Kinetic and thermodynamic approach of organic dye adsorption on biopolymer- kaolin composite

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The removal of cationic dye, Methylene Blue (MB), from aqueous solution using biopolymer-kaolin composite was studied in a batch stirred tank reactor. The effect of various parameters such as, mass of Composite (2 – 10 g), initial MB dye solution concentration (10 - 500 ppm), agitation speed (0 – 1000 rpm) and solution temperature (22 - 65°C) on the mass transfer coefficient, and the rate constant for intraparticle diffusion and pore diffusion coefficient were studied. Using the Arrhenius equation, the energy of activation (E_a) was calculated. Thermodynamic parameters including enthalpy (ΔH), free energy (ΔG) and entropy (ΔS) were calculated and their values showed that adsorption of (MB) on composite was an endothermic reaction process, which was favored at high temperatures. It was found that the higher the composite mass, the higher the mass transfer coefficient, pore diffusion coefficient and the lower rate constant for intraparticle diffusion. In addition, increasing the degree of agitation resulted in an increase in the mass transfer coefficient, pore diffusion coefficient and decrease in the rate constant for intraparticle diffusion. It was also found that the lower the initial MB concentration, the higher the mass transfer coefficient, pore diffusion coefficient and the lower the rate constant for intraparticle diffusion. Temperature was found to increase the rate of mass transfer coefficient, the pore diffusion coefficient and the rate of MB removal while it decreased the rate constant for intraparticle diffusion. Based on the value of E_a = 8.762 KJ/mol confirms the fact that the process of the removal of MB using biopolymer kaolin composite is diffusion controlled.

تمت دراسة لإزالة صبغة الميثيلين الزرقاء القاعدية من المياه الملوثة بالصبغة باستخدام متراكب من الكاولين والبوليمر الحيوى وتم ذلك فى مفاعل دفعى. وقد تم دراسة تأثير بعض العوامل وهى كمية المتراكب (2-10g) وتركيز صبغة الميثيلين الزرقاء القاعدية (500 - 20 ppm) ودرجة التقليب(1000 – 0 rpm) ودرجة الحرارة (22-65°C) على معامل انتقال الكتلة وثابت معدل الانتشار داخل الجزيئات و معامل الانتشار المسامى. و قد تم حساب طاقة التنشيط باستخدام معادلة ارهينيوس وكذلك تم حساب التغير فى قيم الدوال الثرموديناميكية. وقد وجد أن بزيادة كمية المتراكب يحدث زيادة فى كلا من معامل انتقال الكتلة ومعامل الانتشار المسامى ويقل ثابت معدل الانتشار داخل الجزيئات. بالإضافة الى أن زيادة معدل التقليب يؤدى الى زيادة معامل انتقال الكتلة ومعامل الانتشار المسامى والى نقص ثابت معدل الانتشار داخل الجزيئات. كما أن تقليل تركيز صبغة الميثيلين الزرقاء القاعدية يؤدى الى زيادة معامل انتقال الكتلة ومعامل الانتشار المسامى والى نقص ثابت معدل الانتشار داخل الجزيئات. أما بالنسبة للحرارة فقد وجد ان زيادتها تؤدى الى زيادة معامل انتقال الكتلة ومعامل الانتشار المسامى ومعدل ازالة صبغة الميثيلين الزرقاء القاعدية ولكن ثابت معدل الانتشار داخل الجزيئات ينخفض. وبناء على قيمة طاقة التنشيط وهى 8.762 KJ/mol وجد ان عملية ازالة صبغة الميثيلين الزرقاء القاعدية باستخدام المتراكب المستخدم هى عملية انتشار متحكم.

Keywords: adsorption, Methylene blue dye, Mass transfer, Kaolin composite

1. Introduction

Synthetic dyes are extensively used by industries including dye houses, paper printers, textile dyers, colour photography and as additives in petroleum products [1, 2].The effluents of these industries are highly coloured and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm [1]. Moreover, they may also affect photosynthetic activity in aquatic systems by reducing light penetration [3]. Among the various types of dyes, various cationic dyes, including methylene blue, are used in dye, paint production and in wool dyeing [4]. Methylene blue has wider applications, which include coloring paper, temporary hair colorant, dyeing cottons, wools, coating for paper stock, etc. [5-7]. Methylene blue is also used in microbiology,

surgery, diagnostics, trace analysis of anionic surfactants present in aqueous streams and as a sensitizer in photo oxidation of organic pollutants [4]. Though methylene blue is not strongly hazardous, it can cause some harmful effects. Acute exposure to methylene blue was found to cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice, quadriplegia and tissue necrosis in humans [5, 6]. 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 [8]. Although these treatment methods are efficient, they are quite expensive and have operational problems [8, 9]. Sorption of the molecules onto various sorbents is an ideal option for decolourization, which is evidenced by the effectiveness of sorption for various dye types [9, 10]. The main drawbacks which exist at the present time are the high costs involved in the regeneration of the sorbent. Also, since activated carbon is the most widely used and most effective adsorbent, its high cost tends to increase the cost of adsorption systems [8, 9]. This method will become inexpensive if the sorbent used is of derived from inexpensive material and does not require any expensive additional pre-treatment step [5]. 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, fly ash, cereal chaff, pear millet husk carbon, rice husk, perlite, carbonized press mud, bagasse bottom ash [5-7, 11-16].

Clay and kaolin are relatively cheap due to its accessibility and abundance [17, 18]. Clay minerals have great potential to fix pollutants such as heavy metals, dye and organic compounds [19] but still difficult to be separated from the wastewater.

In order to over come the handling problem, biopolymer binding polymers for the granulation of kaolin have a number of advantages such as simplicity of preparation procedure and excellent physicochemical properties [20].

The beads produced from a mixed polymers (alginate and PVA) exhibited rubber like elastic properties, PVA contributed strength and durability to the beads, whereas calcium alginate improved the surface properties, reducing the tendency to agglomerate [21].

The aim of the present work is to study the factors that might affect the rate of the removal of Methylene Blue with biopolymer-kaolin composite in a batch stirred vessel. The present work also focus some light on the probable mechanism of the process, especially the role of mass transfer on the kinetics of MB removal by biopolymer kaolin composite. Finally, activation energy and the thermodynamic data were performed for interpretation of results.

2. Materials and methods

2.1. Materials

kaolin, Hydrated aluminium silicate (SIGMA-Aldrich, Germany).

Poly Vinyl Alcohol (PVA) (MERCK, Germany), Alginic Acid sodium salt (SIGMA, USA.), Methlylene Blue (NICE CHEMICALS Pvt. Ltd., COCHIN).

2.1.1. Preparation of basic dye solution

Methlylene Blue, $C_{16}H_{18}N_3SCI.3H_2O$, is a cationic dye. It was chosen in this study because of its known strong adsorption onto solids. The structure of this dye is shown in Figure 1.The stock dye solution was prepared by dissolving 1g of methylene blue in 1000ml distilled water to obtain 1000ppm dye used for preparing different dye concentrations. The concentration of methylene blue remaining in the supernatant after and before adsorption was determined with a 1.0 cm light path quartz cells using spectrophotometer ((Pirken Elmer model GBC 902)) at λ max of 665 nm. The adsorbed amount of methylene blue was calculated from the concentrations in solution before and after adsorption.

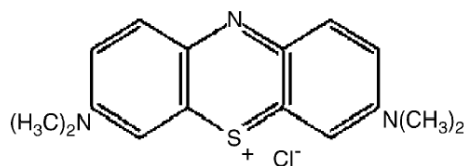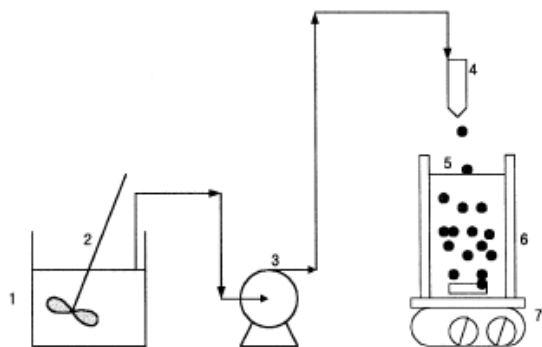Fig.1. Structure of Methlyene blue

Fig. 2. Schematic diagram of kaolin immobilization to form beads: 1, PVA and alginate and kaolin; 2, mechanical stirrer; 3, peristaltic pump; 4, out let tubing; 5, boric acid and CaCl₂; 6, glass beaker; 7, magnetic stirrer.

2.2.2. Preparation of composite Solution

Preparation of composite beads through the following procedures, solution of 4% PVA was prepared by dissolving 20g of PVA (its molecular weight 72000) that has alcoholic structure in the demineralized water by heating the solution to around 60°C with continuous stirring to dissolve PVA. 1% alginate solution that has linear unbranched polymers containing β-(1 → 4)-linked D-mannuronic acid (*M*) and α-(1 → 4)-linked L-guluronic acid (*G*) was prepared by dissolving alginic acid sodium salt (medium viscosity ~3500cps) in water with gentle heating and stirring.

2.2.3. Preparation of biopolymer -kaolin composite

9g kaolin was mixed thoroughly with an aqueous solution of 5% PVA containing 0.5% sodium alginate using the homogenizer for 5min at 14000rpm. This mixture was pumped by a peristaltic pump at 10 ml/min and then dropped into a gently stirred 6% boric acid solution containing 3% CaCl₂ to form

spherical beads as shown in fig. 2. In order to complete gelation inside beads, these beads were stirred gently in the boric acid-CaCl₂ solution for 24h. The beads were then removed and washed with distilled water. Finally the washed beads was dried at 40°C for 24 h. The dried composite was used for detailed studies.

2.2. Setup

The apparatus used consists of a cylindrical Pyrex jacked reactor, with outer diameter 12.3 cm, wall thickness 1.6 cm and 18.2 cm in height. The mixer consists of a stainless steel shaft fitted with four blade propellers, with a diameter 5cm. The stirrer is coated with epoxy resin and is driven by a 35 watt motor which is fixed firmly against a steel frame to prevent vibrations. The rotation speed is controlled automatically by LED display. The jacked reactor was connected with water bath model-ultra term (J.P.SELECTA Co., Spain) to control the temperature.

2.3. Procedure

800 ml of freshly prepared Methylene Blue (MB) solution of known initial concentration (10 - 500 ppm) is placed in the reactor with certain amounts of the biopolymer kaolin composite (2 – 10 g) at the required rotational speed (100 – 1000 rpm) and temperature (22 - 65°C). 2ml samples at different time intervals, are taken from the reactor for MB analysis using "UV-VS spectrophotometery" (Perkin Elmer model GBC 902) (AAS).

3. Results and discussions

3.1. Theoretical aspects

The percent removal of MB was calculated according to the following equation:

$$\% \ Removal = ((C_o - C)/C_o) * 100, \qquad (1)$$

where C_o and C (both in ppm) are the initial concentration and the concentration at any time (min) respectively.

The adsorption capacity q_e (mg/g) after equilibrium was calculated by mass balance relationship equation as follows:

$$q_e = (C_o - C_e) * (V/W), \qquad (2)$$

where V is the volume of the solution (L) , W is the mass of adsorbate (g) and Ce is the equilibrium dye concentration (ppm).

The rate of a heterogeneous reaction in a batch reactor is represented by the following equation [22]:

$$\ln C_O/C = (KA/V)*t . \qquad (3)$$

The above equation is the integrated form of the equation:

$$V(dc/dt) = KAC. \qquad (4)$$

The volumetric mass transfer coefficient (KA) that is used in the present work to express the reaction rate k (min^{-1}) was determined from the slope of the linear plot of ln C_O/C vs. t, where K is the mass transfer coefficient (cm/min), A is the sectional area of the solid reactant (adsorbent) (cm^2), t is the time (min), and V is the solution volume (cm^3). In a batch reactor with rapid stirring, there is also a possibility that the transport of MB from solution into the pores of the biopolymer kaolin composite is the rate controlling step [23-26].

Intraparticle diffusion can be described by three consecutive steps [27]:
1-The transport of sorbate from bulk solution to outer surface of the sorbent by molecular diffusion, known as external (or) film diffusion.
2-Internal diffusion, the transport of sorbate from the particles surface into interior sites.
3-The sorption of the solute particles from the active sites into the interior surface of the pores.

The overall rate of the sorption process will be controlled by the slowest, the rate limiting step. The nature of the rate-limiting step in a batch system can be determined from the properties of the solute and sorbent. In adsorption systems where there is the possibility of intraparticle diffusion being the rate-limiting step, the intraparticle diffusion approach described by Weber and Morris [26]

is used. The rate constants, for intraparticle diffusion (k_p) are determined using equation given by Weber and Morris [26]. This equation can be described as [28–30]

$$q_t = k_p \, t^{0.5} + I, \qquad (5)$$

where k_p and I are the intraparticle diffusion rate constant (mg/g min$^{0.5}$) and a constant, respectively. The k_p is the slope of straight-line portions of plot q_t versus $t^{0.5}$. An extrapolation of the linear portions of the plots back to the axis yield intercepts (I) which are proportional to the extent of boundary layer thickness [31].

These plots have generally the double nature, i.e. initial curve portions and final linear portions. It is explained by the fact that the initial curved portions are boundary layer diffusion effects. The final linear portions are a result of intraparticle diffusion effects.

The pore diffusion coefficient, D (cm^2/s), at different temperatures is determined by using the following equation [32]:

$$t_{0.5} = 0.03 \, r_o^2 / D, \qquad (6)$$

where, $t_{0.5}$ (min) is the time for the removal of half the amount of heavy metal, r_o (cm) is the radius of composite particle. The half time, $t_{0.5}$, for first order reaction is calculated according to the following equation [22]:

$$t_{0.5} = 0.693/KA . \qquad (7)$$

3.1. Effect of mass of biopolymer kaolin composite

Fig. 3, illustrates the effect of the mass of biopolymer kaolin composite that is added to the MB dye solution. It is observed that the removal of MB increases as the mass of biopolymer kaolin composite increases. For instance, the removal of MB increases from 29.2 to 80.1% on increasing the mass of biopolymer kaolin composite from 2 to 10 g after 180 minutes. This may be attributed to the greater availability of the surface area at higher masses of biopolymer Kaolin composite.

Fig. 4, which is a typical plot of ln (C_o/C) vs. t shows that the present data approve the eq. (3). Based on linear regression

(0.99>R^2> 0.96) values, it may be concluded from these plots that the reaction taking place is first order. The values of volumetric mass transfer coefficient, KA are calculated from fig. 4 and presented as function of mass of biopolymer kaolin composite in fig. 6. It may be concluded from the previous figure that as the mass of biopolymer Kaolin composite increased the rate of MB removal increased as indicated by KA. Fig. 5 illustrated the relationship between the amount of Methylene blue dye adsorbed (mg /g) and the square root of time (min$^{1/2}$). The linear regression R^2 values (0.98>R^2>0.93) indicate that an intra-particle diffusion process takes place.

The intraparticle diffusion constant, k_p, at different biopolymer kaolin composite masses was determined and plotted on fig. 6 [23, 24, 33- 35].

Fig. 5. Plot q vs time$^{0.5}$ using different composite mass.
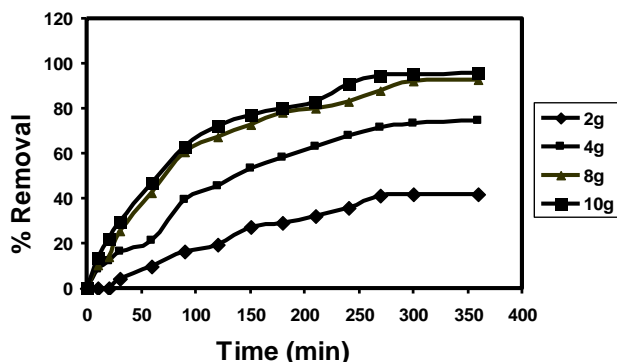
Fig. 3. Effect of composite mass on the % removal of MB dye vs time of adsorption. (agitation speed =500 rpm , MB concentration=20 ppm , PH=9, volume of MB solution= 800 ml and solution temperature = 22°C).
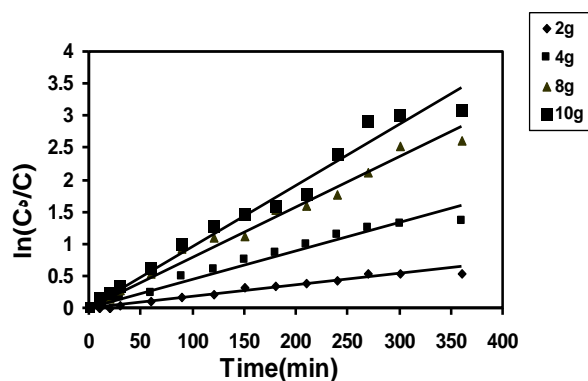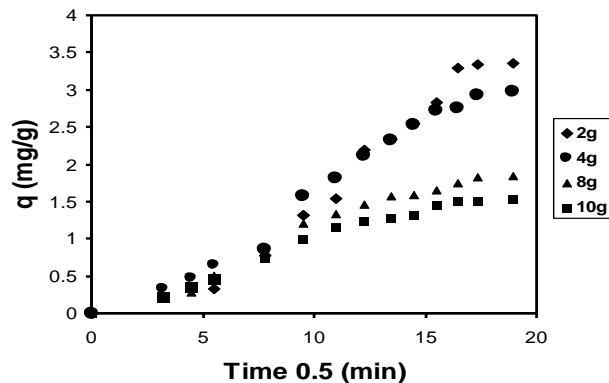
Fig. 6. Effect of composite mass on the volumetric mass transfer coefficient and on the intraparticle diffusion rate constant.
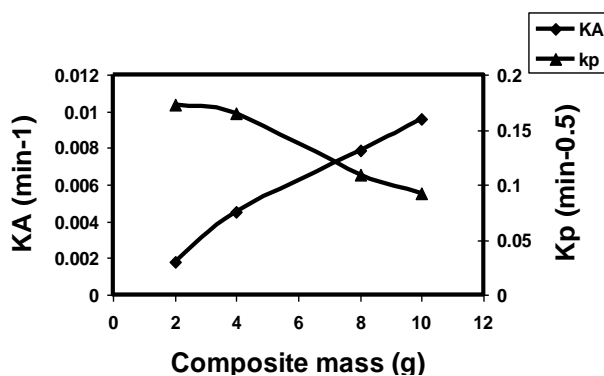

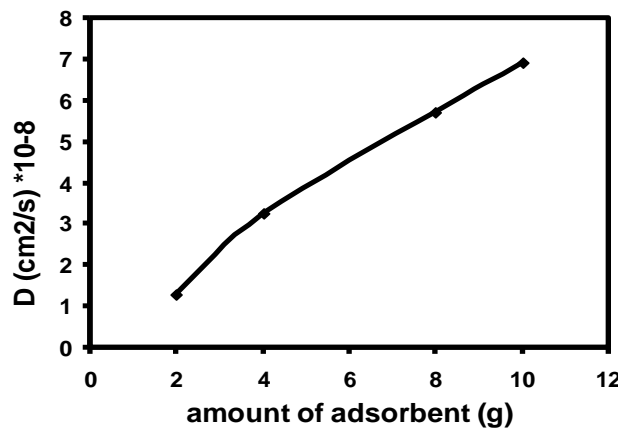Fig. 4. Plot of lnC$_o$ /C vs time using different composite mass.

Fig. 7. Effect of composite mass on the pore diffusion coefficient.

The deviation of straight lines from the origin, as shown in the fig. 5, may be because of the difference between the rate of mass transfer in the initial and final steps of adsorption. Further, such deviation of straight line from the origin indicates that the pore diffusion is not the sole rate-controlling step [34]. From fig. 5, it may be seen that there are two separate regions-the first portion is attributed to the bulk diffusion and the second portion to intraparticle diffusion [36]. It can be noticed from fig. 6 that as the mass of biopolymer kaolin composite increased the rate of MB removal increased as indicated by KA which may be due to higher surface area of composite particles available for the removal of MB, but the rate constant of intraparticle diffusion, k_p decreased.

The values of pore diffusion coefficient, D (cm^2/s), were calculated from eq. (6) where the radius of composite particle r_o equal $1*10^{-1}$ cm. Pore diffusion coefficient was found in the order of 10^{-8} cm^2 s^{-1} as shown in fig. 7 indicating that the rate-controlling step is mainly pore diffusion [23-26] because the overall rate of the exchange process is controlled by whichever is the slowest process. Also, it is observed that the pore diffusion coefficient increased with increasing the mass of biopolymer kaolin composite, which may be attributed to the increase of the mass of biopolymer kaolin composite which increases the volumetric mass transfer coefficient, KA. Accordingly the half time decreases which causes an increase in the pore diffusion coefficient, *D*.

3.2. Effect of agitation speed

It is clear from figure 8 that the increase in agitation speed has a positive effect on MB removal. It increased from 0 to 70.5% at 0 and 100 rpm respectively and slightly increased from 70.5 % to 79.9% at 100 to 750 rpm respectively then decreased to 74.5 at 1000rpm after 180 minutes. The % removal seemed to be affected by the agitation speed for values between 0 and 100 rpm, thus confirming that the influence of external diffusion on the sorption kinetic. In contrast, the small effect of agitation in the range of 100–750 rpm showed that external mass

transfer was not the rate limiting step, and implied that intra-particle diffusion resistance needed to be included in the analysis of overall sorption [37-39].
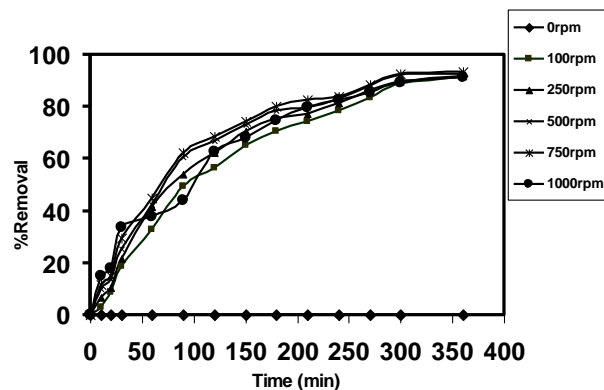

Fig. 8. Effect of agitation speed on the %removal of MB vs time of adsorption. (PH=9, composite mass= 8 g, solution temperature=22°C, volume of MB solution= 800 ml and MB concentration= 20 ppm).
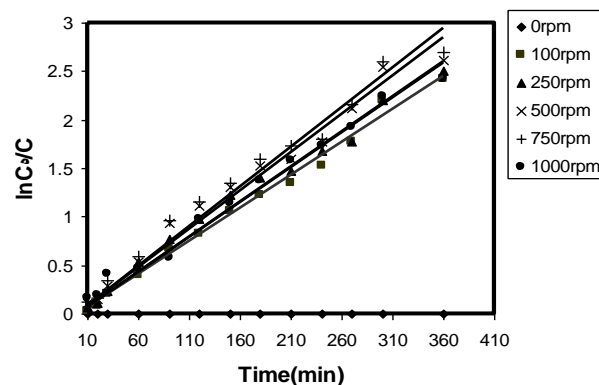

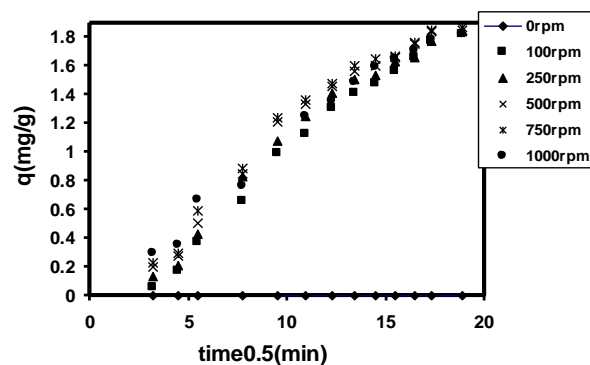Fig. 9. Plot of lnC$_o$/C vs time using different agitation speed.

Fig. 10. Plot q vs time$^{0.5}$ using different agitation speed.

The decrease in the dye removal at 1000 rpm may be attributed to an increase desorption tendency of dye molecules probably because the high shear stress induced by the high degree of stirring strips the weakly adsorbed dye molecules from the kaolin composite particles (physical adsorption) The results were in agreement with Batzias F.A., and D.K. Sidiras [40].

The volumetric mass transfer coefficient, KA, at different agitation speeds was computed from the slopes of fig. 9. The values of the rate constant for intraparticle diffusion, k_p, at different agitation speeds were determined from the slopes of fig. 10. Fig. 11 shows that the volumetric mass transfer coefficient increases with increase in the degree of agitation up to 750 rpm and then decrease at 1000 rpm. The increase in the rate of MB removal as indicated by KA with increasing the degree of agitation within the present range of conditions as shown in figure 11, may be due to the decrease in the liquid phase diffusion layer thickness surrounding each biopolymer kaolin composite particle as a result of the increase in turbulence intensity[41,42].

Solution stirring affects only the liquid phase diffusion layer surrounding each particle. Eddies can not penetrate and enhance intraparticle diffusion depriving the MB from reaching the pore opening [41]. The liquid phase mass transfer contributes a good deal to the process, accordingly intrapartical diffusion may contribute to the process along with liquid phase diffusion but is not controlling. The values of D were found in the order of 10^{-8} cm^2 s^{-1} as shown in fig. 12.

3.3. Effect of initial Methylene Blue (MB) solution concentration

It is observed from fig. 13 that the % removal is inversely proportional to the initial MB solution concentration.

The values of KA and k_p were determined from the slopes of figs. 14 and 15 respectively. Fig. 15 shows that the amount of MB removed per gram biopolymer kaolin composite increases by increasing the MB concentration. Fig. 16 shows that KA decreases with increasing initial MB concentration.
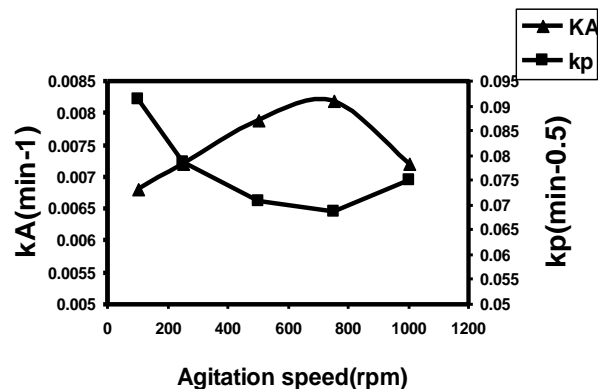

Fig. 11. Effect of agitation speed on the volumetric mass transfer coefficient and on intraparticle diffusion rate constant.
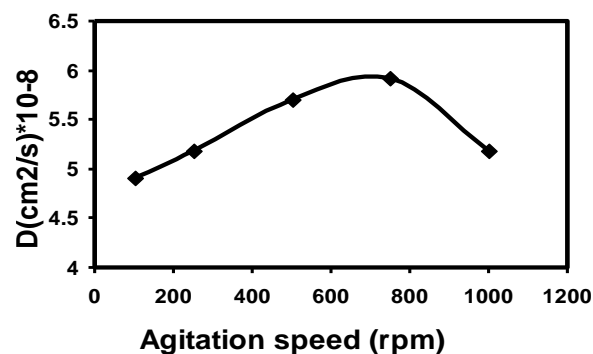

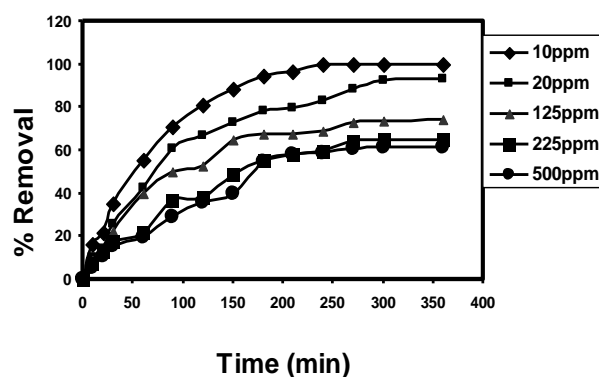Fig. 12. Effect agitation speed on the pore diffusion coefficient.

Fig. 13. Effect of MB concentration on the % removal of MB dye vs time of adsorption.(agitation speed =500 rpm, PH=9, composite mass= 8 g, volume of MB solution= 800 ml and solution temperature =22°C).
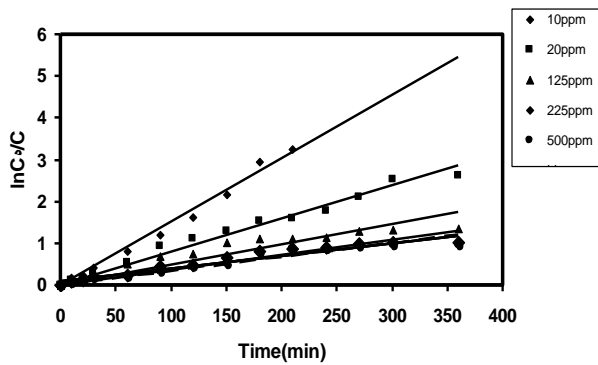
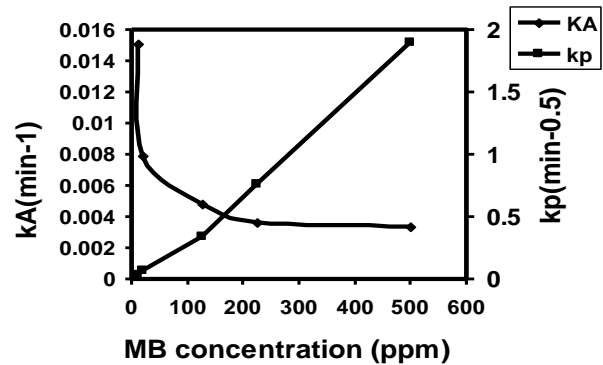Fig.14. Plot of $\ln C_o/C$ vs time using different initial MB concentrations.

Fig. 16. Effect of concentration on the mass transfer coefficient and intraparticle diffusion rate constant.
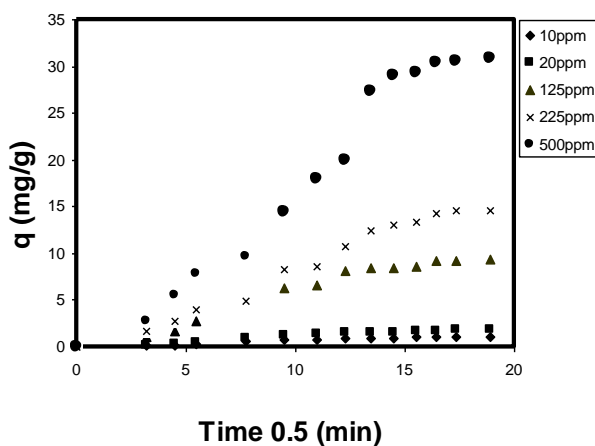

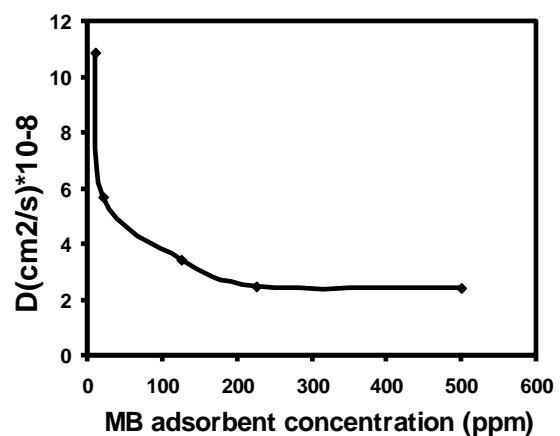Fig.15. Plot of q vs time$^{0.5}$ using different initial MB concentration.

Fig. 17. Effect of adsorbent concentration on the pore diffusion coefficient.

The decrease in the rate of MB removal with increasing initial MB concentration may be due to decreasing MB diffusivity as a result of the association of dye molecules to form bulky aggregates which becomes more pronounced at high dye concentration [43]. It is also observed from the previous figure that the rate constant for intraparticle diffusion increases with increasing initial MB concentration.

It was also found that the pore diffusion coefficient decreases with increasing initial MB concentration. Again this is ascribed to the association of dye molecules when the dye concentration increases in the limited space of the bore [43].

3.4. Effect of solution temperature

The effect of temperature variation on the removal of MB using biopolymer kaolin composite from aqueous solution is presented in fig. 18. From this figure it is seen that the extent of removal of MB increases with temperature.

The volumetric mass transfer coefficient, KA, at different temperatures was derived from the slopes of the lines of fig. 19. The values of the rate constant for intraparticle diffusion, k_p, at different temperatures was determined from the slopes of fig. 20 and was plotted in fig. 21.
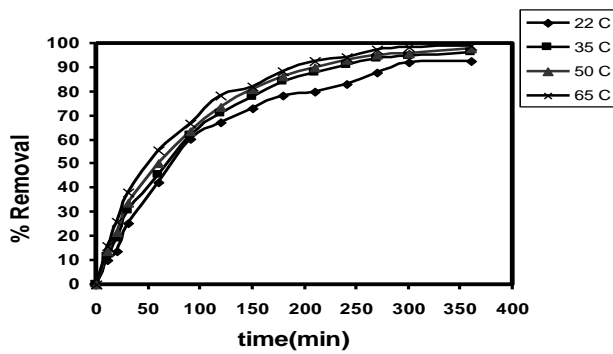
Fig. 18. Effect of solution temperature on the % removal of MB vs time of adsorption. (agitation speed =500 rpm, PH=9, composite mass= 8 g, volume of MB solution= 800 ml and MB concentration= 20 ppm).
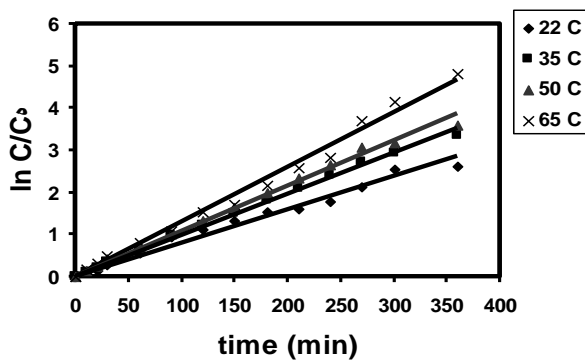

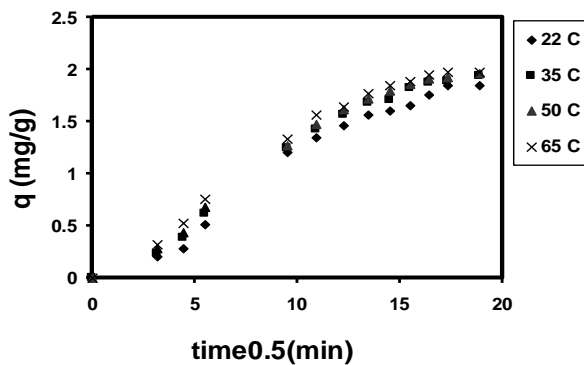Fig. 19. Plot of ln C_o/C vs time for different temperature.

Fig. 20. Plot of q vs time0.5 for different temperature.

Fig. 21 shows that the volumetric mass transfer coefficient increases with temperature with an activation energy of 8.762 KJ/mol .The activation energy, E_a, was determined from the Arrhenius equation:

$$KA = A_o e^{-Ea/RT} \quad . \tag{8}$$

where A_o is the frequency factor, s^{-1} , E_a is the activation energy, kJ mol^{-1} , R is the gas constant [8.314J(mol K^{-1})], T is the absolute temperature in degree Kelvin. Eq. (8) can be written in the natural logarithmic form:

$$ln\ kA = ln\ A_o - E_a/RT \quad . \tag{9}$$

By plotting ln KA vs. $1/T$ a linear relationship was obtained as shown in fig. 22. E_a was determined from the slope $(-E_a/R)$ and A_o from the intercept. The small value of the activation energy below 42 kJmol^{-1} confirms the fact that the process of the removal MB using biopolymer kaolin composite is diffusion controlled [44]. The increase in the rate of MB removal with increasing temperature may be ascribed to the increase in MB diffusivity according to Stokes- Einstein equation [45] and increase in the mobility of the dye.
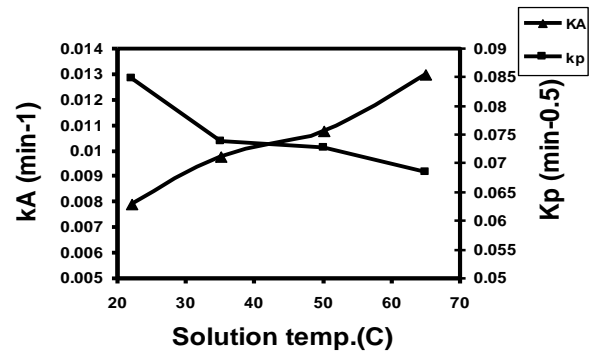
$$D_s\ \mu/T_1 = \text{constant.} \tag{10}$$

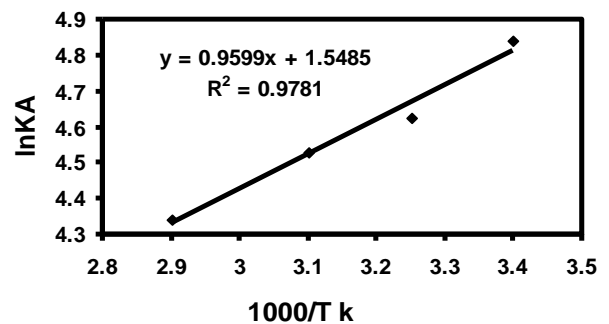Fig. 21. Effect of solution temperature on the mass transfer coefficient and on intraparticle diffusion rate constant.

Fig. 22. Arrhenius plot of MB on biopolymer kaolin composite removal.

where D_s is the diffusivity, cm^2/s, µ is the viscosity, g /cm s and T_1 is the temperature, °C. The increase of temperature leads to increase of pore diffusion coefficient and availability of active sites and subsequently increase of composite capacity.

In spite of this increase in the pore diffusion coefficient but its value is still in the order of 10^{-8}cm^2 s^{-1}, i.e. the rate-controlling step is mainly pore diffusion as shown in fig. 23.

Moreover the increase in dye sorption with a rise in temperature can be explained on the basis of thermodynamic parameters such as change in enthalpy *(ΔH)* and entropy (ΔS) which are calculated using free energy (ΔG), by using the van't Hoff [46,47]:

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \,. \tag{11}$$

Where, $k_c = F_e/(1−F_e)$, and $F_e= (C_o-C_e)/\ C_o$; is the fraction adsorbed at equilibrium, while *T* is the temperature in Kelvin. The plot of $\ln k_c$ versus $1/T$ gives a straight line with acceptable coefficient of determination (R^2) as shown in fig. 24. From the slope and the intercept of van't Hoff plots, the values of ΔH and ΔS have been computed, while the Gibbs free energy change ΔG was calculated using the following eq. [48]:

$$(\Delta G) = -RT\ ln\ k_c. \tag{12}$$

The thermodynamic parameters for the sorption of MB onto organic Kaolin composite at various temperatures were calculated and summarized in table 5. The positive values of ΔH indicate that the studied sorption processes are endothermic in nature. Furthermore the negative values of ΔG° demonstrate the spontaneous behavior of the sorption processes [48]. The decrease in the value of ΔG with the increase of temperature shows that the reaction is more spontaneous at temperature high which indicates that the sorption processes are favored by the increase in temperature [49]. Finally, the positive values of ΔS suggest that the increased randomness at the solid-solution interface during the sorption process. The adsorbed

solvent molecules which are displaced by the adsorbate species gain more translational entropy than ions lost by adsorbate thus allowing for prevalence of randomness in the system [50]. Normally, adsorption of gases leads to a decrease in entropy due to orderly arrangement of the gas molecules on a solid surface. However, the same may not be true for the complicated system of sorption from solution [51].
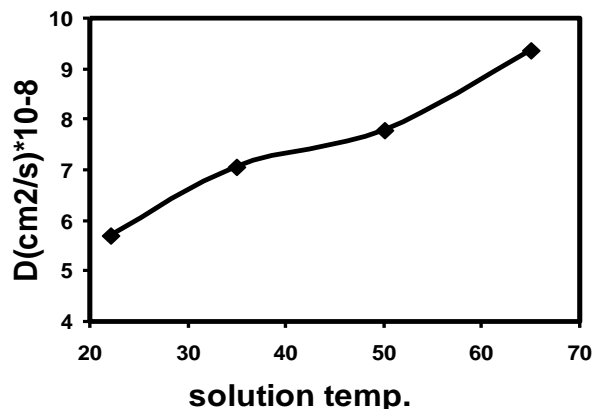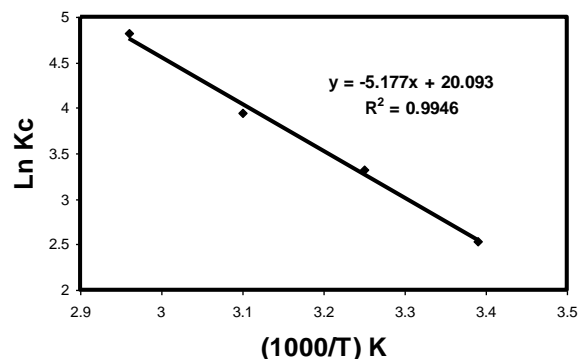

Fig. 23. Effect of temperature on the pore diffusion coefficient.

Fig. 24. Effect of temperature on MB kinetic sorption.

Table1
Thermodynamic parameters for dye sorption

Temperature,°c	ΔG, kJ mol^{-1}	ΔH, kJ mol^{-1}	ΔS, kJ mol^{-1}
22	-6.235		
35	-8.494	5.177	20.093
50	-10.591		
65	-13.55		

4. Conclusions

The results indicated that the use of biopolymer kaolin composite in a batch stirred tank reactor is an effective technique for the removal of methylene blue dye from aqueous solution .The process of the removal of MB using the biopolymer kaolin composite is diffusion controlled with activation energy of 8.762 KJ/mol.

The positive values of ΔH indicate that the studied sorption processes are endothermic in nature. The negative values of ΔG° demonstrate the spontaneous behavior of the sorption processes. The decrease in the value of ΔG with the increase of temperature indicates that the sorption processes are favored by the increase in temperature.

The positive values of ΔS suggest that the increased randomness at the solid-solution interface during the sorption process.

The volumetric mass transfer coefficient , pore diffusion coefficient and intrapartical diffusion rate constant were found to be affected by the mass of composite, degree of agitation, solution temperature, and the initial MB concentration, in accordance with the assumption that the adsorption of MB using the biopolymer kaolin composite is diffusion controlled process.

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