

EFFECT OF TEMPERATURE ON METHYLENE BLUE SORPTION FROM AQUEOUS SOLUTIONS BY ALMOND PEEL: EXPERIMENTAL STUDIES AND MODELLING

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ABSTRACT

In the present work, the influence of temperature on kinetics and equilibrium of methylene blue sorption from synthetic aqueous solutions, in single dye solutions, using almond peel as a sorbent material has been investigated in batch conditions. Temperature played an important part in sorption phenomenon: the methylene blue sorption increased as temperature increased. The pseudo second-order model was selected to describe the experimental data of methylene blue sorption kinetics. The results showed that the process follows pseudo second-order kinetics. Equilibrium data were mathematically fitted to Langmuir equation which gave an acceptable fit over the whole equilibrium dye concentrations range. A high dye sorption was observed by this sorbent material: a maximum sorption capacity about 77 - 118 mg/g was achieved depending on temperature tested. The thermodynamic parameters obtained with this system, indicated spontaneous and endothermic process. Under these experimental conditions, the analysis of mechanistic steps involved in the sorption process confirms that methylene blue sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages.

Keywords: sorption; methylene blue; almond peel; effect of temperature.

INTRODUCTION

Synthetic dyes are extensively used for dyeing and printing in industries. Over 7×10^5 tons and approximately 10,000 different dyes and pigments are produced annually worldwide, of which about 10% are lost in industrial effluents (Fu & Viraraghavan [1], Robinson et al. [2]). Commercial dyes have a great variety of colors, high stability to light, temperature, detergent and microbial attack. They are not toxic, while their colors in industrial effluents cause environmental concern. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm (Zollinger [3]). Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration (O'Mahony [4]). Among the various

types of dyes, various cationic dyes, including methylene blue, are used in dye, paint production and in wool dyeing (Bielska & Szymanowski [5]). Methylene blue has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc (Kumar et al. [6,7], Han et al. [8]). Though methylene blue is not strongly hazardous, it can cause some harmful effects (Kumar et al. [6, 7]). Due to low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical and/or chemical methods (Garg et al. [9]). Although these treatment methods are efficient, they are quite expensive and have operational problems (Garg et al. [9], Kapdan et al. [10]). Sorption of molecules onto various sorbents materials is an ideal option for decolorization, which is evidenced by the effectiveness of sorption for various dye types (Kapdan et al. [10], Porter et al. [11]). The main drawbacks which exist at the present time are the high costs involved in the regeneration of the adsorbent. Also, since activated carbon is the most widely used and most effective adsorbent, its high cost tends to increase the cost of adsorption systems (Kapdan et al. [10], Porter et al. [11]). As a result, there is a search for low-cost, naturally occurring, abundant sorbent materials that can serve as viable alternatives to activated carbon. Sorption of methylene blue has been extensively studied by many researchers using several low cost materials. such as mango seed kernel (Kumar et al. [6]), fly ash (Kumar et al. [7]), cereal chaff (Han et al. [8]), pear millet husk carbon (Inbaraj et al. [12]), *Aspergillus niger* (Fu & Viraraghavan, [13]), rice husk (McKay et al. [14]), Vadivelan & Kumar [15]), hair (McKay et al. [14]), cotton waste (McKay et al. [14]), bark (McKay et al. [14]), perlite (Dogan et al. [16,17]), carbonised press mud (Kumar, [18]), bagasse bottom ash (Kumar [18]), raw kaolin (Gosh & Bhattacharya [19]), pure kaolin (Gosh & Bhattacharya [19]), calcined raw kaoline (Gosh & Bhattacharya [19]), calcined pure kaoline (Gosh & Bhattacharya, [19]), NaOH treated raw kaolin (Gosh & Bhattacharya, [19]), coir pith (Namasiavam et al. [20]), guava seeds activated carbon (Rahman & Saad [21]), iron humate (Janos [22]), neem sawdust (Khattri & Singh [23]), clay (Gürses et al. [24]), durian shell activated carbon (Chandra et al. [25]), steam activated bitimous coal activated carbon (El Qada et al. [26]), activated carbon (Kumar & Sivanesan [27]), neem leaf (Bhattacharyya & Sharma [28]), various carbons (Kannan & Sundaram [29]), oxihumolite (Janos et al. [30]), Indian rosewood sawdust (Garg et al. [31]), palm-tree cobs activated carbons (Avom et al. [32]), water hyacinth root (Low et al. [33]), giant duckweed (Waranusantigul et al. [34]), modified sawdust (De & Basu [35]). Almond peel waste can be an alternative and favourable sorbent material for pollutants such dyes. To date, except the works carried out in our laboratory about the kinetics and equilibrium of methylene blue sorption from synthetic aqueous solution by almond peel (Benaïssa [36, 37]), no information are available in the literature for dye sorption from aqueous solutions by almond peel. This low-cost material may be particularly suitable for application in small industries and developing countries.

As a continuation of our previous works (Benaïssa [36, 37]) in this field, the aim of this study is focussed on the effect of temperature on Methylene blue sorption from synthetic aqueous solutions, in single dye solutions, using a biological natural waste: almond peel as an inexpensive sorbent material. Experiments of dye sorption kinetics

and equilibrium were performed in batch conditions. Pseudo second-order model was selected to analyze the data obtained from the dye sorption kinetics. In order to obtain information about the maximum dye sorption capacity of almond peel, the model of Langmuir was selected to analyse the experimental sorption equilibrium data. Using the equilibrium constants obtained at different temperatures, various thermodynamic parameters such as ΔG^0 , ΔH^0 and ΔS^0 , have been determined to explain the process feasibility. The kinetics controlling mechanisms of Methylene blue by almond peel: external mass transfer and intraparticle diffusion were also investigated.

MATERIALS AND METHODS

1. Sorbent material and dye

In this work, an agricultural by-product waste: almond peel has been employed as a low-cost sorbent material in the removal of methylene blue from synthetic aqueous solutions. This waste was collected in summer 2004 from the region of Bensekrane, in Tlemcen-Algeria-, in the form of large flakes, cut in small particles of size 1-5 mm and sun/air dried at ambient temperature. It was used as a sorbent material after the following treatment chosen arbitrary: 10 g of almond peel were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of $25\pm 1^\circ\text{C}$ during 4 hours, then filtered, washed with distilled water for several times to remove all the dirt particles until constant pH (4.90-5.75) and no color, and oven-dried at 80°C for 24 hours after filtration. This material was crushed and sieved into different particles size ranges. Only the size 1.6-2 mm was used for further batch sorption experiments.

The basic dye, methylene blue (REACTIF RAL – France Lot N°.169) was used as such without further purification, in single component aqueous solutions. 1000 mg/L stock solutions of methylene blue were prepared in distilled water. All working solutions of the desired concentration were prepared by successive dilutions.

2- Uptake kinetics

The initial solution Methylene blue concentration was 100 mg/L for all experiments to examine the effect of temperature in the range $10\text{-}50^\circ\text{C}$ on the kinetics of Methylene blue sorption by almond peel. For dye removal kinetics studies, 1 g of almond peel was contacted with 1 L of dye solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature. In all cases, the working pH was that of the original solution and was not adjusted. Samples from the clear supernatant, at appropriate time intervals, were pipeted from the reactor by the aid of the very thin point pipette, which prevented the transition to solution of sorbent samples. Their dye concentrations were determined using a UV-visible spectrophotometer (model Beckman 52, USA) by monitoring the absorbance changes

at a wavelength of maximum absorbance ($\lambda_{\max} = 663 \text{ nm}$). The dye uptake q_t (mg dye/g sorbent) was determined as follows:

$$q_t = (C_o - C_t) \times V/m \quad (1)$$

where C_o and C_t are the initial and time dye concentration (mg/L), respectively, V is the volume of solution (mL), and m is the sorbent weight (g) in dry form.

Blank runs, with only the sorbent in distilled water, were conducted simultaneously at similar conditions to account for any colour leached by the sorbent and sorbed by the glass container. Blanks were also run simultaneously, without any sorbent to determine the impact of pH change on the dye solutions. Preliminary experiments had shown that dyes adsorption losses to the container walls were negligible.

3- Uptake equilibrium

The dye equilibrium isotherms were determined by contacting a constant mass 1 g/L of sorbent material with a range of different concentrations of dye solutions: 5-800 mg/L. The mixture obtained was agitated in a series of 250 ml conical flasks with equal volumes of solution 100 ml for a period of 24 h at a constant temperature in the range 10-50°C. The contact time in the range 6-8 h was previously determined (Benaïssa [36]) but in order to avoid sorption error i.e. a pseudo-equilibrium, 24 h was chosen to study sorption equilibrium. The mixture pH was not controlled after the initiation of experiments. After shaking the flasks for 24 h, the final pH was measured. The equilibrium concentration of unbound dye was determined with a UV-visible spectrophotometer, model Beckman 52, at $\lambda_{\max} = 663 \text{ nm}$ value. The equilibrium dye uptake q_e (mg dye/g sorbent) was determined by difference between concentrations: initial and at equilibrium, respectively.

For at least two temperatures tested, experiments were carried out in duplicate and the average results are presented in this work. Duplicate tests showed that the maximum standard deviation of the results was $\pm 5\%$.

RESULTS AND DISCUSSION

1- Sorption kinetics

Different parameters related to the sorbent, to dye and the medium can influence the kinetics of methylene blue sorption by almond peel. In this context, to study the influence of temperature on the kinetics of methylene blue sorption, four temperatures were selected namely: 10, 25, 40 and 50°C. As shown in Fig. 1, all curves obtained have the same shape characterized by a strong increase of the amount of dye sorbed by almond peel during the first minutes of contact solution – sorbent, follow-up of a slow increase until to reach a state of equilibrium. As an approximation, the sorption of dye

can be said to take place in two distinct steps: a relatively fast one followed by a slower one. These results also indicate that an increase of the temperature in the range 10-50°C deals to an increase in the amount of dye sorbed at equilibrium: 47.16 mg/g ($T = 10^{\circ}\text{C}$) and 60.54 mg/g ($T = 50^{\circ}\text{C}$), indicating the endothermic nature of process. In general, the necessary time to reach equilibrium was in the range 5-7 h depending on temperature tested, and, an increase of sorption time to 24 h did not show notable effects. Generally, this equilibrium time decreased as temperature increased: 7 h ($T = 10^{\circ}\text{C}$) and 5 h ($T = 40^{\circ}\text{C}$), and, an increase of sorption time to 24 h did not show notable effects.

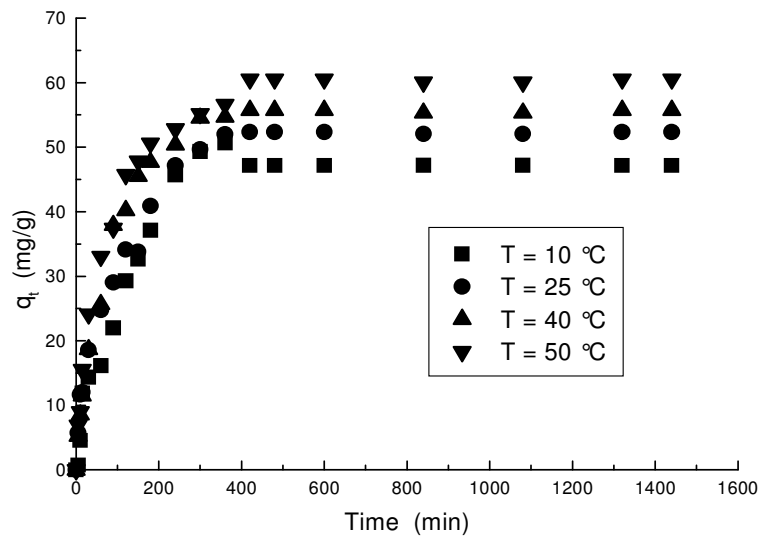


Figure 1. Effect of temperature on methylene blue sorption kinetics by almond peel. (Initial dye concentration = 100 mg/L, sorbent dose = 1 g/L, particles size = 1.6 – 2 mm, natural initial solution pH, agitation speed = 400 rpm)

During the dye sorption experiments, for all temperatures studied (see Fig. 2 as a typical example), an increase in the initial pH value of solution was observed: $\Delta\text{pH} = 0.13\text{-}0.18$ unit between the initial and equilibrium time, depending on temperature used. The pH value at equilibrium was in the range 3.98-4.56 units which decreased with the temperature increase. This phenomenon can be interpreted as a possible release of OH^- ions from the almond peel due to dye sorption or by a possible fixation of H_3O^+ ions by the negative groups present on the sorbent surface. At this stage, further investigations are required to understand the mechanisms involved in dye sorption by this type of complex materials.

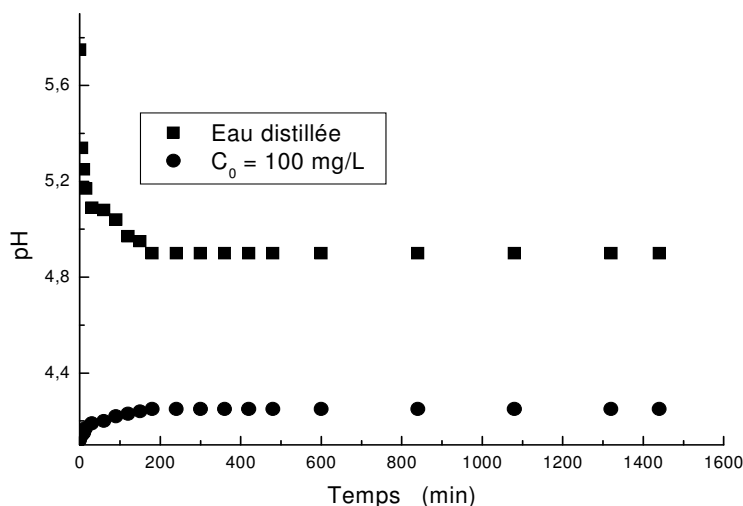


Figure 2. Evolution of initial pH in absence and in presence of methylene blue in solution as a typical example. (sorbent dose = 1 g/L, particle size = 1.6-2 mm, natural initial solution pH, agitation speed = 400 rpm)

The kinetics of methylene blue sorption by almond peel has been only modelled using the pseudo second-order rate equation (Ho [38], Ho & McKay [39]) which had shown its ability to analyse adequately the data of sorption kinetics for this system (Benaïssa [36]) and shown below as:

$$t/q_t = 1/k \cdot q_e^2 + t / q_e \quad (2)$$

where k is the pseudo second-order rate constant of sorption ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$); q_e and q_t are the amounts of dye sorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t , respectively.

For all temperatures tested, when the experimental data were fitted to the pseudo second-order rate equation, straight lines (Fig. no shown here) were obtained from the plot of t/q_t vs. t with good correlation coefficients ($R^2 = 0.9745 - 0.9987$) indicating that the process follows a pseudo second-order kinetics. The different values of constants from the slope and intercept of linear plot are summarized in the Table 1. The values of q_e obtained from the fitting to the pseudo second-order kinetics model are very similar to the experimental values obtained from the dye sorption kinetics at equilibrium.

Table 1: Effect of temperature on pseudo second-order rate constants for methylene blue sorption by almond peel. Initial methylene blue concentration = 100 mg/L

| Temperature (°C) | 10 | 25 | 40 | 50 |
|-----------------------------|--------|--------|--------|--------|
| $q_{e \text{ exp.}}$ (mg/g) | 47.16 | 52.35 | 55.98 | 60.54 |
| $q_{e \text{ cal.}}$ (mg/g) | 51.81 | 54.88 | 58.14 | 62.50 |
| $k \cdot 10^4$ (g/mg/min) | 2.10 | 3.56 | 3.78 | 3.38 |
| R^2 | 0.9745 | 0.9977 | 0.9987 | 0.9968 |

2– Sorption equilibrium

Figure 3 shows the dye sorption isotherms by almond peel obtained at different temperatures. For all isotherms, the amount of dye sorbed increases initially with the dye concentration at equilibrium but then reaches saturation. These isotherms obtained are of type-2 class L type (Langmuir type) according to the classification of isotherms of Giles et al. [40] for sorption from solution, implying strong preferential sorption of the solute. The results obtained indicate that an increase of the temperature in the interval 10-50°C deals to an increase in the maximum amount of dye sorbed: about 77 mg/g ($T = 10^{\circ}\text{C}$) and 118 mg/g ($T = 50^{\circ}\text{C}$). The increase of methylene blue sorption in the interval of temperature 10-50°C means that the process of dye sorption by almond peel is endothermic. If this sorption of methylene blue by almond peel is governed only by a physical phenomenon, an increase in temperature will be followed by a decrease in sorption capacity. During all experiments of dye sorption equilibrium (results not presented here), it was observed that the initial pH value of solution increased, and, the equilibrium pH varied with the initial concentration of dyes and the temperature tested.

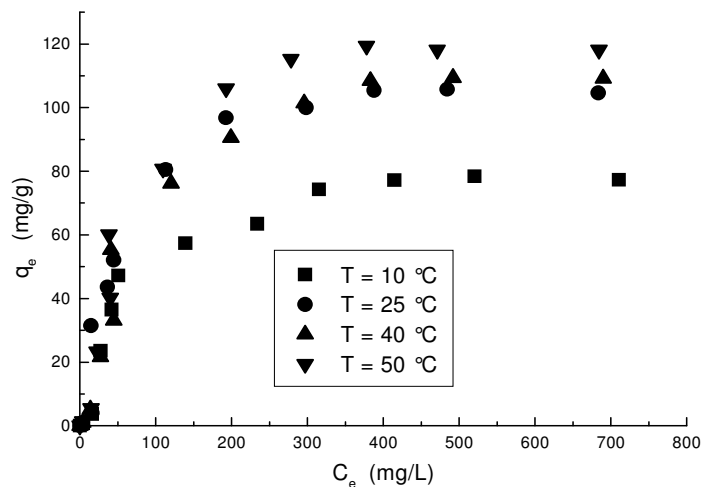


Figure 3. Effect of temperature on Methylene blue sorption isotherm by almond peel.
 ($m = 1 \text{ g/L}$, $dp = 1.6 - 2 \text{ mm}$, natural initial solution pH,
 agitation speed = 400 rpm)

In order to optimise the design of a sorption system to remove pollutants from effluents, it is important to establish the most appropriate correlation for the equilibrium curve. The model of Langmuir [41] commonly used to fit experimental data when solute uptake occurs by a monolayer sorption, has been tested in the present study. Its form is given as follows:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (3)$$

The linearized form on this equation can be written as follows:

$$C_e/q_e = 1/K_L q_m + C_e/q_m \quad (4)$$

where: q_e is the amount of dye sorbed at equilibrium per g of sorbent (mg/g); C_e the equilibrium concentration of dye in the solution (mg/L); q_m and K_L are the Langmuir model constants. If the equation of Langmuir is valid to describe the experimental results, it must verify the linearized shape of the basis equation, in system of coordinates C_e/q_e vs. C_e , that will permit us to obtain the constants q_m and K_L from the intercept and slope. Results of the modelling of isotherms of Methylene blue sorption by almond peel (Figures no presented here) according to this model are presented in Table 2.

Table 2: Langmuir model constants for the sorption of methylene blue by almond peel

| T (°C) | q_m (mg/g) | K_L (L/mg) | R^2 |
|--------|--------------|--------------|--------|
| 10 | 85.18 | 0.017 | 0.9964 |
| 25 | 113.77 | 0.023 | 0.9979 |
| 40 | 128.04 | 0.011 | 0.9859 |
| 50 | 135.14 | 0.014 | 0.9891 |

It appears that the Langmuir model acceptably fits the experimental results over the experimental range with good coefficients of correlation ($R^2 = 0.9859 - 0.9979$). A high dye sorption was observed by this sorbent material confirming the previous tendencies observed in the kinetics sorption. The applicability of this model should be considered as a mathematical representation of the sorption equilibrium over a given dye concentration range. The mechanistic conclusions from the good fit of the model alone should be avoided. In spite of the above limitations, this model can provide information on dye uptake capacities and differences in dye uptake between various species (Kapoo & Viraraghavan [41]). At this stage, no information about the mechanism of dye sorption by this material is available. The sorption of dyes by this kind of complex materials might be attributed to different kinds of sites present on the sorbent surface.

3- Thermodynamic parameters of sorption

In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change, ΔG^0 , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^0 is a negative quantity. To estimate the

effect of temperature on the Methylene blue sorption by almond peel, the free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were determined.

The free energy of the dye sorption, considering the sorption equilibrium constant, K_L , is given by the following equation:

$$\Delta G^0 = -RT \cdot \ln K_L \tag{5}$$

where: ΔG^0 is the standard free energy change (J), R the universal gas constant, 8.314 J/ mol. K and T the absolute temperature (K).

The Gibbs free energy change, G^0 , can be represented as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{6}$$

As shown in Fig. 4, a plot of ΔG^0 versus T was linear. Enthalpy change, ΔH^0 , and entropy change, ΔS^0 , were determined from the slope and intercept of the plots. The thermodynamic parameters obtained for the dye sorption are shown in Table 3.

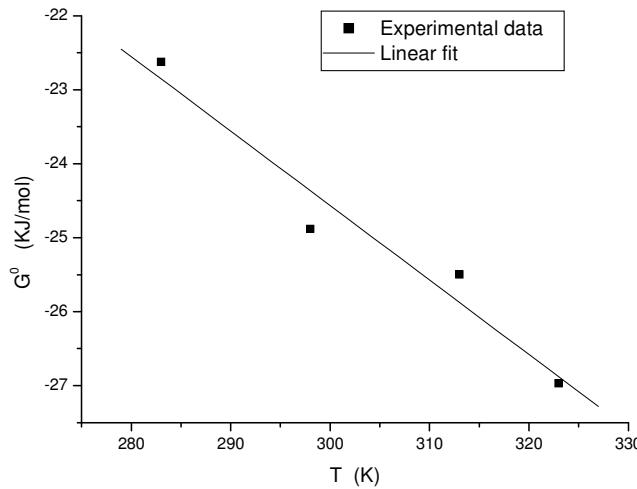


Figure 4: A plot of (G^0 versus T for Methylene blue sorption by almond peel

Table 3. Thermodynamic parameters of Methylene blue sorption by almond peel

| | | | | |
|-------------------------|---------|---------|---------|---------|
| T (K) | 283 | 298 | 303 | 313 |
| G^0 (KJ/Mol) | - 22.62 | - 24.88 | - 25.50 | - 26.97 |
| ΔH^0 (KJ/Mol) | 5.63 | | | |
| ΔS^0 (KJ/Mol/K) | 0.10 | | | |

$R^2 = 0.9518$

The negative ΔG^0 values of methylene blue sorption at various temperatures, confirmed the feasibility of the process and the spontaneous nature of sorption. The positive value of ΔH^0 confirms the endothermic character of dye sorption, whereas the positive ΔS^0 value confirms a certain increased randomness at the solid-solute interface during sorption. The low value of ΔS^0 also indicates that no remarkable change on entropy occurs.

4. Rate determining steps

From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during the sorption process. It is generally agreed that there are four consecutive steps which describe the overall sorption process of solute from a solution by a sorbent particle (Furusawa & Smith, [43]). These steps, as adapted to apply to the sorption of dye by a sorbent particle, are as follows:

- 1- External mass transfer of dye from the solution bulk to the boundary film;
- 2- Dye transport from the boundary film to the surface of the sorbent particle;
- 3- Diffusion of dye within the sorbent particle to the sorption sites: internal diffusion of dye;
- 4- Final uptake of dye at the sorption sites, which is fast.

The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the agitation given here to the solution (400 rpm) is considered as sufficient to avoid steps 1 and 2 being controlling steps. In a well – agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step (Sag & Aktay, [44]). In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis (Findon et al. [45]). The sorption rate will be controlled by the rate of diffusion (Peniche-Covas et al. [46]). Consequently, the two rate limiting steps investigated are external film mass transfer and intraparticle diffusion, either singly or in combination. Models were established to determine the two coefficients initially based on single resistance mass transport analysis (McKay et al. [47]). The approach chosen in this study was restricted to an interpretation and subsequent identification of mass transfer coefficients by separating the two mechanisms, based on the adequacy of correspondence models with experimental data of these parameters. Weber and Morris [48] demonstrated that in intraparticle diffusion studies, rate processes are usually expressed in terms of square root of time. So, q_t or fraction metal sorbed is plotted against $t^{0.5}$ as follows:

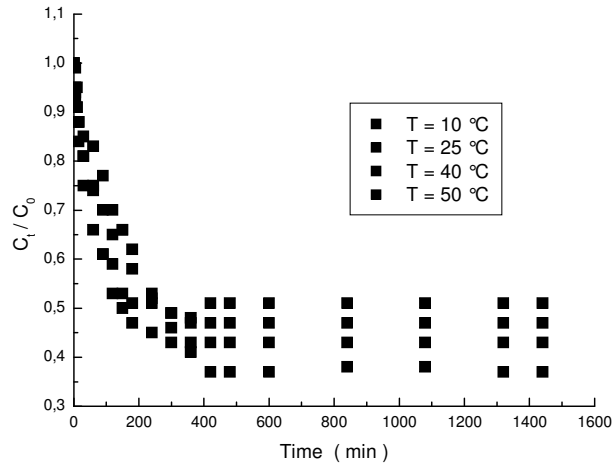
$$q_t = k_i \times t^{0.5} \quad (7)$$

where: q_t is the solute concentration in the solid and k_i the slope of the plot defined as an intraparticle diffusion rate parameter. If particle diffusion is rate controlling, the plots q_t versus $t^{0.5}$ is linear and the slope of the plots is defined as an intraparticle diffusion rate parameter, k_i ($\text{mg metal g}^{-1}\text{sorbent time}^{-0.5}$) (McKay [49]). In theory, the plot between q_t and $t^{0.5}$ is given by four regions representing the external mass transfer followed by intraparticle diffusion in macro, meso and micropore (Ho and McKay [50]). From the Fig. 5b, as a typical example, it was observed that there are two linear portions: a first linear portion followed by another before equilibrium, indicating multiple-stage diffusion of methylene blue onto almond peel particles. Such a multiple nature of the curve confirms that intraparticle diffusion is not a fully operative mechanism for this system and reflects two stages: external mass transfer at initial time periods followed by intraparticle diffusion of methylene blue onto almond peel particles. The slope of the second linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept, e (mg/g), is proportional to the boundary layer thickness: the larger intercept the greater is the boundary layer effect (Kumar et al. [51]). Figure 5a, as a typical example, shows plots of q_t versus $t^{0.5}$ for the effect of temperature on methylene blue sorption by almond peel. Table 4 summarises the diffusion coefficients for different models tested as a function of temperature.

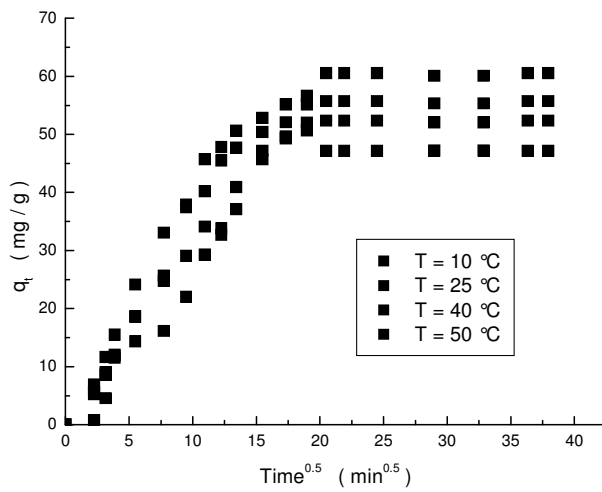
The initial biosorption rate constant corresponding to external mass transfer at initial time intervals was determined using the simplified classic mass transfer equation (5) which describes the evolution of metal ion concentration C_t in solution (McKay et al. [47], Weber and Morris [48], Ho & McKay [49]):

$$d(C_t / C_o) / dt = - \beta_L S \quad (8)$$

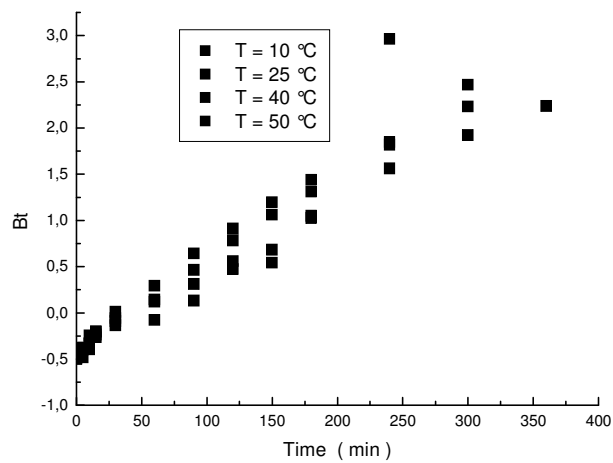
where β_L is the external mass transfer coefficient, C_o and C_t the liquid phase solute concentrations at $t = 0$ and any time t , respectively, and S the specific surface area for mass transfer. The external mass transfer rate, $\beta_L S$, is approximated by the initial slope of the C_t / C_o vs. time graph and can be calculated either by assuming a polynomial relation between C_t / C_o and time that is used here or based on the assumption that the relationship was linear for the first initial rapid phase. Figure 5b, as a typical example, shows plots of C_t / C_o versus time for the effect of temperature on dye sorption by almond peel. The values of external mass transfer rate, $\beta_L S$, obtained under different temperatures, are also given in Table 4.



(a)



(b)



(c)

Figure 5. Effect of temperature on Methylene blue sorption kinetics by almond peel: C_t/C_0 versus t , (b) q versus $t^{0.5}$ and (c) Bt versus t

Table 4: Effect of temperature on diffusion coefficients for Methylene blue sorption by almond peel. ($C_0 = 100 \text{ mg L}^{-1}$; sorbent dose= 2 g L^{-1} ; natural solution pH, agitation speed = 400 rpm; particle size = 1.60 - 2.00 mm)

| T (°C) | External mass transfer model $\beta_L S \times 10^3 \text{ (min}^{-1}\text{)}$ | Intraparticle diffusion model k (mg g ⁻¹ min ^{-0.5}) e (mg/g) | | Boyd model B.10 ³ (min ⁻¹) R ² | |
|--------|---|---|--------|---|--------|
| 10 | 6.04 | 3.80 | -13.43 | 11.57 | 0.8708 |
| 25 | 8.76 | 1.38 | 25.71 | 9.02 | 0.9721 |
| 30 | 7.73 | 1.36 | 29.12 | 9.39 | 0.9853 |
| 40 | 9.78 | 1.10 | 35.80 | 7.60 | 0.9684 |

The results presented demonstrate that temperature is a parameter which affects the sorption kinetics, within the temperature range studied. In general, an increase in temperature is followed by an increase in the diffusivity of the dye, and consequently by an increase in the sorption rate if diffusion is the rate controlling step. Here in the temperature range studied, an increase in temperature is followed by an increase in the $\beta_L S$ value and a decrease in the k value. Except temperature 10°C, the linearization of q_t versus $t^{1/2}$ gave a positive and significant ordinate intercept, indicating the influence of external rate control (Sag and Aktay [44]). These observations indicate that methylene blue sorption by almond peel is a complex process. Thus, in order to determine the actual rate-controlling step involved in methylene blue sorption process, the sorption data were further analysed by the kinetic expression given by Boyd et al. [51]:

$$Bt = -0.4967 - \ln(1 - q_t/q_\infty) \quad (9)$$

where: Bt is a mathematical function, q_t and q_∞ represents the amount of solute sorbed (mg/g) at any time t and at infinite time.

The values of Bt can be calculated for each value of q_t/q_∞ . These values were plotted against time as shown in Fig. 5c, as a typical example. The linearity of this plot will provide useful information to distinguish between external transport and intraparticle transport controlled rates of sorption (Kumar et al. [50]). For all temperatures studied, it was observed that the plots were linear but did not pass through the origin, indicating that external mass transport mainly governs the rate-limiting process (Boyd et al. [51]).

CONCLUSION

This work shows the interest of a concept based on the waste to treat another waste or to resolve an environmental problem. The results obtained confirm that almond peel can remove Methylene blue from aqueous solution. Temperature plays an important part in Methylene blue sorption by almond peel: the amount of Methylene blue sorbed increased as temperature increased. The results also showed that the process follows

pseudo second-order kinetics. Langmuir model gave an acceptable fit to experimental data over the whole equilibrium dye concentrations range. The thermodynamics of the system pointed out the system was spontaneous and endothermic. The process mechanism was found to be complex, consisting of external mass transfer and intraparticle mass transfer diffusion. Analysis of mechanistic steps involved in the sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages for the different experimental parameters studied.

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