Jurnal Teknologi

Full Paper

OPTIMIZATION OF BATCH CONDITIONS FOR THE REMOVAL OF BORON BY AMBERLITE IR743

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Article history
Received
19 May 2015
Received in revised form
24 March 2016
Accepted
1 May 2016

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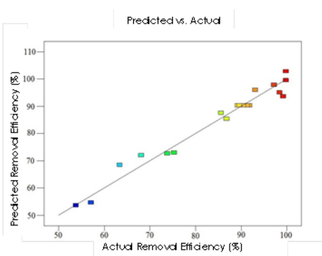
Graphical abstract



Abstract

This study is aimed at optimizing the treatment parameters in boron adsorption using a commercial resin, Amberlite IRA 743, via response surface methodology (RSM). The effect of adsorbent dosage, pH and initial boric acid concentration were optimized using RSM in order to obtain high removal efficiencies at low adsorbent dosage and pH levels and high concentrations. The central composite design (CCD) was used to generate the experimental design. The experiments were conducted in a batch process according to the experimental design obtained. The analysis of variance (ANOVA) was performed to obtain a statistical validation of regression models and to study the interaction between treatment parameters. The optimum conditions recommended by the developed model for 100% removal efficiency , was at adsorbent dosage, pH and initial boron concentration of 51g/L, pH 7 and 40mg/L.

Keywords: Boron, Amberlite IRA743, optimization, response surface methodology, central composite design

Abstrak

Objektif kajian ini adalah pengoptimuman parameter proses penjerapan boron oleh resin komersial Amberlite IRA 743 yang diubahsuai dengan glucamine menggunakan kaedah gerak balas permukaan. Kesan dos adsorben, pH dan kepekatan asid boric mula telah dioptimumkan menggunakan RSM untuk mendapatkan peratusan penyingkiran boron yang tinggi pada dos adsorben rendah dan kepekatan yang tinggi dalam proses kelompok . Rekabentuk komposit usat telah digunakan untuk menjana reka bentuk eksperimen manakala analisis varians (ANOVA) telah dilaksanakan untuk mendapat pengesahan statistik model regresi dan untuk mengkaji interaksi antara parameter input . Keadaan optimum yang disyorkan oleh model untuk dos adsorben , pH dan kepekatan awal ialah 51g/L, pH 7 and 40mg/L

Kata kunci: Boron, Amberlite IRA74, pengoptimuman, gerak balas permukaan, reka bentuk komposit pusat

1.0 INTRODUCTION

Boron naturally exists in sea water and in minerals widely dispersed in the environment in various forms bounded to oxygen such as, boric acid or salts. Boron takes the form of boric acid and partial borate salts in aqueous environments. Boric acid, a very weak Lewis acid, is formed when boron oxide (B_2O_3) reacts with water. It acts as an acid by accepting OH^- to form $B(OH)_4^-$. Boron leaks to ground water from areas with volcanic geology.[1] It also leaks to the environment from the wide usage of its compounds in various industries leading to its large presence in wastewater, soil and surface water, wherein boron forms complexes with heavy metal ions such as Cu^{2+}, Cd^{2+}, Pb^{2+} and Ni^{2+} leading to more toxicity than original heavy metal ions.[2]

Water-soluble boron compounds contaminating surface and ground waters originate from a variety of applications including the use of boronated fertilizers, insecticides and more significantly in the manufacture and subsequent utilization of sodium perborate found in an array of detergent formulations and cleaning products as a bleaching agent. The presence of boron in potable and agricultural water even at relatively small amounts (ppm) has proven to be harmful to human, plants and animals alike.[3] The effect of exposure to high boron levels in most crops include yellowing of the leaf tips that progress into the blades, burned edges on the older leaves, accelerated decay and subsequently death of the plant.[4-6] As for animals, chronic exposure of boron has been shown to cause cutaneous disorders, retarded growth and negatively impact the male reproductive system as has been observed in rats and mice).[6-7] A guideline value of 2.4 mg/L has been set by the World Health Organization (WHO) for potable water while wastewater discharge standards range from 4.0mg/L globally.[8]

Numerous separation technologies have been employed for boron removal from water and waste water including precipitation–coagulation, electrocoagulation (EC), electrodialysis (ED), adsorption on various adsorbents such as oxides, activated carbon, clays and fly ash, liquid-liquid extraction, reverse osmosis (RO), phytoremediation and ion exchange. However, it has been established that ion exchange is the most efficient method for boron removal from water and wastewater. [4,8]

Boron can be effectively removed from various streams using boron-selective resins (BSRs). These resins contain functional hydroxyl groups in the 1–2 or 1–3 positions, thus enabling boron capture by the formation of borate-diol complexes.[8-9] Amberlite IRA 743 is a typical example of a commercial BSR. This resin is prepared by condensation of N-methylglucamine with cross-linked chloromethylated polystyrene.[9] A previous study conducted by Parsaei et al. to study the effect of initial boron concentration, pH and dosage on removal efficiency using Amberlite IRA 743 reported that to achieve a maximum removal efficiency of between 70-98 %, an adsorbent dosage, pH and initial boron concentration of 70g/L, pH 9.5 and 40mg/L was needed.[10] It can be observed that a high pH level is required to achieve high removal efficiency. Extreme operating conditions cause an increase higher operational cost. Hence, it is necessary to optimize the treatment parameters to minimize cost.

Various studies have been conducted to test the capacity and behavior of Amberlite IRA743 towards boron removal. However, there has yet to be one on the optimization of its treatment parameters. In recent years, response surface methodology (RSM) has been vastly employed for improving and optimizing operating parameters in water treatment systems, while determining the significance of each parameter and the presence of complex interactions between them.[11] Although RSM does not enable the complete understanding of the mechanism, it still remains a powerful tool for statistical modeling and optimization of separation processes as it eases the task of searching for the optimum conditions for a process.[12-13] This study will enable the determination of the optimum combination of treatment parameters to achieve a high boron removal efficiency and to study the interaction between the parameters.

The objective of this study is to optimize the treatment parameters such as initial boron concentration, pH and adsorbent dosage using the central composite design in RSM to achieve maximum removal efficiency at reasonable operating conditions to minimize cost.

2.0 EXPERIMENTAL

2.1 Materials

The commercial anion exchange resin used in this study Amberlite IRA743 was purchased from Sigma-Aldrich Germany. Boric acid supplied by Merck Darmstadt-Germany was used for the preparation of boric acid stock solution. Mannitol solution was prepared from D(-)-Mannitol supplied by Systerm, by dissolving 200g in 1L of deionized water. Sodium hydroxide solution (0.1M and 0.01M) was prepared from pellets supplied by J.T Baker. Hydrochloric acid solution (0.1M, 0.01M and 0.001M) was prepared from hydrochloric acid (HCL Approx. 37%) purchased from Mallinkdrot.

2.2 Experimental Design

The central composite design (CCD) was employed in the present study to determine the optimum process variables for boron adsorption by Amberlite IRA743 using Design Expert (Version 9.0) by Stat-Ease. In this study the CCD of 3 variables i.e. adsorbent dosage(g/L), pH and initial boron concentration (mg/L), each with five levels (±1for the factorial points, 0 for the center point and ±afor the axial points) were chosen as independent variables with designated coded factors A, B and C as shown in Table 1. To estimate the coefficients of each model through linear regression, a number of 19 runs were necessary. The statistically designed experiments were performed on a batch basis.

Table 1 Coded and actual values of variables used

Factor	Symbol	Ranges				
		-α	-1	0	1	α
Adsorbent dosage (g/L)	A	15	30	45	60	75
pH	B	5	6	7	8	9
Initial concentration (mg/L)	C	20	40	60	80	100

2.3 Adsorption Studies

Prior to the experiments, the resin (Amberlite IRA743) was pre-treated by immersing in distilled water for 3-4 h. Pre-equilibration was performed by rinsing the resin with HCl 0.1M, 0.01M, and 0.001M, successively. The resin was then washed with deionized water in triplicates and dried in the oven for 24 h.

An amount of the pre-treated Amberlite IRA 743 resin (according to the experimental design in Table 2) was added to 100ml of boric acid, of known concentration and pH (which was adjusted with drops of 0.01M HCL or 0.01M NaOH) in a volumetric flask according to the experimental design obtained. The flasks were then put in a rotary shaker at 150rpm for 1 h after which the supernatant liquid samples were extracted from the volumetric flasks to be analyzed in order to determine the removal efficiency.

The 848/877 Titrino Plus auto-titrator (by Metrohm) was used to perform titrations on the extracted supernatant liquid samples. Since boric acid is a weak acid (pKa=9.24), the samples were first reacted with 50ml of mannitol solution to increase the acidic strength. The addition of poly-alcohols such as mannitol leads to the formation of complexes with a higher acidic strength that behave like a monovalent acid which can be easily titrated with 0.1M NaOH to determine the final boron content, the removal efficiency was calculated as follows:

$$\text{Removal Efficiency (\%)} = [(C_o - C_e)/C_o] \times 100 \qquad (1)$$

Where C_o is the initial concentration and C_e is the solution concentration at the end of the adsorption process. Table 2 presents the dependent output response i.e. removal efficiency (Y_1) which was obtained from the independent input variables in the CCD obtained.

Table 2 Experimental design matrix and responses for the adsorption of boron using Amberlite IRA 743

Run	A (g/L)	B	C (mg/L)	Actual Y_1	Predicted Y_1
1	60	8	80	93.1	95.96186
2	30	6	80	57.1	54.63585
3	45	7	20	97.2	97.840055
4	15	7	60	53.8	53.545185
5	60	6	40	98.4	95.02774
6	30	8	80	68.1	72.01097
7	30	8	40	85.6	87.55217
8	45	7	60	91.8	90.336855
9	75	7	60	99.8	99.546765
10	60	6	80	86.8	85.38654
11	45	7	60	91.3	90.336855
12	45	7	60	89.6	90.336855
13	30	6	40	75.3	72.97705
14	45	7	60	89.2	90.336855
15	45	7	60	90.1	90.336855
16	45	7	60	90.5	90.336855
17	45	7	100	73.8	72.657655
18	45	9	60	99.2	93.621155
19	45	5	60	63.4	68.470715

3.0 RESULTS AND DISCUSSION

3.1 Regression Model Analysis

The quadratic model was suggested by the software for removal efficiency of boron (Y_1) using Amberlite IRA743 due to higher-order polynomial as reported in Table 3 and is presented as follows in terms of coded factors:

$$Y_1 = 90.33 + 11.68A + 6.29B - 6.30C - 1.70AB + 2.18AC + 0.70BC - 3.45A^2\ 2.32B^2 - 1.27C^2 \qquad (2)$$

The analysis of variance corresponding to equation (2) is reported in Table 4. The model F-Value of 33.96 implies that the model is significant. P vales less than 0.05 indicate the model terms are significant.

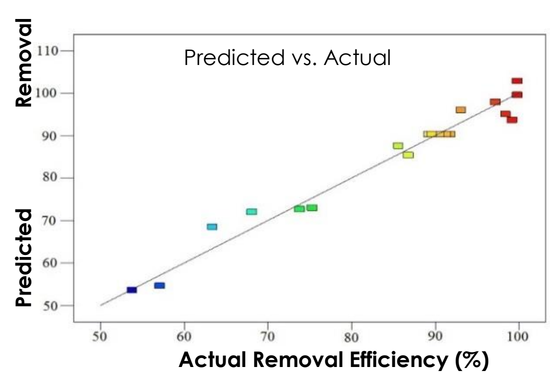


Figure 1 Actual and predicted boron removal efficiency plot using Amberlite IRA 743

In this case A, B, C, A2 and B2 are significant model terms. Values greater than 0.1 indicate the model terms are not significant.

Based on equation (2), the actual and predicted plots for removal efficiency I of boron using Amberlite IRA743 is shown in Figure 1. The values that were obtained for R^2 and R^2_{adj} were 0.9683 and 0.9398 respectively.

Table 3 Model summary statistics for removal efficiency of boron using Amberlite IRA 743

Source	Std. Dev.	R^2	R^2_{adj}	Predicted R^2	Press	Comments
Linear	5.90	0.8588	0.8323	0.7715	900.37	
2F1	6.15	0.8752	0.8177	0.6959	1198.02	
Quadratic	3.53	0.9683	0.9398	0.7440	1008.78	Suggested
Cubic	1.00	0.9985	0.9952	0.9460	212.78	Aliased

Table 4 Analysis of variance (ANOVA) for response surface quadratic model for removal efficiency of boron

Source	Sum of Squares	Df	Mean Square	F Value	P Value	Comments
Model	3815.19	9	423.91	33.96	< 0.0001	
A	2116.00	1	2116.00	169.53	< 0.0001	
B	632.52	1	632.52	50.68	< 0.0001	
C	635.04	1	635.04	50.88	< 0.0001	
AB	23.12	1	23.12	1.85	0.2034	
AC	37.85	1	37.85	3.03	0.1123	
BC	3.92	1	3.92	0.31	0.5875	
A^2	298.87	1	298.87	23.94	0.0006	
B^2	135.65	1	135.65	10.87	0.0081	
C^2	40.73	1	40.73	3.26	0.1010	
Residual						
Lack of fit	119.87	5	23.97	24.22	0.0016	Significant
Pure Error	4.95	5	0.99			
Cor total	3940.01	19				

The interaction effect of adsorbent dosage and pH on removal efficiency of boron using Amberlite IRA743 is shown in Figure 2. It can be observed that the maximum removal efficiency was obtained at a pH of 8. This is because borate ions, which are readily adsorbed onto the active sites of the resins, predominate at pH 7.5 and above whereas the boric acid species which is not in its active form predominates at a lower pH.[8] From Figure 2 an optimized initial concentration of 60mg/L for a removal efficiency of 100% was obtained at a pH and adsorbent dosage of 8 and 57.8g/L.

The interaction effect of initial concentration and adsorbent dosage on removal efficiency of boron using Amberlite IRA743 is shown in Figure 3. It can be observed that the removal efficiency increased with increasing dosage, this can be attributed to the increase in adsorbent surface area. From Figure 3 an optimized pH of 7 for a removal efficiency of 100% was obtained at initial concentration and adsorbent dosage of 40mg/L and 51g/L.

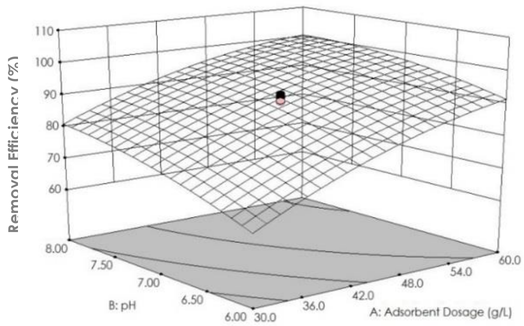


Figure 2 3D surface plot of interaction effect of pH and adsorbent dosage on removal efficiency

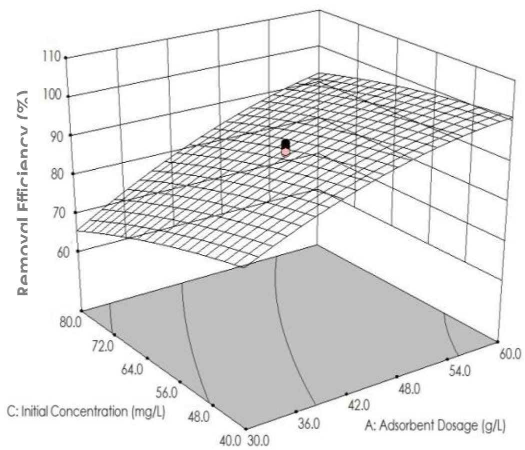


Figure 3 3D surface plot of interaction effect of initial concentration and adsorbent dosage on removal efficiency

The interaction effect of initial concentration and pH on removal efficiency of boron using Amberlite IRA743 is shown in Figure 4. The removal efficiency of boron was found to decrease with increasing initial concentrations this is as the ratio of boron to resin increases the exchangeable sites within the resin become saturated, resulting in a decrease in removal efficiency. From Figure 4 an optimized adsorbent dosage of 45g/L for a removal efficiency of 90.3578% was obtained at pH and initial concentration of 8 and 72mg/L.

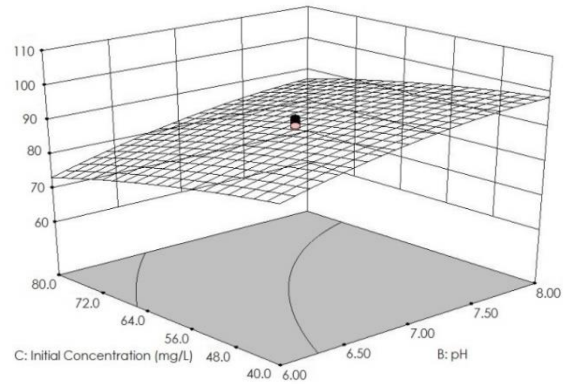


Figure 4 3D surface plot of interaction effect of interaction effect of initial concentration and pH on removal efficiency

From the experiments conducted the maximum removal efficiency achieved was 99.8% at adsorbent dosage, pH and initial concentration of 75g/L, pH 7 and 60mg/L as can be found in table 2. However, using the mathematical model obtained via RSM, the optimum treatment parameters for a removal efficiency of 100% at lower pH and adsorbent dosage was found to be at adsorbent dosage, pH and initial concentration of 51g/L, pH 7 and 40mg/L.

4.0 CONCLUSION

The treatment parameters for the adsorption of for the adsorption of boron by Amberlite IRA 743 resin were optimized using RSM. The CCD was employed to obtain the effect of adsorbent dosage, pH and initial boron concentration on the removal efficiency. A number of 19 runs were carried out in batch basis according to the experimental design obtained. The quadratic model was suggested as the best fit by the software for removal efficiency wherein all three treatment parameters were found to be significant. The optimum condition suggested by the model for 100% removal efficiency was at adsorbent dosage, pH and initial concentration of 51g/L, pH 7 and 40mg/L. This study suggests that the use of RSM is highly effective in optimization of selective removal of boron from solutions.

Acknowledgement

The authors wish to thank Malaysian Ministry of Higher Education (MOHE) for financial support under LRGS project (vote # 4L817). Madana Leela Nallappan is grateful for the financial support from the same project.

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