

# The Applicability of Fe (III)-Chitosan Complex for the Sorption of Single-Phase Acid Blue-15 Dye from Water

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## Abstract

The objective of this work concern with the applicability of Fe (III)-chitosan complex for the adsorption of single-phase Acid Blue-15 (AB-15) dye from water through a batch process. The maximum removal of dye increased with the increase of pH, the dosage of Chitosan-Fe (III) adsorbent and temperature of the reaction vessel. However, the percentage of removal decreases with the increase in the initial concentration of the AB-15 solution. The results show that the pH of the interaction medium shows a significant influence in the adsorption process achieving the maximum removal in the basic medium. The adsorption of AB-15 on the Fe (III)-chitosan complex sorbent fits better with the Langmuir ( $R^2 = 0.998$ ) than the Freundlich model. The adsorption Kinetics follows the pseudo-second-order ( $R^2 > 0.998$ ) and not the pseudo-first-order model. The obtained results of this study show that Fe (III)-chitosan complex sorbent has a potential application as a membrane to remove the AB-15 from industrial effluents.

**Keywords:** Acid Blue-15; Dye; Sorption; Fe (III)-chitosan complex; Langmuir; Pseudo-second order

## Introduction

It is known that dyes contaminate the water medium through industrial processes and washing clothes and textiles [1-2]. Acid Blue-15 dye is considered as one of these dyes that has health and environmental impacts [3-5]. Acid Blue-15 dye is a type of azo dyes, which has a complex and resonance-stabilized triphenylmethane (TPM). This complex resists degradation in the environment causing a threat for human life. Therefore, our efforts are going toward the removal of such dyes from the aqueous system. The traditional processes focus on the removal of dyes by using physical and chemical methods such as coagulation [6], membrane filtration [7], photocatalytic degradation [8-9], Nano filtration and ozonolysis, oxidation [10], and microbiological decomposition [11]. In general, 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 many dyes cannot be easily decomposed [12]. Therefore, the most efficient one is the adsorption process [13-16]. Several cheap and safe adsorbent is 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 *Lemna minor* [29]. More example for a removal of AB15 dye from aqueous solutions are Red mud [30], wood and sawdust [31], fly ash [32], wheat straw [33], apple pomace [33], orange peel [34-36], banana peel [37], leaf [38], Soybean cake [39], eggshell membrane [40], lignocellulosic waste biomass activated carbon [41]. Therefore, in literature, we find little works in the removal and sorption of Acid Blue 15. These articles focus into the utilization of the various adsorbents, for example, *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 freshwater algae [53].

Recently, our research group utilizes the chitosan as flocculating and chelating agents in wastewater treatment and drinking water for removing heavy metals and synthetic dyes as a potential application as membrane filters. One of our recent publication concerns with the sorption of Acid Blue-15 (AB-15) dye from the water by using chitosan. The batch process achieves the highest removal percentage (99%) during the first 50 minutes (equilibrium time) of batch physisorption [54]. The new reported study, concerning with the sorption of iron (III) ion from water by chitosan [55], guide us to produce Fe (III)-chitosan complex as an adsorbent for

removal of anionic dyes such as AB-15. This may produce large macromolecular cross linked chitosan; however it increase the positive.

Up to date, we do not find any work related to the sorption of the Acid Blue-15 by using Fe (III)-chitosan complex sorbent. Therefore, the main purpose of the study is to utilize the Fe (III)-chitosan complex as adsorbent to remove of Acid Blue dye from water. 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 Fe (III)-chitosan complex sorbent.

## Material and Methods

### Preparation of Fe (III)-chitosan complex sorbent

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  $(228 \pm 5)\mu\text{m}$ . Iron (III)-chitosan complex formed by adsorption of iron(III) ion onto chitosan as either Penta- or hexacoordinated Fe (III) [55]. Twenty milligrams of the chitosan sample {in flakes forms  $(228 \pm 5)\mu\text{m}$ }, and a 4-mL sample of an aqueous iron (III)  $(\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O})$  solution with a  $100\text{ mg L}^{-1}$  concentration at  $\text{pH} = 1.42$  of 1%  $\text{HNO}_3$  were mixed in the reaction vessel and thermostatically maintained at 80 rpm and  $30^\circ\text{C}$  for 40 minutes.

### Reagents

All chemicals were used as received as an analytical grade. Acid Blue-15 (AB-15) was purchased from Alvan Sabet CO ( $M_{\text{wt}} = 775.95\text{ g/mol}$ ; the chemical formula is  $\text{C}_{42}\text{H}_{46}\text{N}_3\text{NaO}_6\text{S}_2$ ). The stock solution ( $1000\text{ mg L}^{-1}$ ) was prepared by dissolving a stoichiometric amount of AB-15 powders in 1 L of distilled water. Standard solutions of AB-15 ( $10, 30, 50, 70,$  and  $100\text{ mg L}^{-1}$ ) were prepared by appropriate dilution from  $1000\text{ mg L}^{-1}$  stock solution. An "initial" pH and its subsequent adjustment for all experimental runs were conducted less than 7.00 at the maximum value. NaOH ( $0.1\text{ mol L}^{-1}$ ), HCl ( $0.1\text{ mol L}^{-1}$ ) and  $\text{HNO}_3$  (65%) were purchased from Merck (Darmstadt, Germany). 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  $(228 \pm 5)\mu\text{m}$ . The salt of Iron (III) ion  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was purchased by commercial providers from Fluka Chemika.

### 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 by using the Ultraviolet Visible Spectroscopy (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  $55^\circ\text{C}$ , Isothermal Gefellschaft Fur 978). To ensure accuracy in the preparation, analytical balance is used (Sartorius, CP324-S/ management system certified according to ISO 9001). The chemical functional groups of the Fe (III)-Chitosan complex are detected by Fourier-Transform Infrared Spectroscopy (Thermo Scientific Nicolet IR200 FT-IR,  $400\text{-}4000\text{ cm}^{-1}$ ).

### 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 Fe (III)-chitosan complex sorbent. It equals a number of AB-15 removed from the aqueous solution. Mathematically can be expressed in equations 1-2 [54,56,57]:

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

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

Where

$q_e$ : AB-15 amount adsorbed on the Fe (III)-chitosan sorbent surface at equilibrium ( $\text{mg g}^{-1}$ ).

$q_t$ : AB-15 amount adsorbed on Fe (III)-chitosan sorbent surface at a specific time ( $\text{mg g}^{-1}$ ).

$C_i$ : Initial concentration of AB-15 in the aqueous solution ( $\text{mg L}^{-1}$ ).

$C_e$ : Equilibrium concentration or final concentration of AB-15 in the aqueous solution ( $\text{mg L}^{-1}$ ).

$C_t$ : The final concentration of AB-15 in the aqueous solution ( $\text{mg L}^{-1}$ ) at a specific time.

S: Dosage (slurry) concentration of Fe (III)-chitosan complex 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 Fe (III)-chitosan complex sorbent. The percent adsorption (%) was also calculated using the following equation

$$\% \text{ adsorption} = \frac{C_i - C_e}{C_i} \times 100\% \quad (4)$$

### Effect of AB-15 Initial Concentration

Adsorption measurements were made by a batch technique at a temperature of  $35 (\pm 1) ^\circ\text{C}$ . The stopper plastic flasks containing 50 mL of different initial concentrations ( $C_i = 10, 30, 50, 70$  and  $100 \text{ mg L}^{-1}$ ) of AB-15 and  $2 \text{ g L}^{-1}$  of Fe (III)-Chitosan complex were shaken vigorously using a thermostatic mechanical shaker for 50 minutes. The agitation speed (80 rpm) was kept constant for each run to ensure equal mixing. At the end of the equilibrium time, the flasks were removed from the shaker and then the supernatant solution in each flask was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

### Effect of Temperatures

The adsorption experiments were carried out by shaking vigorously the stopper plastic flasks containing 50 mL of  $100 \text{ mg L}^{-1}$  of AB-15 dye and  $2 \text{ g L}^{-1}$  of Fe (III)-Chitosan complex by using a thermostatic mechanical shaker at constant contact time (50 minutes) and agitation speed (80 rpm) with varying temperatures (25, 35, 45 and  $55 ^\circ\text{C}$ ). At the end of the equilibrium time, the flasks were removed from the shaker, and then Fe (III)-Chitosan complex particles was filtered using filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed. All the reported results were the average of at least triplicate measurements.

### Effect of dosage

The adsorption experiments were carried out by a batch technique at a temperature of  $35 ^\circ\text{C} (\pm 1 ^\circ\text{C})$ . Different doses of Fe (III)-Chitosan complex (2, 6, 10, 14 and  $20 \text{ g L}^{-1}$ ) were placed in a 100 mL stopper plastic flask containing 50 mL of aqueous AB-15 ( $C_i = 100 \text{ mg L}^{-1}$ ). The solutions were shaken vigorously by using a thermostatic mechanical shaker for 50 minutes. The agitation speed (80 rpm) was kept constant for each run to ensure equal mixing. At the end of the equilibrium, the flasks were removed from the shaker, and then the solution was filtered using filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed. All the reported results were the average of at least triplicate measurements.

### Effect of contact time

The sorption experiments were carried out by shaking 0.1 g of the Fe (III)-chitosan complex 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  $55 ^\circ\text{C}$ ). 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 flasks were removed from the shaker and then the supernatant solution in each flask was filtered using filter paper (Whatman No. 41). The filtrate samples were analyzed. All the reported results were the average of at least triplicate measurements.

### Effect of pH

The adsorption experiments were carried out by a batch technique at a temperature of  $35 ^\circ\text{C} (\pm 1 ^\circ\text{C})$ . Different doses of Fe (III)-chitosan complex sorbent (2, 4, 7 and  $10 \text{ g L}^{-1}$ ) were placed in a 100mL stopper plastic flask containing 50mL of aqueous AB-15 ( $C_i = 100 \text{ mg L}^{-1}$ ). The solutions were shaken vigorously by using a thermostatic mechanical shaker for 90 minutes. The agitation speed (80 rpm) was kept constant for each run to ensure equal mixing. At the end of the equilibrium, the flasks were removed from the shaker, and then the solution was filtered using filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed. All the reported results were the average of at least triplicate measurements.

### Adsorption Isotherm Models

The isotherm experiments were conducted by using 10, 30, 50, 70 and  $100 \text{ mg L}^{-1}$  of AB-15 dye solutions. The mixtures containing 0.1 g Fe (III)-chitosan complex sorbent and 50 ml of AB-15 dye solutions were stirred under the shaking conditions of 80 rpm, 50 minutes and  $35 ^\circ\text{C}$ . Afterward, the flasks were removed from the shaker, and then Fe (III)-chitosan solid was filtered by filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed. All the reported results were the average of at least triplicate measurements.

### Adsorption Kinetic Models

For the kinetic studies, a number of samples containing 0.1 g Fe (III)-chitosan complex sorbent and 50 ml of AB-15 solutions ( $C_i = 100 \text{ mg L}^{-1}$ ) were placed in the 100 ml flasks. The initial pH was 7. These flasks were agitated using a temperature-controlled shaker (study at various  $T = 25, 35, 45$  and  $55 ^\circ\text{C}$ ) at 80 rpm for 50 minutes. Afterwards, the flasks were removed from the shaker at every 10 minutes in the first 60 minutes and then 30 minutes until the end of 180 minutes. The Fe (III)-chitosan complex solid

was filtered using filter paper (Whatman No. 41). The filtrate supernatant solutions were analyzed. All the reported results were the average of at least triplicate measurements.

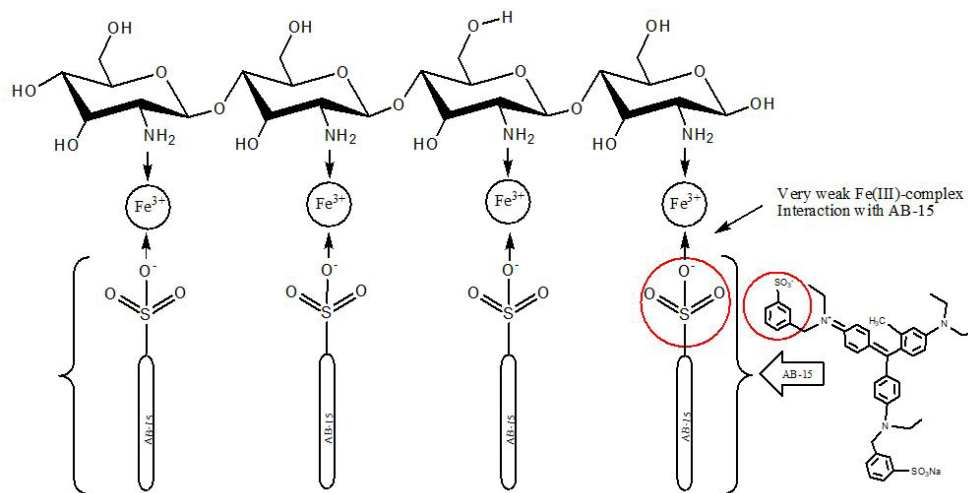
## Results and Discussion

### FTIR Spectroscopy

FTIR spectra of chitosan [53] and Fe (III)-chitosan complex show that both two spectra are identical except for the loss of the peak at  $1554\text{ cm}^{-1}$  due to N-H bending vibrations of chitosan. This can be interpreted as the formation of a Fe (III)-chitosan complex through the involvement of N atoms on the chitosan backbone. The nonexistence of any new absorption band or shifting indicates the adsorption of Fe (III) ion onto chitosan forming a weak Fe (III)-chitosan complex. Therefore, physical and chemical properties of chitosan may be modified by using Fe (III) ion to make it a suitable to capture anionic dyes and anionic pollutant species.

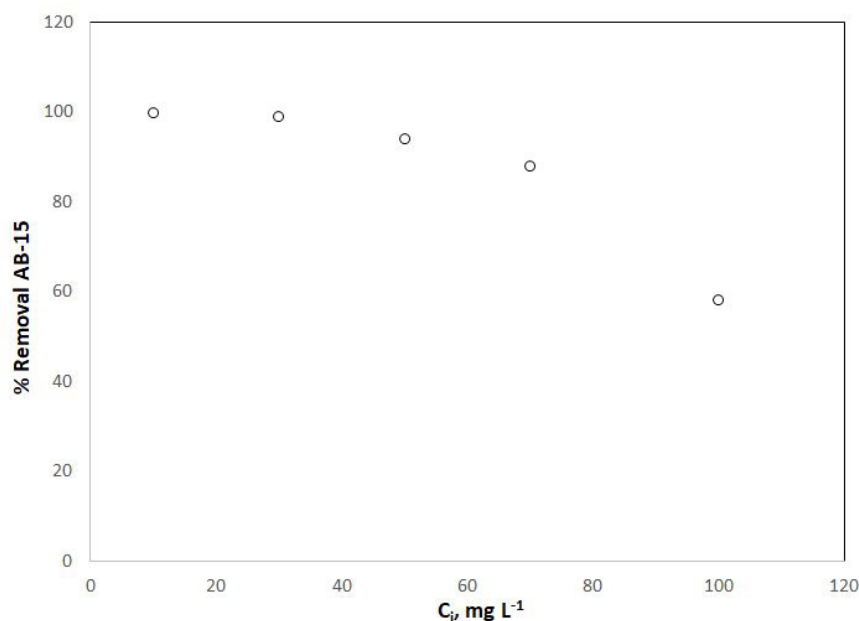
### The sorption of AB-15 onto the Fe (III)-chitosan complex sorbent

The sorption of AB-15 onto the solid particles of the Fe (III)-chitosan complex sorbent could be performed through the suggested chemisorption mechanism through the electrostatic interaction of AB-15 with the iron onto on the Fe (III)-chitosan sorbent surface (see Scheme 1). The sorption of AB-15 onto Fe (III)-chitosan complex sorbent achieves the suggestion of a chemisorption mechanism of Lagergren pseudo-second-order model (ca.  $R^2 = 0.998$ ). This idea can be confirmed by the FTIR spectra of Fe (III)-chitosan complex sorbent before and after sorption of AB-15 dye. In contrast with the reported of our study [54] and others [58,59], regarding the sorption of AB-15 onto chitosan only, achieve the suggestion of a physisorptions mechanism of Lagergren pseudo-first-order model.



**Scheme 1:** The possible mechanism of adsorption of AB-15 onto Chitosan adsorbent

### Effect of AB-15 Concentration



**Figure 1:** Effect of initial concentration of AB-15 ( $t = 50$  min,  $35\text{ }^\circ\text{C}$ ,  $50\text{ ml}$ ,  $0.1\text{ g}$  Fe (III)-chitosan complex sorbent,  $80\text{ rpm}$ )

The effect of the initial AB-15 concentration on the sorption efficiency is investigated in the concentration range of 10-100 mg L<sup>-1</sup> at 35 °C. Figure 1 shows that the initial concentration of AB-15 has a highly significant influence on the sorption process; in general the percentage of removal decreases with increasing the initial concentration of AB-15 causing, which causes a decrease in the sorption efficiency of the Fe (III)-Chitosan adsorbent. This may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand, the increase in initial dye concentration will cause an increase in the adsorption capacity of the adsorbent, which may be due to the high driving force for mass transfer at a high initial dye concentration. This behavior agrees relatively with the results obtained by using chitosan [54] and Red mud for removal of AB15 dye from aqueous solutions [30].

### Effect of Temperature

The influence of temperature on the removal of AB-15 from the aqueous solution by using Fe (III)-chitosan complex sorbent has been studied through the applied of a variety of temperatures 25, 35, 45 and 55 °C. It is observed that the removal percentage increased with increasing temperature (Figure 2); wherein it is highly influenced by raising the value of temperatures. The maximum removal percentage at 55 °C is 85 %, while the lowest percentage is 58 % (approx.) at a temperature of 25 °C. This indicates that high temperature could enhance the chemical interaction of AB-15 with Fe (III)-chitosan sorbent surface (chemisorption) [59]. This type of interaction is not typical to the adsorption of the AB-15 dye by chitosan [54].

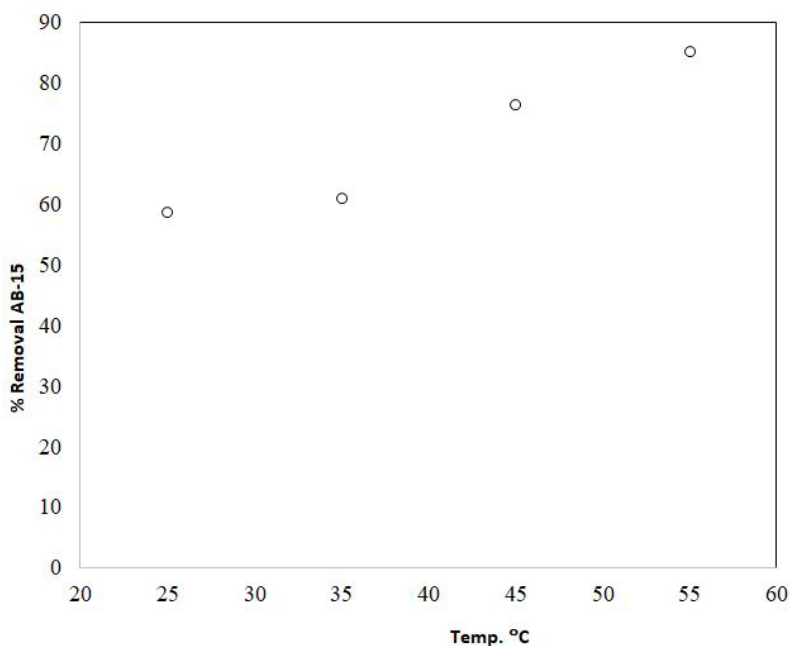


Figure 2: Effect of temperature (dosage of Fe (III)-chitosan sorbent = 2 g L<sup>-1</sup>, C<sub>i</sub> = 100 mg L<sup>-1</sup>, 80 rpm, pH<sub>i</sub> = 7.00)

### Dosage effects of Fe (III)-chitosan complex sorbent

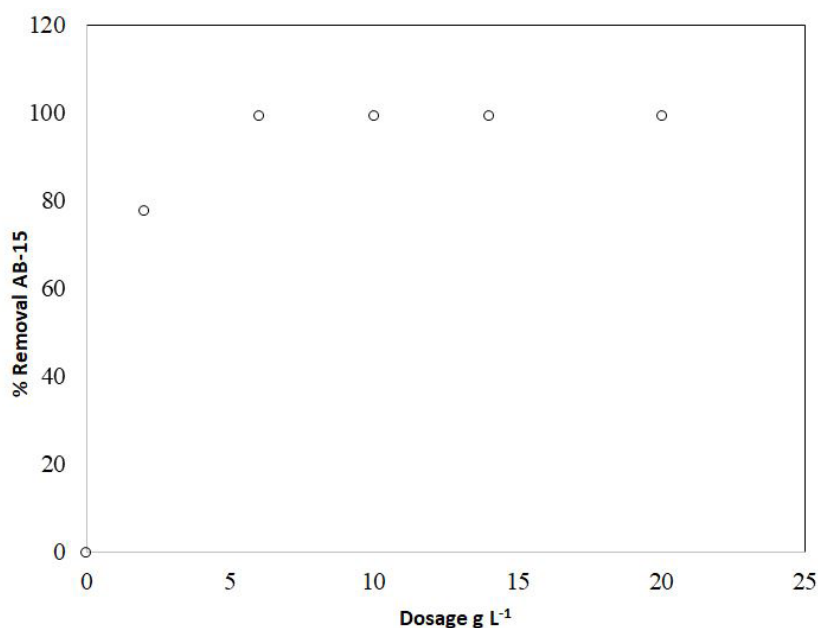


Figure 3: Effect of Fe (III)-chitosan complex sorbent dosage (t = 50 min, 50 ml, T = 35 °C, C<sub>i</sub> = 100 mg L<sup>-1</sup>, 80 rpm, pH<sub>i</sub> = 7.00)

The removal percentage of AB-15 from 100 mg L<sup>-1</sup> solutions using different dosages of Fe (III)-chitosan complex sorbent (2, 6, 10, 14 and 20 g L<sup>-1</sup>) has been described in Figure 3. The removal percentage increases sharply as the adsorbent dose increases up to dosage = 6 g L<sup>-1</sup>. This is due to the reason of increasing the number of the iron (III) ion as an active site in the Fe (III)-chitosan sorbent surface area, as mentioned before in pieces of literature [58,60]. The maximum removal (Ca 100%) has been observed using the dosage of 6 g L<sup>-1</sup>. These results are in line with our study by using chitosan sorbent [54,62], and others such as adsorption of Acid Dyes onto Bentonite and Surfactant-modified Bentonite [60-62].

### 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 Ca 99% is achieved with pH = 10, while it is 88% by using pH = 2. This indicates that a significant influence of the pH value on the sorption process of AB-15 onto Fe (III)-chitosan complex sorbent. In general, the percentage removal of AB-15 from water was higher in basic solutions than in neutral and acidic conditions. From another direction, amino groups (-NH<sub>2</sub>) in the Fe (III)-chitosan complex sorbent can be easily protonated to form -NH<sub>3</sub><sup>+</sup> groups and eliminate Fe (III) ion from the surface (destroy the Fe (III)-chitosan complex). This lead to decrease the number of the iron ion on the surface and then decrease the active sites and efficiency of sorption AB-15 in the Fe (III)-chitosan complex surface. When the pH increases toward the basic medium (pH > 7), the number of protonated amines decrease. This will fixed the Fe (III) on the surface of chitosan, and the AB-15 interaction increases on the surface. This behavior is confirmed by Borsagli, *et al.* [63].

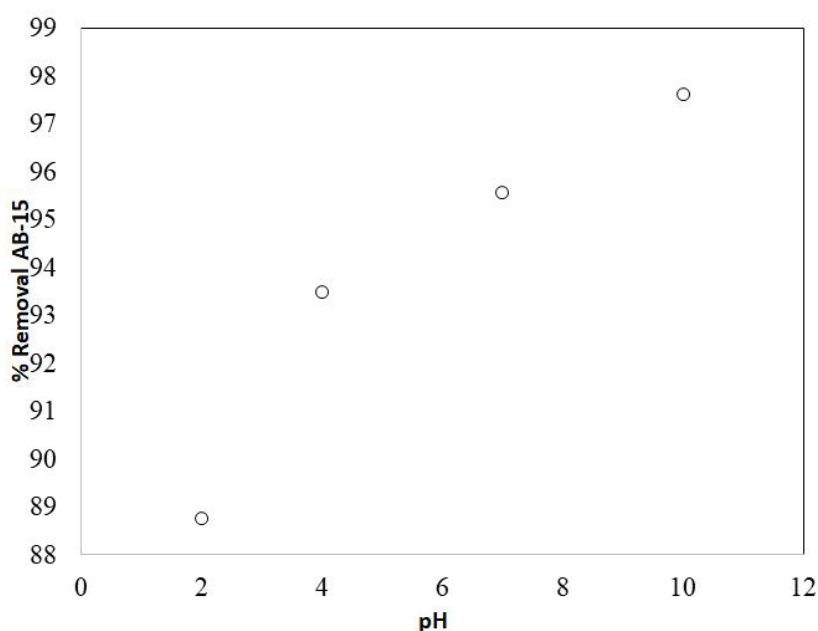


Figure 4: Effect of pH (t = 90 min, C<sub>i</sub> = 100 mg L<sup>-1</sup>, 35 °C, dosage of Fe (III)-chitosan complex = 2 g L<sup>-1</sup>, 80 rpm)

### Adsorption Isotherm

The maximum sorption capacity of AB-15 can be determined by the equilibrium distribution between the Fe (III)-chitosan complex 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 and resulted data as reported in selected kinds of literature [57,64-67]. Isotherm studies were conducted at 35 °C by varying the initial concentration of AB-15. The representative initial concentration (10, 30, 50, 70, and 100 mg L<sup>-1</sup>) of AB-15 were mixed with slurry concentrations (dose) of Fe (III)-chitosan complex (=2 g L<sup>-1</sup>) for 50 minutes, which was the equilibrium time for the Fe (III)-chitosan complex and AB-15 chemisorptions mixture.

The linear form of the Langmuir model is given by:

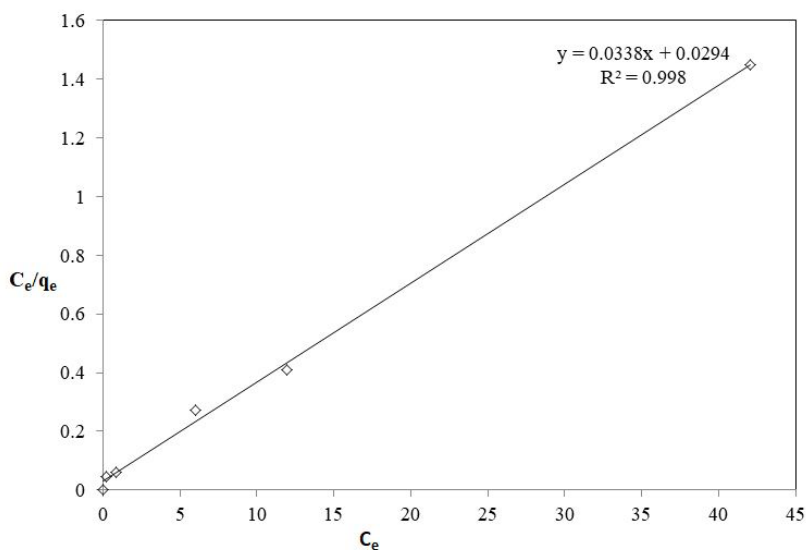
$$\frac{C_e}{q_e} = \frac{1}{q_{max}b} + \frac{1}{q_{max}}C_e \quad (5)$$

Where:

$q_e$ : AB-15 amount (mg) on the Fe (III)-chitosan complex (g) at equilibrium (mg g<sup>-1</sup>); and  $q_{max}$  is the maximum dye uptake per unit dosage of Fe (III)-chitosan complex sorbent (mg g<sup>-1</sup>), which is related to adsorption capacity. The  $b$  is Langmuir constant (L.mg<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 = 7.00 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 ( $R^2= 0.998$ ), which is a measure of goodness-of-fit and the general empirical formula of the Langmuir model by  $\frac{C_e}{q_e} = 0.0338C_e + 0.0294$ , as shown in Figure 5. Our results are in a good qualitative agreements with those found from adsorption of AB-15 onto our recent study by using chitosan [54], red muds adsorbent [30] and the adsorption of the Acid Blue-25 (AB-25) onto raw diatomite [68].



**Figure 5:** The linearized Langmuir adsorption isotherms for AB-15 adsorption onto Fe (III)-chitosan complex sorbent (dosage = 2 g L<sup>-1</sup>, Temperature = 35 °C, agitation speed = 80 rpm and contact time = 50 min)

On the other side, 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.

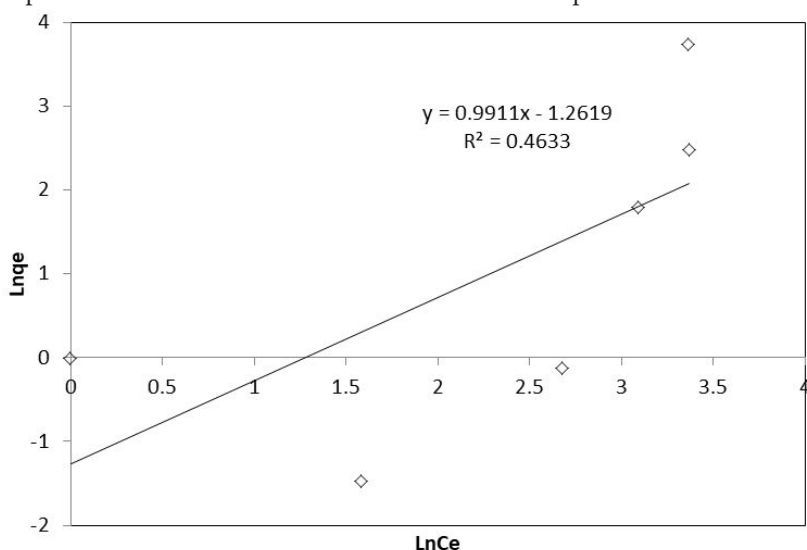
The linear form of the Freundlich model is also given by:

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

Where  $K_F$  and  $n$  are 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  $\ln q_e = 0.9911 \ln C_e - 1.2619$  with  $R^2 = 0.4633$ . The Langmuir model has a better fitting model than the Freundlich model does. Figure 6 shows that the Langmuir model has a higher correlation regression coefficient ( $R^2 = 0.998$ ) than the Freundlich model. The smaller the value of the heterogeneity parameter ( $1/n$ ) means the greater the expected heterogeneity [69,70]. The results exhibit a value of  $\frac{1}{n} \left( 0 < \left(\frac{1}{n}\right) < 1 \right)$  indicating the

more heterogeneous physiosorptions of AB-15 onto Chitosan as mentioned in the reported works of literature [57,71].



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

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 [71,72] 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:

$$RL = 1/(1+bC_i) \quad (7)$$

Where  $C_i$  is the initial AB-15 concentration  $\text{mg L}^{-1}$ . The calculated  $R_L$  was less than 1.0, indicating for the favorable adsorption as shown in Figure 7.

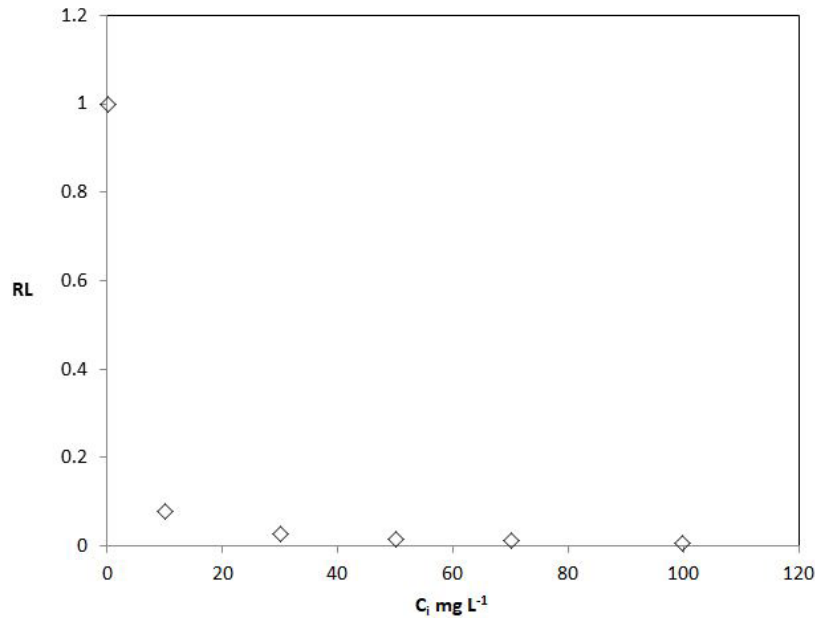


Figure 7: The separation factor of sorption vs. initial concentration of AB-15 dye

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

$$\Delta G^\circ = -RT \ln K_L \quad (8)$$

Wherein,  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  is the absolute temperature in Kelvin

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

Where  $M_A$  is the molar weight of sorbate ( $\text{AB-15} = 775.95 \text{ g mol}^{-1}$ , where  $K_L = 892.110 \text{ L mol}^{-1}$ , and  $b$  is the equilibrium constant, related to the Langmuir constant,  $b (=1.1497)$ .

The value of standard Gibbs free energy change calculated at  $35^\circ \text{C}$  is found to be  $-17.405 \text{ kJ mol}^{-1}$ . The negative sign for ( $\Delta G^\circ$ ) indicates the spontaneous nature of AB-15 adsorption on the Fe (III)-chitosan complex sorbent surface.

To justify the validity of Fe (III)-chitosan complex as a sorbent for the removal of AB-15 from the aqueous solution, the adsorption potentials, as shown in Table 1.

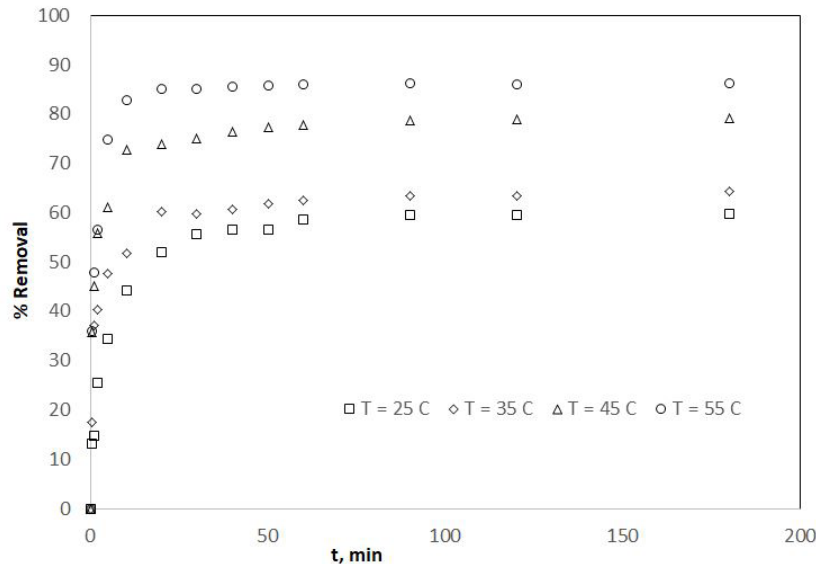
Adsorbent		Langmuir			Freundlich				
		$q_{\max}$ ( $\text{mg g}^{-1}$ )	$b$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_f$	—	$R^2$	Isotherm	Ref
1	Activated carbons prepared from sunflower seed hull	75 - 110		0.994				Langmuir	[43]
2	Mud red	3.11	0.41	0.995	1.74	0.39	0.921	Langmuir	[30]
3	<i>Azolla filiculoides</i> 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	[54]
5	Fe(III)-chitosan complex sorbent	29.586	1.1497	0.998	0.28	0.99	0.463	Langmuir	herein

Table 1: List the compression of the adsorption isotherm of AB-15 onto various adsorbents



### Sorption Kinetic Model

Figure 8 shows the effect of contact time regarding the adsorption of Ab-15 onto Fe (III)-chitosan complex sorbent. 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 surface area of the Fe (III)-chitosan complex sorbent. The final equilibrium of sorption starts after 40 minutes yielded a maximum removal of 99% (approx.) at T = 55 °C. 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 iron (III) ion onto Fe (III)-chitosan complex sorbent as an active site. Similar results have been reported in the literature for the removal of dyes by chitosan [54,59] and activated clay [73] adsorbents.



**Figure 8:** Effect of contact time on AB-15 sorption by using different temperature (25, 35, 45, and 55 °C), dosage = 2 g L<sup>-1</sup>, 80 rpm, and C<sub>i</sub> = 100 mg L<sup>-1</sup>, pH<sub>i</sub> = 7.0

The kinetics sorption models of pseudo-first-order and pseudo-second-order assume that adsorption of AB-15 from the 100 mg L<sup>-1</sup> of an aqueous solution onto Fe (III)-chitosan complex is a pseudo-chemical reaction. The role of contact time was studied under the shaking conditions, for instance, the pH of the solution was 7.0, 80 rpm, 2 g L<sup>-1</sup> dosage of Fe (III)-chitosan complex sorbent and by applying 25, 35, 45 or 55 °C. Samples were collected at regular intervals and then analyzed after filtration. The adsorption rate can be determined, respectively, for the pseudo-first-order kinetic model (Eq. 10) [74,75] and the pseudo-second-order kinetic model (Equation 11) [75,76] in their integral expression by the following equations:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{10}$$

Where  $q_e$  and  $q_t$  (mg g<sup>-1</sup>) = the amounts of adsorbed AB-15 at equilibrium and at the time ( $t$ ), respectively,

$k_1$  (min<sup>-1</sup>) = the pseudo-first-order rate constant,

$t$  (minutes) = contact time of adsorption.

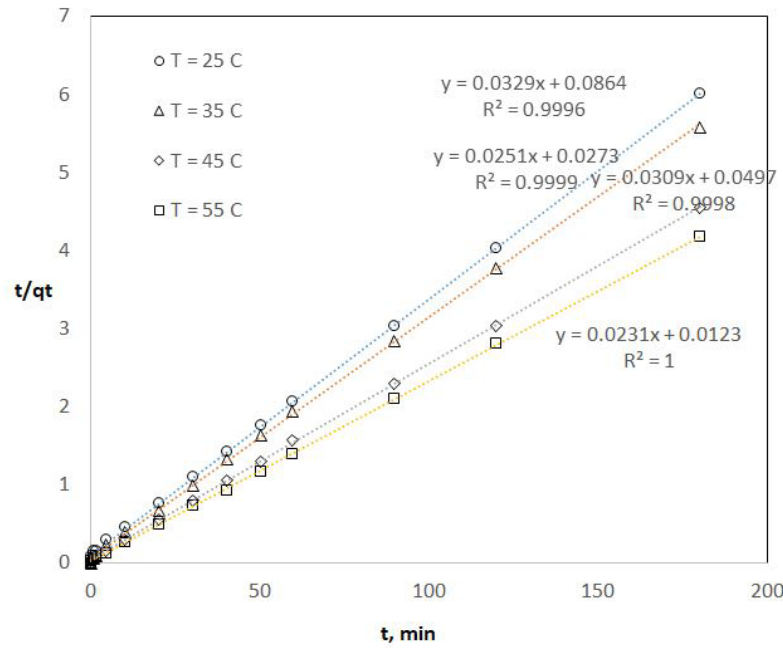
The plot of  $\ln(q_e - q_t)$  versus  $t$  results the determination coefficient value  $R^2$  very small (approx. 0.564). Therefore, the experimental data does not fit to the pseudo-first order. Therefore, it is better to use the pseudo-second-order kinetic model as an integrated form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

Where  $k_2$  = the equilibrium rate constant of the pseudo-second-order kinetic model (g mg<sup>-1</sup> min<sup>-1</sup>). The plot of  $\frac{t}{q_t}$  versus  $t$  results the determination coefficient value ca.  $R^2 = 0.999$  as shown in Figure 9. Therefore, the experimental data fit better to the pseudo-second-order. The rate constant of  $k_2$  and  $q_e$  can be determined a straight line of slope  $1/q_e$  and intercept of  $1/(k_2)$  as shown in Table 2.

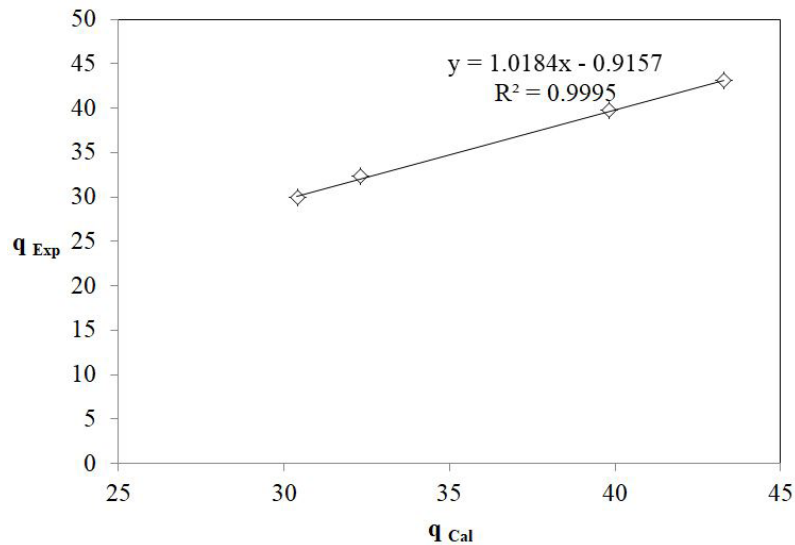
T, °C	Eq.time (min.)	k <sub>2</sub> (g mg <sup>-1</sup> min <sup>-1</sup> )	q <sub>e</sub> , Exp (mg g <sup>-1</sup> )	q <sub>e</sub> , Calc (mg g <sup>-1</sup> )	R <sup>2</sup>
25	60	0.01253	29.88913	30.3951	0.9996
35	50	0.02308	39.66522	39.840	0.9999
45	30	0.0192114	32.21957	32.3624	0.9998
55	20	0.04339	43.1413	43.2900	1.0000

**Table 2:** The parameters of the pseudo-second-order kinetic model



**Figure 9:** Pseudo-second order model of AB-15 by using different Temperature (25, 35, 45, and 55 °C), dosage = 2 g L<sup>-1</sup>, 80 rpm, and C<sub>i</sub> = 100 mg L<sup>-1</sup>

The adsorption model of AB-15 transport onto Fe (III)-chitosan complex surfaces are regarded as pseudo-second-order. Furthermore, the comparison of  $q_e$  values from the experimental work of this study and calculated one of the pseudo-second-order kinetic model (difference smaller) also show the availability of this model (see Figure 10).



**Figure 10:** The relationship and trend of the  $q_{exp}$ . Vs.  $q_{cal}$ . Obtained by Pseudo-second order model

To determine the diffusibility of the AB-15 into the Fe (III)-chitosan complex adsorbent, Weber-Morris intraparticle diffusion model [77] were 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 (mg g<sup>-1</sup>) and  $k_{int}$  is the intraparticle diffusion rate constant (mg g<sup>-1</sup> min<sup>-0.5</sup>). A plot of  $q_t$  vs.  $\sqrt{t}$  giving straight line confirms intraparticle diffusion sorption. Figure 11 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 (from 0 up to 30 minutes of adsorption period) is the external surface adsorption or instantaneous adsorption stage. The second portion is the sharper portion stage (from 30 up to 60 minutes of adsorption period), where the intraparticle diffusion is rate- controlled ( $k_{int} = 5.8493$  mg g<sup>-1</sup> min<sup>-0.5</sup> and  $R^2 = 0.9506$ , see Figure 11). The third portion is the final equilibrium stage ( $t > 60$  min.) where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution.

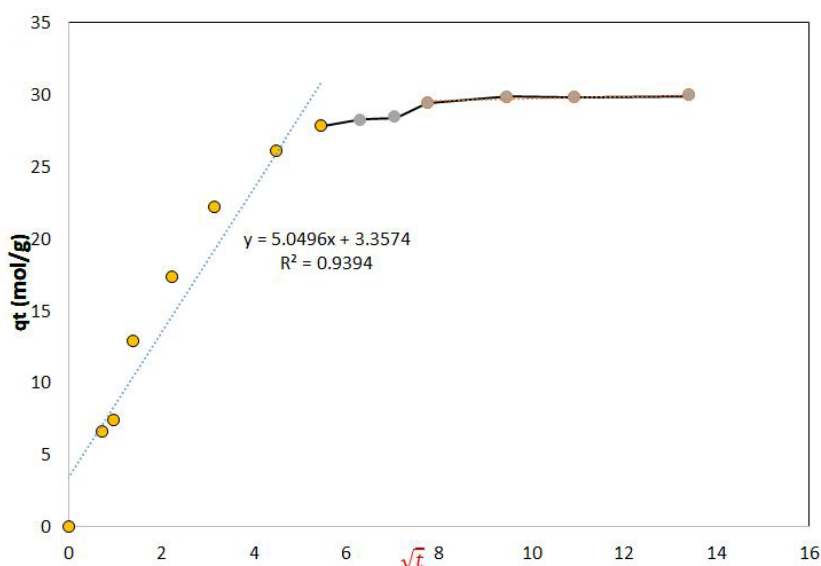


Figure 11: Weber-Moris intra-particle diffusion kinetic model,  $T = 55\text{ }^{\circ}\text{C}$ ,  $t = 30\text{ min}$ ,  $C_i = 100\text{ mg L}^{-1}$

## Conclusion

In this work, Acid Blue-15 (AB-15) dye is removed from the water using Fe (III)-chitosan complex adsorbent, achieving the highest removal percentage (99%) during the first 50 minutes (equilibrium time) of batch sorption. The sorption of AB-15 by Fe (III)-chitosan complex adsorbent is 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 ( $T = 55\text{ }^{\circ}\text{C}$ ).

The sorption of AB-15 onto Chitosan has followed the pseudo-second-order model. The highest kinetic rate constant  $k_2$  of sorption is achieved at  $T = 55\text{ }^{\circ}\text{C}$ . Wherein, the physical meaning indicates that the sorption of AB-15 onto Fe (III)-chitosan complex adsorbent achieve chemisorption. The equilibrium parameter ( $R_L$ ) is less than 1.0 indicating for the favorable sorption. The experimental isotherm is largely identical with the Langmuir isotherm model. The negative sign for ( $\Delta G^{\circ}$ ) indicates the spontaneous nature of AB-15 adsorption on the Fe (III)-chitosan complex adsorbent surface.

Weber-Moris intraparticle diffusion model shows that two or more steps occur as follows: (i) the first stage is the external surface adsorption or instantaneous adsorption stage within 0 up to 30 minutes of adsorption period; (ii) The second stage is the intraparticle diffusion stage (rate- controlled step) within 30 up to 60 minutes of the adsorption period (it is a chemisorption process); (iii) Equilibrium and saturation stage from  $t > 60\text{ min}$ . The final stage is the equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentrations in the solution

The new information in this study suggests for using the Fe (III)-chitosan complex adsorbent as natural filtering materials for removing the AB-15 from the water.

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