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Research paper

Optimization of Iron (Fe2+) Adsorption on Commercial Granular Activated Carbon in A Fixed-Bed Column

Novi Sylvia[1*], Meriatna[1], Fikri Hasfita[1], and Nur Fardian[2]

1Department of Chemical Engineering, Malikussaleh University, Lhokseumawe, 24351, Indonesia,
2Department of Nutrition, Medical School, Malikussaleh University, Lhokseumawe, 24351, Indonesia,
**Corresponding author E-mail:* nxsylvia@gmail.com

Abstract

Adsorption process can also establishes a mathematical relationship between the interaction process of variables and process optimization is essential in measuring factors values to obtain maximum respons number.The adsorption of Fe from ground water was optimized by using the methodology of response surface based on design idea of Box-Behnken. Adsorption data was analyzed using isotherm models. The process was measured using continue experiments. Variables in the process were bed depths (7,5, 10 and 12,5 cm), time (20, 40 and 60 min), flow rate (6, 10 and 14 L/min). Regression analysis was used to analyze the value of models developed. The result of this research showed the number of 95,598 % from the variations in removal rate of efficiency respectively are applied to three processes which variables considered, that is, bed depths, time and flow rate. Therefore, the models used as well to predict the interaction of the process variables. Optimization tests showed the optimum process conditions for the adsorption process occurred at bed depths 11,36 cm, time 55,61 min and flow rate 6 L/min. These were considered as optimum operating conditions. There are two isotherm equations which have been tested, those are Langmuir and Freundlich. The Equilibrium adsorption data can be optimized when formulated in the Langmuir isotherm model.

Keywords: *Adsorption, Box-Behnken design, Optimization, iron (Fe2+), isotherm*

1. Introduction

Water is very useful natural resource for life. The need of clean water is increasing along with the development of society and technology. The rapid population growth requires various facilities including clean water. Meanwhile, increasing industry will likely to produce form pollution including industrial waste.

Waste is waste its presence at a particular time and place undesirable environment because it has no economic value. Groundwater relatively has high iron (Fe2+) content. Iron content in the least amount required for the formation of red blood cells, but if the levels are too high may adversely affect human's health and environment.

Therefore, some groundwater sources should be processed before use. One treatment used to eliminate the metal Fe in groundwater is adsorption. Adsorption is a process which is involving process of a substance, then originally present in one phase and removed by the accumulation at the interface between those phases and separate (solid) phase. Adsorption is processed one with the addition of the adsorbent, active carbon or the like.

Adsorption systems are divided into two kinds of batch system and continuous system (column) (Mohammad, 2013). The Response surface methodology (RSM) developed by Box and Wilson in 1951 used to enhance the manufacturing processes in chemical industry (Dean et.al, 1991). It focused on optimizing adsorption to prevail , high yield and economic price purity

The result was accomplished through sequential experimentations which involving subjects like temperature, pressure and also duration of the reaction and proportion of the reactants. Response Surface Methodology (RSM) gets an important application for analyzing the effects of several independent variables which include interactive effects of the variables as the response**.**

A mathematical and statistical approach in modeling and analyzing problems to define some variables which resulted responses of interest namely Response Surface Methodology (RSM) had been used in multivariate experimental design, statistical modeling and process optimization. Influence of numerous process markers i.e initial metal concentration, pH, adsorbent dosage, contact time, and type of adsorbent on adsorption process were measured investigated in batch system (Mohammad et al, 2014; Ivana et al, 2012; Turkyilmaz et al, 2014; Roy et.al, 2014; Maria, et.al 2014; Anupam et.al, 2011; Khatee, 2010; Gottipati et.al, 2012; Lalitendu et.al, 2012; Sahu et. al, 2009; Liu et.al 2010; Han et.al 2008;). Messaoudi et.al (2016) run experiment regarding the column from aqueous solution using jujube for biosorption of Congo red in a fixed-bed shell. Variables in the process were bed depths (2, 4 and 6 cm), flow rate (2.8, 4.5 and 6.4 L/min), influent CR concentrations (100, 200 and 300 mg/L) and particles size (50–100, 100–315, 315–500 and 500–1000 μm). The highest number of biosorption capacity (80.49 mg/g) of a 100 mg/L of CR solution is considered at a flow rate of 2.8 mL/min, bed depth of 4 cm and JS particles size of 50–100 μm. The series of number gathered from column study then considered matched well with the

Thomas model. Nevertheless, no study was ascertained in literature for optimizing adsorption of iron in a continous system. The objective of the present research was to optimize the adsorption conditions of iron using granular activated carbon deploying Response Surface Methodology (RSM in a fixed-bed column). Results of variables bed depth, contact time and flow rate the adsorption yield were investigated by three variables of three level Box-Behnken Design (BBD). Empirical correlation model responses to the three variables that was then also developed; Langmuir and Freundlich isotherm models that were measured for its appropriateness. The granular activated carbon supplied method, is used as the adsorbent. Activated carbons were produced from coconut shell. Optimization of adsorption using activated carbon adsorbent carried by flowing groundwater into the adsorption column filled with continuous system with an activated carbon adsorbent bed depth, vary 7.5 cm, 10 cm, 12.5cm consecutively; a contact time of 20, 40 and 60 minutes and a flow rate of 6, 10 and 14 l/min as shown in fig.1.

Fig.1: Fixed-Bed Column used to experiment

2. Modeling and Optimization

2.1. Experimental procedure and design

The independent variables in this study were bed depth (X1;7.5 cm, 10 cm, 12.5 cm), adsorption time (X2; 20 minutes, 40 minutes and 60 minutes) and flow rate (X3; 6, 10 and 14 l/min). This research aimed to separate Fe metal ion in groundwater used granular activated carbon by a fixed-bed column in continuous system. Initial concentration Fe (II) (C0) was 0,169 mg/l. Analyzed dependent variables were e Fe removal efficiency (Y1), isoterm Freundlich and isoterm Langmuir. The level and code in this study presented in Table 1.

Table 1: Experimental ranges and levels of Independent Variables

Independent variables	Coded level and range		
	-1	0	+1
Bed depth, cm (X_1)	7,5	10	12,5
Adsorption time, min (X_2)	20	40	60
Flow rate, L/min (X_3)	6	10	14

Table 1 contains all the independent variables of Experimental upper and lower limits and scale of the A number of 17 runs that were randomly performed to optimize the process variable, together with predicted results and simulated experimental of the dependent variable as figured in Table 2. The experimental data analyzed by RSM with the use of Design Expert software (Version 7.5, State-Ease Inc, Minneapolis, USA) to fit the following second-order polynomial equation:
to fit the following second order polynomial equation:

$$Y_k = \beta_o + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum\sum_{i<j} \beta_{ij} X_i X_j + \varepsilon_j \qquad (1)$$

where Y is the predicted responses and X1, X2, and X3 are coded independent variables corresponding to bed height, adsorption time and flow rate diameter using column adsorption with a flow system in which sample is applied to the filtration tube containing active carbon respectively.

The constants βo, βi, βii, and βij were defined as the linear term, quadratic term and cross product term coefficients. The coded values are related to the real values through equation [2] presented below.

[2]

where Z is the coded value (-1, 0, or +1) and X is the corresponding original un-coded value, while Xo the mid value of the domain. X represents as the increment of X for every unit of Z.
It is essential to set up the optimum criteria in order to match the goals of optimizing multiple response variables with the desirability function (DF) approach, as recommended by Derringer and Suich (1980). The upper or lower number of the variable response is measured based on technical and/or economical sensitivity. The common way is first to convert each response Yi, into an individual desirability function di , which differ from 0 < di < 1, and di = 1 defined as e response Yi meets the goal or target value, and di = 0 if the response falls under yond the acceptable limit.
Experimental design matrix based on Box-Behnken Adsorption removal efficiency was establish by using the equation [3] (Garg et.al, 2008; Lo et.al, 2012; Saad et.al, 2010)
Y = (C_(A0)- C_A)/C_A0 [3]

where Y is the percentage of adsorbed Fe(II) ions, CAo is the first concentration of Fe(II), and CA is the residual concentration of Fe(II).

TABLE 2: Experimental design matrix based on Box-Behnken

Run	Bed depth (X_1)	Adsorption time (X_2)	Flowrate (X_3)	Removal Efficiency		
				Experiment	Prediction	Error, %
1	0	+1	-1	91,72	94,156	-2,661
2	+1	-1	0	92,31	92,307	0,001
3	+1	0	+1	89,35	91,789	-2,731
4	0	0	0	89,94	89,940	0,000
5	0	-1	+1	84,62	82,174	2,885
6	+1	0	-1	95,86	94,156	1,775
7	0	0	0	89,94	89,940	0,000
8	0	0	0	89,94	89,940	0,000
9	0	+1	+1	85,80	84,097	1,983
10	0	0	0	89,94	89,940	0,000
11	+1	+1	0	94,67	93,934	0,782
12	0	0	0	89,94	89,940	0,000
13	-1	+1	0	76,92	76,923	0,000
14	-1	0	-1	84,62	82,174	2,885
15	-1	-1	0	71,60	72,337	-1,033
16	0	-1	-1	88,17	89,867	-1,929
17	-1	0	+1	65,09	66,790	-2,613

Two theoretical isotherm models Langmuir (applied to homogeneous adsorption) and Freundlich (applied to heterogeneous adsorption) isotherms were adopt to fit the adsorption data collected at 35°C. In Langmuir isotherm by equation [4] (Benefield et.al, 1982):
C_e/Q=1/(Q_0 b)+C_e/Q_0
where C_e for the equilibrium concentration (mg/L), Q for number of metal adsorbed (mg/g), and b for sorption constant (L/mg) (at 35°C) related to the energy and Q_0 for maximum sorption capacity (mg/g).
In Freundlich isotherm (Benefield et.al, 1982):
Q_e=K_F 〖C_e〗^(1/n),
where Q_e indicate the number of metal adsorbed at the equilibrium (mg/g), K_F (mg/g)(L/mg)1/n) and n (dimensionless, those is Freundlich constants related to the adsorption capacity and adsorption intensity. The regression analysis and calculation of constants of Eq.
(4) and (5) were obtain by the solver add-in function of MS Excel

3. Results and Discussion

Model for the response variable
Table 2 presented the design matrix of the coded units in conjunction with the results of experimental data and the predicted number of response variable using the model (iron removal efficiency). The predicted values of the response were calculated using model fitting calculation using Design Expert software. The experimental data, the removal of efficiency were utilized to develop the statistical model using multiple regression analysis method. The resulted relationship of the response variable of removal efficiency and independent variables of bed depth, adsorption time and flow rate is shown in Equation 6. Based on the data, the highest removal efficiency (Y1) of 95,86 % was obtained and this was followed by the removal efficiency of 94.67%.
The percentage error of the RSM presented in Table 2 shows that the highest-lowest error for response Y1 is 2.885-0.

$$Y1 = -6.97115 + 16.89349X1 + 0.52145X2 - 2.49630X3 - 0.014793X1X2 + 0.32544X1X3 - 0.00739645X2X3 - 0.79290X12 - 0.00277367X22 - 0.078587X32 \quad [6]$$

Where Y is iron removal (response) in percentage, X1, X2 and X3 were the coded values of variables bed depths in cm (X1); adsorption time in min (X2), and flow rate in L/min (X3).
Correlation between the surface response and factors were developed using Box-Behnken of the Design Expert Software. According to a bunch model sum of squares, the models were choosen according to the highest order polynomials where the additional terms are significant and the models were not aliased (Chaudhary and Balomajumder, 2014). Correlation coefficient and standard deviation are used to evaluate the fitness of the models that developed.
The closer the 2 value is to unity. Smaller standard deviation showed better model in in predicting the response (Tan et. al, 2009). Table 3 shows the quadratic model has a relatively small standard deviation of 2,28 and relatively high $R2$ value of 0,9657 with predicted $R2$ (0,4518) in reasonable agreement with adjusted $R2$ (0,9217).

Table 3: Regression statistics for removal efficiency (model for response YI)

Source	Standard Deviation	R^2	Adjusted R^2	Predicted. R^2	Comment
Linear	3,97	0,8000	0,7637	0,6518	-
2FI	3,98	0,8511	0,7618	0,4585	-
Quadratic	2,28	0,9657	0,9217	0,4518	Suggested
Cubic	0	1	1	-	Aliased

It was also observed on the table that the model for response Y1 was not aliased. This implies that this model can be used to outline the relationship between response Y1 and the interaction variables.

Table 4: Analysis of variance (ANOVA) for removal efficiency

Factor	Sum square	df	Mean square	F-Value	P Value	Remark
Model	1028,75	9	114,31	21,92	0,0003	Significant
X_1	683,84	1	683,84	131,15	<0,0001	Significant
X_2	19,30	1	19,30	3,70	0,0958	
X_3	157,56	1	157,56	30,22	0,0009	Significant
X_1X_2	2,19	1	2,19	0,42	0,5378	
X_1X_3	42,37	1	42,37	8,12	0,0247	
X_2X_3	1,40	1	1,40	0,27	0,6203	
X_1^2	103,40	1	103,40	19,83	0,0030	Significant
X_2^2	5,18	1	5,18	0,99	0,3520	
X_3^2	6,66	1	6,66	1,28	0,2957	
Residual	36,50	7	5,21			
Error	0,000	4	0,000			
Cor Total	1065,25	16				

Table 4 shows the results of analysis of variance quadratic model removal efficiency of Fe.ANOVA for the quadratic model in Table 5 looks variables X1 and X3 have probabilit y value (Prob> F) is smaller than 0,05. This shows that the quadratic model, the variable X1 = bed height, X3 = the flow rate and the X12 quadratic variables significantly affect the removal efficiency of Fe. Instead, X2 = contact time, and the interaction variables X1X2, X1X3 and X2X3 and quadratic variable X22 and X32 looks insignificant.

This shows that statistically these variables only gives little influence on the removal efficiency of Fe. However, these variables remain included in the model, given the possibility of these variables a significant impact on the adsorption.

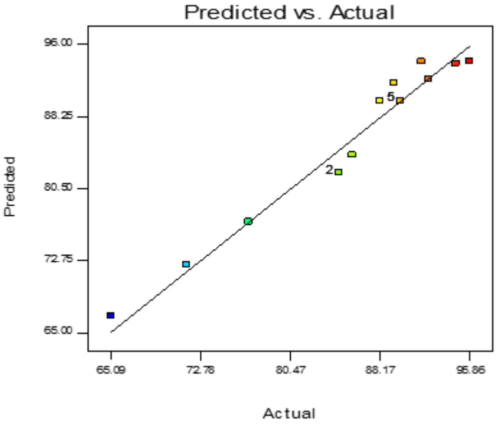

Fig.2: Comparison of predicted and actual values of Removal Efficiency Fe (symbol –actual data; line – predicted model)

Figure 2 presented the comparison of predictions of removal efficiency compared to the experimental measurements or actual data. The solid line entitled to the calculation based on the statistical model shown in Equation 6, while the symbol depicts the experimental values. It is obvious most of the experimental data are falling on or having in contact with the prediction line, confirming an excellent agreement between the predictions and experimental data. All the above discussions indicate outstanding adequacy of the proposed quadratic model to represent the relationship between the response variable, removal efficiency and independent variables of bed depth, adsorption time and flow rate. .

The determination of optimum operating conditions for the independent variable is aimed at obtaining the highest removal efficiency of iron. A parameter desirability function, DF, is used to judge the optimum operating condition. As mentioned earlier, if the DF is closer to unity, the response of the target is the best. Table 5 presents alternative solutions with different DF values. The highest DF value is 1, obtained under conditions of bed depth of 11.36 cm, adsorption time of 55.61 min and flow rate of 6 l/min. The lowest DF value of 0.991 is obtained under conditions of bed depth of 11.39 cm, adsorption time of 56.45 min and flow rate of 6 l/min. Both conditions produce a similar removal efficiency of 95.60%. Applying the DF method, the Design Expert software produced four solutions, as shown in Table 5. On the consideration of DF value, solution number 1 is selected to represent the optimum response variable. Messaoudi et al., (2016) reported the highest removal efficiency at the lowest flow rate.

Table 5. Numerical optimization of the model obtained by desirability function

No	Criteria	Solution	Desirability
1	Bed Depth: in range	11,360	1
	Adorption Time: in range	55,610	
	Flow Rate: in range	6	
	Iron Removal: maximize	95,598	
2	Bed Depth: in range	11,350	0,992
	Adorption Time: in range	55,910	
	Flow Rate: in range	6	
	Iron Removal: maximize	95,598	
3	Bed Deptht: in range	11,340	0,992
	Adorption Time: in range	56,170	
	Flow Rate: in range	6	
	Iron Removal: maximize	95,597	
4	Bed Depth: in range	11,390	0,991
	Adorption Time: in range	56,450	

Flow Rate: in range	6
Iron Removal: maximize	95,596

Isotherm

The study of the kinetics of adsorption of iron that carried out at 30°C on powder then activated the carbon from commercial sources. This is to measure the time needed for reaching equilibrium carbon adsorption for metal. Generally, the small adsorption seems to show at low number of pH and it is often attributed to a competition between H+ and metal ion on the same sites. The activated carbon surface has a positive charge and an electrostatic repulsion takes place between the same charge of the cations and the activated carbon. The increase of pH will cause the negative charges density on the form to increase cause of the deprotonation of positively charged groups on the surface of activated carbon (Kouakou et al, 2013). In order to show the design of a sorption system to remove iron from effluents, it is crucial to have the most appropriate correlation for the equilibrium curve. Two isotherm equations have been tested; Langmuir and Freundlich.

The experimental adsorption data were fitted to these isotherm models for synthetic solutions and shown in Figure 3.

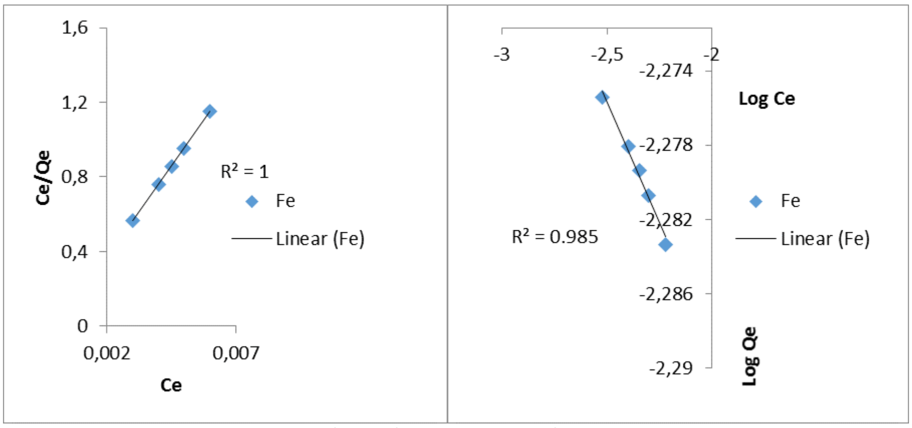

Fig. 3: Isotherm adsorption of Fe2+ from Langmuir (left) and Freundlich model (right)

The values of the constant of Langmuir KL and Qm with correlated coefficients for Fe are listed in Table 6. Correlaction coefficient number of Langmuir model showed higher value compared to .

The Langmuir equation represented the best fit of experimental data than Freundlich isotherm equation. So, Langmuir model is more appropriate to describe this adsorption and Table 6 shows the initial and final concentration of iron in groundwater. Activated carbon adsorbed high concentrations of metal. These high rates should not only attribute to activated carbon but to the very low concentrations of the initial iron contained in these waters. This activated carbon is a excellent adsorbent for removing these metals in groundwater since approximately 95% of iron is removed. After adsorption, the ground water are good to be rejected due to its low content concentration of metal.

Table 6: Isotherm model constans for the adsorption of iron on coconut shell

Langmuir Model			Freundlich Model		
Qm	K_L	R^2	Ln K	1/n	R^2
0,005	4,299	1	2,340	0,026	0,985

5. Conclusion

A desirability function approach has been utilized to optimize the process variables of bed depths (7,5, 10 and 12,5 cm), time (20, 40 and 60 min), flow rate (6, 10 and 14 L/min) on the removal efficiency of iron in the fixed-column adsorption. The optimum conditions to produce high removal efficiency of iron were obtained at a condition of Bed Depth=11.36 cm, Adsorption time=55.61 min and Flowrate=6 l/min. With minimum numbers of experimental runs, this technique is an efficient solution for cyclone optimization problems. Beetween two isotherm equations tested; Langmuir and Freundlich, equilibrium adsorption data will be best represented using the Langmuir isotherm model.

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