901 min. To obtain the Cu(II) adsorption capacity for each adsorbate at certain adsorption time, Eq. (7) can be used [33].

$$q_{t=n} = \frac{\left(C_{t=0} - C_{t=n}\right)V_S}{m_{AC}} \tag{7}$$

where $C_{t=0}$ (mg/L) is Cu(II) ions concentration in liquid phase at the time of zero (t = 0 min), which is the Cu(II) initial concentration; $C_{t=n}$ (mg/L) represents Cu(II) ions concentration in liquid phase at the time of $t=n$ (min); $q_{t=n}$ (mg/g) is the Cu(II) adsorption capacity of adsorbate used at a certain adsorption time of $t=n$; V_S (L) is the batch mode of Cu(II) aqueous solution volume (L); and m_{AC} (g) denotes as the mass of adsorbate. The Cu(II) removal can be calculated using the expression of $C_{t=0}$ - $C_{t=n}$ (mg/L). Therefore, the maximum copper adsorption capacity of the NB, IB and PB were obtained to be approximately 27.101, 27.568 and 28.969 mg/g respectively.

4. Conclusions

From the results obtained, it can be summarized that natural bentonite, intercalate bentonite and pillared bentonite utilized were a promising adsorbate for copper removal in water treatment. Optimization of adsorption using by response surface methodology was success to obtain the maximum copper removal. The maximum copper removal by the PB being 289.699 mg/L was greater than by the NB and IB which were 271.017, 275.685 mg/L respectively. The maximum copper adsorption capacity of the NB, IB and PB were 27.101, 27.568 and 28.969 mg/g respectively with the optimum condition with initial copper concentration of 300 mg/L and agitation time of 75.901 min.

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