



## Original Research Article

# Removal the acid blue-15 dye from water by chitosan: kinetic and thermodynamic study

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### KEYWORDS

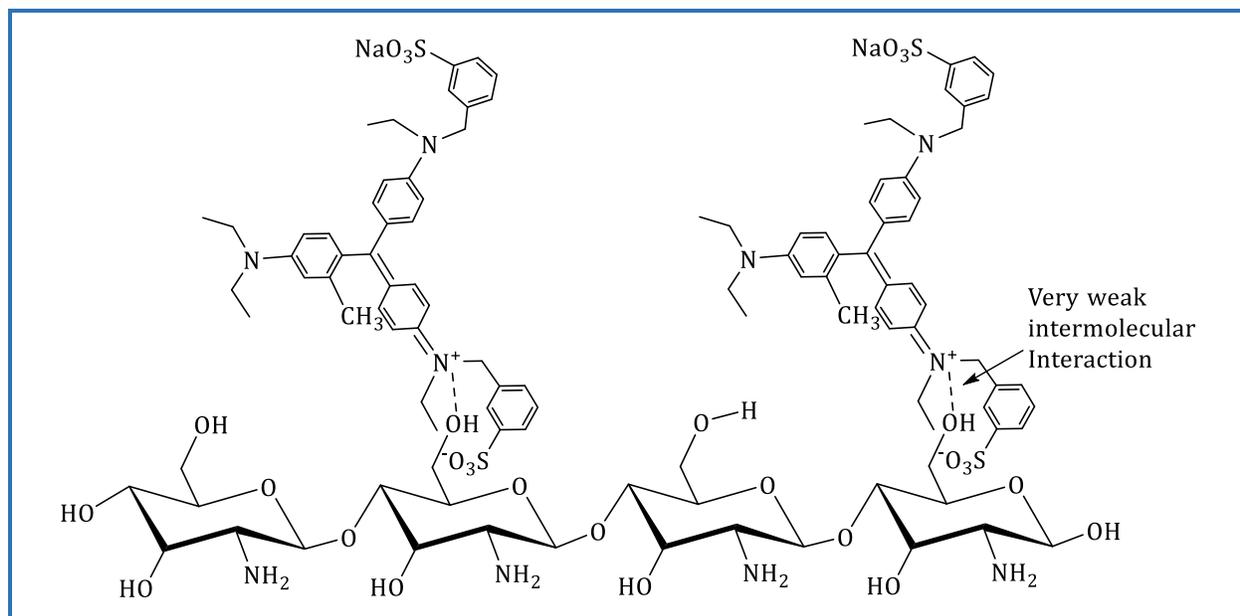
Acid blue-15 dyes  
Chitosan  
Pseudo-first order model  
Freundlich isotherm

### ABSTRACT

This study concerns the removal of acid blue-15 (AB-15) from water using chitosan through the batch sorption. To get the best percentage of removal, several experimental parameters have been used such as the initial concentration, temperature, and pH. The results show that the pH of the interaction medium does not indicate a significant influence in the adsorption process. In addition, the percentage of removal increased with the increase of dosage of chitosan and temperature of the reaction vessel. Furthermore, the percentage of removal decreases with the increase in the initial concentration of the AB-15 solution. The adsorption of AB-15 on the chitosan fits better with the Freundlich ( $R^2= 0.998$ ) than the Langmuir model. The adsorption kinetics follows the pseudo-first order ( $R^2> 0.998$ ) but not the pseudo-second-order model. The obtained results of this study show that chitosan has a potential application as a membrane to remove the AB-15 from industrial effluents.

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## Graphical Abstract



## Introduction

Nowadays, environmental and water pollution are growing dramatically, this is due to a large number of chemical industries, especially the textile, leather, paper and cosmetic industries [1, 2]. Acid blue-15 is one of the organic dyes that are used for dyeing the product of such textile industries. It enters the water through dyeing or/and washing processes. It is considered as one of the azo dyes. It is a complex and resonance-stabilized triphenylmethane (TPM) textile dye. The triphenylmethane (TPM) group of textile dyes has a complex aromatic molecular structure, which resists degradation in the environment. These kinds of dyes cause adverse effects on human health in case of exposure to high concentration. For example, many reports in the pieces of literature provide information regarding the toxicity and carcinogenic potential of different TPM dyes [3–5]. Furthermore, the TPM dyes can hinder light penetration and then disturb life processes of the living organisms in the water. Therefore, the researchers direct their efforts toward the removal of dyes and color from the aqueous system.

The traditional processes focus on the removal of dyes and color by physical and chemical methods such as coagulation [6], membrane filtration [7], photocatalytic degradation [8, 9], nanofiltration and ozonolysis, oxidation [10], and microbiological decomposition [11]. Generally, these processes break down the azo dyes to form carcinogenic aryl-amines; it decomposes to simple metabolic intermediates. This process leads to a more and more increasing problem. Wherein, the decomposition procedures are not efficient because of the fact that many dyes cannot be easily

decomposed [12]. Therefore, the most efficient one is the adsorption process [13–16]. Several cheap and safe adsorbents are used and investigated for removing dyes from water, such as: orange peel [17], dolomitic [18], calcine alunite [19], clay [20], bottom ash [21], zeolite [22], chitosan [23], bentonite [24], silica fume [25], *azolla filiculoides* [26], rice husk [27], canola [28] and chitin [29]. In literature, we find little works in the removal and sorption of acid blue-15. These articles focus on the utilization of variant biomass adsorbent for the removal of acid blue-15 from water such as red mud [30], wood and saw dust [31], fly ash [32], wheat straw [33], orange peel [34–36], banana peel [37], leaf [38], soy meal hull [39], eggshell membrane [40], lignocellulosic waste biomass activated carbon [41], macroalga *azolla filiculoides* [42], activated carbons of sunflower seed hull [43–44], *azolla rongpong* [45], *azolla filiculoides* biomass [46], immobilized cell bioreactor [47], activated carbon of melon seed hull [48], activated carbon of delonix regia (DR) seed pod [49], bagasse, groundnut shells, cow dung, pea shells, wheat straw, and tea leaves [50],  $\beta$ -cyclodextrin (CD), hydroxypropyl  $\beta$ -cyclodextrin (HPCD), poly (vinyl alcohol) (PVOH) [51], activated carbon from pomelo skin [52], and fresh water algae [53]. In particular, it can use chitosan as flocculating and chelating agents in wastewater treatment and drinking water. It can also be used as an ecological polymer for removing heavy metals and synthetic dyes. Therefore, it can be considered that chitosan can be a potential adsorbent.

Chitosan is a type of fiber taken from the shells of crustaceans such as shrimp, clams, or lobster. It is available in huge quantity through the waste product of the crabbing and shrimp canning industry. Wherein the chemistry of chitosan is a linear polysaccharide composed of  $\beta$ -(1,4)-2-amino-2-deoxy-D-glucose and  $\beta$ -(1,4)-2-acetamido-2-deoxy-D-glucose repeating units. Because of the lack of research works that are related to the removal of acid blue-15 using chitosan, we have studied the sorption and the removal of the acid blue-15 (AB-15) dye from water onto chitosan.

Little studies are found in the pieces of literature, which are related to the adsorption and removal of acid blue-15 dye from water. Furthermore, we do not find any work related to the sorption of the acid blue-15 by using chitosan. Therefore, the main purpose of the study is to remove acid blue dye from water by chitosan. Herein, the objectives of this work is: *I*) to determine maximum removal of AB-15 by using different environmental parameters of interaction, such as initial concentration of AB-15, dosage of adsorbent, contact time and pH, *II*) to study the thermodynamic and kinetic model parameters, and *III*) to estimate the interaction mechanism between AB-15 and chitosan surface.

## Experimental

### *Materials and methods*

All chemicals were used as received as an analytical grade. Acid blue-15 (AB-15) was purchased from Alvan Sabet CO. ( $M_{wt}=775.95$  g/mol; the chemical formula is  $C_{42}H_{46}N_3NaO_6S_2$ ). The stock solution ( $1000$  mg/L<sup>-1</sup>) was prepared by dissolving a stoichiometric amount of AB-15 powders in 1 L of distilled water. Standard solutions of AB-15 (30, 50, 100, 150, and 200 mg/L<sup>-1</sup>) were prepared by appropriate dilution from 1000 mg/L<sup>-1</sup> stock solution. An “initial” pH and its subsequent adjustment for all experimental runs were conducted less than 7.4 at the maximum value. NaOH (0.1 mol/L<sup>-1</sup>) and HCl (0.1 mol/L<sup>-1</sup>) were purchased from Merck (Darmstadt, Germany).

### *Apparatus and instruments*

AB-15 absorbs light in the field between about 530 to 700 nm so that the peak is at about 560 nm. Therefore, the AB-15 concentration in the solution was measured using the UV-vis spectrophotometer (Shimadzu UV-1800 UV-vis spectrophotometer). All the reported results were the average of at least triplicate measurements at 560 nm. The mixtures were mixed by a thermostatic mechanical shaker at constant temperature (25, 35, 45 and 55 °C, isothermal Gesellschaft für 978). To ensure accuracy in the preparation, analytical balance is used (sartorius, CP324-S/management system certified according to ISO 9001). Chitosan (synonym: deacetylated chitin, poly(*D*-glucosamine) is used as received from Sigma-Aldrich without further purification as medium molecular weight. The mass median diameters of the chitosan flakes were estimated to be ( $228 \pm 5$ ) μm.

### *Equilibrium studies*

The batch removal of the AB-15 was calculated from the mass balance, which was stated as the amount of AB-15 adsorbed onto the solid particles of the chitosan or chitosan-Fe sorbent. It equals a number of AB-15 removed from the aqueous solution. Mathematically, it can be expressed in equations 1-2:

$$q_e = \frac{(C_i - C_e)}{S} \quad (1)$$

$$q_t = \frac{(C_i - C_t)}{S} \quad (2)$$

Where  $q_e$ : AB-15 amount adsorbed on the chitosan sorbent surface at equilibrium (mg/g<sup>-1</sup>).  $q_t$ : AB-15 amount adsorbed on chitosan or chitosan-Fe sorbent surface at a specific time (mg/g<sup>-1</sup>).  $C_i$ : Initial concentration of AB-15 in the aqueous solution (mg/L<sup>-1</sup>).

$C_e$ : Equilibrium concentration or final concentration of AB-15 in the aqueous solution ( $\text{mg/L}^{-1}$ ).  $C_i$ : The initial concentration of AB-15 in the aqueous solution ( $\text{mg/L}^{-1}$ ) at a specific time.  $S$ : Dosage (slurry) concentration of Chitosan sorbent and it is expressed by:

$$S = \frac{m}{v} \quad (3)$$

Where  $v$  is the initial volume, of AB-15, the solution used (L) and  $m$  is the mass of chitosan sorbent. The percent adsorption (%) was also calculated using the following equation

$$\% \text{ Removal of AB - 15} = \frac{C_i - C_e}{C_i} \times 100\% \quad (4)$$

#### *Effect of contact time*

The sorption experiments were carried out by shaking 0.1 g of the chitosan or chitosan-Fe sorbent with 50 mL of  $100 \text{ mg/L}^{-1}$  of AB-15 solution ( $\text{pH}_i = 7.4$ , dosage =  $2 \text{ g/L}^{-1}$ ). The solutions were shaken vigorously using thermostatic mechanical shaker at constant temperature (25, 35, 45 and  $55 \text{ }^\circ\text{C}$ ). The agitation speed was fixed at 80 rpm for a known period in the interval of 0.5 to 180 minutes with increment of 10 minutes from 10 to 60 minutes, and then 30 minutes from 60 to 180 minutes. At the end of the predetermined time, the filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

## **Results and Discussion**

### *The sorption of AB-15 onto the chitosan sorbent*

The sorption of AB-15 onto the solid particles of the chitosan sorbent could be performed through the suggested physisorption mechanism through the electrostatic interaction of AB-15 with the  $-\text{OH}$  functional group on the sorbent surface (see [Scheme 1](#)). The sorption of AB-15 onto chitosan achieved the suggestion of a physisorptions mechanism of Lagergren pseudo-first-order model ( $R^2 = 0.999$ ). This idea can be supported by the reported studies such as the sorption of omega chrome red ME through fly ash to coal [54]. Wherein, these studies report that pseudo-first order Lagergren kinetics is considered as the sorption of dyes. Based on this suggestion, the kinetic sorption of AB-15 onto chitosan adsorbent is considered in our explanations.

### *Effect of AB-15 dye initial concentration*

The effect of the initial AB-15 concentration on the sorption efficiency is investigated in the concentration range of  $10\text{-}100 \text{ mg/L}^{-1}$  at  $35 \text{ }^\circ\text{C}$ . [Figure 1](#) shows that the initial concentration of AB-

15 has no significant effect on the sorption process; in general, the percentage of removal decreases with increasing the initial concentration of AB-15. This behavior agrees with the results obtained by using red mud for removal of AB-15 dye from aqueous solutions [30]. Whereas, a reported study, concerning the adsorption of the anionic compounds, shows an opposite behavior [55].

#### *Effect of temperature*

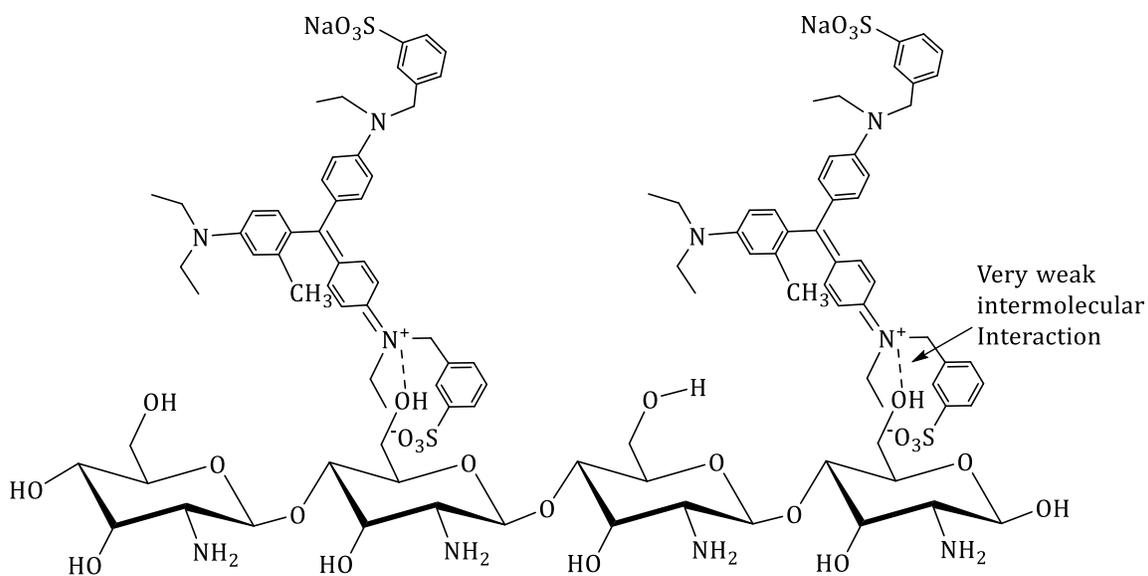
The influence of temperature on the removal of AB-15 from the aqueous solution has been studied through the applied of a variety of temperatures 25, 35, 45 and 55 °C. It is observed in [Figure 2](#) that the removal percentage increased with increasing temperature; wherein it is not highly affected by raising the value of temperatures. The maximum removal percentage at 55 °C is 98%, while the lowest percentage is 81% (approx.) at a temperature of 25 °C. This indicates that high temperature could enhance the chemical interaction of AB-15 with chitosan surface (Physisorptions) [56]. This type of interaction is not typical to the adsorption of the dyes by activated clay [57].

#### *Dosage effects of chitosan adsorbent*

The removal percentage of AB-15 from 100 mg/L<sup>-1</sup> solutions using different dosages of chitosan (2, 6, 10, 14 and 20 g/L<sup>-1</sup>) has been described in [Figure 3](#). The removal percentage increases slightly sharp as the adsorbent dose increases. This is due to the reason of increasing the number of the functional group and adsorption active site in the chitosan surface area, as mentioned before in kinds of literature [58]. The maximum removal (99 %) has been observed using the dosage of 10-20 g/L<sup>-1</sup>. These results are in line with the study, which are related to the study of adsorption of acid dyes onto bentonite and surfactant-modified bentonite [59].

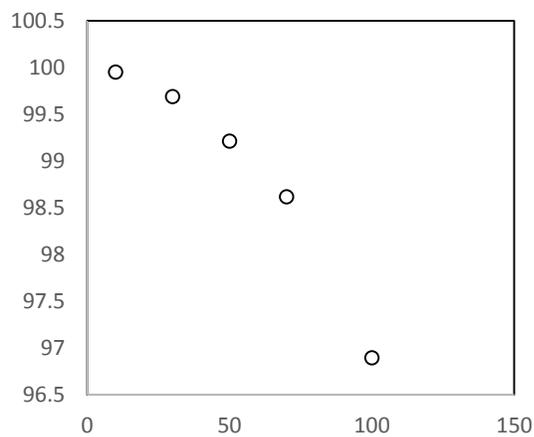
#### *Effect of pH*

[Figure 4](#) represents the removal percentage of AB-15 from 100 mg/L<sup>-1</sup> aqueous solutions using different pH values (2, 4, 7 and 10). The maximum removal percentage 99% is achieved with pH = 4, while it is 96% by using pH = 2. This indicates no significant influence of the pH value on the sorption process. In general, the percentage removal of AB-15 from water was higher in acidic solutions than in neutral and alkaline conditions. The minor decrease (ca. pH<4) in adsorption may be due to the repulsion between acidic dye molecules and the abundance of OH<sup>-</sup> ions at higher pH values [59]. From another direction, amino groups (-NH<sub>2</sub>) of chitosan molecules can be easily protonated to form -NH<sub>3</sub><sup>+</sup> groups, which increase the electrostatic attractions between negatively charged dye anions and positively charged adsorption sites of the amino group in the chitosan surface. Two factors play an opposite effect that leads to minor pH effect [60].

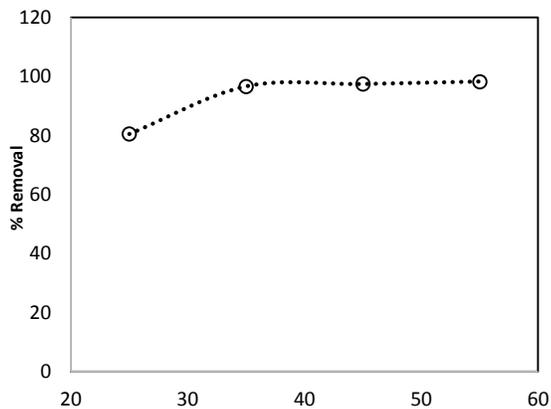


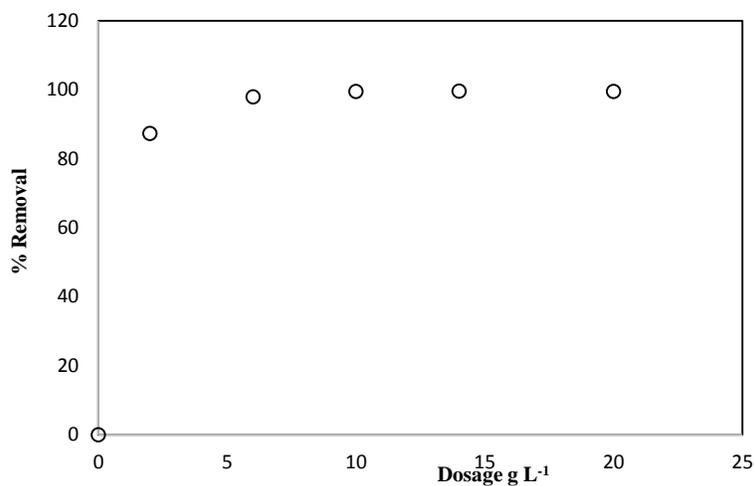
**Scheme 1.** The possible mechanism of adsorption of AB-15 onto chitosan adsorbent

**Figure 1.** Effect of initial concentration of AB-15 ( $t = 50$  min,  $35^\circ\text{C}$ ,  $50$  mL,  $0.1$  g chitosan,  $80$  rpm)

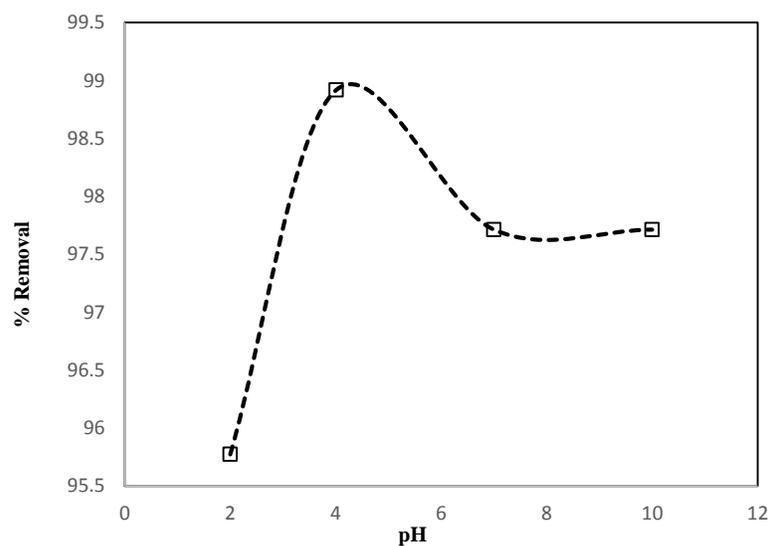


**Figure 2.** Effect of temperature ( $t = 40$  min,  $50$  mL,  $C_i = 100$  mg/L<sup>-1</sup>,  $0.1$  g chitosan,  $80$  rpm)





**Figure 3.** Effect of chitosan dosage ( $t = 50$  min,  $50$  mL,  $T = 35$  °C,  $C_i = 100$  mg/L<sup>-1</sup>,  $80$  rpm)



**Figure 4.** Effect of pH ( $t = 90$  min,  $C_i = 100$  ppm,  $35$  °C,  $0.1$  g chitosan,  $50$  mL,  $80$  rpm)

#### *Adsorption isotherm*

The maximum sorption capacity of AB-15 can be determined by the equilibrium distribution between the chitosan and the solution. For this target, various isotherm models are used to describe the equilibrium such as Langmuir and Freundlich models. Wherein, they are used to fit the experimental data as reported in selected works of literature [61–64]. Isotherm studies were conducted at  $35$  °C by varying the initial concentration of AB-15. Representative initial concentrations ( $10$ ,  $30$ ,  $50$ ,  $70$ , and  $100$  mg/L<sup>-1</sup>) of AB-15 were mixed with slurry concentrations

(dose) of 2 g/L<sup>-1</sup> for 50 minutes, which was the equilibrium time for the Chitosan and AB-15 chemisorptions mixture. The linear form of the Langmuir model is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{1}{q_{max}} C_e \quad (5)$$

Where:  $q_e$ : AB-15 amount (mg) on the chitosan (g) at equilibrium (mg/g<sup>-1</sup>); and  $q_{max}$  is the maximum dye uptake per unit dosage of adsorbent (mg/g<sup>-1</sup>), which is related to adsorption capacity; and  $b$  is Langmuir constant (L/g<sup>-1</sup>) which is exponentially proportional to the heat of adsorption as well as it related to the affinity of binding sites and is a measure of the energy of adsorption. Therefore, a plot of  $\frac{C_e}{q_e}$  versus  $C_e$ , gives a straight line of slope  $\frac{1}{q_{max}}$  and intercept  $\frac{1}{q_{max}b}$ . The thermodynamic and the equilibrium results were obtained at the pH = 7.4 model solution of AB-15, which are summarized in [Table 1](#).

The Langmuir isotherm model is used to fit the experimental data, giving a correlation, regression coefficient ( $R^2= 0.919$ ), which is a measure of goodness-of-fit and the general empirical formula of the Langmuir model by  $\frac{C_e}{q_e} = 0.0186C_e + 0.0103$ , as shown in [Figure 5](#). Our results are in a good qualitatively agreements with those found from adsorption of AB-15 onto red muds adsorbent [30] and the adsorption of the acid blue-25 (AB-25) onto raw diatomite [65].

On the other hand, the Freundlich model is commonly used to describe the adsorption characteristics of the heterogeneous surface. It represents initial surface adsorption followed by a condensation effect resulting from strong adsorbate-adsorbate interaction. The linear form of the Freundlich model is also given by

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (6)$$

Where  $K_F$  and  $n$  are the Freundlich constants determined from the slope and intercept of plotting  $\ln q_e$  versus  $\ln C_e$ .

The experimental data fit into the Freundlich model as shown in [Figure 6](#). The empirical formula of this model is found as  $\ln q_e = 0.5522 \ln C_e + 3.3154$  with  $R^2$  value equals 0.998. The Freundlich model has a better fitting model than the Langmuir model does. [Figure 6](#) shows that the Freundlich model has a higher correlation regression coefficient ( $R^2=0.998$ ) than the Langmuir model. Furthermore, [Figure 7](#) shows that the experimental isotherm is “look like” identical with the

Freundlich isotherm model ( $R^2=0.899$ ). The smaller the value of the heterogeneity parameter ( $1/n$ ) means the greater the expected heterogeneity [66, 67]. The results exhibit a value of  $\frac{1}{n}$  ( $0 < \frac{1}{n} < 1$ ) indicating the more heterogeneous physisorptions of AB-15 onto chitosan as mentioned in the reported literature [68, 69].

The effect of isotherm shape is discussed from the direction of predicting the weather and adsorption system is “favorable” or “unfavorable”. It was previously reported [68] that the dimensional analysis, separation factor, or equilibrium parameters “ $R_L$ ” was as an essential feature of the Langmuir isotherm to predict adsorption system to be “favorable or “unfavorable” by equation 7:

$$R_L = \frac{1}{1 + bC_i} \quad (7)$$

Where  $C_i$  is the initial AB-15 concentration mg/L<sup>-1</sup>. The calculated  $R_L$  was less than 1.0, indicating for the favorable adsorption as shown in Figure 8.

The apparent Gibbs free energy of sorption ( $\Delta G^\circ$ ) is the fundamental criterion of spontaneity. The reaction occurs spontaneously at a given temperature if  $\Delta G^\circ$  is negative in value. The standard Gibbs free energy change ( $\Delta G^\circ$ ) for the adsorption of AB-15 molecule on the chitosan surface can be calculated using the following thermodynamic equation

$$\Delta G = -RT \ln K_i \quad (8)$$

Wherein,  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup>/K<sup>-1</sup>) and  $T$  is the absolute temperature in Kelvin and  $b$  is the equilibrium constant, related to the Langmuir constant,  $b$  (= 1.806).

$$K_L = b \times M_A \quad (9)$$

Where  $M_A$  is the molar weight of sorbate (AB-15 = 775.95 g/mol<sup>-1</sup>, where  $K_L = 1401.366$  L/mol<sup>-1</sup>).

The value of standard Gibbs free energy change calculated at 35 °C is found to be -18.562 kJ/mol<sup>-1</sup>. The negative sign for ( $\Delta G^\circ$ ) indicates the spontaneous nature of AB-15 adsorption on the chitosan framework surface.

To justify the validity of chitosan as an adsorbent for the removal of AB-15 from the aqueous solution, the adsorption potentials were considered, as shown in Table 2.

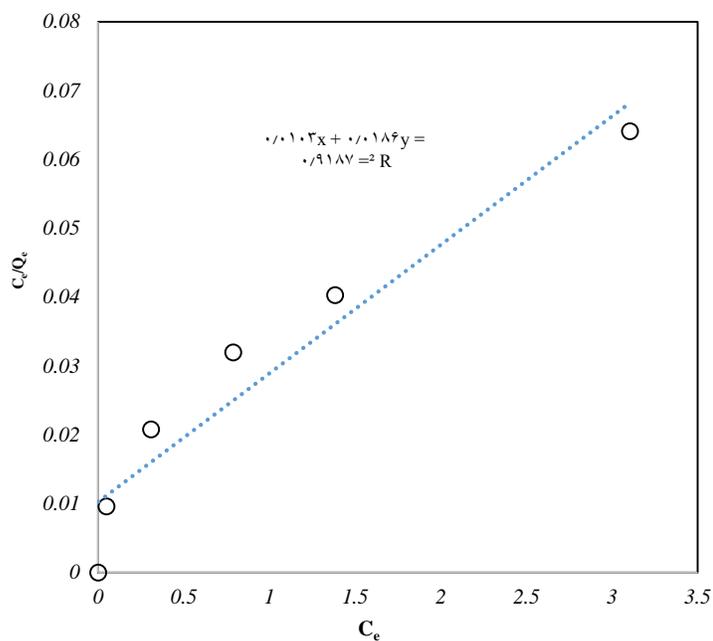
#### *Sorption kinetic model*

The effect of contact time is shown in Figure 9. At the initial stage, the removal rate of AB-15 is high during the first 5 minutes. The initial faster rate may be due to the availability of the uncovered

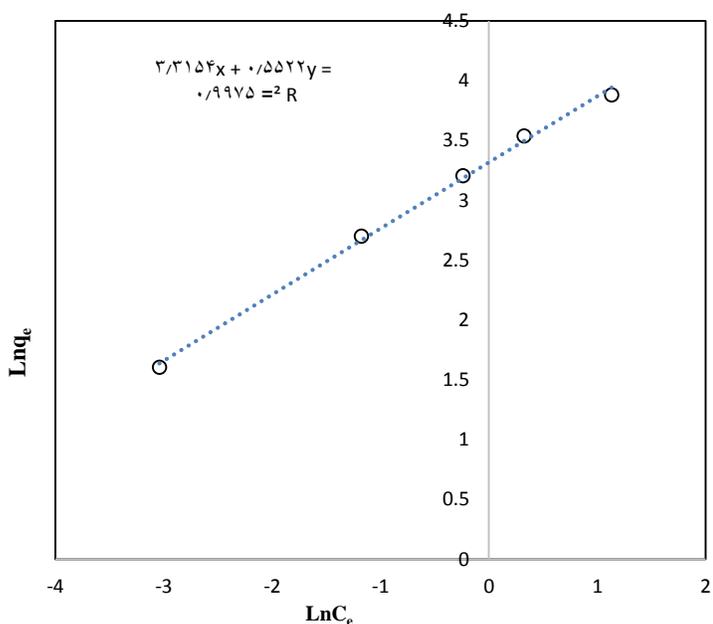
**Table 1.** The parameters of the pseudo-first-order kinetic model

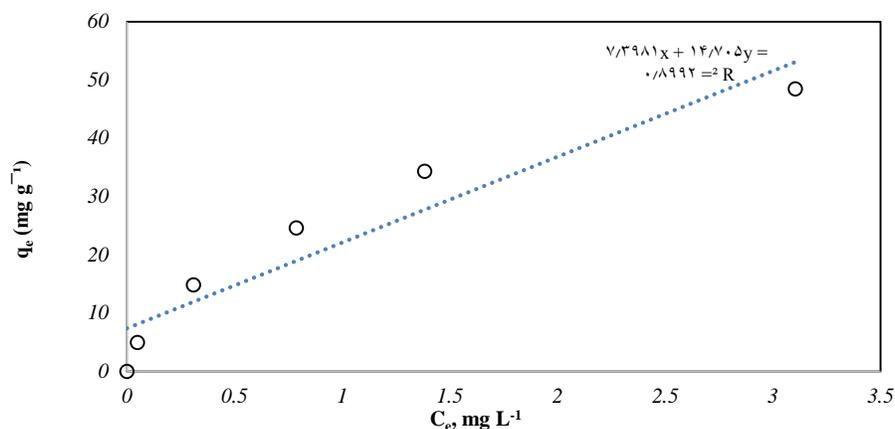
| Temp. (°C) | $K_1$ (g/mg <sup>-1</sup> min <sup>-1</sup> ) | $q_{e, \text{Exp}}$ (mg/g <sup>-1</sup> ) | $q_{e, \text{Calc}}$ (mg/g <sup>-1</sup> ) | $R^2$  |
|------------|---|---|--|--------|
| 25         | 0.0027  | 45.435                                    | 45.291                                     | 0.9991 |
| 35         | 0.0085  | 48.768                                    | 49.166                                     | 0.9952 |
| 45         | 0.0126  | 47.804                                    | 47.971                                     | 0.999  |
| 55         | 0.0128  | 46.968                                    | 47.0824                                    | 0.9987 |

**Figure 5.** The linearized Langmuir adsorption isotherms for AB-15 adsorption by chitosan (dosage = 2 g/L<sup>-1</sup>, temperature = 35 °C, agitation speed = 80 rpm and contact time = 50 min)

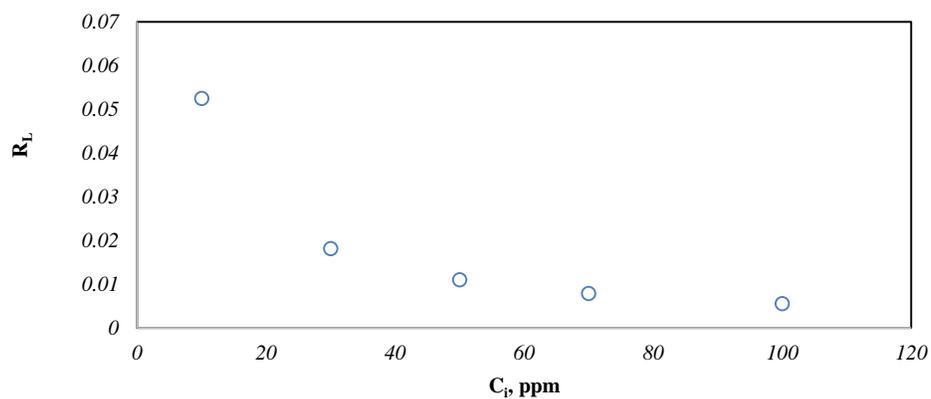


**Figure 6.** The linearized Freundlich adsorption isotherms for AB-15 adsorption by chitosan (dosage = 2 g/L<sup>-1</sup>, temperature = 35 °C, agitation speed = 80 rpm and contact time = 50 min)





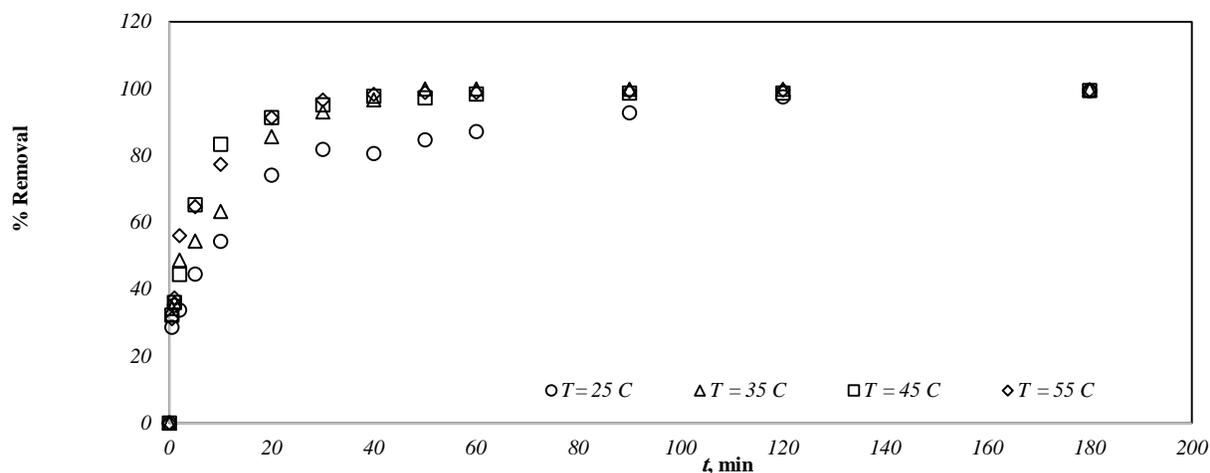
**Figure 7.** Experimental isotherms for AB-15 adsorption by chitosan (dosage = 2 g/L<sup>-1</sup>, temperature = 35 °C, agitation speed = 80 rpm and contact time = 50 min)



**Figure 8.** Separation factor vs. the initial concentration of AB-15 dye

**Table 2.** List the compression of the adsorption isotherm of AB-15 onto various adsorbents

|   | Adsorbent   | Langmuir                            |                              |       | Freundlich |               |       | Isotherm   | Ref          |
|---|---|-------------------------------------|------------------------------|-------|------------|---------------|-------|------------|--------------|
|   |   | $q_{\max}$<br>(mg/g <sup>-1</sup> ) | $b$<br>(L/mg <sup>-1</sup> ) | $R^2$ | $K_f$      | $\frac{1}{n}$ | $R^2$ |            |              |
| 1 | Activated carbons<br>prepared from<br>sunflower seed hull | 75 - 110                            |                              | 0.994 |            |               |       | Langmuir   | 43           |
| 2 | mud red   | 3.11                                | 0.41                         | 0.995 | 1.74       | 0.39          | 0.921 | Langmuir   | 30           |
| 3 | Azolla filiculoides<br>biomass                            | 7.11                                | 1.11                         | 0.998 | 51.2       | 1.02          | 0.963 | Langmuir   | 46           |
| 4 | Chitosan  | 53.76                               | 1.806                        | 0.919 | 27.5       | 0.55          | 0.998 | Freundlich | Our<br>study |



**Figure 9.** Effect of contact time on AB-15 sorption,  $C_i = 100 \text{ mg/L}^{-1}$

surface area of the chitosan. The final equilibrium of sorption starts after 50 minutes yielded a maximum removal of 99% (approx.). At the later stages, there is slightly increasing removal efficiency within increasing the contact time. This is due to the decreased or lesser number of active sites. Similar results have been reported in the literature for the removal of dyes by activated clay [57] and carbon biomass [70].

The kinetics sorption describes the removal rate of AB-15 from the  $100 \text{ mg/L}^{-1}$  of an aqueous solution. The kinetic sorption was analyzed using two kinetic models including the pseudo-first-order and pseudo-second-order. The role of contact time was studied under the shaking conditions, for instance, the pH of the solution was 7.4, 80 rpm,  $2 \text{ g/L}^{-1}$  dosage of chitosan and by applying 25, 35, 45 or 55 °C. Samples were collected at regular intervals and then analyzed after filtration.

The pseudo-first-order kinetic model and its integral can be expressed by the following the equation [71, 72]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (10)$$

Where  $q_e$  and  $q_t$  ( $\text{mg/g}^{-1}$ ) are the amounts of adsorbed AB-15 at equilibrium and at the time ( $t$ ), respectively,  $k_1$  ( $\text{min}^{-1}$ ) is pseudo-first-order rate constant, and  $t$  (minutes) is contact time. The coefficient of determining the value ( $R^2$ ) is ca. 0.999 as shown in Figure 10 and Table 1. The pseudo-second-order kinetic model and its integral form. This model is expressed by the following equation [72, 73]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where  $k_2$  is the equilibrium rate constant of the pseudo-second-order kinetic model ( $\text{g}/\text{mg}^{-1}/\text{min}^{-1}$ ). The value of  $k_2$  can be determined by plotting  $t/q_t$  versus  $t$  to obtain a straight line of slope  $1/q_e$  and intercept of  $1/(k_2)$ . From the determination coefficient value  $R^2$  was very small (approx. 0.45). Therefore, the experimental data fit better to the pseudo-first order.

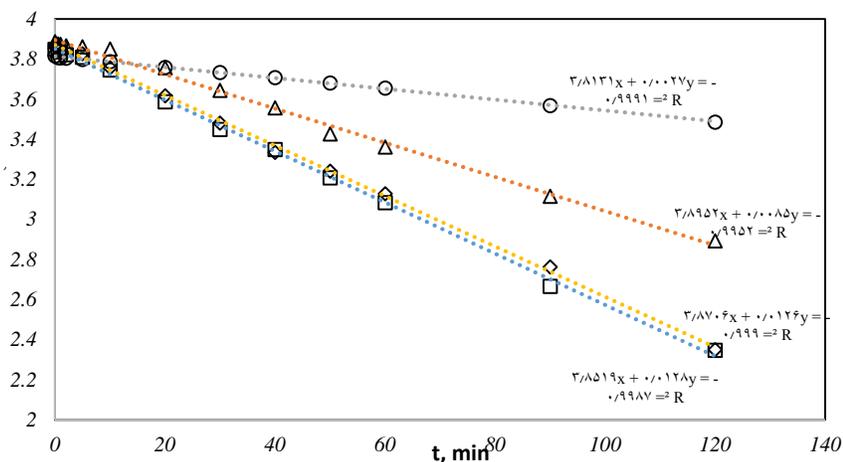
The adsorption model of AB-15 transport onto chitosan surfaces is regarded as pseudo-first-order. Furthermore, the comparison of  $q_e$  values from the experimental work of this study and the calculation of the pseudo-first-order kinetic model (difference smaller) also show the availability of this model (Figure 11). This result was found matching with the reported one [74].

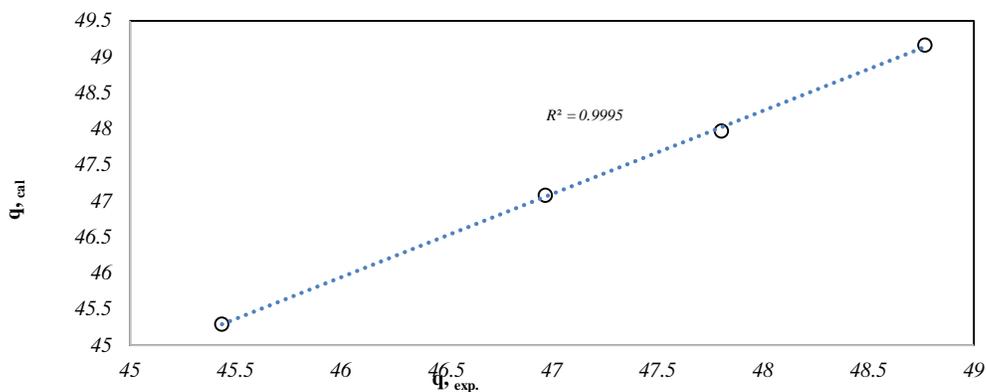
To determine the diffusibility of the AB-15 into the chitosan adsorbent, weber-morris intraparticle diffusion model [75] was used in the form of the Equation 12:

$$q_t = k_{int}\sqrt{t} + C \quad (12)$$

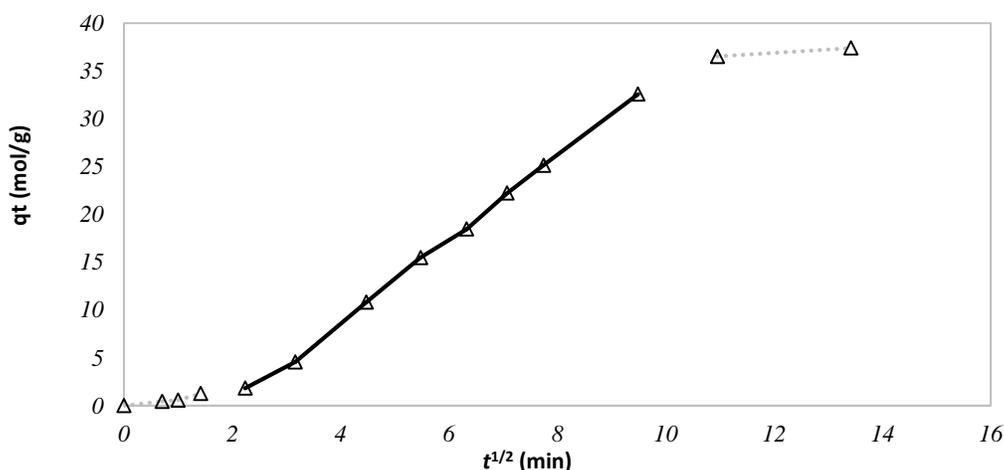
Where  $C$  is constant,  $q_t$  the amount of AB-15 adsorbed at the time ( $\text{mg}/\text{g}^{-1}$ ) and  $k_{int}$  is the intraparticle diffusion rate constant ( $\text{mg}/\text{g}^{-1}/\text{min}^{-0.5}$ ). A plot of  $q_t$  vs.  $t^{0.5}$  giving straight line confirms intraparticle diffusion sorption. Figure 7 shows that the plot is not linear, and the moreso do not pass through the origin. The presence of multi-linearity indicates that two or more steps occur, and then the intraparticle diffusion could not be the only mechanism involved. The first, the gradual adsorption stage (ca.  $t^{0.5}$  range from 0 to 2.24  $\text{min}^{0.5}$ ; i.e. from 0 up to 5 minutes of adsorption period) is the external surface adsorption or instantaneous adsorption stage. The second portion is the sharper portion stage (ca.  $t^{0.5}$  range from 3.36 to 9.49  $\text{min}^{0.5}$ ; i.e. from 10 up to 90 minutes of adsorption period), where the intraparticle diffusion is rate- controlled ( $k_{int} = 5.8493 \text{ mg}/\text{g}^{-1}/\text{min}^{-0.5}$  and  $R^2 = 0.9506$ , see Figure 12). The third portion is the final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution

**Figure 10.** Pseudo-first order model of AB-15 by using different temperature (25, 35, 45, and 55 °C), dosage = 2  $\text{g}/\text{L}^{-1}$ , 80 rpm, and  $C_i = 100 \text{ mg}/\text{L}^{-1}$





**Figure 11.** The relationship and trend of the  $q_{exp}$ . vs.  $q_{cal}$ . Obtained by pseudo-first order model



**Figure 12.** Weber-morris intra-particle diffusion kinetic model,  $T = 55\text{ }^{\circ}\text{C}$ ,  $t = 30\text{ min}$ ,  $C_i = 100\text{ mg/L}^{-1}$

## Conclusion

In this work, acid blue-15 (AB-15) dye has been successfully removed from the water using chitosan, achieving the highest removal percentage (99%) during the first 50 minutes (equilibrium time) of batch sorption. The sorption of AB-15 by chitosan is not highly influenced by the initial concentration of AB-15 ( $C_i=10$  to  $100\text{ mg/L}^{-1}$ ), pH of the basic medium, dosage ( $>2\text{ g/L}^{-1}$ ) and temperature ( $T>35\text{ }^{\circ}\text{C}$ ). The sorption mechanism of AB-15 dye onto chitosan has spontaneous and favorable physisorption process. Weber-morris intraparticle diffusion model shows that two or more steps occur following the external surface adsorption, and then followed by the intraparticle diffusion or physisorption process (rate- controlled step), and finally equilibrium and saturation stage. The new information in this study suggest using the Chitosan as natural filtering materials for removing the AB-15 from the water.

## Disclosure Statement

No potential conflict of interest was reported by the authors.

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