

Technical paper

# Removal of Methylene Blue from Aqueous Solutions by Wheat Bran

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## Abstract

In this work, a fundamental investigation on the removal of methylene blue from aqueous solutions by wheat bran is conducted in batch conditions. Removal kinetic data are determined, and the effects of different experimental parameters, such as wheat bran mass, initial concentration of methylene blue, agitation speed, solution pH, particle size, temperature, and ionic strength on the kinetics of methylene blue removal are investigated. The cationic dye recovery increases with an increase of sorbent mass, solution pH, and temperature. Methylene blue removal decreases with an increase of initial concentration, particle size, and ionic strength. The agitation speed showed a limited influence on the removal kinetics. Modeling of kinetic results shows that sorption process is best described by the pseudo-second order model, with determination coefficients higher than 0.996 under all experimental conditions. The applicability of both internal and external diffusion models shows that liquid-film and particle diffusion are effective sorption mechanisms. The activation energy of sorption calculated using the pseudo-second order rate constants is found to be 13.41 kJ mol<sup>-1</sup> from an Arrhenius plot. The low value of the activation energy indicates that sorption is an activated and physical process. Thus, wheat bran, a low cost and easily available biomaterial, can be efficiently used as an excellent sorbent for the removal of dyes from wastewater. It can be safely concluded that wheat bran is much economical, effectual, viable, and can be an alternative to more costly adsorbents.

**Keywords:** Removal; methylene blue; wheat bran; sorption; kinetics.

## 1. Introduction

Contamination of the environment from a variety of sources has become an increasingly serious problem in recent years. The release of dyes into wastewaters by various industries poses serious environmental problems due to various dyes persistent and recalcitrant nature. The presence of dyes in waterways is easily detectable even when released in small concentrations. For some dyes, the dye concentration of less than 1 ppm in receiving water bodies is highly visible, so that even small quantities of dyes can color large water bodies. This is not only unsightly, but the coloration of the water by the dyes may have an inhibitory effect on photosynthesis affecting aquatic ecosystems. Dyes may also be problematic if they are broken down anaerobically in the sediment, as toxic amines are often produced due to incomplete degradation by bacteria.<sup>1</sup> Some of the dyes or their metabolites are either toxic or mutagenic and carcinogenic.<sup>2,3</sup>

Synthetic dyes have complex aromatic structures which provide them physicochemical, thermal, biological, and optical stability.<sup>4,5</sup> They require usually special treat-

ment strategies. Recently, all governments have been under severe pressure by their people to stop dye-laden effluents to the public watercourses, unless it is treated properly. The USEPA (Environmental Protection Agency) has classified textile wastes into four groups, dispersible, hard-to-treat, high-volume, and hazardous and toxic wastes.<sup>6</sup> Basic dyes are the brightest class of soluble dyes used by the textile industry.<sup>7</sup>

Among the various dyes, methylene blue is a thiazine (cationic) dye, which is most commonly used for coloring among all other dyes of its category. Methylene blue is an important basic dye widely used for printing calico, dyeing, printing cotton and tannin, indicating oxidation-reduction, and dyeing leather, and in purified zinc-free form, it is used as an antiseptic and for other medicinal purposes. Although not strongly hazardous, methylene blue can have various harmful effects. The dye causes eye burns, which may be responsible for permanent injury to the eyes of human and animals. If swallowed, the dye causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting, and diarrhea. It may also cause methemoglobinemia,

cyanosis, convulsions, tachycardia, and dyspnea, if inhaled. It is likely to cause irritation to the skin.<sup>8,9</sup> Hence, it is necessary to remove methylene blue from waste-waters.

Many methods are available for the removal of methylene blue from waters. Among these methods, adsorption is by far the most versatile and widely used method because of its initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances. A number of agricultural waste and by-products of cellulosic origin have been studied in the literature for their capacity to remove dyes from aqueous solutions, such as barley husks, sugarcane bagasse, wheat straw, corncobs, barley husks, tree ferns, wood chips, and corn-cob shreds.<sup>10–13</sup> There are a few works of metal ions sorption by wheat bran, as a by-product of a flour factory.<sup>14–17</sup>

Therefore, there is a need for the search of low cost and easily available biomaterials, which can sorb dyes from waste waters. In this paper, we attempt to use an agricultural by-product, wheat bran, as a sorbent for the removal of methylene blue from water. The bran of wheat is the shell of the wheat seed and is a complex material basically containing lignin and cellulose as the major constituents. Cellulose can be a sorbent for removing dyes from solution.<sup>18</sup>

The objective of this paper is to study the removal of methylene blue from aqueous solutions using wheat bran as abundant and low-cost sorbent. In order to design sorption treatment systems, knowledge of kinetic and mass transfer processes is essential. The applicability of kinetic and mass transfer models has been reported. Additionally, the influence of various operating parameters such as wheat bran mass, methylene blue initial concentration, agitation speed, solution pH, particles size, temperature, and ionic strength on the dye removal has been investigated.

## 2. Materials and Methods

### 2.1. Sorbate and Chemicals

A cationic dye of amorphous nature, methylene blue, having molecular formula  $C_{16}H_{18}N_3S$ Cl (mol. wt. 319.86) with CI Classification Number 52015, is chosen

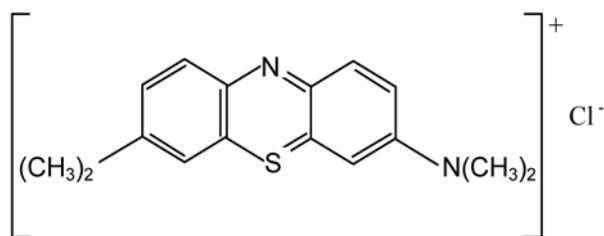


Figure 1. Chemical structure of methylene blue (basic blue 9).

as sorbate. Methylene blue (Basic Blue 9), a basic blue dyestuff, of spectroscopic grade is purchased from Merck; Class: thiazine; Water solubility: 50 g L<sup>-1</sup> (20 °C). Its chemical structure is presented in Figure 1.

The solutions of methylene blue at the desired concentration were prepared with bidistilled water. Freshly prepared bidistilled water was used in all of the experiments. Analytical-grade HCl or NaOH, purchased from Merck, was added for the variation of pH. Analytical-grade NaCl (Merck) was used to study the effect of ionic strength.

### 2.2. Sorbent

The wheat bran was obtained from a market as solid waste and was used for sorption experiments without any treatment. The wheat bran was sieved repeatedly, in order to eliminate wheat semolina, non-wheat bran solids, and fine particles of the material, and dried to constant weight. Finally, the sorbent material is screened to obtain a particle size in the range 0.3–1.25 mm and stored in a vacuum desiccator before use.

### 2.3. Sorption Kinetics

The initial solution methylene blue concentration was 10 mg L<sup>-1</sup> for all experiments, except for those carried out to examine the effect of the initial concentration of methylene blue. For kinetic studies, the batch technique was used because of its simplicity. For dye-removal kinetic experiments, 2 g of wheat bran was contacted with 0.5 L of methylene blue solutions in a beaker agitated vigorously by a mechanic stirrer using a water bath maintained at a constant temperature of 20 °C. The stirring speed was kept constant at 400 rpm. At predetermined intervals of time, solutions were centrifuged for 15 min at 3000 rpm and the supernatant solutions were analyzed for the final concentration of methylene blue by using a UV-vis spectrophotometer (Hewlett Packard 8453) set at a wavelength of 665 nm, maximum absorbance. In all cases, the working pH was that of the solution and was not controlled.

The dye uptake  $q$  (mg g<sup>-1</sup>) was determined as follows:

$$q = \frac{(C_0 - C)V}{W} \quad (1)$$

where  $C_0$  and  $C$  are the initial and final dye concentrations (mg L<sup>-1</sup>), respectively,  $V$  is the volume of solution (L), and  $W$  is the sorbent weight (g).

Calibration experiments were carried out to exclude the experimental mistake raised from sorption of methylene blue on wall of the glass vessels. All the experiments were carried out in triplicate and the mean values are presented.

### 3. Results and Discussion

#### 3.1. Characterization of Sorbent Material

The wheat bran (1 g) was stirred (400 rpm) with bidistilled water (150 mL, pH 5.6, electric conductivity  $0.5 \mu\text{S cm}^{-1}$ ) for 60 min and an increase in the pH and the electric conductivity of the water to 6.6 and  $190 \mu\text{S cm}^{-1}$ , respectively, was observed. The increase of pH can be interpreted by a possible fixation of  $\text{H}^+$  ion by the negative groups present on the sorbent surface. The surface area of the sorbent as calculated by the Brunauer-Emmett-Teller (BET) method was  $378 \text{ m}^2 \text{ g}^{-1}$ . Scanning electron microscopy (SEM) images of the wheat bran (Figure 2) at different magnifications clearly indicate the surface texture and different levels of porosity of the material.

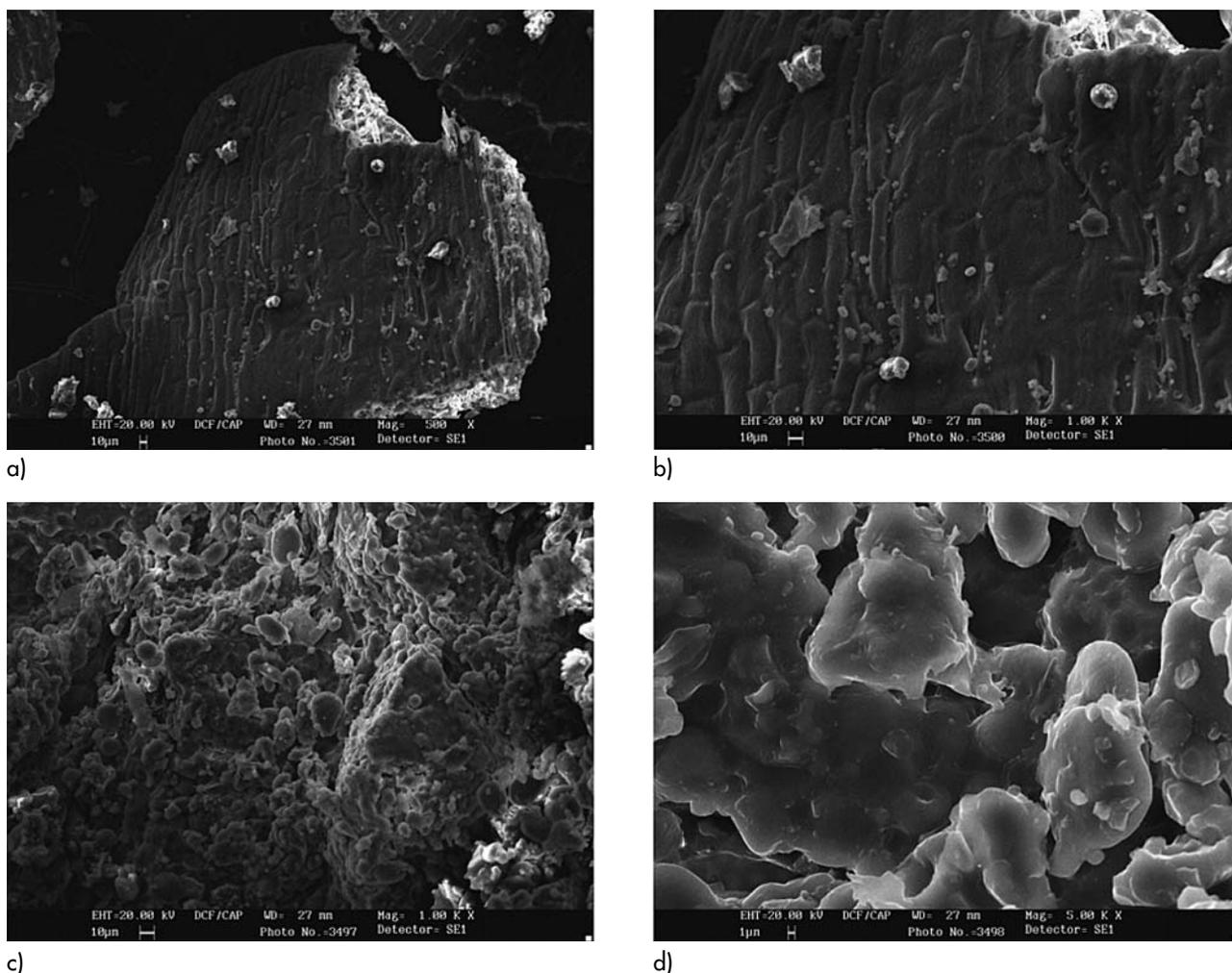


Figure 2. SEM images of wheat bran at different magnifications (a) 500 $\times$ , (b) 1000 $\times$ , (c) 1000 $\times$ , and (d) 5000 $\times$  magnification.

#### 3.2. Sorption Kinetic Models

The main issue when searching for an appropriate sorption mechanism is to select a mathematical model that not only fits the data with satisfactory accuracy but also complies with a reasonable sorption mechanism. Gene-

rally, several steps are involved during the sorption process by porous sorbent particles: (i) bulk diffusion; (ii) external mass transfer (boundary layer or film diffusion), between the external surface of the sorbent particles and the surrounding fluid phase; (iii) intraparticle transport within the particle; and (iv) reaction kinetics at phase boundaries. The majority of research on dye sorption systems confirmed that only two mechanisms controlled dye sorption: external and internal diffusion.<sup>19</sup> In the case of chemisorption, the rate of sorption is generally controlled by the kinetics of bond formation.<sup>20</sup>

Several kinetic models have been proposed to clarify the mechanism of a solute sorption from aqueous solution onto an adsorbent: (a) a pseudo-first order kinetic model of Lagergren<sup>21</sup> based on solid capacity, (b) a pseudo-sec-

ond order kinetic model of Ho<sup>22,23</sup> based on solid phase sorption, (c) external diffusion model of Spahn and Schlunder,<sup>24</sup> and (e) intra-particle diffusion model of Weber and Morris.<sup>25</sup>

### 3. 2. 1. Pseudo-first Order Kinetic Model

The sorption kinetics can be described by a pseudo-first order equation as suggested by Lagergren:<sup>21</sup>

$$\frac{dq}{dt} = k_1(q_e - q_t) \quad (2)$$

where  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of the pseudo-first order sorption,  $q$  ( $\text{mg g}^{-1}$ ) denotes the amount of sorption at time  $t$  ( $\text{min}$ ), and  $q_e$  ( $\text{mg g}^{-1}$ ) is the amount of sorption at equilibrium. After definite integration by application of the conditions  $t = 0$  to  $t = t$  and  $q = 0$  to  $q = q_e$ , Eq. (2) becomes

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (3)$$

The sorption rate constant,  $k_1$ , can be experimentally determined by the slope of linear plots  $\ln[(q_e - q)/q_e]$  vs.  $t$ .

### 3. 2. 2. Pseudo-second order Kinetic Model

The pseudo-second order equation developed by Ho<sup>22,23</sup> can be written as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (4)$$

where  $k_2$  ( $\text{g mg}^{-1} \text{min}^{-1}$ ) is the rate constant of the pseudo-second order.

Integrating Eq. (4) for the boundary conditions  $t = 0$  to  $t = t$  and  $q = 0$  to  $q = q_e$  gives

$$\frac{1}{(q_e - q)} = \frac{1}{q_e} + k_2 t \quad (5)$$

which has a linear form of

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

$k_2$  and  $q_e$  can be obtained from the intercept and slope of plotting  $t/q$  vs.  $t$ .

### 3. 2. 3. External Diffusion Sorption Model

Providing sufficient agitation to avoid particle and solute gradients makes it possible to ignore bulk diffusion and assume that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. Diffusion from the film to the surface of the adsorbent, also called external diffusion or liquid film diffusion, might govern the sorption process. An examination of the dependence of the dye concentration on the rate constant helps to describe the mechanism of dye removal taking place.<sup>26</sup> In the case of strict surface adsorption, the variation in the rate should be proportional to the first power of the concentration. However, when pore diffusion limits the

sorption process, the relationship between the initial solute concentration and the rate of reaction is no longer linear.<sup>27</sup>

In the present study, the Spahn and Schlunder<sup>24</sup> model was chosen to describe external diffusion on the sorbent

$$\ln \frac{C}{C_0} = -k_s \frac{A}{V} t \quad (7)$$

where  $C_0$  and  $C$  are the solution concentrations ( $\text{mg L}^{-1}$ ) at time  $t = 0$  and at time  $t$ , respectively;  $t$  is the time ( $\text{s}$ ),  $k_s$  represents the external mass-transfer coefficient ( $\text{m s}^{-1}$ ),  $V$  is the volume of the equilibrating solution ( $\text{L}$ ), and  $A$  indicates the surface area ( $\text{m}^2 \text{g}^{-1}$ ) of sorbent.

Therefore,  $k_s$  may be calculated by plotting  $\ln(C/C_0)$  against the adsorption time,  $t$ .

### 3. 2. 4. Internal Diffusion (Pore and Surface Diffusion) Sorption Model

Assuming constant diffusion through adsorbent pores, the relation between the amount adsorbed and the reaction time can be expressed as follows

$$q = K_w t^{1/2} \quad (8)$$

where  $K_w$  is the intra-particle diffusion rate constant ( $\text{mg g}^{-1} \text{min}^{-1/2}$ ). In this model, due to the porous nature of adsorbent, pore diffusion is expanded to be surface sorption. Therefore, the rate constant of intraparticle transport ( $K_w$ ) is estimated from slopes of linear portion of the plots of amount sorbed against square root of time. Although it does not have the conventional rate constant units,  $K_w$  can be conveniently used to quantitatively describe the kinetics in the sorption systems.

Eq. (8) indicates that a plot of the average particle loading,  $q$  ( $\text{mg g}^{-1}$ ), versus the square root of time,  $t^{1/2}$ , would yield a straight line passing through the origin if the sorption process obeyed the intraparticle diffusion model. The slope of the straight line equals to  $K_w$ , the intraparticle diffusion rate constant.

### 3.3. Effect of Contact Time and Sorbent Dose

Preliminary tests carried out by using a volume of 0.5 L of methylene blue solution at different initial concentrations (5, 10, and 20  $\text{mg L}^{-1}$ ) and various masses of wheat bran (1 to 5 g) showed that 180 min is sufficient time to reach the sorption equilibrium.

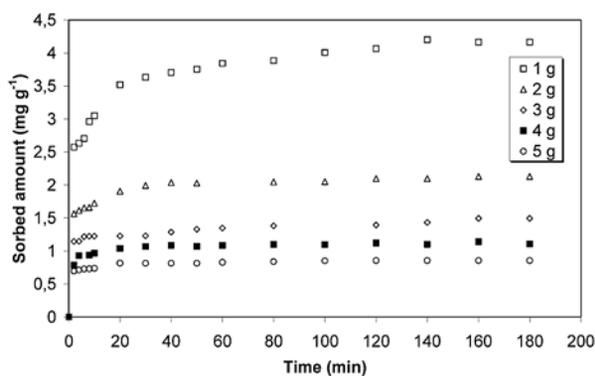
The extent of removal of dye by wheat bran increased with increasing contact time. The removal of dye by sorption on wheat bran was found to be rapid at the initial period of contact time and then to become slow with the increase of contact time. Consequently, the removal of methylene blue is carried out in two distinct stages: a relatively fast one followed by a slower one. This was caused

by strong attractive forces between the dye molecules and the sorbent; fast diffusion onto the external surface was followed by fast pore diffusion into the intraparticle matrix to attain rapid equilibrium.

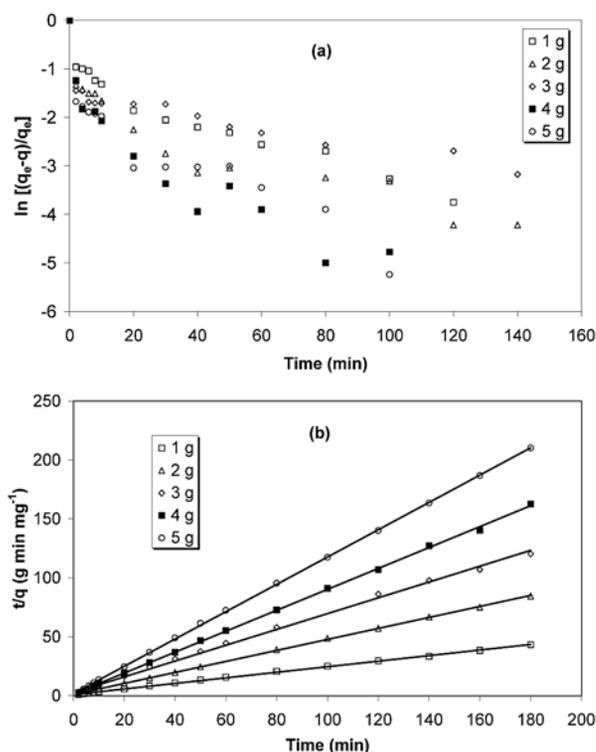
During the course of methylene blue ( $10 \text{ mg L}^{-1}$ ) removal by wheat bran, we noticed an evolution in the value of the initial pH of the solution from 6.1 to 6.6 at the equilibrium. This can be interpreted by a competition between methylene blue molecules and proton ions for binding sites.

In order to investigate the effect of sorbent mass on the sorption of basic dye, a series of sorption experiments was carried out with different sorbent dosages at initial dye concentration of  $10 \text{ mg L}^{-1}$ . Figure 3 shows the effect of sorbent dosage on the removal of methylene blue. The sorption of methylene blue increased with an increase in sorbent dosage. This may be attributed to increased sorbent surface area and availability of more sorption sites resulting from the increase dose of the sorbent. But amount of dye sorbed per unit mass of sorbent decreased with increase in sorbent dose. At higher wheat bran to solute concentration ratios, there is a very fast superficial sorption onto the sorbent surface that produces a lower solute concentration in the solution than when the biomaterial to solute concentration ratio is lower. This is because a fixed mass of wheat bran can only sorb a certain amount of dye. Therefore, the more the sorbent dosage, the larger the volume of effluent that a fixed mass of wheat bran can purify is. The decrease in amount of dye sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent. Thus with increasing sorbent mass, the amount of dye sorbed onto unit weight of sorbent gets reduced, thus causing a decrease in sorption capacity with increasing sorbent mass concentration.

As can be seen in Figure 3, the wheat bran mass has an influence on the time of contact necessary to reach equilibrium. The smallest wheat bran mass (1 g) appears to have reached equilibrium after 140 min, while the high-



**Figure 3.** Effect of sorbent mass on the sorption kinetics of methylene blue by wheat bran.



**Figure 4.** Modeling of methylene blue sorption kinetics by wheat bran: (a) pseudo-first order equation; (b) pseudo-second order model

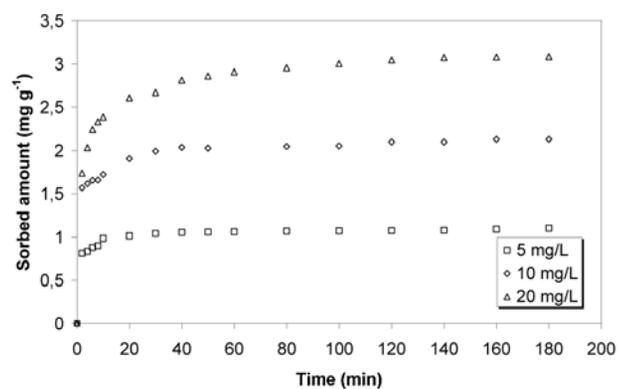
er wheat bran mass (5 g) has achieved equilibrium after 100 min. As above, the same phenomenon in the initial pH variation (slight increase) during the sorption experiment was observed.

Kinetics of methylene blue sorption by wheat bran can be modeled by the pseudo-first order Lagergren equation and the pseudo-second order Ho model. The plots of  $\ln[(q_e - q)/q_e]$  versus time, illustrated in Figure 4 (a), show that the pseudo-first order model can not describe the sorption kinetics of the studied dye. Linear regression of the observed values of  $t/q$  on  $t$  afforded lines with coefficients of determination better than 0.998, allowing estimation of the amount of dye sorbed at equilibrium and the rate constant. It is clearly found that the sorption of methylene blue onto wheat bran can be better described by the pseudo-second order equation (Figure 4 (b)). The values of sorption rate constant of pseudo-second order are  $0.056$  ( $R^2 = 0.999$ ),  $0.214$  ( $R^2 = 1$ ),  $0.181$  ( $R^2 = 0.998$ ),  $0.557$  ( $R^2 = 1$ ), and  $0.742$  ( $R^2 = 1$ )  $\text{g mg}^{-1} \text{ min}^{-1}$  for 1, 2, 3, 4, and 5 g, respectively. The obtained results show that the sorption rate constant of methylene blue onto wheat bran increases with the sorbent mass. The values of sorbed amount at equilibrium determined by the pseudo-second order equation are  $4.241$ ,  $2.140$ ,  $1.490$ ,  $1.126$ , and  $0.863 \text{ mg g}^{-1}$  for, respectively, 1, 2, 3, 4, and 5 g. These values are in agreement with experimental data.

### 3.4. Effect of Methylene Blue Initial Concentration

The experimental results of sorption of methylene blue by wheat bran at various initial concentrations (5, 10, and 20 mg L<sup>-1</sup>) with contact time are shown in Figure 5. In all experiments, the temperature was maintained at 20 °C and the agitation speed maintained at 400 rpm. Percent sorption decreased with increase in initial methylene blue concentration. But the amount of methylene blue sorbed per unit mass of wheat bran increased with increase in dye concentration. The equilibrium sorption capacity is increased from 1.1 to 3.08 mg g<sup>-1</sup> as the methylene blue concentration increased from 5 to 20 mg L<sup>-1</sup>. The results indicate that the obtained curves have the same shape. The necessary time to reach equilibrium is variable according to the initial concentration in methylene blue: about 140 min ( $C_0 = 20$  mg L<sup>-1</sup>), 120 min ( $C_0 = 10$  mg L<sup>-1</sup>), and 60 min ( $C_0 = 5$  mg L<sup>-1</sup>). During sorption of dye, initially the dye molecules reach the boundary layer; then they have to diffuse into the sorbent surface; and finally, they have to diffuse into the porous structure of the sorbent. Hence, this phenomenon will take a relatively longer contact time. Figure 5 reveals that the curves are single, smooth, and continuous, leading to saturation, suggesting the possible monolayer coverage of methylene blue on the wheat bran surface.

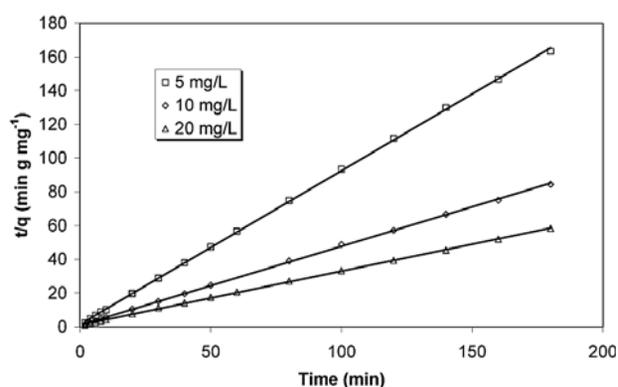
Additionally, during the process of methylene blue removal by wheat bran, it is also noticed an increase of the initial pH of the solution for all studied concentrations



**Figure 5.** Effect of initial sorbate concentration on the sorption kinetics of methylene blue by wheat bran.

The application of the pseudo-first order model of Lagergren to the experimental results of the methylene blue sorption kinetic by wheat bran for various initial concentrations shows that this model cannot describe the sorption kinetics. When the previous data were fitted to the pseudo-second order rate equation (Figure 6) straight lines are obtained indicating that the process follows pseudo-second order kinetics. The values of the rate constant obtained from pseudo-second order kinetics are

0.543 ( $R^2 = 1$ ), 0.214 ( $R^2 = 1$ ), and 0.092 ( $R^2 = 1$ ) g mg<sup>-1</sup> min<sup>-1</sup> for initial dye concentrations of 5, 10, and 20 mg L<sup>-1</sup>, respectively. An increase in initial methylene blue concentration led to a decrease in the rate constant values; the differences in rate constants being significant. The values of determination coefficients obtained from the plots of pseudo-second order kinetics, given in Figure 6, are equal to unity for all initial dye concentrations. The values of equilibrium sorption capacity are 1.099, 2.140, and 3.132 mg g<sup>-1</sup> for, respectively, 5, 10, and 20 mg L<sup>-1</sup> initial dye concentrations. These values are in agreement with experimental data.

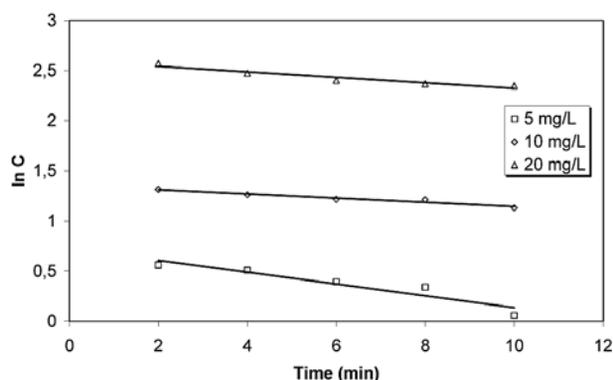


**Figure 6.** Application of the pseudo-second order kinetic model for the sorption of methylene blue by wheat bran at different sorbate initial concentrations.

Sorption kinetics are mainly controlled by various stages including (i) solute transfer from the solution to the boundary film surrounding the particle (bulk diffusion), (ii) diffusion from the film to the surface of the sorbent (external diffusion), (iii) diffusion from the surface to the intraparticle sites (intraparticle diffusion), and (iv) solute adsorption by complexation or physicochemical sorption or ion exchange. Providing sufficient agitation to avoid particle and solute gradients makes it possible to ignore bulk diffusion and assume that the rate is not limited by mass transfer from the bulk liquid to the particle external surface. Additionally, it is generally accepted that process (iv) is very rapid and does not represent the rate-determining step in the uptake of sorbate. Therefore, two mechanisms may be controlled methylene blue sorption by wheat bran: external and internal diffusion.

If the sorption process is controlled by the external resistance, the plot  $\ln C$  versus time must be linear. This kind of relation is shown for the first stage ( $\leq 10$  min) of sorption kinetics of methylene blue by wheat bran (Figure 7). It seems that the external diffusion is the rate-controlling step of the initial fast sorption of methylene blue onto wheat bran.

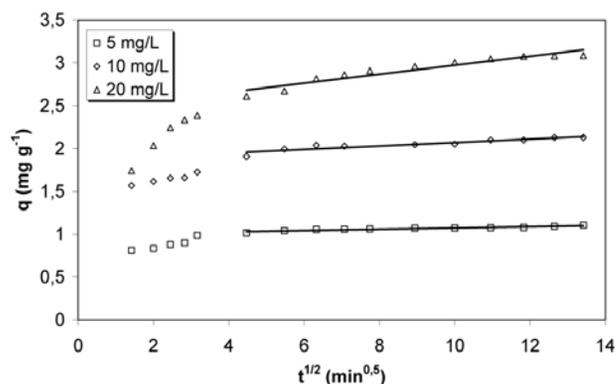
As stated earlier, the mass-transfer coefficient was determined using Spahn and Schlunder<sup>24</sup> model, Eq. (7). The model is applied to the first terms of the kinetic



**Figure 7.** Plots of  $\ln C$  versus time for the sorption of methylene blue by wheat bran for various dye initial concentrations.

curves (Figure 7), when  $t$  tends towards zero. The mass-transfer coefficient was found to vary with the initial concentration. The external mass transfer coefficients obtained for various concentrations are  $4.67 \times 10^{-6}$ ,  $2.17 \times 10^{-6}$ , and  $1.67 \times 10^{-6} \text{ m s}^{-1}$  at 5, 10, and  $20 \text{ mg L}^{-1}$ , respectively.

The kinetic results can be used to determine if intraparticle diffusion is the rate-limiting step for methylene blue sorption by wheat bran. Weber and Morris<sup>25</sup> reported that if intraparticle diffusion is involved in the sorption process then a plot of sorbate uptake versus the square root of time (Eq. (8)) would result in a linear relationship and that particle diffusion would be the rate-controlling step if this line passes through the origin. As elucidated in Figure 8, the results can be represented by such a linear relationship but they do not pass through the origin. This indicates that intraparticle diffusion is involved in the sorption process but it is not the only rate-limiting mechanism and that some other mechanisms are involved. Such a deviation of the straight line from the origin may be due to the difference in the rate of mass transfer in the initial stage of sorption. Moreover, the intercept of the plot gives an idea about boundary layer thickness, the larger the value of the intercept, the greater is the boundary layer effect. For various initial concentrations, the intercepts of the plots  $q$  vs.  $t^{1/2}$  for 20, 10, and  $5 \text{ mg L}^{-1}$  are, respectively, 2.45, 1.87, and  $1 \text{ mg g}^{-1}$ . It seems that the boundary layer effect increases with the initial concentration of dye. Intra-particle diffusion rate constants obtained for different initial concentrations are  $52.45 \times 10^{-3}$ ,  $20.14 \times 10^{-3}$ , and  $7.49 \times 10^{-3} \text{ mg g}^{-1} \text{ min}^{-1/2}$  at 20, 10, and  $5 \text{ mg L}^{-1}$ , respectively. Figure 8 shows that the plots have the same general features, initial curved portion followed by linear portion. The initial curved portion is attributed to the liquid-film mass transfer and the linear portion to the intraparticle diffusion. At a certain time limit, the curves reveal a linear characteristic that the intraparticle diffusion controls the sorption process. These phenomena have been reported for the adsorption of dye on activated carbon.<sup>28</sup>

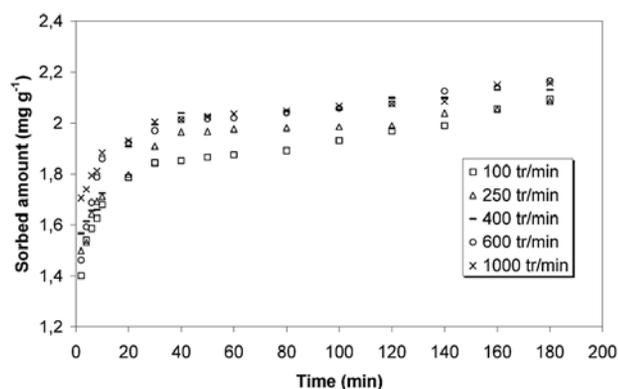


**Figure 8.** Plots of methylene blue sorption versus square root of time for various dye initial concentrations.

The sorption of methylene blue by wheat bran is a process carried out in two stages comprising a fast initial phase and a second slower phase. In the first phase, methylene blue molecules are sorbed on the external sites of the sorbent material in a fast process, which dominates the initial kinetics of sorption. In the second phase, molecules of dye slowly diffuse in the pores of material, and are sorbed onto internal sites.

### 3.5. Effect of Agitation Speed

Taking into account that the sorption kinetics is influenced by mass transfer parameters, such as agitation speed, five agitation speeds were selected to study their effects on the sorption of methylene blue by wheat bran. Figure 9 illustrates the sorption kinetics of methylene blue by wheat bran for different agitation speeds ranging from 100 to 1000 rpm. The result shows that the sorption of methylene blue by wheat bran particles is faster at higher agitation speeds than at lower ones. The amount of dye sorption increases with the increase of the agitation speed from 100 to 400 rpm. This may be explained that with low agitation speed a greater contact time would be required for reaching equilibrium. For agitation speeds higher than 400 rpm (600 and 1000 rpm), the sorption increases with the agitation speed during the initial stage of the sorption kinetics. The dye concentration in each of the suspensions where sorption took place at various higher agitation speeds ( $\geq 400 \text{ rpm}$ ) is gradually approaching the final equilibrium sorbed amount. When increasing the agitation speed, the diffusion rate of dye molecules from the bulk liquid to the liquid boundary layer surrounding particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. Under these conditions, the value of the external diffusion coefficient became larger. Finally, the boundary layer became very thin and approached to the laminar sublayer at high agitation speeds. Therefore, the external diffusion resistance and the diffusion coefficient are constant or they can be neglected. The same phenomenon was ob-



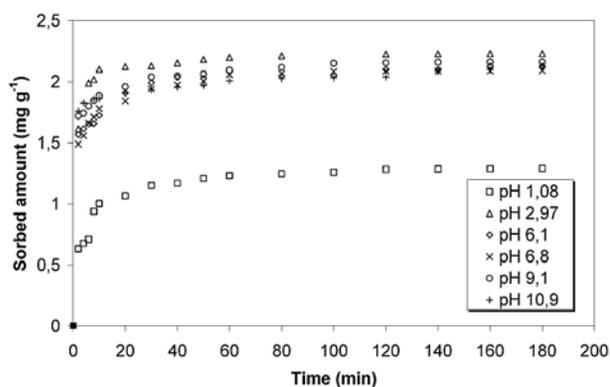
**Figure 9.** Effect of agitation speed on the sorption kinetics of methylene blue by wheat bran.

served in the kinetic experiments of the cupric ion adsorption on the corncob particles.<sup>29</sup> Thus, it can be noticed that the sorption rate has a slight increase with increasing the speed of agitation.

Lagergren pseudo-first order rate equation can not model adequately the sorption kinetics result, whatever the agitation speed is. When kinetic data were fitted to the pseudo-second order rate equation (results not shown here), straight lines were obtained indicating that the process follows pseudo-second order kinetics. The rate constants calculated from their slopes and intercepts were found to be 0.140 ( $R^2 = 0.998$ ), 0.205 ( $R^2 = 0.999$ ), 0.214 ( $R^2 = 1$ ), 0.187 ( $R^2 = 0.999$ ), and 0.225 ( $R^2 = 0.999$ )  $\text{g mg}^{-1} \text{min}^{-1}$  at 100, 250, 400, 600, and 1000 rpm, respectively. The values of equilibrium sorption capacity are 2.066, 2.074, 2.140, 2.157, and 2.145  $\text{mg g}^{-1}$  for, respectively, 100, 250, 400, 600, and 1000 rpm. Results indicate that the agitation speed influences the kinetic rate constant; in contrast, its effect on the sorption capacity is very limited.

### 3.6. Effect of Solution pH

The solution pH is one of the most important factors that control the sorption of dyes on sorbent material. The initial pH influences the kinetics of sorption because the proton concentration decreases when the initial pH increases, and then the dye molecules have more chance to react with the active sites on the surface of wheat bran because of a lower proton competition. Figure 10 shows the effect of pH on dye removal at different initial solution pH for an initial dye concentration of  $10 \text{ mg L}^{-1}$  and a sorbent dosage of 2 g. From the figure, it is observed that the removal of methylene blue by wheat bran increases when the solution pH increased from 1.08 to 2.97. In the pH range 2.97 to 10.9, the effect of pH is not significant. At low initial pH value ( $\text{pH} < 2.97$ ), the  $\text{H}^+$  ion can be considered as competitor of methylene blue cations for sorption sites on the wheat bran surface. For high pH values ( $\text{pH} \geq$



**Figure 10.** Effect of solution pH on the sorption kinetics of methylene blue by wheat bran.

2.97), pH had a poor influence on methylene blue sorption. As the pH of the system increases, the number of positively charged sites decreases and the number of negatively charged sites increases that results in a decrease of the competitive sorption with the methylene blue cations for active sites on the sorbent. The negatively charged sites favor the sorption of dye cations due to electrostatic attraction. This confirms that the charged dye molecules are attached onto wheat bran due to ion exchange mechanism. A similar observation was previously reported for methylene blue sorption on fly ash particles.<sup>30</sup>

It also appears that the surface charge of the sorbent has a considerable influence on the dye removal. With increase in pH, the net electronegativity of the biosorbent increases due to deprotonation of different functional groups. When the surface is negatively charged, sorption is favored by electrostatic attractions between the dye cations and the sorbent surface. On the other hand, when it is charged positively, the electrostatic repulsions involve a reduction in sorption. Moreover, the weak differences in sorption for high pH values ranging from 2.97 to 10.9 cannot be explained by these phenomena. It seems that the phenomenon of dye removal by wheat bran is carried out by several sorption processes (adsorption, ion exchange or chelation, for example).

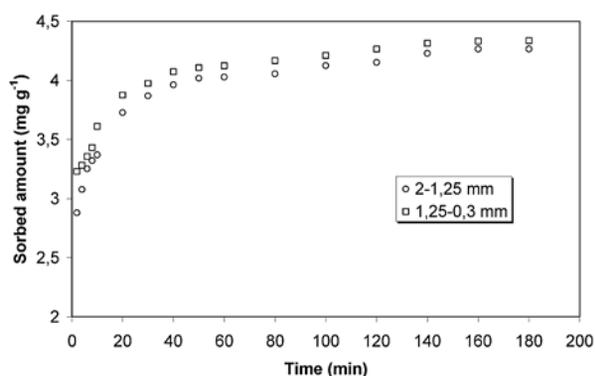
Since the dye solution was not buffered, a change in pH of the dye solution is expected during the sorption process. So, both initial and equilibrium pH were measured. It was observed that the final pH was higher than the initial pH for the biosorption of methylene blue. This indicated competitive sorption of  $\text{H}^+$  ions during the biosorption of methylene blue.

Kinetic experimental results of dye sorption by wheat bran are modeled using the pseudo-first and the pseudo-second order rate equations. Sorption kinetics can not be described adequately by the Lagergren model due to lower values of determination coefficients. The plots of kinetic data to pseudo-second order model give straight lines with high coefficients of determination (0.999) indi-

cating that the process follows pseudo-second order kinetics. The rate constants calculated from their slopes and intercepts were found to be 0.189 ( $R^2 = 1$ ), 0.409 ( $R^2 = 1$ ), 0.214 ( $R^2 = 1$ ), 0.239 ( $R^2 = 1$ ), 0.265 ( $R^2 = 1$ ), and 0.213 ( $R^2 = 0.999$ )  $\text{g mg}^{-1} \text{min}^{-1}$  for various initial pH of 1.08, 2.97, 6.1 (natural), 6.8, 9.1, and 10.9, respectively.

### 3.7. Effect of Particle Size

The surface of contact between any sorbent and the liquid phase plays an important role in sorption processes. The effect of particle size of wheat bran on the methylene blue removal was studied using two particle size ranges: 0.3–1.25 and 1.25–2 mm. Figure 11 shows the sorption kinetics of the dye at two different particle sizes. As can be seen, the kinetic curves obtained have an identical shape, and that the removal is improved as the particle size decreased. This is because the smaller particles have more surface area and access to the particle pores is facilitated when their size is small. It is also believed that the breaking up of large particles to form smaller ones opens some tiny sealed channels, which might then become available for adsorption, and so the sorption by smaller particles is higher than that by larger particles. Additionally, the decrease in particle size leads to a decrease of the equilibrium time. This is in agreement with the kinetic principle: smaller particles have a larger contact area by unit of mass of the sorbent to react with reactant than larger ones, resulting in a faster sorption. These observations indicate that methylene blue sorption occurs by a surface mechanism. As mentioned above, the same phenomenon in the initial pH variation (slight increase) during the sorption experiment was observed.



**Figure 11.** Effect of sorbent particle size on the sorption kinetics of methylene blue by wheat bran.

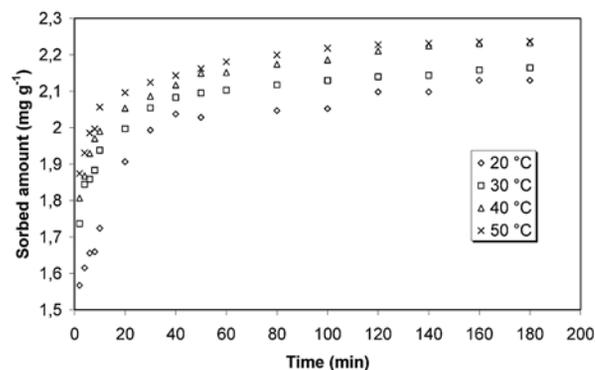
The sorption kinetics of methylene blue by wheat bran for two different particle sizes can be described adequately using the pseudo-second order kinetic model. The obtained coefficients of determination are equal to unity showing the very good quality of linearization. The values

of the rate constant are 0.096 and 0.083  $\text{g mg}^{-1} \text{min}^{-1}$  for the particle size range of 0.3–1.25 and 1.25–2 mm, respectively. Equilibrium sorption capacities are 4.369  $\text{mg g}^{-1}$  for particle size range of 0.3–1.25 mm and 4.297  $\text{mg g}^{-1}$  for particle size range of 1.25–2 mm. These values are in agreement with experimental data.

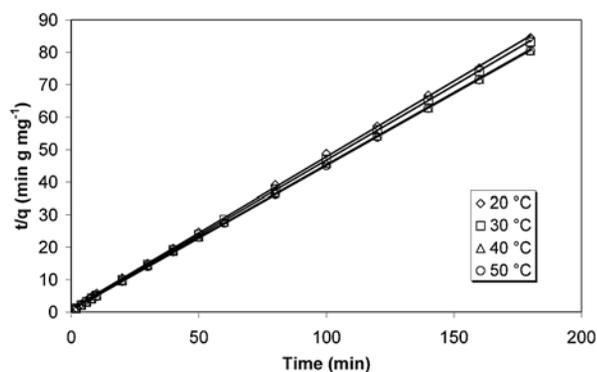
### 3.8. Effect of Temperature

A parameter with great significance in the sorption process is temperature. To determine the effect of temperature, sorption studies of methylene blue were performed at four different temperatures, i.e., 20, 30, 40, and 50 °C, and the results are shown in Figure 12. Similar shape of the kinetic curves is observed for all the temperatures. Figure 12 indicates that the methylene blue sorption uptake increases with increasing temperature. The equilibrium sorption capacity increases from 2.13 to 2.24  $\text{mg g}^{-1}$  when the temperature of dye solutions increases from 20 to 50 °C. The fact that the sorption of dye is in favor of temperature indicates that the mobility of the dye molecule increases with a rise in the temperature, and it can be suggested that the dye molecule should interact more effectively with the sorbent surface. The increase in sorption capacity with increasing temperature indicates that the process of removal of the dye by wheat bran is endothermic in nature and activated process.

Figure 13 illustrates the effect of temperature on pseudo-second order sorption kinetics of methylene blue onto wheat bran. The obtained rate constants, determined from the slopes and intercepts of the plots, are 0.214 ( $R^2 = 1$ ), 0.238 ( $R^2 = 1$ ), 0.278 ( $R^2 = 1$ ), and 0.360 ( $R^2 = 1$ )  $\text{g mg}^{-1} \text{min}^{-1}$  at 20, 30, 40, and 50 °C, respectively. Similar results have been reported by Ho and McKay<sup>31</sup> for the sorption of basic blue 69 onto peat. The values of determination coefficients obtained are greater than 0.999 for all the temperatures. The values of equilibrium sorption capacity are 2.140, 2.169, 2.243, and 2.248 for 20, 30, 40, and 50 °C, respectively, and these values are in agreement with experimental data.



**Figure 12.** Effect of temperature on the sorption kinetics of methylene blue by wheat bran.



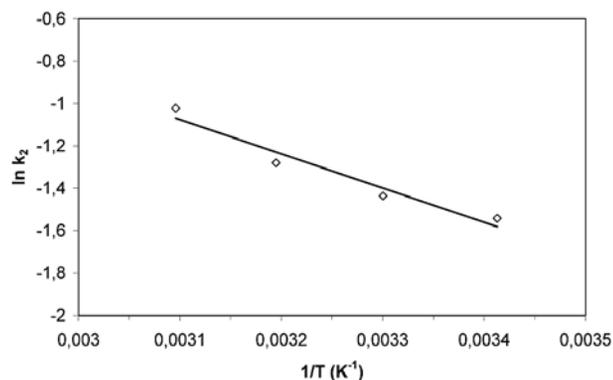
**Figure 13.** Effect of temperature on pseudo-second order sorption kinetics of methylene blue by wheat bran.

Generally, a rise in temperature of a chemical reaction increases the rate of the reaction, and the temperature dependence results in a change in the rate constant. Activation energy of the sorption of methylene blue by wheat bran can be estimated by Arrhenius equation providing the relationship between rate constant ( $k_2$ ) and temperature as shown in the following:

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g T} \quad (9)$$

where  $k_2$  is the pseudo-second order rate constant of sorption ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $k_0$  the Arrhenius constant which is a temperature independent factor ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $E_a$  the activation energy ( $\text{kJ mol}^{-1}$ ),  $R_g$  the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the solution temperature in Kelvin (K).

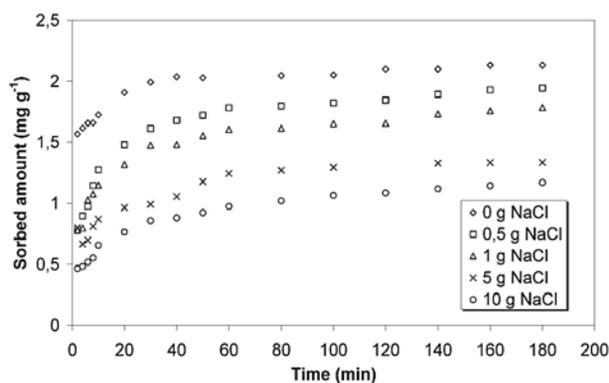
In this work, activation energy of sorption process has been calculated using the values of rate constant from a pseudo-second order kinetic equation and using the appropriate solution temperatures. An Arrhenius plot drawn of  $\ln k_2$  versus  $1/T$  is shown in Figure 14. The value of activation energy from the slope of the plot is  $13.41 \text{ kJ mol}^{-1}$  and Arrhenius constant ( $k_0$ ) is  $50.68 \text{ g mg}^{-1} \text{min}^{-1}$ . Therefore, the activation energy obtained is very low, and thus the sorption of methylene blue by wheat bran may involve not only an activated process but a physical sorption.



**Figure 14.** Arrhenius plot for sorption of methylene blue by wheat bran.

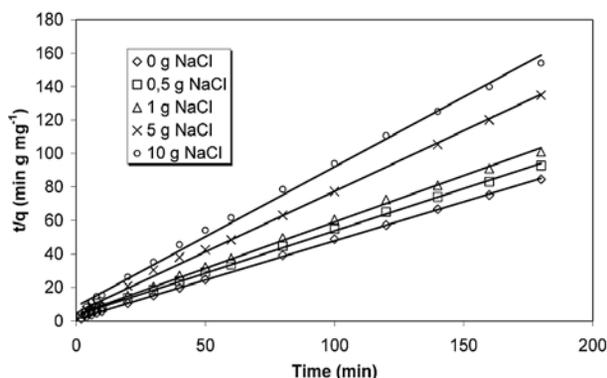
### 3.9. Effect of Ionic Strength

Dye-laden wastewaters released from different industries contain various types of salts. The presence of ions leads to high ionic strength, which may significantly affect the performance of the biosorption process. In order to study the effect of ionic strength on the sorption of methylene blue by wheat bran, sorption kinetics of the dye were determined for different concentrations of sodium chloride ( $0\text{--}20 \text{ g L}^{-1}$ ). Sorption kinetics were carried out for methylene blue initial concentration of  $10 \text{ mg L}^{-1}$ , solution volume of  $0.5 \text{ L}$ , and a sorbent mass of  $2 \text{ g}$ . Figure 15 presents the effect of ionic strength on the uptake of dye by wheat bran. It was observed that sorption potential decreased with increase in ionic strength. The adverse effect of ionic strength on dye uptake suggests the possibility of ion exchange mechanisms being in operation in the biosorption process. It may be due to competition of  $\text{Na}^+$  (present in salt used to change the ionic strength of dye solution) with positively charged dye molecules for the same binding sites on the biosorbent surface. Additionally, ionic atmosphere may be progressively formed around methylene blue molecules with increased  $\text{NaCl}$  concentration and results in the reduction of methylene blue sorption on the tested material.



**Figure 15.** Effect of ionic strength on the sorption kinetics of methylene blue by wheat bran.

Figure 16 shows pseudo-second order sorption kinetics of methylene blue by wheat bran for different ionic strengths. The values of the rate constant obtained from pseudo-second order kinetics are  $0.214$  ( $R^2 = 1$ ),  $0.081$  ( $R^2 = 0.999$ ),  $0.086$  ( $R^2 = 0.998$ ),  $0.105$  ( $R^2 = 0.998$ ), and  $0.082$  ( $R^2 = 0.996$ )  $\text{g mg}^{-1} \text{min}^{-1}$  for  $0, 0.5, 1, 5,$  and  $10 \text{ g}$ , respectively. The values of determination coefficient obtained from the plots of pseudo-second order kinetics are higher than  $0.996$  for all salt concentrations. The values of equilibrium sorption capacity are  $2.140, 1.979, 1.804, 1.382,$  and  $1.198 \text{ mg g}^{-1}$  for, respectively,  $0, 0.5, 1, 5,$  and  $10 \text{ g}$  of  $\text{NaCl}$ . These values are in agreement with experimental data.



**Figure 16.** Effect of ionic strength on pseudo-second order sorption kinetics of methylene blue by wheat bran.

## 4. Conclusion

The goal of this work was to explore the potential use of wheat bran as low-cost sorbent for the removal of methylene blue from aqueous solutions. The sorption amounts increase with an increase of initial concentration of methylene blue, solution pH, and temperature. The cationic dye recovery increases with an increase of sorbent dose. An increase of the dye removal is obtained by a decrease of particle size and ionic strength in the aqueous phase. The agitation speed showed a restricted influence on the removal kinetics. The sorption kinetics could be quite successfully fitted by a pseudo-second order kinetics equation. The sorption of methylene blue by wheat bran is a process carried out in two stages comprising a fast initial phase and a second slower phase. In the first phase, methylene blue molecules are sorbed on the external sites of the sorbent material in a fast process, which dominates the initial kinetics of sorption. In the second phase, molecules of dye slowly diffuse in the pores of material, and are sorbed onto internal sites. The calculated activation energy of the sorption process is  $13.41 \text{ kJ mol}^{-1}$ . The low value of activation energy may involve not only an activated process but a physical sorption.

Biosorption technology, utilizing natural materials or industrial and agricultural wastes to passively remove dyes from aqueous media, offers an efficient and cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques. Wheat bran, a low cost and easily available material, may be particularly appropriate for the treatment of small quantities of wastewaters containing cationic dyes and the data reported here should be useful for the design of batch or stirred-tank flow reactors.

Further experiments need to be conducted to test the dynamic sorption of methylene blue in fixed bed by wheat bran.

## 5. Acknowledgement

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## Povzetek

Raziskovali smo pogoje odstranjevanja barvila metilen modro iz vodnih raztopin z adsorpcijo na pšeničnih otrobih. V članku so opisani vplivi različnih eksperimentalnih parametrov (masa adsorbenta, začetna koncentracija barvila, hitrost stresanja, pH, velikost delcev, temperatura in ionska moč zmesi) na kinetiko adsorpcije. Ugotovili smo, da adsorpcijo preiskovanega sistema najbolje opišemo kot proces psevdo-drugerega reda z aktivacijsko energijo  $13.41 \text{ kJ mol}^{-1}$ . Velikost aktivacijske energije kaže, da gre za fizikalno adsorpcijo. Z uporabo tako internega okot eksternega modela difuzije smo ugotovili, da sta bistvenega pomena difuzija delcev in nastanek tekočinskega filma. Pšenični otrobi kot poceni in dostopen material je torej lahko koristno uporabljen kot odličen adsorbent za odstranjevanje barvil iz odpadnih voda.