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Removal of Reactive Red 4 Dye Using Chitosan- Epichlorohydrin/ TiO_2 nanocomposite: Application of Response Surface Methodology

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ABSTRACT

Chitosan-epichlorohydrin/TiO_2 composite was synthesized to be employed as an adsorbent for the removal of reactive red 4 (RR4) dye from aqueous solution. Response surface methodology (RSM) with 3-level Box-Behnken design (BBD) was utilized for the optimization of the removal of RR4. The process key variables which include adsorbent dose (A: 0.5 – 1.5 g), pH (B: 4 – 10) and time (30 – 80 min) were selected for the optimization process. The experimental data for RR4 removal were statistically analysed using analysis of variance (ANOVA). The significant interaction between key parameters on RR4 removal efficiency was observed by interaction between AB and AC. The highest RR4 removal (95.08%) was obtained under the following conditions; adsorbent dose (1.0 g), pH 4 and time of 80 min.

Keywords: *Chitosan; Epichlorohydrin; TiO_2; Box-Behnken Design; Reactive red 4*

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INTRODUCTION

Synthetic dyes are composed of organic chemicals and mostly are aromatic compounds which can be grouped into non-ionic, cationic and anionic dyes [1]. Various industries such as textile, paper, plastic and pharmaceutical has have been widely used these dyes due to their better dyeing process conditions and more vivid colours [2]. However, a serious environmental problem has been generated by the immense usage of the synthetic dyes [3]. A range of conventional treatment methods available for the removal of dyes from aqueous solution such as biotreatment [4], adsorption [5], photocatalytic degradation [6] and flocculation-coagulation [7]. Adsorption has been proven to be the most efficient and versatile technique. Among the materials that have been used, chitosan is cheaper and has potential to be used as an adsorbent.

Chitosan (Cs) is a cationic biopolymer derived from alkaline N-deacytelation of chitin which is the second most abundant biopolymer naturally [8]. Cs is considered as a promising adsorbents for the removal of targeted contaminants owing to its unique characteristics such as low toxicity, biocompatibility, biodegradability and biofunctionality [9]. Cs possess outstanding natural adsorbent attributed to the presence of amine ($-NH_2$) and hydroxyl group (-OH) acting as an active adsorption site for the adsorption of dyes and heavy metals [10]. However, unmodified chitosan has limitation to be used as an adsorbent in acidic solutions and effluents since it tends to be dissolved in acidic effluents [11]. Hence, modification of Cs is important to reinforce its chemical stability.

Crosslinking reaction is one of chemical modification pathway increasing the chemical stability of Cs in acidic environment [12]. Utilizing different types of crosslinking agents, for instance, glutaraldehyde [13], ethylene glycol diglycidyl ether [12], tripolyphosphate [14] and epichlorohydrin [9] helps to enhance the pore size, chemical and mechanical stability, and adsorption properties [15]. Epichlorohydrin (Ech) is a crosslinking mono-functional agent used to form covalent bonds with the carbon atoms of the hydroxyl groups of chitosan, resulting in the rupturing of the epoxide ring and the removal of a chlorine atom [16]. Many chitosan derivatives have been synthesized by incorporating new functional groups onto the backbone of chitosan in order to boost its adsorption capacity [9].

A lot of research has been done by incorporating inorganic materials, especially metal oxides such as TiO_2 as a composite to be used as adsorbent in various water treatment procedures [17-21]. TiO_2 is an inert chemical material with low toxicity and comprises a large amount of hydroxyl groups [2]. TiO_2 possess various good characteristics such as high surface area, low-cost, widely available, low toxicity and high chemical stability [14]. Hence, TiO_2 play a vital role in improving physiochemical properties of Cs such as surface area, porosity and adsorption capacity [12]. In this current research paper, a composite chitosan-epichlorohydrin/ titanium (IV) dioxide (Cs-Ech/TiO_2) adsorbent was synthesized by introducing TiO_2 nanoparticles into the polymeric chain of cross-linked chitosan-epichlorohydrin for the removal of RR4 dye as a model pollutant from aqueous solution. Box-Benhken design (BBD) was used as a tool for optimizing the adsorption key parameters such as adsorbent dose, pH and time.

EXPERIMENTAL

Materials

Chitosan flakes (degree of acetylation ≥ 75) was supplied by Sigma-Aldrich. Reactive Red 4 (RR4) was purchased from Aldrich Chemical (molecular weight 995.23 g mol^{-1}; chemical formula $C_{32}H_{23}ClN_8Na_4O_{14}S_4$; λ_{max} = 517nm). Epichlorohydrin (≥ 98% [w/v] aqueous solution) was purchased from Fluka. Titanium (IV) dioxide P-25 (TiO_2) was bought from R&M Chemicals. Acetic acid (CH_3COOH) and sodium hydroxide (NaOH) were obtained from HmbG Chemicals. Ultra-pure water (18 MΩ/cm) was used to prepare all reagents and solutions throughout the experiment.

Preparation of Cs-Ech/ TiO_2 nanocomposites

2.0 g of chitosan flakes and 0.2 g of TiO_2 powder were mixed and dissolved in 90 mL of 5% of acetic acid solution. The solution was left to stir for 24 h to allow complete dissolution of chitosan flakes. The viscous solution Cs/TiO_2 was beaded through a 10 mL syringe into 1000 mL of NaOH (0.5 M) under stirring. The Cs/TiO_2 beads were washed with distilled water several times to remove any remaining NaOH until it reaches pH ≈7. The crosslinking reaction was carried out by adding 85 mL of 1% Ech solution and stirred gently for 2 h at 40°C. After that, the cross-linked Cs-Ech/TiO_2 beads were washed again with distilled water and air dried for 24 h. The dried Cs-Ech/TiO_2 was ground to powder form and sieved to constant particle size of ≤ 250 µm.

Characterization of Cs-Ech/TiO_2

Fourier transform infrared (FTIR) spectra of Cs-Ech/TiO_2 before and after adsorption of RR4 dyes were obtained by Perkin Elmer, Spectrum RX I spectrophotometer from 4000 to 450 cm^{-1} using the KBr disk method at ambient temperature [22]. Morphological of the composite Cs-Ech/TiO_2 was performed by using Hitachi TM3030Plus Scanning Electron Microscope (SEM) with an acceleration voltage of 5 kV and magnification of 5000x. The point of zero charge (pH_{pzc}) was measured using following the method by Jawad, et al. [23].

Design of experiments

Optimization of three independent variables including adsorbent dose (A), pH (B) and time (C) for the adsorption of RR4 onto Cs-Ech/TiO_2 were completed by using Box-Behnken Design (BBD) in Response Surface Methodology (RSM). Design Expert 11.0 Software (Stat- ease, Minneapolis, USA) was employed for the designing and statistical analysis of the experimental data. Table 1 shows the codes and levels of the independent variables.

Table 1: Coded and actual variables and their levels

Codes	Variables	Level 1 (-1)	Level 2 (0)	Level 3 (+1)
A	Adsorbent dose (g)	0.5	1.0	1.5
B	pH	4	7	10
C	Time	30	55	80

The experimental data were fitted to a second-order polynomial equation of quadratic order as shown in Eq. (1)

$$Y=\beta_0+\sum\beta_i X_i+\sum\beta_{ii} X_i^2+\sum\sum\beta_{ij} X_i X_j \qquad (1)$$

where Y is the response for RR4 dye removal (%), while 0, i, ii and ij are the constant coefficient, the linear coefficient, the quadratic coefficient and the interaction coefficient, respectively. Xi and Xj are the coded values of the independent variables.

A total of 17 runs have been conducted to optimize the levels of the independent variables including; A: adsorbent dose (0.5 – 1.5 g), B: pH (4 – 10) and C: time (30 – 80 min). In the 250 mL of Erlenmeyer flasks containing 100 mL of RR4 dye solution, a certain amount of Cs-Ech/TiO_2 was added. The flasks were capped and shaken continuously (100 strokes/ min) in water bath shaker (WNB7-45, Memmert, Germany). The syringe filter (0.45µm) was then used to separate adsorbents from the RR4 dye solutions and the initial and final concentrations of RR4 dye were recorded using UV-Vis Spectrophotometer (HACH DR 2800) at λ_{max} of 517 nm. The RR4 dye removal (DR%) was calculated by using the following Eq. (2):

$$DR\%=\frac{(C_o-C_e)}{C_o}\times 100 \qquad (2)$$

where Co (mg/L) and Ce (mg/L) are the initial and equilibrium RR4 concentrations, respectively.

The actual BBD experimental design matrix is represented in Table 2.

Table 2: The 3-factors BBD matrix and experimental data for RR4 dye removal

Run	A:Adsorbent dose (g)	B:pH	C:Time (min)	RR4 Removal (%)
1	0.5	4	55	56.58
2	1.5	4	55	86.50
3	0.5	10	55	31.71
4	1.5	10	55	37.99
5	0.5	7	30	34.23
6	1.5	7	30	53.02
7	0.5	7	80	55.69
8	1.5	7	80	82.45
9	1.0	4	30	70.19

10	1.0	10	30	33.78
11	1.0	4	80	95.08
12	1.0	10	80	55.58
13	1.0	7	55	65.83
14	1.0	7	55	65.98
15	1.0	7	55	65.18
16	1.0	7	55	65.13
17	1.0	7	55	65.61

RESULTS AND DISCUSSION

Characterization of Cs-Ech/TiO_2

FTIR

The FTIR spectra of Cs-Ech/TiO_2 before and after adsorption of RR4 are provided in Figure 1. The peak located at 3452 cm^{-1} indicated the presence of O-H and N-H bonds. The peak at 1636 cm^{-1} was assigned to stretching vibration of N-H bond. The peak at 1318 cm^{-1} was a characteristic of C-N amide II stretching vibration [10]. The peak at 1050 cm^{-1} was attributed to the stretching vibration of C-O-C. The FTIR spectrum for Cs-Ech/TiO_2 loaded with RR4 showed a shifting in the wavenumber from 3452 cm^{-1} to 3462 cm^{-1}. This indicated a possible hydrogen bonding between –OH group of Cs-Ech/TiO_2 and RR4 molecules. Additionally, an obvious shift can be observed of the C-O-C stretching vibration which suggesting a possible involvement of the Cs-Ech/TiO_2 functional groups with RR4 molecules.

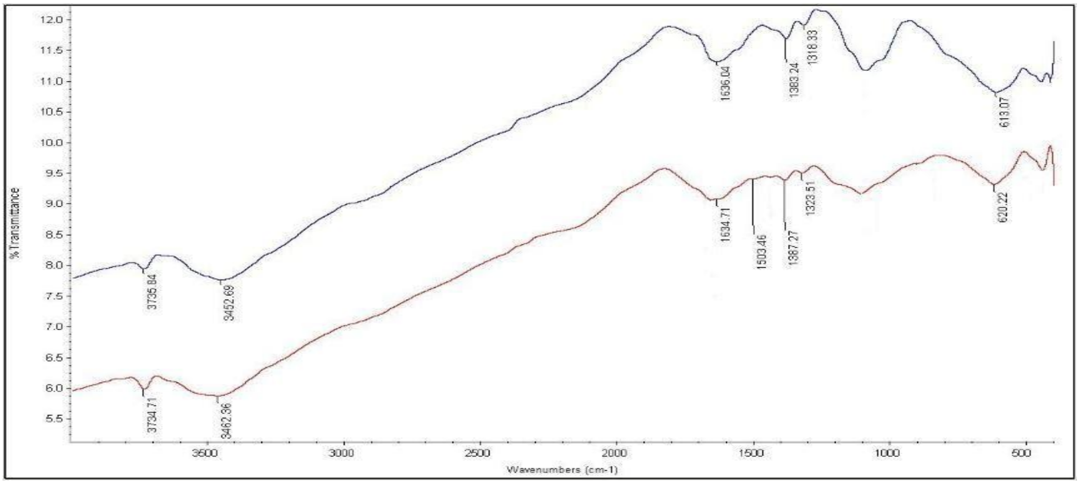

Figure 1: FTIR spectra of (a) Cs-Ech/TiO_2 before adsorption, and (b) Cs-Ech/TiO_2 after adsorption of RR4

SEM analysis

The surface morphology of Cs-Ech/TiO_2 was examined by SEM analysis and is shown in Figure 2. The surface of the Cs-Ech/TiO_2 appears to be irregular, rough and heterogeneous. In addition, rough surface shows a great potential for the adsorption of dyes into the pores of the adsorbent [1].

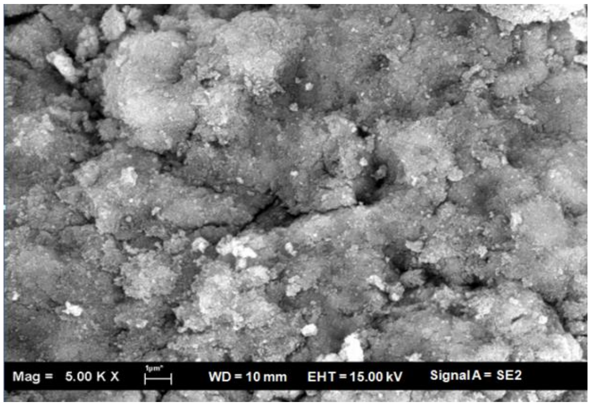

Figure 2: SEM image of Cs-Ech at magnification power 5000x

Response surface methodology

Box-Behnken design

A total of 17 runs were used in this study to assess the effects of three parameters which are adsorbent dose (A), pH (B) and time (min) on the removal of RR4 by Cs-Ech/TiO_2. The experimental result of the empirical relationship was obtained on the basis of Box-Behnken experimental model and the input variables. The final equation obtained with respect to the coded factors is given in Eq. (3):

$$\text{RR4 removal (\%)} = +65.55+10.22A-18.66B+12.20C-5.91AB+1.99AC -0.77BC-9.83A^2-2.52B^2+0.63C^2 \tag{3}$$

where A, B and C are the coded levels of adsorbent dose, pH and time, respectively. Based on Eq. (3), parameters including dose and time demonstrate a positive impact on the removal of RR4 (%). Meanwhile, pH had a negative effect. A positive sign in Eq. (3) suggesting a synergistic impact of the factors whereas an antagonistic effect of the factor is indicated by negative sign [24].

Effect of input parameters

The perturbation plots as shown in Figure 3 was used to investigate the individual impact of the studied variables including adsorbent dose (A), pH (B) and time (C) on the RR4 removal efficiency (%). The steep curvature in curve A indicates that RR4 removal was sensitive to this variable. The relatively sharp line of C shows the high sensitivity to change in time levels. The pH curve shows a slow curvature indicating that this factor has effect on the response.

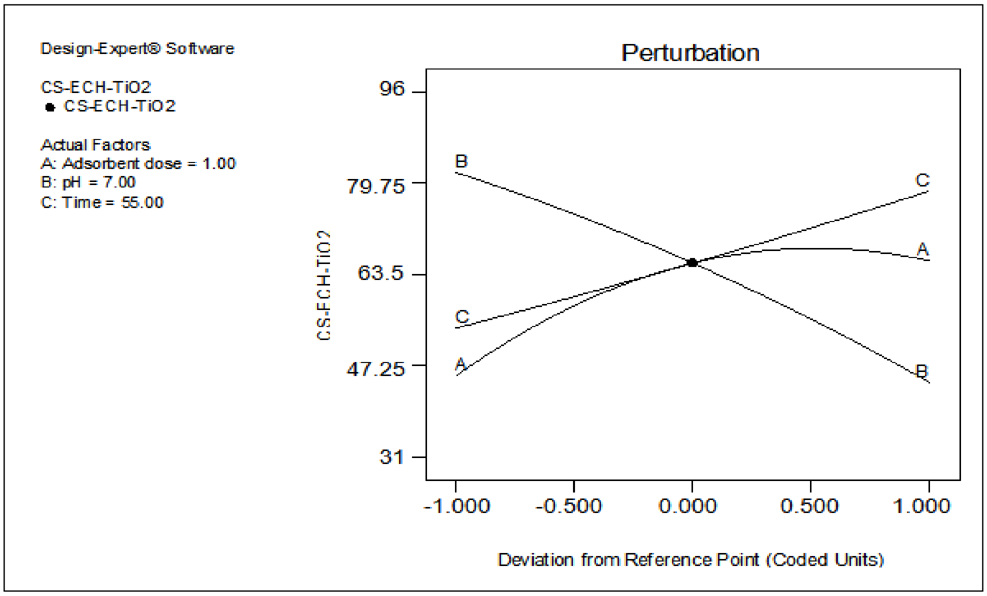

Figure 3: Perturbation plots for the RR4 removal efficiency. (A) Adsorbent dose, (B) pH and (C) time

Analysis of variance (ANOVA)

ANOVA test was utilized to determine the regression model as shown in Table 3. This approach describes the significance of three types of variables based on F-value, p-value and sum of the squares. According to results of the ANOVA F-value for RR4 removal efficiency was 290.22. The items are significant when p-value < 0.0001 and the probability of noise in the model was 0.01%. Low p-value and high F-value show that the terms are significant [25]. It can be observed from Table 3, the term coefficients like A, B, C, A^2, B^2, AB and AC are significant due to very small p-values ($p < 0.05$) and the other term coefficients with $p > 0.05$ are not significant.

Table 3: Analysis of variance (ANOVA) of the response surface quadratic model for RR4 removal efficiency

Source	Sum of Squares	DF	Mean Square	F-value	p-value	Remarks
Model	5415.41	9	601.71	290.22	< 0.0001	Significant
A-Adsorbent dose	835.38	1	835.38	402.93	< 0.0001	Significant
B-pH	2785.94	1	2785.94	1343.73	< 0.0001	Significant
C-Time	1190.23	1	1190.23	574.08	< 0.0001	Significant

A^2	406.90	1	406.90	196.26	< 0.0001	Significant
B^2	26.75	1	26.75	12.90	0.0088	Significant
C^2	1.68	1	1.68	0.81	0.3977	Insignificant
AB	139.71	1	139.71	67.39	< 0.0001	Significant
AC	15.88	1	15.88	7.66	0.0278	Significant
BC	2.39	1	2.39	1.15	0.3189	Insignificant
Residual	14.51	7	2.07			
Cor Total	5429.92	16				

Normality of the residuals was also validated by graphical approach as illustrated in Figure 4 (a). All the data points are relatively close to the linear line supporting that the chosen variables to be relevant and the basic assumptions of the study are met [14]. The relationship between predicted and actual response values for the removal of RR4 by Cs-Ech/TiO_2 is shown in Figure 4 (b). The model is statistically valid since the predicted and actual values are close to each other on the straight lines [26].

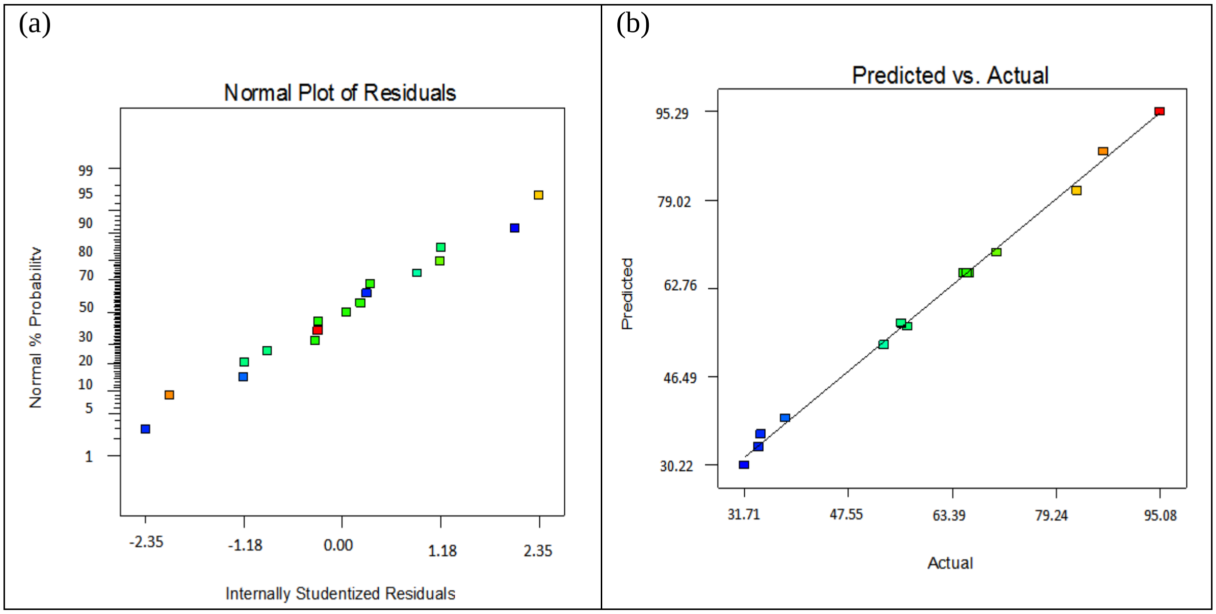

Figure 4: (a) Normal probability of plot of residuals for RR4 removal efficiency; (b) Plot of the relationship between the predicted and actual values of RR4 removal (%)

Three-dimensional (3D) response surface

The correlation effect between each of two parameters on the removal of RR4 dye was investigated. The interaction was found to be statistically significant (p-value < 0.0001) between adsorbent dosage (A) and pH (B) on the removal of RR4 dye. Figure 5 (a) and 5(b) presented the 3D surfaces and 2D contours for AB interaction, respectively.

It can be seen clearly from the Figure 5(a) that the efficiency of RR4 removal increases from 31.71% to 95.08 % by increasing the adsorbent dose up to 1.5 g and by decreasing the pH of the solution from 10 to 4 at a fix time (t= 55 min). Generally, increasing the adsorbent dose will increase the removal of RR4 (%). The increased in the adsorption as the adsorbent dose increases can be explained by larger surface area and availability of more adsorption sites at greater adsorbent dose [27].

The impact of pH between 4 and 10 is analysed on the removal of RR4 dyes by Cs-Ech/TiO_2 (Figure 5). As shown in Figure 5, the amount of dye adsorbed by Cs-Ech/TiO_2 is higher at lower pH and by increasing the pH from 4-10, the efficiency of RR4 removal decreased. The pH_{pzc} of the Cs-Ech was 6.2 (Figure 5), indicating that Cs-Ech/TiO_2 exhibit cationic characteristics. The amine groups of Cs become protonated at lower pH condition and interact with the anionic functional groups of the RR4 dye and thus more adsorption takes place at lower pH conditions [25]. At pH above pH_{pzc}, the removal efficiency decreases due to the deprotonation of the amine groups of Cs which led to the decreased in positive charge density of Cs and thus lessened the electrostatic interaction between Cs and dye molecules [28].

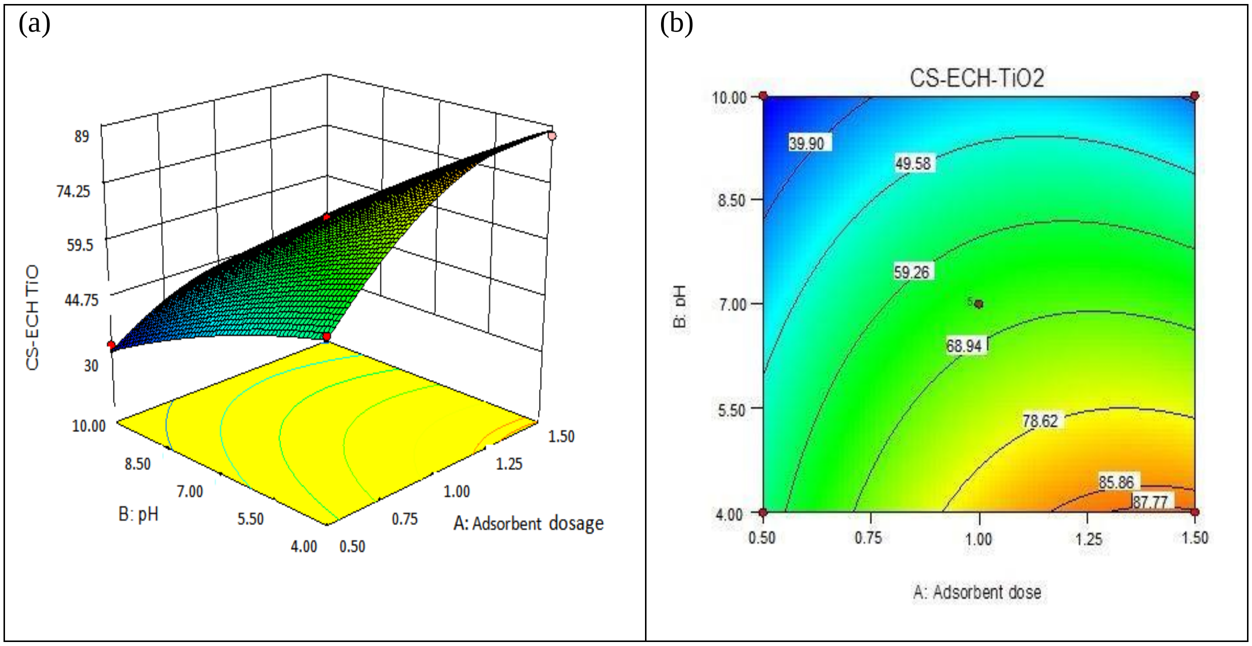

Figure 5: (a) 3D response surface plot; (b) contour plot for RR4 removal efficiency showing interaction between adsorbent dosage (A) and pH (B)

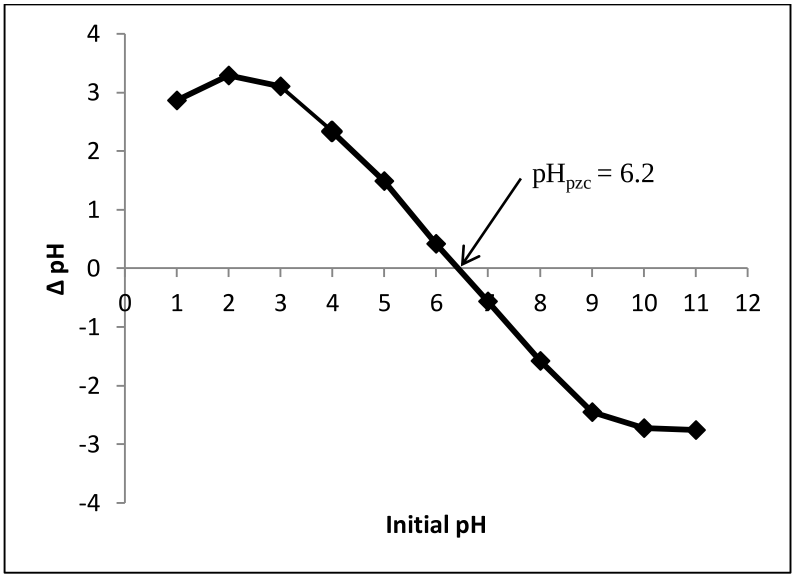

Figure 6: pH_{pzc} of Cs-Ech/TiO_2 suspension

The effect of interaction between adsorbent dose (A) and time (C) was significant on efficiency of RR4 removal (p-value = 0.0278) as recorded in Table 3. The 3D surface and 2D plot for AC interaction are displayed in Figure 7(a) and 7(b) respectively.

It was observed from Figure 7 that the removal efficiency of RR4 increased to a certain degree when the adsorbent dose increased and remained nearly constant which can be explained by the availability of the exchangeable adsorption sites for the adsorption [29]. The incremental of RR4 removal becomes almost insignificant at adsorbent dose > 1.25 g since the surface RR4 concentration and the solution RR4 concentration come to equilibrium with each other.

At any particular adsorbent dose, RR4 removal (%) increases with an increase in time (Figure 7). Moreover, amount of RR4 removal increases as the time increases from 30 min to 80 min. The RR4 dye molecules are able to penetrate deeper into the inner active adsorption sites of Cs-Ech/TiO_2 as the contact time increases [30].

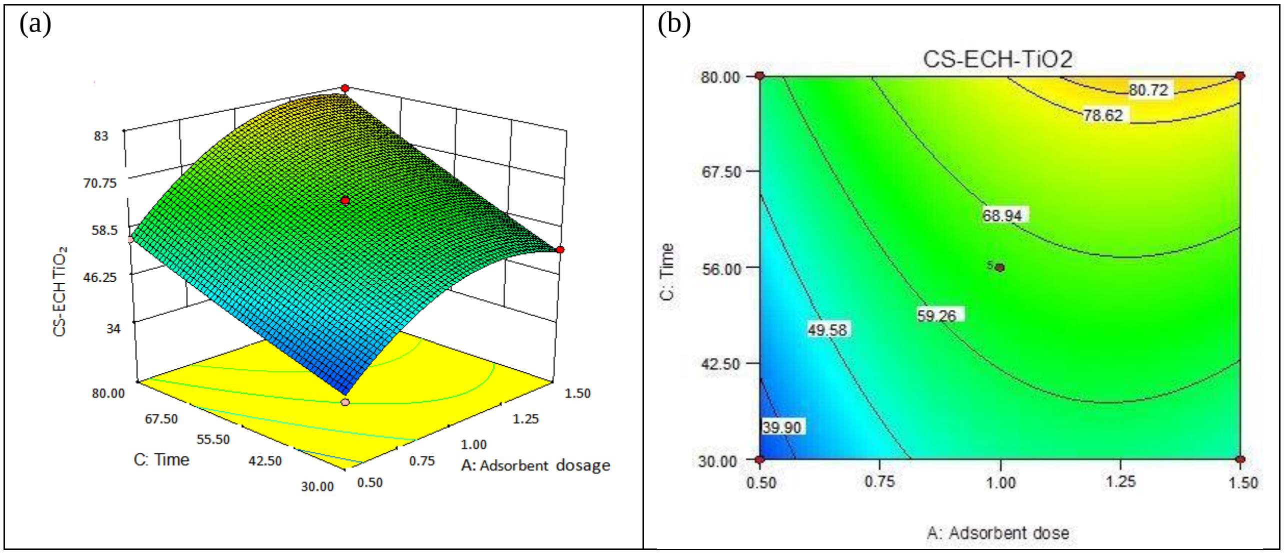

Figure 7: (a) 3D response surface plot; (b) contour plot for RR4 removal efficiency showing interaction between adsorbent dosage (A) and time (C)

CONCLUSIONS

The composite chitosan-epichlorohydrin/ TiO_2 (Cs-Ech/TiO_2) was synthesized and applied for removing RR4 dye from aqueous solution. Box-Behnken design was successfully used as statistical tool to optimize key parameters namely adsorbent dose (A: 0.5 – 1.5 g), pH (4-10) and time (30 – 80 min). The findings demonstrate that the highest RR4 dye removal of (95.08%) was obtained by simultaneous interactions between AB and AC. The optimum conditions for the removal of RR4 dye were found at adsorbent dose (1.0 g), pH of the solution ~4 and time (80 min).

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