Boron removal from aqueous solution using coagulation-flocculation with curcumin : A response surface methodology

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Abstract

Aim: Application of response surface methodology (RSM) to determine optimum parameters in the coagulation-flocculation process aided by curcumin for boron removal from aqueous solution was investigated.

Methodology: Different parameters such as pH, coagulant dosage, and curcumin dosage that effect boron removal were tested. Application of central composite design in RSM was used to design the coagulation-flocculation experiment.

Results: The results showed 75% of boron removal, while the optimum parameters for boron removal were observed at pH 2.8, 132.05 ppm poly aluminium chloride dose and 1161.4 ppm curcumin dose, respectively.

Interpretation: Quadratic regression showed that the model was significant and lack of fit P value was 0.107 ($p > 0.05$), implying a significant model correlation between the variables and responses. The experimental data and predicted model proved that RSM is an appropriate approach for optimising the coagulation-flocculation process in removing boron from aqueous solution.

Key words: Boron, Coagulation, Curcumin, Flocculation, Response surface methodology

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Introduction

The presence of boron can be detected naturally in low concentrations in soil, water and rocks (Yilmaz *et al.*, 2007). Total boron dose recommended by the World Health Organization is 1-13 mg day⁻¹ is safe and adequate for human health (Simsek *et al.*, 2003). The element of boron is widely used especially in production of glass and detergents (Ozturk and Kavak, 2005; Magara *et al.*, 1998), cosmetics, heat-resistant glasses, ceramics, and fire retardants materials (Demey *et al.*, 2019; Kartikaningsih, 2016) and as a moderator in nuclear reactor (Coughlin, 1998; Silva *et al.*, 2019). The use of inactive sepiolite waste (ISW) and the remaining active sepiolite waste (ASW) as coagulants can help in the removal of boron from aqueous solutions by adsorption processes using batch and column (Ozturk and Kavak, 2004). Electrocoagulation process has also been used for treating wastewater containing boron in an effective and efficient manner (Yilmaz *et al.*, 2008; Halim *et al.*, 2012).

Removal of boron from aqueous solutions can be carried out done through precipitation and coagulation (Yilmaz *et al.*, 2007; Halim *et al.*, 2012), electro-coagulation (Silva *et al.*, 2019), activated carbon adsorption, fly ash and oxides (Cengelloglu *et al.*, 2007; Kurkumin *et al.*, 2013; Hu *et al.*, 2020), ion exchange (Bai *et al.*, 2020; Boncukcuoglu *et al.*, 2004), extraction solvent after complexation (Matsumoto *et al.*, 1997), reverse osmosis (Cengelloglu *et al.*, 2008) and electrodialysis (Yazicigil and Oztekin, 2006). Coagulation and flocculation are considered as one of the effective methods for wastewater treatment. Addition of chemicals in the process of coagulation and flocculation has aided in the removal and modification of physical state of suspended solids and dissolved (Verma *et al.*, 2004). High cost required for wastewater treatment, and biological treatment is said to be less productive for the removal of boron from industrial wastewater (Melnyk *et al.*, 2005).

Curcumin, demethoxycurcumin and bisdemethoxy curcumin are known as curcuminoids. Curcumin (diferuloyl methane) is a polyphenol and active ingredient of *Curcuma longa*. Curcumin I (curcumin), Curcumin II (demethoxy curcumin) and Curcumin III (bisdemethoxy curcumin) are three main yellow pigments of turmeric (Goel *et al.*, 2008). Curcumin can be used as a coagulant in the wastewater treatment. Halim *et al.* (2012) found that curcumin-based coagulant was able to remove boron from aqueous solution by 95% as compared to normal coagulant 62%. Electrocoagulation process aided by curcumin was more efficient in removing boron than the unaided electrocoagulation process (Halim *et al.*, 2012). In view of the above, this study was carried out to determine the optimal process involved in removal of boron from the aqueous solution by curcumin aided coagulation-flocculation using response surface methodology.

Materials and Methods

Poly-aluminum chloride was used as a coagulant in this study. Poly-aluminum chloride and curcumin were purchased from Merck Company. Boron stock solution was prepared from boric acid powder. Optimum parameters like pH, poly-aluminum chloride and curcumin doses were determined based on the effectiveness of boron removal.

Estimation of optimum parameters (pH, coagulant dosage and curcumin dosage): For pH, 400 ml of boron solution with concentration at 50 mg l⁻¹ was filled in each of six beakers to 500 ml. Each beaker was adjusted between pH 6 to 11. After that, 90 ml PAC and 5 ml curcumin were loaded into the beaker. Next, after the jar test was completed, a total of 50 ml of the test sample was taken and stored in bottles for the determination of boron content. For PAC dosage, jar tests were conducted using different doses of PAC in the range of 50-100 ml. Each beaker was then filled with 400 ml of boron and 5 ml of curcumin. After 30 min, 50 ml of sample was taken and stored in a bottle for estimation boron by Carmine method (Eaton and Franson, 2005). For curcumin dosage, six beakers containing 400 ml of boron were prepared and filled with different doses of curcumin (2, 4, 6, 8, 10 and 12 ml). After that, all the beakers were prepared for the test tube for the time chosen. Finally, 50 ml samples were taken and stored for further process.

Optimization by response surface methodology and statistical analysis: Design of the experiments and statistical analysis were conducted using Minitab software (ver. 16). Central composite design (CCD) in the response surface methodology was employed to determine the optimisation parameters. The effects on response were compared after different variables that were expressed in different units and variation limits were coded. Variables X_i were coded as x_i based on the equation below:

$$X_i = \frac{x_i - x_{i0}}{\delta x_i} \quad (1)$$

Where, X_i refers to the coded value of independent variable i ; x_i is the uncoded value of independent variable i ; x_{i0} is the median of data array x_i ; and δx_i is the step change. Step change δx_i is expressed as below:

$$\delta x_i = \frac{\max(x_i) - \min(x_i)}{2} \quad (2)$$

pH (x_1), dose of coagulant, PAC (x_2), dose of coagulant aid, curcumin (x_3) were selected as three independent variables. The dependent variable or response was fitted by a second-order model in the form of a quadratic polynomial equation:

$$Ym = b_0 + \sum_{i=1}^k b_i X_i + \sum_{i=1}^k b_{ii} X_i^2 + \sum_{i < j}^{i,j} b_{ij} X_i X_j \dots \dots \dots (3)$$

Table 1 : Coded and non-coded values of RSM application for curcumin aided coagulation-flocculation process

Order of study	Coded value			Non-coded value			Response(Y), % boron removal
	pH (X_1)	Dose of PAC (X_2)	Dose of curcumin (mg l^{-1}) (X_3)	pH	Dose of PAC (mg l^{-1})	Dose of curcumin (mg l^{-1})	
1	-1	1	-1	4.5	65	500	75
2	0	0	0	7	90	1000	67
3	0	0	-1.68	7	48	159.1	25
4	0	0	1.68	7	132	1840.9	58
5	0	0	0	7	90	1000	42
6	1	-1	1	9.5	115	1500	42
7	0	0	0	7	90	1000	58
8	-1	-1	-1	4.5	65	500	25
9	0	0	0	7	90	1000	58
10	1.68	0	0	11.2	90	1000	25
11	0	0	0	7	90	1000	50
12	1	-1	-1	9.5	65	500	50
13	-1.68	0	0	2.8	90	1000	75
14	1	1	-1	9.5	65	500	33
15	0	0	0	7	90	1000	42
16	0	1.68	0	7	90	1000	42
17	1	1	1	9.5	115	1500	58
18	-1	-1	1	4.5	115	1500	50
19	-1	1	1	4.5	115	1500	58
20	0	-1.68	0	7	90	1000	50

Where, i is the linear coefficient, j is the quadratic coefficient; b is the regression coefficient; and k is the number of factors studied and optimised in the experiments. A two-dimensional contour plot was used to illustrate the interactive effects of independent variables on dependent variables. Each parameter was calculated to obtain relevant data to be included in the RSM for the next forecast. Coagulation-flocculation process was carried out using the parameters obtained by RSM based on the non-coded values as shown in Table 1.

Results and Discussion

Fig. 1(a) shows a surface plot for efficient removal of boron which PAC dose at coded value of 0.75 or at 108.6 ppm and the dose of curcumin was observed at coded value of 0.75 or at concentration of 1375 ppm. Based on these plots, the removal of boron was 55%. Fig. 1(b) shows the surface plot for the removal of boron was effective at a pH coded value of -1.25 (pH 3.9), while the dose of curcumin was at coded value of 0.5 (1250 ppm). Percentage removal of boron at this pH and curcumin dose was 60%. Fig. 1(c) shows the surface plot for the efficient removal of boron, where the pH coded value was at -1.5 (pH 3.3), and the coagulant dose coded value was 1.4 (125 ppm). Percentage removal of boron at this pH and coagulant dose was 80%.

Each pH level varied to affect the effectiveness of boron removal either in acidic, alkaline or neutral conditions. In Fig. 1(b) shows that at pH 3.9 (acidic condition) the percentage of boron removal was > 60%. High boron content in the aqueous soluble in

acidic conditions can remove boron more effectively from the aqueous solution. At acidic pH, the positive charge present in the solution is easily generated. It is reasonable to make the adsorption of borate anion in acidic condition (Polowczyk *et al.*, 2013).

Fig. 1© shows that the removal of boron was > 80% at pH 3.3. This removal was higher than the percentage of boron removal between pH and the dosage of PAC, implying the coagulant material was more effective in the removal of boron in surface charge (Moghaddam *et al.*, 2010). According to Wei *et al.* (2011), borate ions in solution become more predominant species below pH 7 that leads to a negatively charged surface. Below pH 7, boron exists as boric acid. It can exist predominantly as boric acid, B(OH)_3 , which cannot be separated in the aqueous liquid (Avraham *et al.*, 2011). According to Oo *et al.* (2009), the total percentage of dissociation of boric acid to borate containing negative charges occurring at an alkaline pH level. Therefore, boric acid in aqueous solution can be removed in the form of borate.

In Fig. 1 (a), at PAC concentration of 108.8 ppm, the boron removal efficiency was above 55%. High coagulant doses content helps in destabilization of the colloidal particles in solution (Syafalni *et al.*, 2012). Fig. 1(c) shows that the boron removal was above 80% at PAC concentration of 105 ppm and pH 3.3. The behavior of coagulation of PAC is associated with the ability of high charge neutralization, adsorption and sweep flocculation

Fig. 1 : Surface plot of boron removal (in percentage) vs (a) coagulant and curcumin, (b) pH and curcumin, (c) pH and coagulant in coded value.

Fig. 2 : Optimization plot of curcumin aided coagulation-flocculation process for boron removal.

(Moghaddam *et al.*, 2010). The high rate of boron removal was due to sweep mechanism for flocculation, which occurs at high-dose PAC. Fig. 2 associates the percent removal of boron correlated between pH and dosage of PAC. According to Han-Qing *et al.* (2011), colloidal particles in solution are destabilized by the coagulant, and flocculant consumption in the coagulation-flocculation process helps in clotting particles of colloidal size to merge into larger particles.

Dose of curcumin is one of the variables used in the coagulation-flocculation to influence the process of boron removal, which acts as a coagulant aid. As shown in Fig. 1 (a), at curcumin dose of 1375 ppm, boron removal was higher than 55%. Total

removal of boron is associated with high concentration of coagulant dosage. This indicates that high curcumin dose is not appropriate for producing high boron removal. In Fig. 1 (b), the removal of boron was > 60% resulting in doses of curcumin at high concentrations of 1,250 ppm. Total removal was low due to low pH. In acidic solution, boric acid reacts with curcumin to form rosocyanine (Lee *et al.*, 2011). Rosocyanine is a large molecule that coagulates/ precipitate in the presence of Al^{3+} ions. This study shows that the boron removal in the coagulation-flocculation process was assisted by the addition of curcumin as a coagulant aid.

Fig. 2 shows the suggested optimum parameters for the most efficient boron removal. Suggested optimum coded

Fig. 3 : Predicted vs. Experimental plot of boron removal by curcumin aided coagulation-flocculation process.

values for pH, coagulant dose and curcumin dose were -1.6818 (pH2.8), 1.6818 (123.05 ppm) and 0.3228 (1161.4 ppm), respectively. For the recommended pH, reading was at low pH, which causes lower boron removal rate due to the acidic pH conditions. In addition, high concentrations of PAC at 132.05 ppm, helped in increasing the removal of boron. The optimal concentrations of curcumin at 1,161.4 ppm also helped in the effective removal of boron.

In this study, important factors such as pH, PAC and curcumin doses affected the percentage of boron removal from aqueous solution. Regression equation model for boron removal in curcumin aided coagulation-flocculation process is given below:

$$Y = 52.72 - 7.99X_1 + 3.19X_2 + 5.89X_3 - 0.27X_1^2 - 1.68X_2^2 - 3.27X_3^2 - 7.37X_1X_2 + 1.13X_1X_3 - 1.13X_2X_3 \quad (4)$$

Based on the above equation, the correlation between X_1 (pH), X_2 , and X_3 (coagulant and curcumin dose in ppm) towards boron removal, Y was determined. Referring to this equation, the removal of boron (%) with linear and quadratic relationships with pH, PAC and curcumin. Analysis of variance (ANOVA) was used to analyse the interaction between process variables and responses. The lack of fit F-test was used to test whether the regression function adequately fits in the data. The quadratic regression showed that the model was significant, lack of fit P value was 0.107 ($P > 0.05$), implying a significant model correlation between the variables and responses. Fig. 3 shows that the predicted boron removal values plot versus experimental boron removal values were distributed close to the straight line. The correlation coefficient value ($R^2 = 0.8442$) indicates that only 15.58% of total variation could not be explained by the empirical model (Ahmad et al., 2005).

A coagulation-flocculation test was carried out to remove boron from aqueous solution, using poly-aluminum chloride as a coagulant, aided with curcumin. A full factorial central composite design and response surface design were

used to optimize the coagulant dosage, curcumin dosage and pH levels. The results showed that optimal conditions for boron removal were at a coagulant dosage of 132.05 ppm, curcumin dosage of 1161.4 ppm and pH 2.8. The significant correlation between experimental data and predicted model proved that RSM is a suitable approach for optimizing the coagulation-flocculation process in removing boron from aqueous solution.

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Add-on Information

Authors' contribution: A.A. Halim: Research idea, experimental design, data analysis, manuscript writing; M.M. Hanafiah: Manuscript writing; M. Asmi: Laboratory work and experimental, data analysis and manuscript writing; Z. Daud: Manuscript writing.

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