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Removal of reactive black 5 from aqueous solution using chitosan beads: optimization by Plackett–Burman design and response surface analysis

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ABSTRACT

Contaminations due to dyes pose not only a severe public health concern, but also many serious environmental problems. The present project aims to prepare an inexpensive and efficient sorbent that could remove dyes that are commonly used in the industry. Chitosan has been seen as a promising sorbent due to its significant properties, such as biocompatibility, biodegradability and non-toxicity. Batch studies were performed under various experimental conditions and the parameters studied included pH, contact time, initial concentration and agitation rate. The kinetics of dye sorption fitted a pseudo-second-order rate expression. Equilibrium data could be fitted into both Langmuir and BET isotherms. Plackett–Burman design was applied to identify the most significant factors in the removal of Reactive Black 5 (RB5) by chitosan. The effect of operating parameters on RB5 uptake was studied and a mathematical model showing the influence of each variable was obtained. The interaction between the factors and their optimum levels for maximum percentage uptake of RB5 were determined using Response Surface Methodology. The optimum sorption conditions were determined as initial pH 7.00 and at contact time greater than 200 min.

Keywords: Sorption; Chitosan; Plackett-Burmann; Response surface analysis; Reactive dye

1. Introduction

Effluents from textile industries contain different types of dyes and most of them show low level of biodegradability because of high molecular weight and complex chemical structures. It has been reported that approximately 10,000 different types of dyes and pigments are used in industries and over 7×10^5 tons of these dyes are annually produced world-wide [1]. Due to inefficiencies of the industrial dyeing process, about 10–15% of the dyes are lost in the effluents of textile units, rendering them highly coloured. Hence, direct deposition of these effluents into sewage networks, resulted disturbance in ecology system. Besides, the high concentrations of inorganic salts, acid and bases in these effluents also lead to the increase in treatment costs [2].

The demand and usage of reactive dyes in textile industries has greatly increased due to the high

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reactivity of such compounds with fibers and their colour stability. However, contaminations due to reactive dyes pose a serious environmental problem as they are generally stable to light, oxidizing agent, and are resistant to aerobic digestion. Besides, the presence of these highly coloured wastes, even in trace quantities are sufficient to impart noticeable colour to the effluent. This reduces light penetration into water thereby decreasing the efficiency of photosynthesis in aquatic plants and resulting in impairment on their growth. Thus, the ecosystem of streams can be seriously affected. Consequently water contamination originated from the dyeing and finishing in textile industry has become a major concern.

Some of the conventional methods for dye removal include adsorption, chemical coagulation, coagulation-flocculation, chemical oxidation, reverse osmosis, photochemical degradation, membrane filtration, aerobic and anaerobic biological degradation [3,4]. Amongst all, adsorption still remains as an attractive option because of its relatively low initial treatment cost, ease of operation, flexibility and simplicity of design, insensitivity to toxic pollutants and the availability of wide range of adsorbents.

Although activated carbon appeared to be one of the most efficient adsorbents to remove dyes from effluents, the relatively high operating costs and problems with regeneration of the spent carbon hamper its large-scale application. Therefore, effort has been attempted to search for more economical alternative sorbent. From the literature review, it shown that biosorption capacity can be significantly influenced by the operating parameters such as pH, initial concentration, contact time and sorbent dosage. Conventional and classical methods of studying a process by maintaining other factors involved at an unspecified constant level does not describe the combined effect of all the factors involved [5]. Besides time consuming, this method also does not guarantee the determination of optimal conditions [6,7].

Therefore, in our continued effort to use low cost materials for the removal of dye from aqueous environment, the sorption ability of chitosan was evaluated. Besides, the interaction between the operational parameters was also studied and optimized using experimental design such as Plackett Burmann and Response Surface Methodology (RSM).

2. Materials and methods

2.1. Sorbent

Chitosan beads were prepared by dissolving 3.0 g of chitosan powder (degree of deacetylation 67.29%) in 100 mL of 3% (V/V) acetic acid solution. The mixture was stirred and being left overnight at room temperature to ensure a complete mixing. Spherical chitosan beads with the diameter size ranging from 2 to 5 mm were obtained by adding the chitosan solution dropwise into an alkaline coagulant bath consisting of 0.125 M NaOH under magnetic stirring. The formed chitosan beads were remained in NaOH bath for 1 h to neutralize the acetic acid within chitosan beads. The chitosan beads were removed by simple filtration and the wet chitosan beads were washed with distilled water until neutral before it was air-dried. The dried chitosan beads are sealed in a container until further use.

2.2. Sorbates

Reactive Black 5 (RB5) which was purchased from Sigma–Aldrich (M) Sdn. Bhd., was used without any further purification. It has a molecular formula of $C_{26}H_{21}N_5Na_4O_{19}S_6$ with molecular weight 991.82 g mol^{-1}. A 500 mg L^{-1} of RB5 stock solution was prepared by dissolving accurately weighed sample of dye in deionized water and dilution was carried out to obtain the desired concentration when necessary. The stock solution was kept in a dark condition at all times to prevent degradation from direct sunlight.

2.3. Batch experiments

All the batch experiments were carried out in duplicate. Control experiments without sorbent was carried out to ascertain that the sorption was by the sorbent and not the wall of the container. Sorption experiments were performed by agitating 0.5 g of sorbent in 20 mL of 20 mg/L dye solution in a centrifuge tube at 150 rpm on an orbital shaker for 6 h at room temperature (25 ± 2˚C) unless otherwise stated. The supernatant was analyzed for its dye concentration using a Double-beam UV/visible—1700 Pharmaspec SHIMADZU spectrometer. All measurements were made at the wavelength corresponding to maximum absorption for RB5 is 597 nm. The percent uptake (% uptake) is defined as $\frac{C_o - C_t}{C_o} \times 100$ where C_o is the initial dye concentration and C_t is the concentration of dye at time t.

To study the effect of pH, 0.5 g of chitosan beads were agitated at 150 rpm in 20 mL of 20 mg L^{-1} dye solution with different pH values for 6 h. The initial pH of dye solutions was adjusted to the range of 2–10 by adding dilute HCI or NaOH. No buffer was added to maintain constant pH. At the end of experimentation pH of dye solutions were measured.

The effect of initial dye concentration and contact time on the dye uptake was studied by using 20, 50 and 100 mg L^{-1} of dye solutions. For each concentration, 0.5 g of chitosan beads were added to 20 mL of dye solution and agitated at 150 rpm over periods of 5, 10, 15, 30, 60, 120, 180, 240, 300, and 360 min. The effect of agitation rate was studied by shaking 0.5 g of chitosan beads in 20 mL of 20 mg L^{-1} RB5 dye solution at the rate of 50, 150, and 200 rpm.

The sorption isotherms were obtained by agitating 0.5 g of chitosan beads at 150 rpm in 20 mL of RB5 solution with different dye concentrations, ranging from 50 to 80 mg L^{-1} for 6 h.

2.4. Selection of significant variables by Plackett–Burman design

For the selection of significant variables for dye adsorption, a total of four variables with replicates were tested and identified via the Plackett–Burman design experiment. In this study, the variables used were: contact time, pH, initial concentration, and agitation rate. All the experimental design and statistical analysis of the data were done by using Design-Expert Version 7.1.3.1.

2.5. Optimization by response surface methodology

The statistical analysis that involves the determination of the optimum levels of significant variables for dye adsorption was performed using Response Surface Methodology (RSM) with central composite design (CCD). The variables involved the contact time, pH, initial concentration, and agitation rate. Each of the variables was assessed at three coded levels, −1, 0, and +1 (Table 1). A total of 30 experiment runs were conducted (Table 2). All variables were taken at a central coded value, which was considered as zero. The minimum and maximum ranges of the variables were used, and the full experimental plan with regard to their values in coded form is provided. All the experimental design and statistical analysis of the data were done by using Design-Expert Version 7.1.3.1.

Table 1
Experimental range and levels of independent variables for RB5

Dye	Factors	Factor code	Range and levels (coded)		
			−1	0	+1
RB5	Contact time (min)	A	5	182.5	360
	Initial concentration (mg/L)	B	20	60	100
	pH	C	2	6	10
	Agitation rate (rpm)	D	100	150	200

3. Results and discussion

3.1. Surface morphology

The surface morphology of chitosan was studied using field emission scanning electron microscopy (FESEM) which is operated at emission current of 3.0 kV with working distance of 4.6 mm-JEOL FESEM JSM 6701F. Fig. 1 is the FESEM micrograph of the synthesized chitosan. As shown in the image, the chitosan has a non porous configuration due to the absence of pores and cavities.

3.2. Effect of pH

Fig. 2 shows the result for the effect of pH on the uptake of RB5 by chitosan beads. The lowest uptake, 38.56% was recorded at pH 2. The percentage uptake increased greatly to 79.39 at pH 3 and becomes almost constant thereafter. The highest uptake was observed at pH 7, which is 92.14%. The low uptake at pH 2 is closely related to the sensitivity of chitosan towards pH change. It has been reported that the addition of strong acid has significant effect on the surface properties and physical strength of chitosan beads [8]. Similar result was reported in removal of RB5 from aqueous solutions using magnetic chitosan resins [9]. The pH independent profile indicates that both adsorbent and dye are completely disassociated and this is attributed to the fact that the adsorbent is a strong basic anionic exchanger and the dye sulfonate is derived from a strong acid [10].

The pH at point of zero charge (pH_{pzc}) of chitosan was determined by the mass titration method [11] and found to be 8.0. At pH above 8, surface charge of chitosan beads is negative which hinders the adsorption due to the repulsion between the negatively charged RB5 dye molecule and adsorbent. But the result shows that, there is an appreciable amount of dye being adsorbed above this pH, which suggests the simultaneous occurrence of different kinds of interactions such as entrapment, physical adsorption, hydrophobic attraction and etc. [12,13]. Under caustic conditions, reactive dye adsorption was also affected by the covalent bonding of dye and hydroxyl groups of chitosan [14]. As the natural pH of RB5 dye was 6.07, which falls in the optimum range of dye removal, therefore, no pH adjustment was carried out for the further parameters studied.

Table 2
The CCD matrix for four independent variables and the observed response for RB5 in aqueous solution

Experimental run	Coded values of variables				Observed response (%)	Predicted response (%)
	A	B	C	D		
1	−1	1	−1	−1	37.53	21.82
2	0	0	0	0	97.18	89.65
3	−1	−1	−1	−1	17.97	11.92
4	0	0	−1	0	30.98	63.53
5	0	0	0	0	97.18	89.65
6	0	0	0	0	97.18	89.65
7	0	0	0	0	97.18	89.65
8	−1	0	0	0	13.65	35.19
9	−1	1	1	−1	3.96	4.19
10	1	−1	1	1	81.01	86.89
11	1	1	1	−1	69.15	69.07
12	1	1	1	1	71.52	83.62
13	−1	1	1	1	11.72	4.19
14	1	−1	1	−1	85.86	83.7
15	0	0	0	1	75.59	96.22
16	0	−1	0	0	89.16	80.84
17	0	0	0	0	97.18	89.65
18	1	0	0	0	89.17	82.7
19	1	−1	−1	−1	29.81	27.52
20	−1	−1	1	−1	8.08	29.29
21	−1	−1	1	1	30.1	21.84
22	0	0	0	0	97.18	89.65
23	1	1	−1	1	97.97	66.93
24	0	0	0	−1	97.94	92.38
25	0	0	1	0	98.03	80.55
26	−1	−1	−1	1	14.8	5.06
27	0	1	0	0	60.76	84.15
28	1	−1	−1	1	21.56	31.3
29	−1	1	−1	1	18.1	26.32
30	1	1	−1	−1	37.47	51.79

3.3. Effect of initial dye concentration and contact time

Fig. 3 shows the result of the effect of initial dye concentration and contact time for the uptake of RB5 dye solution. The uptake for three different initial dye concentrations (20, 50 and 100 mg L^{-1}) shows the similar adsorption trend whereby the uptake increase with increasing contact time before it attains equilibrium. The percentage of uptake decreased with increasing dye solution concentration while the amount of dye sorbed increased. Similar observation was reported in the adsorption behavior of reactive red 189 by cross-linked chitosan beads whereby an increase in initial dye concentration leads to an increase in the adsorption capacity of dye on chitosan [15]. For all the concentrations under studied, the fast uptake at the beginning may be attributed to the rapid attachment of the dye molecules to the surface of the adsorbent. The high availability vacant binding sites of adsorbent explain the fast uptake at the beginning. The following slower adsorption pattern is closely related to intraparticle diffusion. With increasing contact time, the adsorbates tend to diffuse into the interior sites of chitosan. Finally, equilibrium is attained and this indicating that the binding sites are saturated with the adsorbates particles. From the same figure, it also shows that the extent and rate of dye uptake are initial dye concentration dependent.

This experimental result is similar with most of the reported work whereby the first stage in the adsorption process involves the external mass transfer or instantaneous adsorption step. The second stage is the gradual adsorption step where the intra-particle

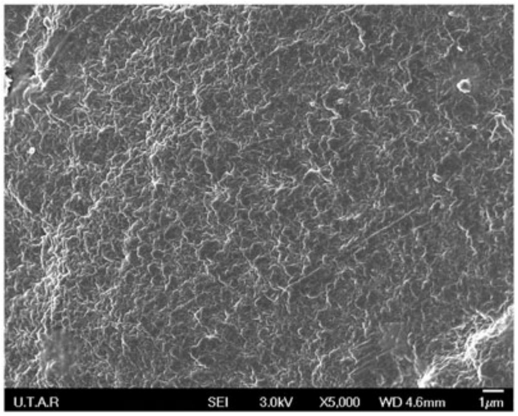

Fig. 1. SEM micrograph of chitosan with magnification of 5000×.

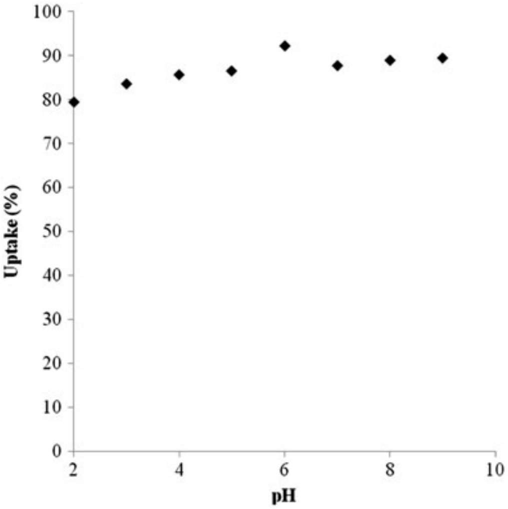

Fig. 2. Effect of pH on percentage uptake of RB5 by chitosan beads. (0.50 g chitosan beads; 20 mL of 20 mg L^{-1} of RB5; natural pH of dye solution; 150 rpm).

diffusion can be rate controlling step. The third stage is the final equilibrium step where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in the solution [16,17].

3.4. Adsorption kinetic study

Adsorption equilibrium and kinetics are important for the proper design of adsorption processes. The experimental data obtained from the adsorption of chitosan beads was analyzed using pseudo-first order equation of Lagergren (1898) [18] and pseudo-second-order adsorption kinetics model [19]. The best-fit model was selected based on the linear regression correlation coefficient, R^2 values.

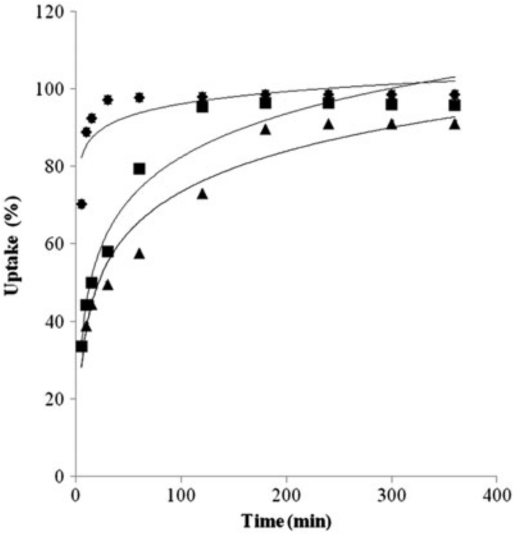

Fig. 3. Effect of initial dye concentration and contact time on percentage uptake of RB5 by chitosan beads. ◆, ■, ▲—20, 50, and 100 mg L^{-1} of RB5 (0.50 g chitosan beads; 20 mL; natural pH of dye solution; 150 rpm).

3.4.1. Pseudo-first-order kinetic model

The pseudo-first-order rate expression of Lagergren is generally described using the following linear equation:

$$\mathrm{Log}\,(q_e - q_t) = log\, q_e - k_1 t/2.303 \quad \text{(pseudo-first-order equation of Lagergren, 1898)} \quad (1)$$

where q_e = the amount of dyes sorbed at equilibrium (mg/g), q_t = the amount of dyes sorbed at time t (mg/g), k_1 = the rate constant of pseudo-first order sorption (1/min).

Fig. 4 shows the pseudo first-order model presented low linear correlation coefficients values (R^2) for all the three studied concentrations. Besides, the equilibrium sorption capacities determined from the first order kinetic model show a great difference than those determined experimentally.

3.4.2. Pseudo-second-order kinetic model

Since the experimental results can not be adequately explained by pseudo-first-order kinetic model, the sorption data was further analyzed using pseudo-second-order kinetic model. The related equation was as follows:

$$t/q_t = 1/h + t/q_e \,\text{(pseudo-second-order)} \quad (2)$$

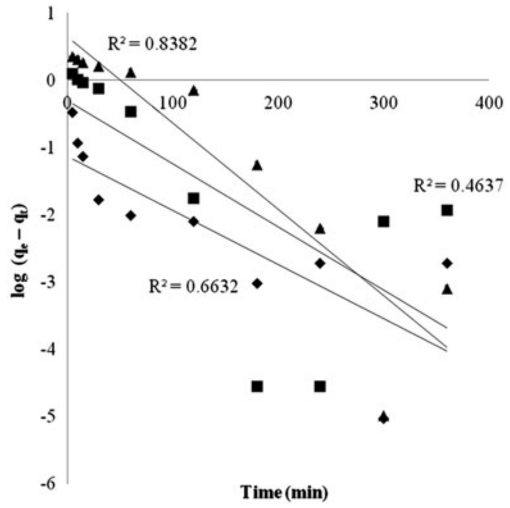

Fig. 4. Pseudo-first-order plot for the sorption of RB5 by chitosan beads. ◆, ■, ▲—20, 50, and 100 mg L^{-1} of RB5 (0.50 g chitosan beads; 20 mL; natural pH of dye solution; 150 rpm).

h ($k_2 q_e^2$) = the initial sorption rate (mg/g min) and k_2 = the rate constant of pseudo-second-order kinetics (g/mg min), other terms are as previously defined.

Fig. 5 shows the pseudo-second-order model presented high linear correlation coefficients for 20, 50, 100 mg L^{-1} of RB5 dye solution on chitosan beads with R^2 values of 1, 0.9987 and 0.9933 respectively. The correlation coefficient values obtained are close to unity and therefore, this indicating the validity of the pseudo-second-order model for the adsorption of RB5 on the chitosan beads. Based on the results in Table 3, the experimental q_e values also agreed well with the calculated q_e values obtained from pseudo-second-order kinetics model. It thus appears that the system under study is more appropriately described by the pseudo-second-order model which was based on the assumption that the rate limiting step may be chemical sorption or chemisorption involving valency forces through sharing or exchange of electron between sorbent and sorbate [20].

In the study involving the adsorption kinetics of the Cu(II) and Ni(II) ions by chitosan modified with Reactive Blue 2, the experimental results fitted well in pseudo-second-order kinetic model [21]. This suggested that the external mass transfer limitations in the system can be neglected and the chemical sorption is the rate-limiting step. The applicability of pseudo-second-order kinetics model has also been reported in the adsorption process involving Methylene Blue by fruit peels [22], Methylene Blue by wheat shells [23], Methylene Blue and Methyl Violet by wood sawdust [24] and basic dyes by sugarcane bagasse [25].

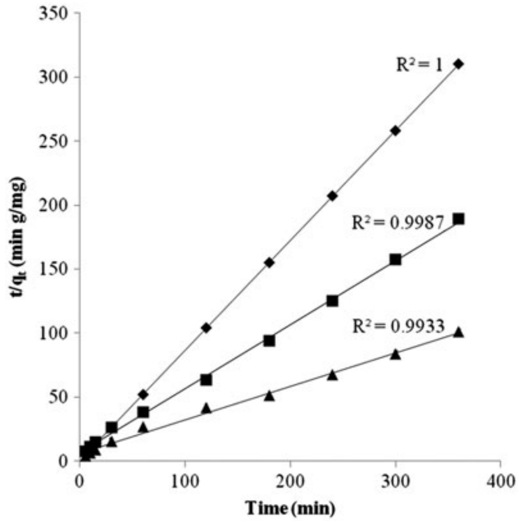

Fig. 5. Pseudo-second-order plot for the sorption of RB5 by chitosan beads. ◆, ■, ▲—20, 50, and 100 mg L^{-1} of RB5 (0.50 g chitosan beads; 20 mL; natural pH of dye solution; 150 rpm).

The generalized predictive models for RB5 adsorbed at any contact time and initial concentration within the given range with relationship of q_t, C_0 and t can be expressed using the following equation:

$$q_t = \frac{C_o t}{A_h C_o + B_h + (A_q C_o + B_q)t} \tag{3}$$

where A_q, B_q, A_k, B_k, A_h and B_h are constants obtained through regression from linear plots based on pseudo-second-order kinetic model [20]. By substituting the calculated constant values, the theoretical model for RB5 with chitosan beads can be represented as:

$$q_t = \frac{C_o t}{9.386 C_o - 226.6 + (0.0304 C_o + 24.444)t} \tag{4}$$

Eq. (4) can be employed to represent the generalized predictive models for RB5 sorbed at any contact time and initial dye concentration within a given range. The theoretical model derived for RB5 by chitosan beads was applied and the result was compared to the experimental values in Fig. 6. It is clear that the theoretically generated curves agreed well with the experimental data for 50 mg/L of RB5, but deviation was observed at higher concentration. The deviation could imply the formation of multilayers on chitosan beads as the concentration of RB5 increased. Similar phenomenon has been observed in the uptake of Reactive Orange 16 by etyhlenediamine modified rice hull [17].

Table 3
Kinetic model parameters, sorption capacities and correlation coefficients based on pseudo-first and second order kinetics

Initial RB5 concentration (mg L^{-1})	Pseudo-first order				Pseudo-second order				
	$q_{e,\ cal}$ (mg g^{-1})	$q_{e,\ exp}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,\ cal}$ (mg g^{-1})	$q_{e,\ exp}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	h (mg mg^{-1} min^{-1})	R^2
20	0.0745	1.1611	0.0186	0.6632	1.1643	1.1611	0.8061	1.0928	1
50	0.4949	1.9150	0.0216	0.4637	1.9992	1.9150	0.0375	0.1499	0.9987
100	4.4637	3.5710	0.0295	0.8382	3.8124	3.5710	0.0115	0.1667	0.9933

3.5. Effect of agitation

Fig. 7 shows the experimental results obtained from a series of contact time study for the adsorption of RB5 onto chitosan beads in which the degree of agitation was varied from 100 to 200 rpm. It was noted that the uptake of RB5 increased with increasing agitation rate from 100 to 150 rpm; thereafter the effect was minimal. The effect of increasing agitation is to decrease the film resistance to mass transfer surrounding the sorbent particles thus increasing sorption of dye molecules. The negligible effect of agitation rate on dye uptake beyond 150 rpm could implies that external mass transfer is not the sole rate-limiting factor in a well-agitated system.

A similar study was conducted for the removal of basic and reactive dyes using quartenized sugar cane bagasse [26]. The percentage removal of RO16 was found to be increased with increasing agitation rate and the authors attributed this observation to the decreasing film resistance to the mass transfer surrounding the sorbent particles, which would be beneficial to the dye sorption onto the sorbent.

3.6. Sorption isotherm

The equilibrium adsorption isotherm provides the information of the adsorption capacity of an adsorbent, which is important in the development of a treatment system. In order to have some insight into both the sorption mechanisms and the surface properties and affinities of the sorbent, the equilibrium sorption data were analysed using three different isotherm models, namely Langmuir, Freundlich and the Brunauer-Emmett-Teller (BET). From the sorption isotherms, the adsorption capacity, energy of adsorption, number of layers and the rate constants were evaluated.

3.6.1. Langmuir isotherm

In this study, the Langmuir isotherm essentially provides a framework for describing the extent and strength of adsorption on the surface of chitosan. The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \tag{5}$$

where C_e = equilibrium liquid phase dye concentration (mg L^{-1}), q_e = amount of dye adsorbed at equilibrium (mg g^{-1}), Q_0 = maximum adsorption capacity (mg g^{-1}), K_L = adsorption equilibrium constant (L mg^{-1}).

3.6.2. Freundlich isotherm

The linear form of Freundlich isotherm model was given by:

$$\log q_e = \log K_F + 1/n \log C_e \tag{6}$$

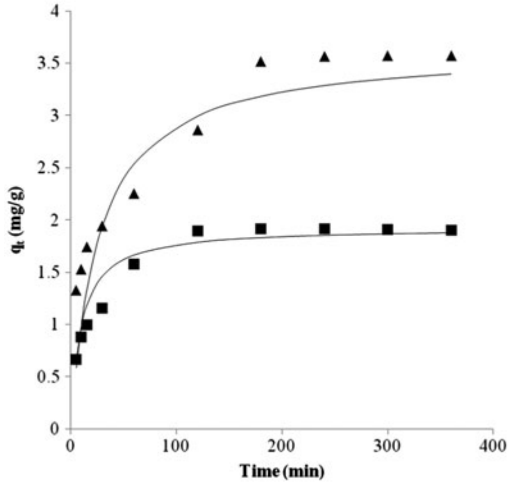

Fig. 6. Comparison between experimental data and theoretical data for RB5 sorption by using chitosan beads. ■, ▲—50 and 100 mg L^{-1} of RB5. Symbol—experimental; Line—theoretical. (0.50 g chitosan beads; 20 mL; natural pH of dye solution; 150 rpm).

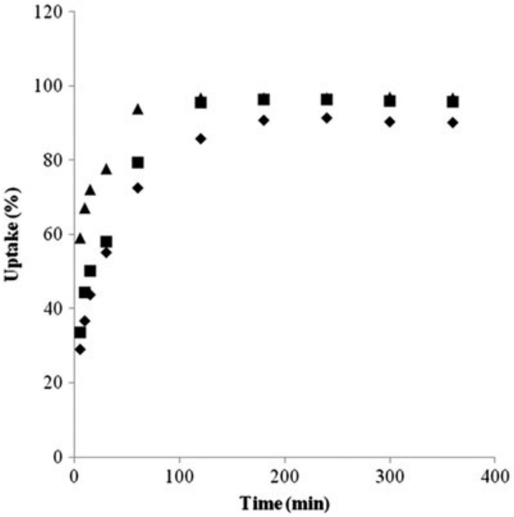

Fig. 7. Effect of agitation rate on percentage uptake of RB5 by chitosan beads. ◆, ■, ▲—100, 150 and 200 rpm (0.50 g chitosan beads; 20 mL of 50 mg L^{-1} of dye solutions; natural pH of dye solution).

where n = Freundlich constant for intensity and K_F = Freundlich constant for sorption capacity. The Freundlich isotherm is an exponential equation and therefore, assumes that as the adsorbate concentration increases so does the concentration of adsorbate on the adsorbent surface. Theoretically, using this expression, an infinite amount of adsorption can occur. Equilibrium sorption data of RB5 on chitosan beads is fitted into both Langmuir and Freundlich equations. The linear plots of C_e/q_e vs. C_e and log q_e vs. log are shown in Figs. 8 and 9, respectively. The coefficients for the linearised forms of the isotherm models for the sorption of RB5 on chitosan beads are listed in Table 4.

Based on the R^2 values, it is apparent that both Langmuir and Freundlich models provide reasonable fittings for the sorption data of RB5 on chitosan beads. Although these two models are based on different assumptions, fitting the model to the sorption process does not necessarily imply any physical interpretation attached to them since the sorbent's surface is non-homogeneous and there could be more than one type of sorption sites on the sorbent's surface [27]. Notwithstanding this Langmuir model allows the calculation of limiting sorption capacities that could be useful for the comparison of the sorption efficiency of materials studied.

Table 4
Comparative between Langmuir, Freundlich and BET isotherm models

Langmuir isotherm		Freundlich isotherm		BET isotherm	
Q_o (mg g^{-1})	2.9112	n	4.8333	x_m (mg g^{-1})	2.9075
K_L (L mg^{-1})	1.0133	K_F	1.7033	A	8598.5
R^2	0.9918	R^2	0.9812	R^2	0.9919

3.6.3. BET model

The liner form of the BET isotherm is given as:

$$\frac{C_e}{(C_{eq} - C_e)N_e} = \frac{1}{Ax_m} + \frac{A-1}{Ax_m}\left(\frac{C_e}{C_{eq}}\right) \quad (7)$$

where C_{eq} = saturation concentration of solute (mg/l), $A = a$ constant describing the energy of interaction between the solute and the sorbent surface, x_m = amount of solute in forming a complete monolayer (mg/g), other terms are as previously defined. This model is based on the assumption that the sorbent surface is composed of fixed individual sites and molecules can be sorbed more than one layer thick on the surface of the sorbent (Fig. 10). Using this model, the amounts of solute forming a complete monolayer (Table 4) agreed very well with those obtained from Langmuir isotherm. However conformation to BET model further suggests that sorption of the dye molecules was extended beyond monolayer coverage.

According to Gurusamy and Menjeri [26], the feasibility of the process is expressed in terms of a dimensionless constant, or separation factor or equilibrium parameter (R_L) defined as in Eq. (8).

$$R_L = \frac{1}{1 + K_L C_o} \quad (8)$$

where K_L = adsorption equilibrium constant (L mg^{-1}) and C_0 = initial dye concentration (mg L^{-1})

Table 5 illustrates that the values of R_L denote the types of isotherm of the adsorption process [28,29]. The R_L value calculated from lowest concentration (20 mg L^{-1}) to highest concentration (100 mg L^{-1}) was

Table 5
Types of isotherm with its R_L value

R_L value	Types of isotherm
$R_L > 1$	Unfavorable
$R_{L=}1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 6
Values of R_L for the RB5 dye concentration range

C_o	R_L
20	0.0470
30	0.0318
40	0.0241
50	0.0194
60	0.0162
70	0.0139
80	0.0122
90	0.0108
100	0.0097

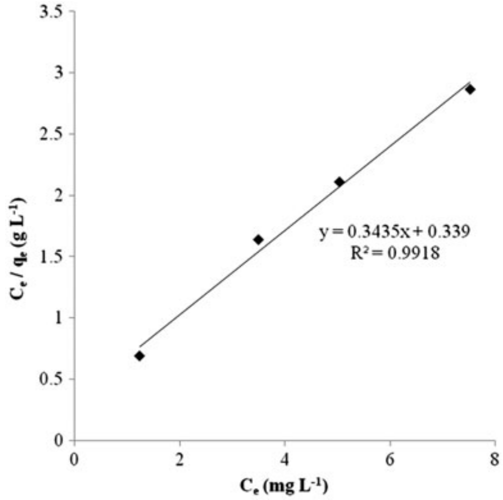

Fig. 8. Langmuir isotherm of RB5 by chitosan beads. (0.50 g chitosan beads; 20 mL of 50, 60, 70, and 80 mg L^{-1} of dye solutions; natural pH of dye solution; 150 rpm).

tabulated in Table 6. All the R_L values calculated fall in the range of $(0 < R_L < 1)$ which shown the favorable adsorption of RB5 onto chitosan beads.

3.7. *Evaluation of variables affecting percentage uptake of dye*

Plackett–Burman design was used to determine the important variables that will have an influential effect in the uptake of RB5. In this study, four parameters (contact time, initial concentration, pH, and agitation rate) were tested on their validity by using Plackett–Burman design (Table 7). Besides, the analysis of variance (ANOVA) was also performed (Table 8). From the same table, the model *F*-value of 10.01 and Prob > *F* of 0.0051 implies that the model was significant. Model terms were defined as significant when the value of Prob > *F* was less than 0.05. The *p*-values were used as a tool to check the significance of each of the interaction among the variables. As shown in Table 8, effect of contact time and pH were significant model terms for the uptake of RB5, while, initial concentration and agitation rate were not significant for the response (Prob > *F* = 0.5588 and 0.3500, respectively).

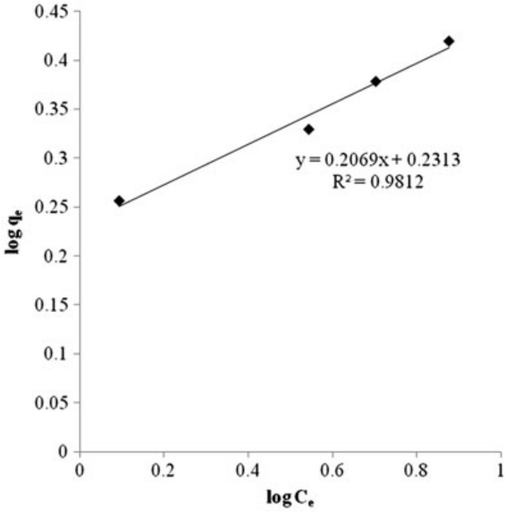

Fig. 9. Freundlich isotherm of RB5 by chitosan beads. (0.50 g chitosan beads; 20 mL of 50, 60, 70, and 80 mg L^{-1} of dye solutions; natural pH of dye solution; 150 rpm).

The results obtained suggest that in the removal of dyes, the effect of pH is a non-negligible factor as it affects the degree of ionization of the sorbate as well as the surface properties of the sorbent. The dependence of dye uptake on contact time could be attributed to the three phases of dye sorption: (i) external mass transfer or instantaneous adsorption step, (ii) gradual adsorption step where the intra-particle diffusion can be rate controlling and (iii) final equilibrium step where the intra-particle diffusion starts to slow down due to the extremely low solute concentration in the solution [16]. The significance of these two factors agrees well with the findings in batch study.

3.8. *Verification of Plackett–Burman design model*

The function of desirability was applied using Design-Expert Version 7.1.3.1 in order to validate the model. The experimental conditions to be verified were selected based on the highest desirability. The percentage error of dye uptake based on the model prediction and experimental response was in the range of 0.6–5%. The deviations observed could be most likely due to the incorporation of insignificant factors into the calculation of dye uptake.

Table 7
Plackett–Burman results for the removal of RB5 by chitosan beads

Experimental	Variables				Experimental % uptake	Predicted % uptake
	Contact time	Initial concentration	pH	Agitation rate		
1	5	100	10	100	17.5	19.52
2	5	100	10	200	18.14	23.02
3	5	100	2	200	12.41	17.36
4	5	20	10	100	16.32	19.65
5	5	20	2	200	9.23	11.81
6	360	100	2	200	37.8	39.99
7	5	20	2	100	12.75	13.34

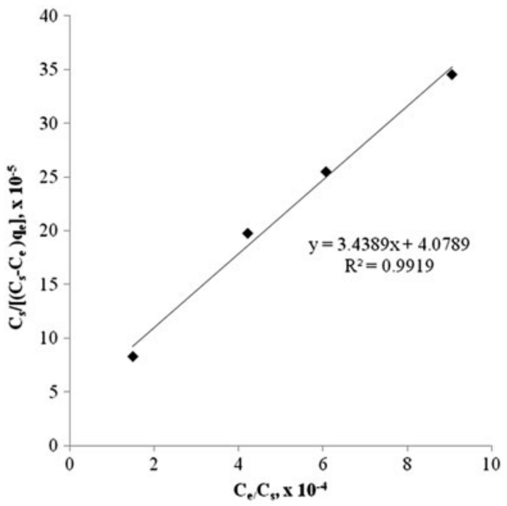

Fig. 10. BET isotherm of RB5 by chitosan beads. (0.50 g chitosan beads; 20 mL of 50, 60, 70, and 80 mg L^{-1} of dye solutions; natural pH of dye solution; 150 rpm).

3.9. Optimization of percentage uptake of RB5 dye using response surface methodology approach

The effects of contact time, initial concentration, pH, and agitation rate on the percentage uptake of RB5 in aqueous solution were studied using RSM. The modified cubic model describing the correlation between the variables and the percentage uptake for RB5 dye was shown as follows:

$$\begin{aligned}\%\text{uptake} = {} & 89.64 + 23.76A + 1.66B + 8.51C \\ & + 1.92D + 3.59AB + 9.70AC + 2.66AD \\ & - 9.73BC + 2.84BD - 0.15CD \\ & - 30.70A^2 - 7.15B^2 - 17.60C^2 + 4.66D^2 \quad (9)\end{aligned}$$

where A = contact time, B = initial concentration, C = pH, D = agitation rate.

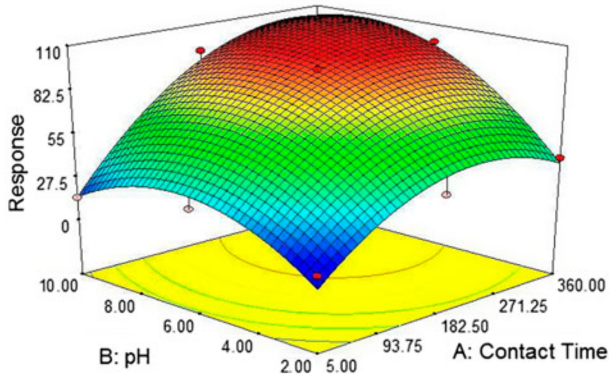

Fig. 11. 3D surface plot for uptake of RB5 as a function of contact time and pH at 50 mg/g of initial dye concentration and 150 rpm of agitation rate.

Fig. 11 shows the 3D surface plot for uptake of RB5 as a function of contact time and pH at 50 mg/g of initial dye concentration and 150 rpm of agitation rate. Table 9 shows the ANOVA regression analysis for RB5 in aqueous solution. The model was significant (p = 0.0009) with F-value of 5.78. The coefficient of determination (R^2) for RB5 was found to be 0.8435. The closer the R^2 is to unity, the stronger the model and the better it predicts the response [30]. The predicted multiple correlation coefficient (predicted R^2) value of 0.1086 was not agreed well with the adjusted multiple correlation coefficient (adjusted R^2) value of 0.6975. The coefficient of variance (C.V.) of this model was reported as 33.16%. The lower the C.V. value, the greater is the precision and reliability of the experiments carried out. Adequate precision indicates the signal to noise ratio and a ratio greater than 4 is desirable.

3.10. Verification of response surface methodology model

In order to determine the validation of the model equations for the studied dye, experiments were

Table 8
Regression analysis (ANOVA) of Plackett–Burman of RB5

Source	Degree of freedom	Sum of squares	Mean square	*F*-value	Prob > *F*	Description
Model	4	11,489.74	2,872.44	10.01	0.0051	Significant
Contact time	1	7,680.57	7,680.57	26.77	0.0013	Significant
Initial concentration	1	108.06	108.06	0.38	0.5588	
pH	1	3,413.48	3,413.48	11.90	0.0107	Significant
Agitation rate	1	287.63	287.63	1	0.3500	
Residual	7	286.89	286.89			
Total	11					

Table 9
Regression analysis (ANOVA) for the removal of RB5 from aqueous solution

Source	Degree of freedom	Sum of square	Mean square	*F*-value	*P*
Model	14	31,117.95	2,222.71	5.78	0.0009
A	1	10,158.35	10,158.35	26.40	0.0001
B	1	49.43	49.43	0.13	0.7250
C	1	1,304.58	1,304.58	3.39	0.0855
D	1	66.51	66.51	0.17	0.6835
AB	1	206.71	206.71	0.54	0.4749
AC	1	1,506.80	1,506.80	3.92	0.0665
AD	1	113.37	113.37	0.29	0.5953
BC	1	1,513.79	1,513.79	3.93	0.0659
BD	1	129.11	129.11	0.34	0.5710
CD	1	0.35	0.35	0.00	0.9765
A^2	1	2,441.85	2441.85	6.35	0.0236
B^2	1	132.44	132.44	0.34	0.5662
C^2	1	802.98	802.98	2.09	0.1692
D^2	1	56.15	56.15	0.15	0.7078
Residual	15	5,772.50	384.83		
Lack of fit	10	5,772.50	577.25		

Note: R^2: 0.8435, adjusted R^2: 0.6975, predicted R^2: 0.1086, adequate precision: 6.916 and C.V.: 33.16%

conducted based on the experimental conditions with the highest desirability which generated by Design-Expert Version 7.1.3.1 software. The comparison between the experimental and predicted results showed a percentage error of less than 5%.

4. Conclusion

In this study, the chitosan beads have been used as an effective low cost sorbent for the adsorption of RB5 dye from aqueous solution. The optimization and the modeling of percentage uptake of RB5 in aqueous solution were conducted using Plackett–Burman design and RSM. Plackett–Burman design was successfully applied to identify the most significant factors which influence the percentage uptake of the dye. By using RSM, a set of optimal reaction conditions for RB5 uptake was obtained with the compromise of this response: contact time (182.5 min), initial concentration (60 mg/L), pH (6), agitation rate (200 rpm). Under optimal values of operating parameters, highest percentage uptake of dye was achieved (96.22%). Overall, chitosan beads have the potential as an effective sorbent for the dye adsorption in wastewater.

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