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ORIGINAL ARTICLE

The dye removal from aqueous solution using polymer composite films

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Abstract

The composite consisted of clay and polymers like polyethylene (GCP) was used to remove methylene blue (MB) from the water. The most effective pH, temperature and initial dye concentration in adsorption process were found to be 9, 55 °C and 5×10^{-6} M, respectively. The results of the experiment showed that the adsorption process was compatible with the pseudo-second-order model. Activation parameters of ΔG: −70.64 K J mol^{-1}, ΔS: −70.64 J mol^{-1} K^{-1}, E_a: 12.37 K J mol^{-1} at 308 °C were calculated and showed that adsorption process was exothermic and spontaneous. The results revealed that adsorption of MB on composite GCP was spontaneous and the composite of GCP_f could be used for removing of MB from the water.

Keywords Adsorption · Composite film · Polyethylene · Thermodynamic parameters

Introduction

Nanotechnology and nanomaterials are being used for various applications such as organic reactions, solar cells, fuel cells, hydrogen storage, sensors, dye removal applications (Celik et al. 2016; Gezer et al. 2017; Giraldo et al. 2014; Wang et al. 2016; Sahin et al. 2018; Young et al. 2018; Abrahamson et al. 2013; Saravanan et al. 2013a, b, c, d, e, 2015a, b; 2016a, b; Ghaedi et al. 2015; Salunkhe et al. 2016; Mittal et al. 2010; Gupta et al. 2011, 2014a, b, 2015; Mohammadi et al. 2011; Robati et al. 2016; Asfaram et al. 2015; Ahmaruzzaman and Gupta 2011; Khani et al. 2010; Devaraj et al. 2016; Gupta and Saleh 2013; Saleh and Gupta 2011; 2012a, b; 2014). From these applications, dye removal applications have an important place among them and removal of dyes from water is extremely important (Saravanan et al. 2015a, b; Yang et al. 2018). The increase in dyes pollutants in water is extremely dangerous for the plant, animal and human life (Saravanan et al. 2016a, b; Fan et al. 2012). Because of having a toxic effect on aquatic life and reducing photosynthetic activity of aquatic life by reducing light transmittance, painted wastewater causes significant environmental problems (Barquist and Larsen 2010; Fu and Viraraghavan 2001). Composite materials are generally based on the principle of combining different materials in a particular manner. The ultimate aim to obtain composite material is to allow a new homogeneous material from different properties. Composite materials consist of a combination of matrix and reinforcing elements (Hahn and Gates 1980). Besides, polyethylene is a thermoplastic material which is chemically stable, inexpensive in cost, showing quite high resistance and non-sensitive in low temperatures (Zhano et al. 2005). Generally, methods used to remove harmful substances from the water are adsorption, bio-sorption, ion-exchange, chemical coagulation–flocculation, ozonation, chemical, and photo-oxidation. Specifically, one of the high treatment methods for the treatment of painted wastewater is adsorption (Kannan and Sundaram 2001; Aksu 2005). Among the mentioned dyes, methylene blue (MB) (3,7-bis (dimethylamino)-fenazotiyony chloride) is a dark blue dye

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which is easily soluble in water, ethanol, and chloroform and has the gripping force in water. This dye is a cationic molecule, its molecular weight is 373.9 g mol^{-1}, and it has a $C_{16}H_{18}N_3SCl{\cdot}3H_2O$ formula. Because it has a strong adsorption capability, it has been chosen for this study. In this work, it was aimed to remove the MB dye from aqueous solutions using the composite consisted of polyethylene and green clay. Kinetics of adsorption process between the composite and MB, the thermodynamic data such as entropy, Gibbs energy, and enthalpy of the process were evaluated. Samples of natural green clay, polyethylene, and the composite GCP_f were characterized by SEM, BET, and TGA analysis, respectively. With the results of the study, it was found that the obtained composite material could be used effectively to remove pollutants like methylene blue from the water solutions.

Experimental

Materials

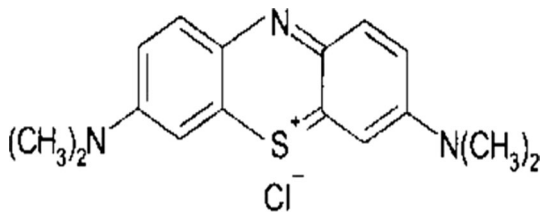
Methylene blue was obtained from Carlo Erba company. Scheme 1 lists chemical formula of methylene blue. Polypropylene (PP) which was used as the matrix at the composite film was obtained from company PETKİM. Green clay used in this study was obtained from the region of Gurpınar (Van-Turkey). The structure of green clay was investigated in scanning electron microscopy (SEM). All the chemicals used in the study are of analytically appropriate quality. BET nitrogen adsorption (Micromeritics Flow Sorb ll-2300) was done for finding the effective surface area. Tables 1 and 2 show the contents and some properties of green clay, respectively.

The process of adsorption experiments

The experiments of adsorption were performed by using mechanical stirring. Pure water was used to prepare methylene blue solutions. The experiment was performed with an initial concentration of methylene blue, 1×10^{-5} M, at room temperature with the stirring speed of 600 rpm (pH 9). The solution of methylene blue was agitated for 1440 min at 600 rpm. For the adjusting of the methylene blue solution, NaOH (5×10^{-2} M) and HCl (5×10^{-2} M) were used. The kinetic experiments were carried out with 1×10^{-5}, 2.5×10^{-5}, 5×10^{-5} M of methylene blue solutions, at pH of 5.5, 7, 9 and at various temperatures such as 298, 308, 318, 328 K. 4 mL sample was taken from the main solution for each adsorption analysis. This sample was centrifuged (Cary 1E UV–Vis spectrophotometer) for 5 min at 3000 rpm stirring speed. The remains of the solution were used for adsorption analysis. The adsorption changes were monitored and Eq. (1), as shown below, was used to calculate the amount of adsorbed methylene blue.

$$q_t = \left[C_0 - C_t\right] \times V/m \quad (1)$$

where q_t is the amount of initial adsorbent, C_0 is the initial concentration of MB, C_t is the concentration of MB at any time, m is the mass of the composite, and V is the volume of the solution.



Scheme 1 Chemical structure of methylene blue

Table 1 The content of green clay used in the study

Constituent	Percentage present (%)
Si	44.79
O	36.80
Al	9.20
Mg	20.74
Fe	12.48
Ca	10.02
Others	2.77

Results and discussion

Effect of initial concentration of methylene blue on adsorption rate

The experiments of the GCP_f blend at different methylene blue concentrations with stirring speed of 600 rpm were performed to determine the equilibrium time. Figure 1 shows that when the concentration of the methylene blue was increased, adsorption kinetics also increased. The time

Table 2 Some properties of green clay

Parameters	Value
Grain size (mesh)	325
Color	Green
pH	9.73
Specific surface area (single point)	148.4 $m^2\ g^{-1}$
Specific surface area (single point)	154.7 $m^2\ g^{-1}$

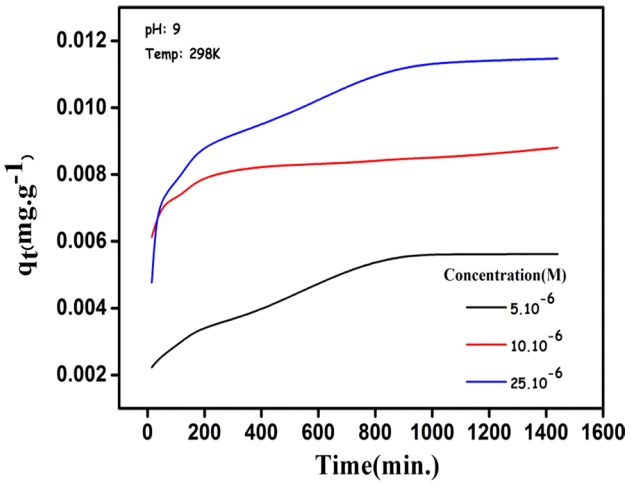


Fig. 1 The change of adsorption kinetics with different methylene blue concentration

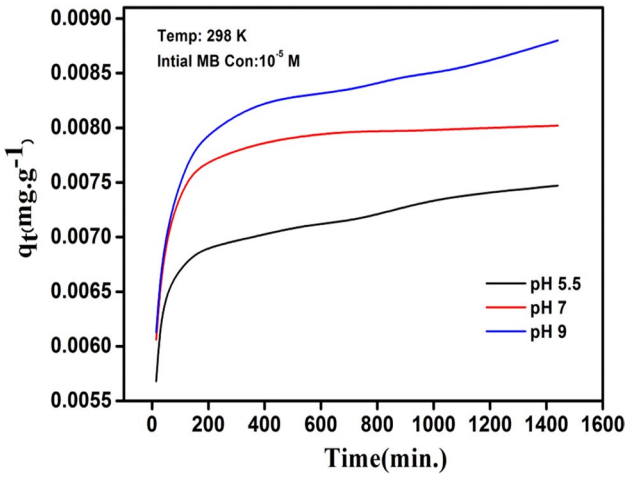


Fig. 2 The exchange of adsorption kinetics with different pH of solution

required to reach a constant concentration according to Fig. 1 is about 800–1000 min.

The exchange of adsorption kinetics with different pH of the solution

The exchange of adsorption kinetics with different pH of the solution is given in Fig. 2. As the pH increased, the adsorption kinetics increased. Generally, adsorbents used in adsorption studies have both negative and positive charges (Burns et al. 1979; Treybal 1963; Nandi et al. 2009). The green composite polyethylene (GCP) used in the study has both positive and negative charges on its surface. These charged particles affect the OH^- ions in the solution medium. The removal of methylene blue (MB) from water solution was found to be effective at range pH of 5.5–9. This can be attributed to the hydrophobic functional groups (originating from polyethylene) present on the surface of the GCP composite material (Ghaedi et al. 2011). This situation can express that when the pH value of the solution increases, the formation of strong electrostatic forces occurred between the positively charged MB and the negatively charged GCP_f composite film (Li et al. 2010; Lim et al. 2015). The formation of GCP_f composite material and the removal of MB dye from water solution are summarized in Scheme 2 and shown in Fig. 3.

The exchange of adsorption kinetics with various temperature of solution

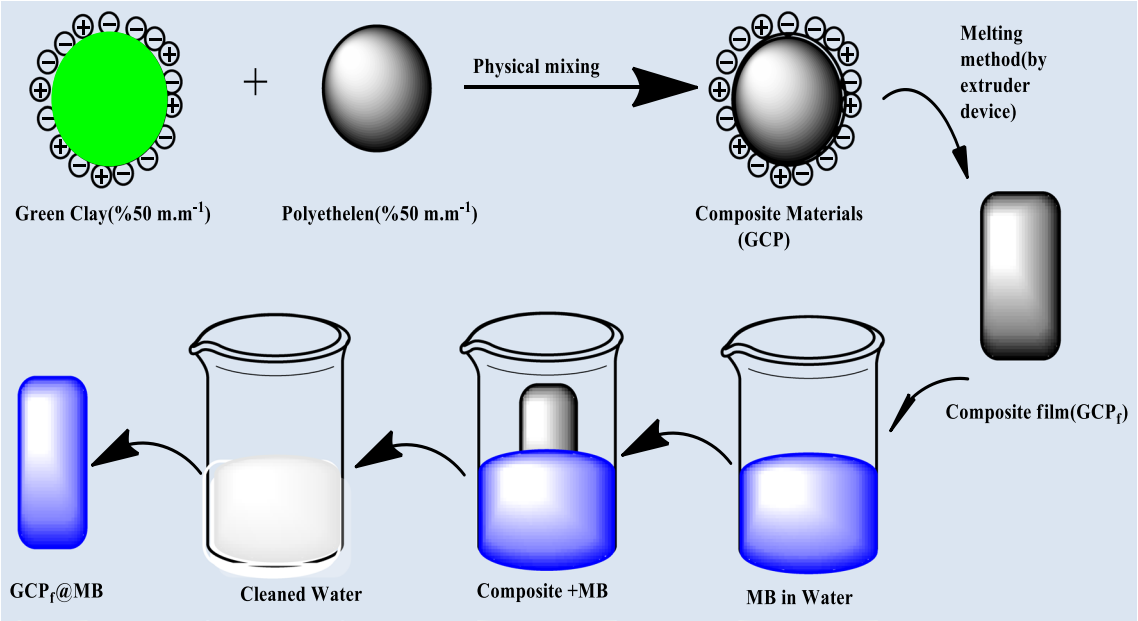
Figure 4 shows the exchange of adsorption kinetics with a variable temperature of the solution. It was seen that the temperature was the very effective parameter in MB dye adsorption experiments. These experiments were performed at 25, 35, 45 and 55 °C, with initial methylene blue concentration of 2×10^{-5} M at pH of 9. The highest adsorption value was obtained at 55 °C. The kinetic energy of the molecules increases with increasing temperature. When the temperature of the solution increased, the diffuse of molecules on the surface composite increased and then adsorption was also increased. The pores of composite increase volume with temperature and the adsorption of MB is positively affected (Dahri et al. 2015).

TGA (thermal gravimetric) analysis of materials and/or composites

TGA analysis was carried out with respect to thermal degradation and mass losses of the samples. Perkin Elmer Pyres model analyzer was used for TGA. The green clay was analyzed at a temperature range of 100–700 °C, and the polyethylene was analyzed at a temperature range of 50–450 °C. All TGA analyses were performed at a nitrogen atmosphere and a heating rate of 10 °C/min. TGA analysis is given in Fig. 5. Figure 5a shows that the loss of water in polyethylene started at 100 °C and the loss of water ratio was 3.2%. Figure 5 shows that the composite (b) shows a more stable structure at the temperature range of 0–100 °C than the pure green clay sample. The situation in other temperatures can be interpreted that mass loss occurs due to the separation of some functional groups and deterioration of the structure at the temperature range of 350–450 °C.

SEM analysis of materials and/or composites

SEM images of pure polyethylene (PE), the composite (GCP_f) film consisted of pure polyethylene–green clay and the composite adsorbed methylene blue (GPC_fM) are given in Fig. 6. Figure 6a shows the SEM image of pure



Scheme 2 Formation of GCP_f and its removal MB from water solution

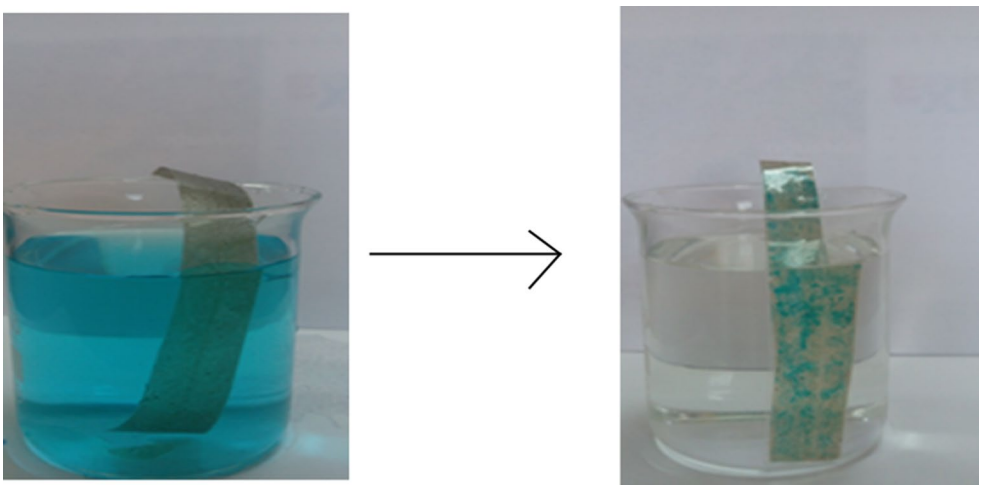


Fig. 3 Removal of MB from water in the laboratory

PE and as shown here, some porous structure is seen on the surface PE. Figure 6b indicates the surface of GCP_f. Bright and dark dots are seen on the surface of the composite. These dots show both polyethylene and green clay. In Fig. 6c, the methylene blue absorbed by the composite material can be clearly visible. After the adsorption, the composite surface appears brighter and smoother. This situation indicates that the composite material is covered with the MB.

Investigation of suitable adsorption kinetic models

Three models were investigated to find the suitable model for the interaction between the composite material and the dye. These models are the pseudo-first-order model, pseudo-second-order model, mass transfer and intra-particle diffusion models. Tables 3 and 4 show the results of experiments and calculated values of models for the adsorption process.

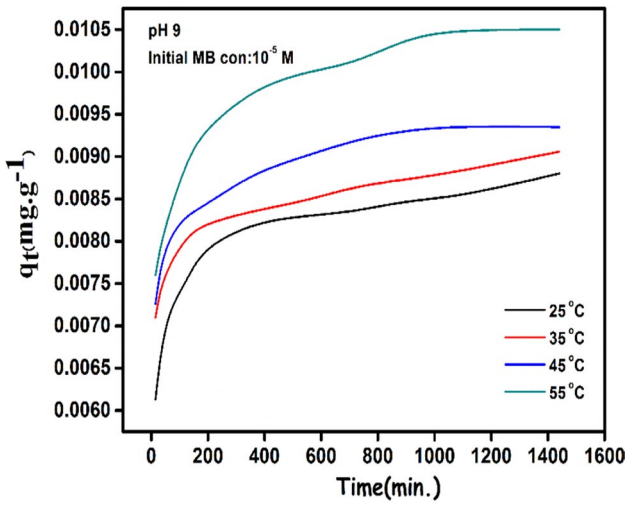


Fig. 4 The exchange of adsorption kinetics with a various temperature of solution

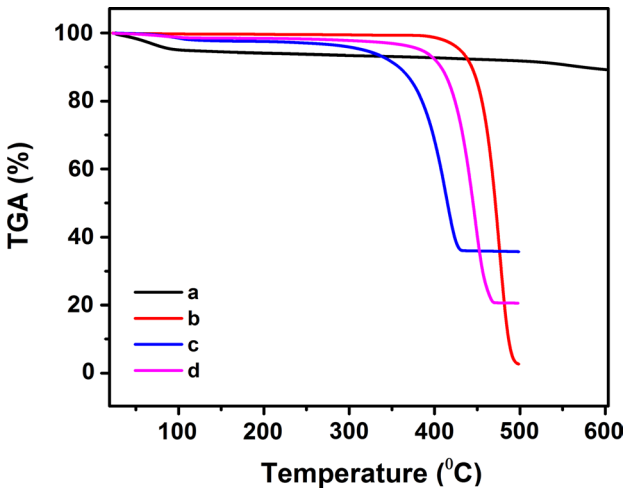


Fig. 5 TGA diagram of pure green clay (**a**), pure polyethylene (**b**), green clay + polyethylene (composite) (**c**), green clay + polyethylene + methylene blue (**d**)

Equation (2) is used to find values of the pseudo-first-order model (Demirbas and Nas 2016). Equation (3) shows the pseudo-second-order model. The half-life time of the adsorbing kinetic is shown in Eq. (4). The first rate of adsorption is shown by Eq. (5). In this equations, q_e and q_t represent, respectively, equilibrium time and at any time amount of adsorption dye. k_1 and k_2 are rate constants, and t is time (min.). These two values were found from the plot of ln $(q_e - q_t)$ (Demirbas and Nas 2016; Laidler and Meiser 1999) with time, respectively, 0.87 and 0.96. $t_{1/2}$ expresses the half-time of the process. Equation (6) was used for calculation of intra-particle diffusion model (Demirbas and Nas 2016). In this equation, k_{int} (mg (g min$^{-1/2}$)$^{-1}$) is a rate constant of diffused intra-particle which was calculated from the slope of the graphic in Fig. 3 and calculated values k_{int} are given in Table 4. q_t is the amount of adsorbed methylene blue. Previous studies (Demirbas and Nas 2016; Ho and McKay 1997) showed that the graph of q_t versus $t_{1/2}$ is multi-linear. Thus, similar adsorption events can be characterized by two or more steps.

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{3}$$

$$t_{1/2} = \frac{1}{k_2 q_e} \tag{4}$$

$$h = k_2 q_e \tag{5}$$

$$q_t = k_{\text{int}} t_{1/2} + C \tag{6}$$

As it can be seen in Fig. 7, the adsorption phenomenon takes place in two phases. The adsorption event occurred according to the initial linear portion in 12–13 min; after this period, the process will occur according to the second linear portion. The first curve in the graph shows rapid adsorption, while the second curve shows that adsorption was slowed by pore filling. It can be said that the adsorption was compatible with pseudo-second-order according to values of R^2 in Table 3. The calculated values $k_{\text{int},1}$ and $k_{\text{int},2}$ at different conditions are given in Table 4. In Table 4, it is found that $k_{\text{int},1}$ values are higher than $k_{\text{int},2}$. The slope of the graph corresponding to the second linear model is expressed as intra-particle diffusion ($k_{\text{int},2}$ (mg/(g min$^{1/2}$)) (Dogan and Alkan 2003). The graph between ln $[(C_t/C_0) - 1(1 + mK)]$ and t (time) is not linear. In this case, the adsorption phenomenon does not match the mass transfer (Kannan and Sundaram 2001; Nas et al. 2017). The calculated values R^1 and R^2 (regression coefficients) are given in Table 4.

Equation (7) and the slope of Fig. 8 were used to find E_a (J mol^{-1}) (activation energy) in which k_2 is rate constant for the second-order model, R_g is constant gas (8.314 J K^{-1} mol^{-1}), and A is Arrhenius factor. By using the slope of Fig. 8, the activation energy was found to be 12.37 K J mol^{-1}. Activation energy values are smaller than 40 K J mol^{-1}. Therefore, the adsorption process considered to be physical interactions. However, interactions between the activation energy values of 40–800 K J mol^{-1} are considered as chemical (Ho and McKay 1997). Equations (8) and (9) were used for calculation of the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS). In these equations, the Boltzmann constant (1.3807×10^{-23} J K^{-1}) is k_B, the Planck constant (6.6261×10^{-34} J s^{-1}) is h. The other expressions are given in the previous rows.

$$\ln k_2 = \ln A - \frac{E_a}{R_g T} \tag{7}$$

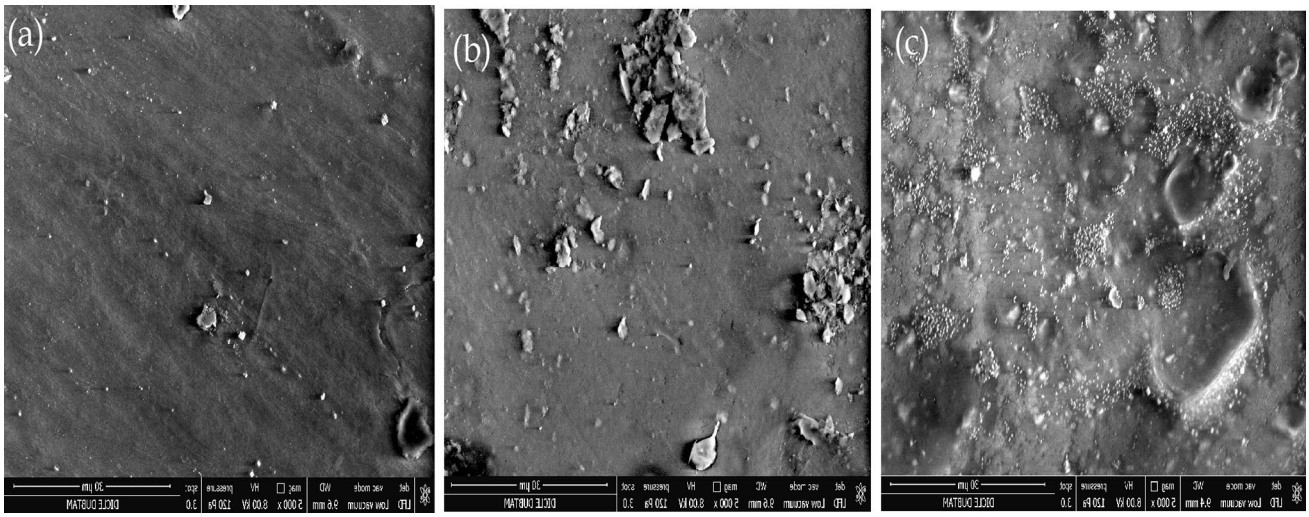


Fig. 6 SEM images of pure polyethylene (**a**), polyethylene with GC (**b**) and the composite with methylene blue (**c**)

Table 3 Calculated kinetic models and some results of experiments

Kinetic models										
Parameters				Pseudo-first-order				Pseudo-second-order		
Temp. (K)	Initial dye conc. ($g\ L^{-1}$)10^4	pH	Stirring speed (rpm)	R^2	q_e (calculated)	q_e (exp.) ($mg\ g^{-1}$)	k_2	R^2	h	$t^{1/2}$
298	0.1	9	600	0.88	0.0088	0.0088	5.992	0.99	0.0527	3.87
308	0.1	9	600	0.94	0.0090	0.0090	6.127	0.99	0.0551	5.47
318	0.1	9	600	0.95	0.0097	0.0094	8.228	0.99	0.0773	7.45
328	0.1	9	600	0.96	0.0105	0.0105	4.7367	0.99	0.0497	10.95
298	0.05	9	600	0.87	0.0059	0.0059	1.662	0.98	0.0095	13.42
298	0.1	9	600	0.92	0.0085	0.0085	6.0671	0.99	0.0516	18.97
298	0.2	9	600	0.96	0.0117	0.0117	1.7841	1.00	0.0209	23.23
298	0.1	5.5	600	0.92	0.0074	0.0074	9.4500	0.99	0.0699	26.83
298	0.1	7	600	0.91	0.0080	0.0080	15.978	0.99	0.1278	30.00
298	0.1	9	600	0.92	0.0085	0.0085	6.0671	0.99	0.0516	32.86

Table 4 Calculated kinetic models and some results of experiments

Mechanism of adsorption								
Parameters			Mass transfer intra-particle diffusion					
Temp. (K)	Initial dye conc. ($g\ L^{-1}$)10^4	pH	Stirring speed (rpm)	R^2	$k_{int,1}$ ($mg\ g^{-1}\ min^{-1/2}$)10^2	R_1^2	$k_{int,2}$ ($mg\ g^{-1}\ min^{-1/2}$)10^2	R_2^2
298	0.1	9	600	0.65	0.0173	0.95	0.0032	0.96
308	0.1	9	600	0.76	0.0141	0.85	0.0042	0.97
318	0.1	9	600	0.78	0.0126	0.95	0.0052	0.95
328	0.1	9	600	0.71	0.0192	0.99	0.0047	0.95
298	0.05	9	600	0.83	0.0124	0.98	0.0032	0.55
298	0.1	9	600	0.78	0.0109	0.93	0.0042	0.97
298	0.2	9	600	0.81	0.0203	0.99	0.0100	0.91
298	0.1	5.5	600	0.62	0.0145	0.87	0.0024	0.98
298	0.1	7	600	0.48	0.0166	0.93	0.0013	0.84
298	0.1	9	600	0.78	0.0109	0.93	0.0042	0.97

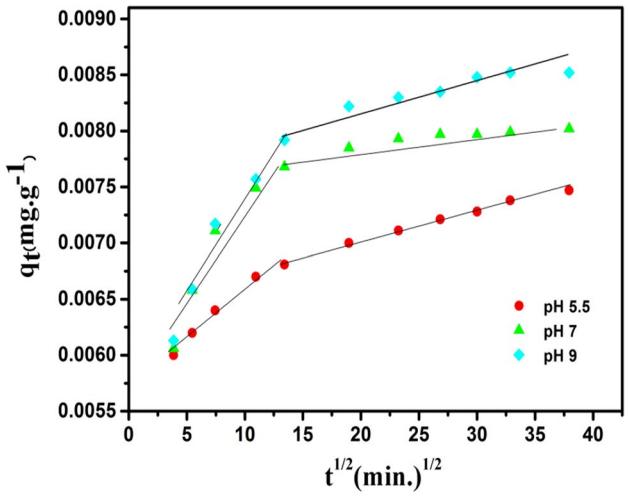


Fig. 7 The plot of intra-particle diffusion for different values of pH

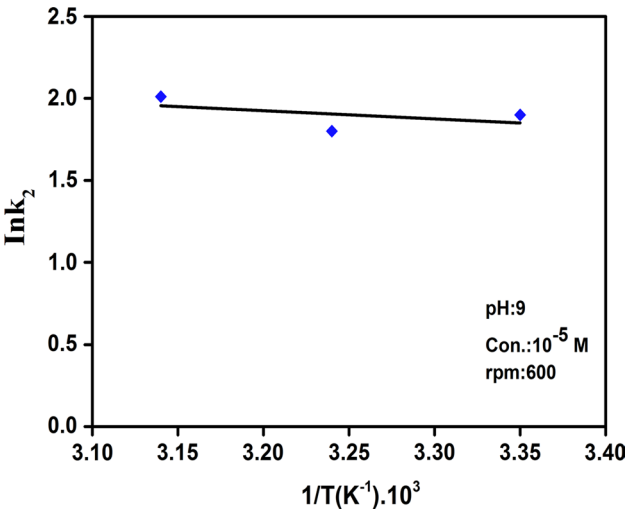


Fig. 8 The plot of $\ln k_2$ versus to $1/T$

$$\ln\left(\frac{k_2}{T}\right) = \ln\left(k_B/h\right) + \frac{\Delta S^\circ}{R_g} - \frac{\Delta H^\circ}{R_g T} \tag{8}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{9}$$

The ΔH was calculated to be -9.81 K J mol^{-1} according to Eq. (8). The enthalpy of the process of adsorption is negative, and physical bonds have taken place between the composite and methylene blue. The calculated values of ΔG and ΔS are seen in Table 5 as negative. These values imply the process of adsorption is spontaneously (Hunter 1999; Mall and Upadhyay 1995).

Conclusions

To conclude, composites film which consists of polyethylene and green clay was successfully formed and performed for methylene blue removal applications. Kinetic parameters of the adsorption between composite and methylene blue were investigated. Temperature, the initial concentration of methylene blue and pH were taken as kinetic parameters. The values initial concentration of methylene blue was 5×10^{-6}, 10×10^{-6} and 25×10^{-6} M, the values of reaction temperature were 25, 35, 45 and 55 °C, and the values of pH were 5.5, 7 and 9. Experimental results showed that the adsorption increased with increasing methylene blue concentration. It was also observed that the adsorption increased with the increase in the pH values from 5.5 to 9. It was also seen that adsorption increased with increasing temperature because of the increased kinetic energies of the molecules. Four models (pseudo-first-order model, pseudo-second-order model, mass transfer and intra-particle diffusion models) were tried to find the fitting kinetic model of adsorption. According to the results of the experiment, the adsorption of GPC$_f$M corresponds to the pseudo-first-model for the first 12–13 min, and for the next time period, it corresponds to the second-order model. Thermodynamic parameters were investigated and calculated according to the results of experiments and equations. Thermodynamic parameters showed that the adsorption event is spontaneous, physical and required low energy. It was shown that the obtained composite material film separated methylene blue easily and spontaneously from the water.

Table 5 Thermodynamic parameters of the MB adsorption

T (K)	ΔG° (K J mol^{-1})	ΔH° (K J mol^{-1})	ΔS° (J mol^{-1} K^{-1})	E_a (K J mol^{-1})
298.0	−68.67	−9.81	−197.51	12.37
308.0	−70.64			
318.0	−72.62			
328.0	−74.59			

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