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To cite this article: Pow-Seng Yap and Viveta Priyaa 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **495** 012052

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Removal of crystal violet and acid green 25 from water using kaolin

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Abstract. The adsorption performances of crystal violet (CV) and acid green 25 (AG 25) from water by using kaolin (KM 20 and KM 40) were investigated. Batch adsorption kinetic and adsorption isotherm experiments were carried out. The fitted models were plotted and analyzed for adsorption kinetic and isotherm studies based on the experimental data obtained. For adsorption kinetics, pseudo-second-order kinetic model was best fitted. For CV, the R^2 values obtained were 0.9990 and 0.9995 for KM 20 and KM 40, respectively. For AG 25, the R^2 values obtained were 0.9971 and 0.9991 for KM 20 and KM 40, respectively. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were plotted and investigated for the adsorption equilibrium studies. Among the isotherm models, Langmuir model was best fitted, thus indicating monolayer adsorption had occurred. For CV, the maximum adsorption capacity ($q_{\max}$) values obtained were 23.64 mg/g and 31.35 mg/g for KM 20 and KM 40, respectively. For AG 25, $q_{\max}$ values of 23.26 mg/g and 30.49 mg/g were obtained for KM 20 and KM 40, respectively. In addition, the effect of solution pH was assessed. The $q_{\max}$ was obtained at pH 11 for CV and pH 7 for AG 25.

1. Introduction

Industries such as textile, beauty care products, printing and papers are utilizing a large amount of dyes to colour their items. The annual worldwide production of dyes is more than 7×10^5 tons [1]. Disposal of dye-containing effluents into water is one of the significant issues as the dyes released may be toxic and carcinogenic [2]. The dyes can be persistent in the environment for a longer time if there is no adequate treatment being carried out.

Therefore, efficient and cost-effective treatments are required. There are a few techniques which have been used for the dye effluent treatment. The techniques encompass coagulation/flocculation, chemical oxidation, membrane separation, electrochemical processes, and adsorption. Among these techniques, adsorption has been perceived as a practical strategy. Adsorption is considerably cheap in terms of cost and simple in operation.

Research has been focused on using cost-effective and good performance adsorbents for the dye removal from aqueous solutions. One of the promising adsorbents for practical application is kaolin. Kaolin is a clay which primarily consists of kaolinite, and it also contains quartz, mica, feldspar, illite, and montmorillonite [3]. Kaolin has been employed to adsorb different types of dyes from water [4].



Adsorption characteristics and properties of kaolin are identified by the surface structure and edges. The adsorption of ions and neutral molecules by kaolin may occur in two ways. The first way is by the exchange of ions on the sites of negative charge which emerged from the replacement of Si (IV) atoms by Al (III) atoms. The second way is by the formation of surface complexes with both Al–OH and Si–OH groups that are situated at the layer edges [5].

Cationic dyes have a net positive charge as a result of the presence of protonated amine or sulphur containing groups. The solubility of cationic dyes is provided by the sulphonic groups in the cationic dye molecule. One example of cationic dye is the basic dye. Anionic dyes have a net negative charge as a result of the presence of sulphonate groups. Example of water-soluble anionic dyes include acid dyes, direct dyes and reactive dyes [6].

Adsorption kinetic study is conducted to determine the rate of solute being adsorbed, and thus the equilibrium time for adsorption can be known. Adsorption isotherm describes the interaction involved between adsorbate and adsorbent and can also yield the data of the adsorption capacity [7].

The objective of this study was to investigate the adsorption kinetic and adsorption isotherm of crystal violet (CV) (a cationic dye) and acid green 25 (AG 25) (an anionic dye), as demonstrated by the kaolin (namely KM 20 and KM 40). To our best knowledge, there were previously no well-documented articles on the adsorption of AG 25 on kaolin. Thus, our study will be able to address this research gap.

2. Materials and methods

2.1. Materials

In this experiment, kaolin KM 20 and KM 40 from Kaolin (Malaysia) Sdn. Bhd. were used. For dyes, CV (Bendosen Limited) and AG 25 (Aldrich Chemistry) were used. Sodium hydroxide (NaOH) (R&M chemicals) and hydrochloric acid (HCl) (Friedemann Schmidt) were used for pH adjustments. Reverse osmosis (RO) water was used for mixing of the solutions.

2.2. Analytical

The aqueous concentrations of CV and AG 25 were determined using the DR 2800 spectrophotometer (HACH) at their wavelengths of maximum absorbance, respectively.

2.3. Adsorption kinetic studies

Adsorption kinetic experiments were conducted by preparing 500 mL of dye solution with an initial concentration of 75 mg/L in a conical flask and appropriate amount of kaolin was added into it. The dye solutions in the flasks were put in an orbital shaker with an agitation speed of 200 rpm and at a temperature of $26 \pm 2^\circ\text{C}$. Aliquots were sampled at pre-determined time, filtered using a cellulose acetate membrane filter paper, and the concentration of samples were analyzed. The amount of dye adsorption on kaolin at time t , q_t (mg/g), was calculated using Equation (1):

$$q_t = \frac{(C_o - C_t)V}{W} \quad (1)$$

where C_o is the initial dye concentration (mg/L), C_t is the dye concentration at time t (mg/L), V is the volume of the solution (L), and W is the mass of the adsorbent (g).

2.4. Adsorption kinetic models

The linear forms of adsorption kinetic models, namely pseudo-first-order kinetic model [8], pseudo-second-order kinetic model [9], and Elovich model [10], (as given in the Equations (2), (3), and (4), respectively) were employed for the determination of adsorption kinetic parameters.

The linear form of pseudo-first-order kinetic model is given in Equation (2):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where q_e is the amount of dye adsorbed on kaolin at equilibrium (mg/g), q_t is the amount of dye adsorbed on kaolin at time t (mg/g), t is time (min), and k_1 is the pseudo-first-order rate constant (min^{-1}).

The linear form of pseudo-second-order kinetic model is given in Equation (3):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_e is the amount of dye adsorbed on kaolin at equilibrium (mg/g), q_t is the amount of dye adsorbed on kaolin at time t (mg/g), t is time (min), and k_2 is the pseudo-second-order rate constant (g/mg min).

The linear form of Elovich model is given in Equation (4):

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (4)$$

where q_t is the amount of dye adsorbed on kaolin at time t (mg/g), t is time (min), α is the initial adsorption rate (mg/g min), and β is a constant related to the surface coverage (g/mg).

2.5. Adsorption isotherm studies

Adsorption isotherm experiments were conducted by preparing 250 mL of dye solution with 6 different initial concentrations. The initial concentrations of the dye used were 10, 20, 30, 40, 50 and 60 mg/L. Appropriate amount of kaolin was added into the respective conical flasks containing different initial concentrations of the dye solution. The flasks were then placed in an orbital shaker with an agitation speed of 200 rpm and at temperature of $26 \pm 2^\circ\text{C}$ for 3 hours. Aliquots were sampled at the end of the contact time, filtered using a cellulose acetate membrane filter paper, and the concentration of samples were analyzed. The amount of dye adsorption on kaolin at equilibrium, q_e (mg/g), was calculated using Equation (5):

$$q_e = \frac{(C_o - C_e)V}{W} \quad (5)$$

where C_o is the initial dye concentration (mg/L), C_e is the dye concentration at equilibrium (mg/L), V is the volume of the solution (L), and W is the mass of the adsorbent (g).

2.6. Adsorption isotherm models

The linear forms of adsorption isotherm models, namely Langmuir isotherm [11], Freundlich isotherm [12], Temkin isotherm [13], and Dubinin-Radushkevich isotherm [14] (as given in the Equations (6), (7), (8) and (9), respectively) were employed for the determination of adsorption isotherm parameters.

The linear form of Langmuir isotherm is given in Equation (6):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (6)$$

where q_e is the amount of dye adsorbed on kaolin at equilibrium (mg/g), C_e is the dye concentration at equilibrium (mg/L), $q_{\max}$ is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant (L/mg).

The linear form of Freundlich isotherm is given in Equation (7):

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (7)$$

where q_e is the amount of dye adsorbed on kaolin at equilibrium (mg/g), C_e is the dye concentration at equilibrium (mg/L), K_F is the Freundlich constant (mg/g)(L/mg)^{1/n}, and n is the intensity of adsorption constant.

The linear form of Temkin isotherm is given in Equation (8):

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e \quad (8)$$

where q_e is the amount of dye adsorbed on kaolin at equilibrium (mg/g), A_T is the Temkin isotherm equilibrium binding constant (L/g), b_T is the Temkin isotherm constant, B is the constant related to heat of sorption (J/mol) and can be calculated as RT/b_T , R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The linear form of Dubinin-Radushkevich isotherm is given in Equation (9):

$$\ln q_e = \ln(q_s) - (K_{DR} \varepsilon^2) \quad (9)$$

where q_e is the amount of dye adsorbed on kaolin at equilibrium (mg/g), q_s is the theoretical isotherm saturation capacity (mg/g), K_{DR} is the Dubinin-Radushkevich isotherm constant (mol²/J²) and ε is the constant which can be calculated using Equation (10).

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (10)$$

where R is the gas constant (8.314 J/mol K), T is the absolute temperature (K) and C_e is the dye concentration at equilibrium (mg/L).

2.7. Effect of solution pH

A 250 mL of dye solution with concentrations in the range of 10, 20, 30, 40, 50, 60 mg/L were prepared. The pH investigated was 3, 7, and 11. 0.1 M of NaOH and 0.1 M of HCl were used for pH adjustments. A pH meter was used to measure the pH of the solution. Appropriate amount of kaolin was added into the conical flask containing the dye solution with different pH values and they were put in an orbital shaker with an agitation speed of 200 rpm and at temperature of $26 \pm 2^\circ\text{C}$ for 3 hours. Aliquots were sampled at the end of the contact time, filtered using a cellulose acetate membrane filter paper, and the concentration of samples were analyzed.

3. Results and discussion

3.1. Adsorption kinetics of CV

3.1.1. Effect of contact time of CV

Figures 1(a) and 1(b) show the effect of contact time on the adsorption of CV on KM 20 and KM 40, respectively. It was observed that the adsorption rate was very rapid in the first 30 min for both KM 20 and KM 40. In the beginning of the adsorption process, there was a high number of active sites available on the adsorbent surface for the CV molecules to be adsorbed [15]. After 30 min, a slow increment in the adsorption capacity was observed. This is due to minimum availability of active sites on the adsorbent surface which prevent further adsorption to occur. The equilibrium stage was reached at the 60th min.

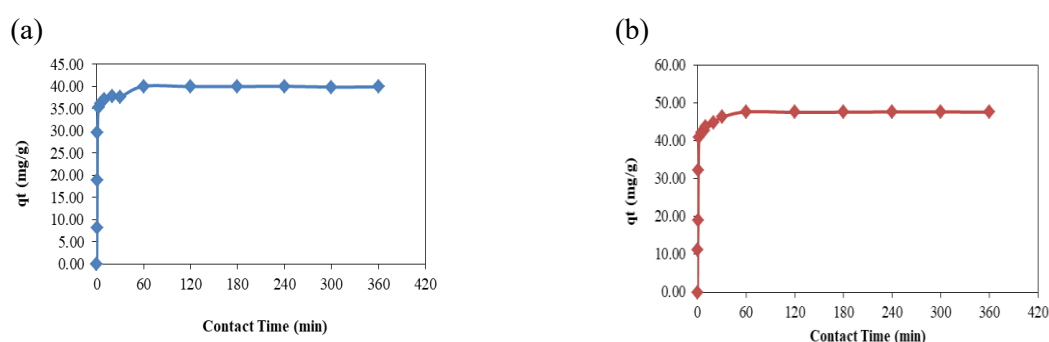


Figure 1. Effect of contact time on the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_0 : 75 mg/L, dosage of adsorbent : 0.6 g/L, solution pH: 6.80 ± 0.2 , total time: 6 hours).

3.1.2. Adsorption kinetic models of CV

Figures 2(a) and 2(b) show the pseudo-first-order kinetic model for the adsorption of CV on KM 20 and KM 40, respectively. The pseudo-first-order kinetic model assumes that the solute uptake rate with time was directly proportional to the difference in the saturation concentration and the adsorbed amount [8]. The coefficient of determination (R^2) values obtained from this model were 0.8707 and 0.9257 for KM 20 and KM 40, respectively.

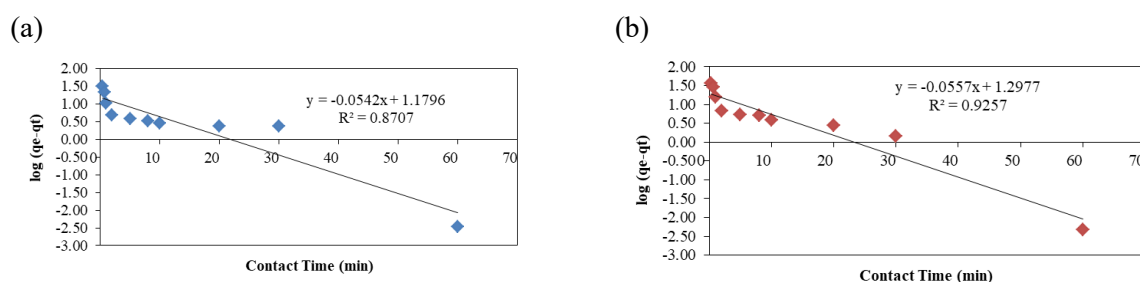


Figure 2. Pseudo-first-order kinetic model for the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_0 : 75 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20).

Figures 3(a) and 3(b) show the pseudo-second-order kinetic model for the adsorption of CV on KM 20 and KM 40, respectively. The pseudo-second-order kinetic model assumes that the rate limiting step would be the chemical adsorption involving valent forces either through sharing or the exchange of electrons [9]. The R^2 values obtained were 0.9990 and 0.9995 for KM 20 and KM 40, respectively.

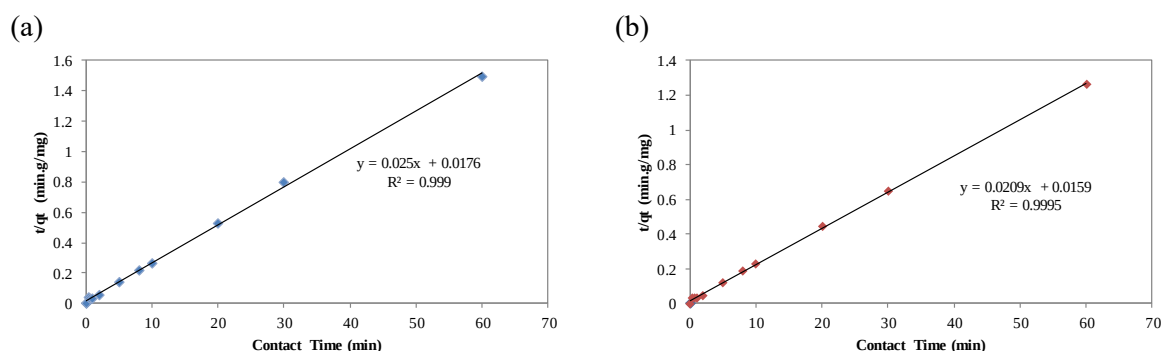


Figure 3. Pseudo-second-order kinetic model for the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_0 : 75 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20).

Figures 4(a) and 4(b) show the Elovich model for the adsorption of CV on KM 20 and KM 40, respectively. While the Elovich was originally used to describe the adsorption of gases on solid systems [10], it has also been used to describe the removal of pollutant in aqueous solutions [16]. The R^2 values obtained from this model were 0.7222 and 0.7873 for KM 20 and KM 40, respectively.

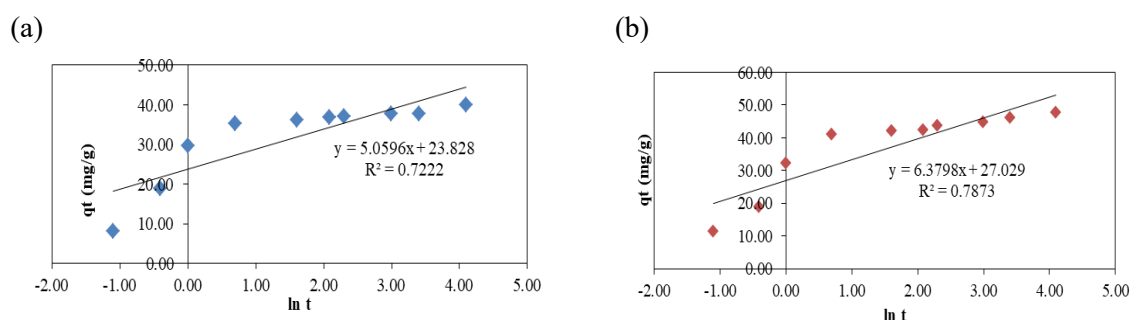


Figure 4. Elovich model for the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_0 : 75 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20).

Table 1: Adsorption kinetic parameters for different adsorption kinetic models for the adsorption of CV on KM 20 and KM 40.

Adsorbent	Parameters								
	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Elovich model		
	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg min)	R^2	α (mg/g min)	β (g/mg)	R^2
KM 20	15.12	0.125	0.8707	40.00	0.036	0.9990	561.58	0.198	0.7222
KM 40	19.85	0.128	0.9257	47.85	0.535	0.9995	440.92	0.157	0.7873

Table 1 shows the adsorption kinetic parameters for the different adsorption kinetic models for the adsorption of CV on KM 20 and KM 40. For pseudo-first-order kinetics, KM 40 achieved a higher adsorption capacity at equilibrium (q_e) of 19.85 mg/g and rate constant (k_1) of 0.128/min as compared to KM 20 which achieved q_e of 15.12 mg/g and k_1 of 0.125/min. For pseudo-second-order kinetics, adsorbent KM 40 achieved a higher value of q_e (47.85 mg/g) as compared to KM 20 (q_e of 40.00 mg/g).

As a comparison, Nandi et al. [15] had reported that their kaolin had demonstrated q_e of 31.95 mg/g when the initial concentration was 40 mg/L. For Elovich kinetics, the constants α and β obtained for adsorption of CV on KM 20 was higher than that of KM 40. Overall, our results were best fitted to the pseudo-second-order kinetic model, as the R^2 values obtained were almost equal to unity. Our results are in agreement with Nandi et al. [15], whereby they had also found that pseudo-second-order kinetic model was best fitted for the adsorption of CV on kaolin.

3.2. Adsorption isotherms of CV

Figures 5(a) and 5(b) show the Langmuir isotherm model for the adsorption of CV on KM 20 and KM 40, respectively. According to the Langmuir isotherm model, the monolayer sorption occurs on the solid surface with identical and homogeneous sites [11]. The R^2 values obtained from this model were 0.9989 and 0.9990 for KM 20 and KM 40, respectively.

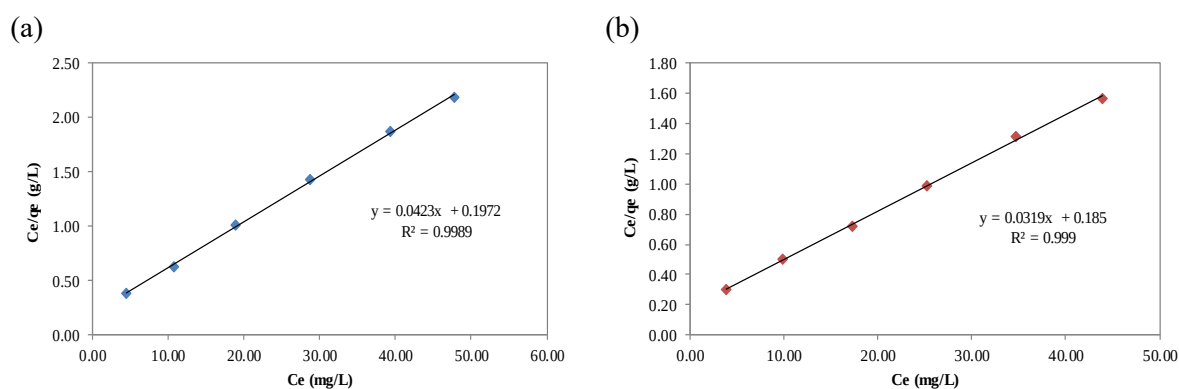


Figure 5. Langmuir isotherm model for the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , contact time: 3 hours).

Figures 6(a) and 6(b) show the Freundlich isotherm model for the adsorption of CV on KM 20 and KM 40, respectively. Freundlich isotherm is an empirical equation which assumes that the distribution of the heat on the adsorbent surface is non-uniform, i.e. the occurrence of heterogeneous adsorption [12]. The R^2 values obtained from this model were 0.9237 and 0.9468 for KM 20 and KM 40, respectively.

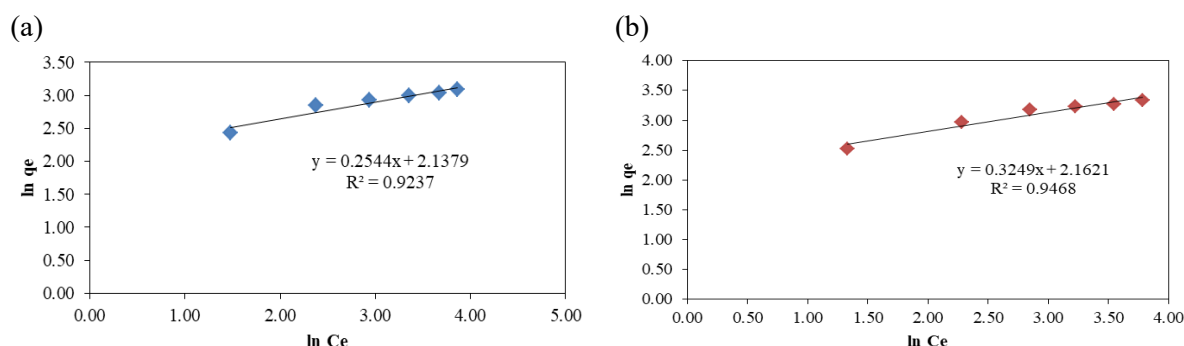


Figure 6. Freundlich isotherm model for the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80, contact time: 3 hours).

Figures 7(a) and 7(b) show the Temkin isotherm model for the adsorption of CV on KM 20 and KM 40, respectively. According to the Temkin isotherm model, the interaction of the adsorbent and adsorbate particles occur in an indirect way, thus causing adsorption heat of the particles in the specific layer to reduce with surface coverage [13]. The R^2 values obtained from this model were 0.9615 and 0.9801, respectively.

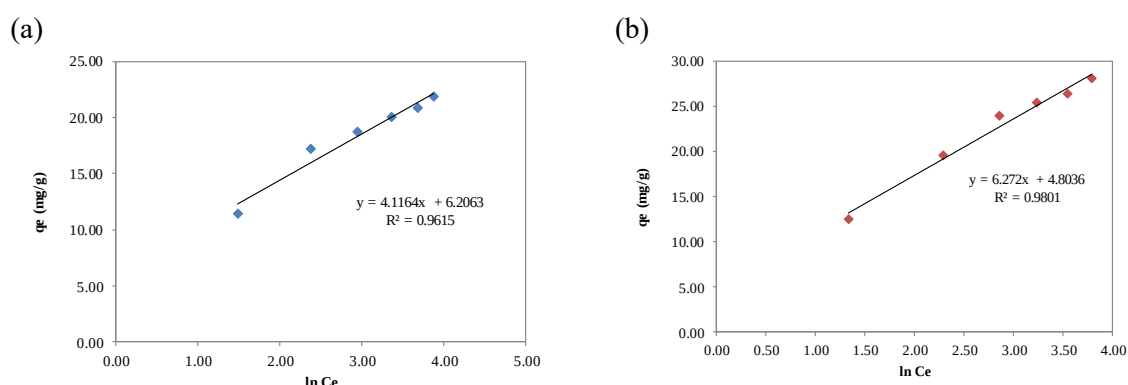


Figure 7. Temkin isotherm model for the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , contact time: 3 hours).

Figures 8(a) and 8(b) show the Dubinin-Radushkevich isotherm model for the adsorption of CV on KM 20 and KM 40, respectively. According to the Dubinin-Radushkevich isotherm model, the mechanism for an adsorption process can be determined based on the potential energy assuming heterogeneous surfaces [14]. The R^2 values obtained from this model were 0.9919 and 0.9832, respectively.

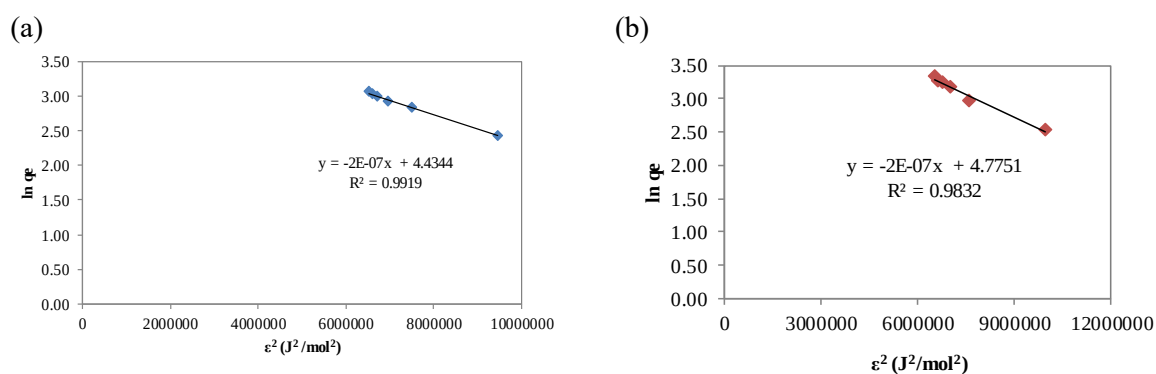


Figure 8. Dubinin-Radushkevich isotherm model for the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , contact time: 3 hours).

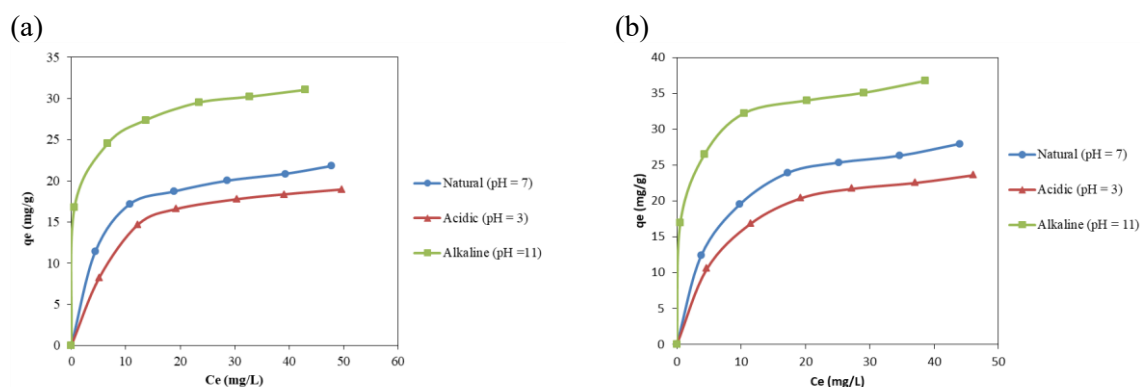
Table 2. Adsorption isotherm parameters for different adsorption isotherm models for the adsorption of CV on KM 20 and KM 40.

Adsorbent	Parameters										
	Langmuir isotherm model			Freundlich isotherm model			Temkin isotherm model			Dubinin-Radushkevich isotherm model	
	q _{max} (mg/g)	K _L (L/mg)	R ²	n	K _F (mg/g)(L/mg) ^{1/n}	R ²	A _T (L/g)	B (J/mol)	R ²	K _{DR} (mol ² /J ²)	R ²
KM 20	23.64	0.215	0.9989	3.93	8.48	0.9237	4.52	608.14	0.9615	2 x 10 ⁻⁷	0.9919
KM 40	31.35	0.173	0.9990	3.08	8.69	0.9468	2.15	398.20	0.9801	2 x 10 ⁻⁷	0.9832

Table 2 shows the adsorption isotherm parameters for different adsorption isotherm models for the adsorption of CV on KM 20 and KM 40. For Langmuir isotherm, the maximum adsorption capacity ($q_{\max}$) values were 23.64 mg/g and 31.35 mg/g for KM 20 and KM 40, respectively. For Freundlich isotherm, the K_F values for KM 20 and KM 40 were 8.48 (mg/g)(L/mg)^{1/n} and 8.69 (mg/g)(L/mg)^{1/n}, respectively. For Temkin isotherm, constants A_T and B were markedly higher for KM 20 as compared to KM 40. For Dubinin-Radushkevich isotherm, the constant K_{DR} was the same for KM 20 and KM 40. By overall comparison, Langmuir model was best fitted due to highest R^2 . Thus, this indicates that monolayer sorption has occurred. As a comparison, Nandi et al. [15] had reported that Langmuir model was best fitted for the adsorption of CV on kaolin with R^2 values of 0.99.

3.3. Effect of solution pH of CV

Figures 9(a) and 9(b) show the effect of solution pH on the adsorption of CV on KM 20 and KM 40 at pH 3, 7, and 11.

**Figure 9.** Effect of solution pH on the adsorption of CV on (a) KM 20 and (b) KM 40 (Experimental conditions: C_0 : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 3, 7, 11, contact time: 3 hours).**Table 3.** The $q_{\max}$ values for the adsorption of CV on KM 20 and KM 40 at different solution pH.

Adsorbent	$q_{\max}$ (mg/g)		
	pH 3	pH 7	pH 11
KM 20	21.74	23.64	31.75
KM 40	27.10	31.35	37.45

Table 3 shows the maximum adsorption capacity ($q_{\max}$) values for the adsorption of CV on KM 20 and KM 40 at three different solution pH. Solution pH plays an important role in the adsorption process, as the charge found on the surface of the adsorbent is basically influenced by the solution pH [6]. At solution pH of 11 (alkaline), maximum adsorption capacity was observed, namely 31.75 mg/g and 37.45 mg/g for KM 20 and KM 40, respectively. It has been reported that the edge charges of kaolin are highly pH-dependent, which may characterize the behaviour of the kaolin. The edge charges of kaolin will become more positive at low pH values as a result of the adsorption of H^+ ions, while the edge charges of kaolin will become more negative at high pH values as a result of the adsorption of OH^- ions [17]. Thus, KM 20 and KM 40 tend to exhibit negative charges if solution pH is alkaline. Meanwhile, the CV is a positively charged dye. This causes electrostatic attraction to occur between CV particles and adsorbents (KM 20 and KM 40) and a high removal of CV was achieved. In acidic medium, the positive charges on the edges of KM 20 and KM 40 tend to oppose the positive charges on CV particles. This causes a lower adsorption capacity of 21.74 mg/g and 27.10 mg/g for KM 20 and KM 40, respectively. It was also observed that the $q_{\max}$ obtained at the solution pH of 7 was higher than the acidic medium. By overall comparison, the optimum solution pH for the removal of CV was at pH 11. Other researchers [18, 19, 20] had also reported that the removal efficiency of cationic dyes by kaolin was more favourable in alkaline conditions as compared to acidic solutions.

3.4. Adsorption kinetics of AG 25

3.4.1. Effect of contact time of AG 25

Figures 10(a) and 10(b) show the effect of contact time on the adsorption of AG 25 on KM 20 and KM 40, respectively. It was observed that the adsorption rate was very rapid in the first 30 min for both KM 20 and KM 40. A slow progression was observed thereafter. The minimum time to achieve equilibrium was 60 min.

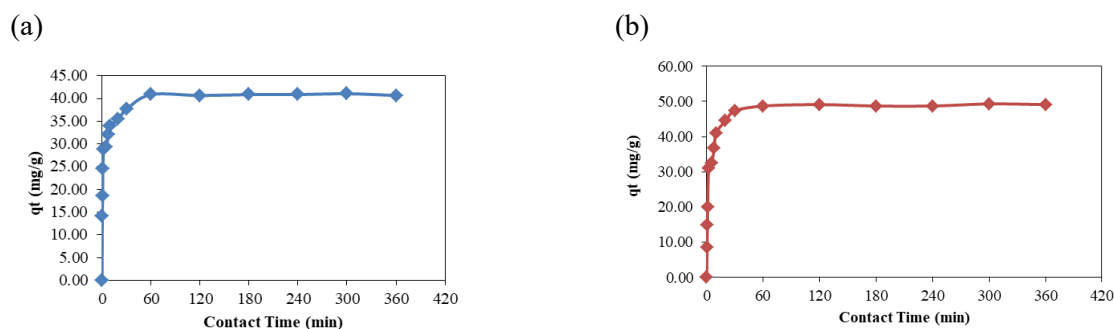


Figure 10. Effect of contact time for the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 75 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , total time: 6 hours).

3.4.2. Adsorption kinetic models of AG 25

Figures 11(a) and 11(b) show the pseudo-first-order kinetic model for the adsorption of AG 25 on KM 20 and KM 40, respectively. The R^2 values obtained from this model were 0.9155 and 0.9596 for KM 20 and KM 40, respectively.

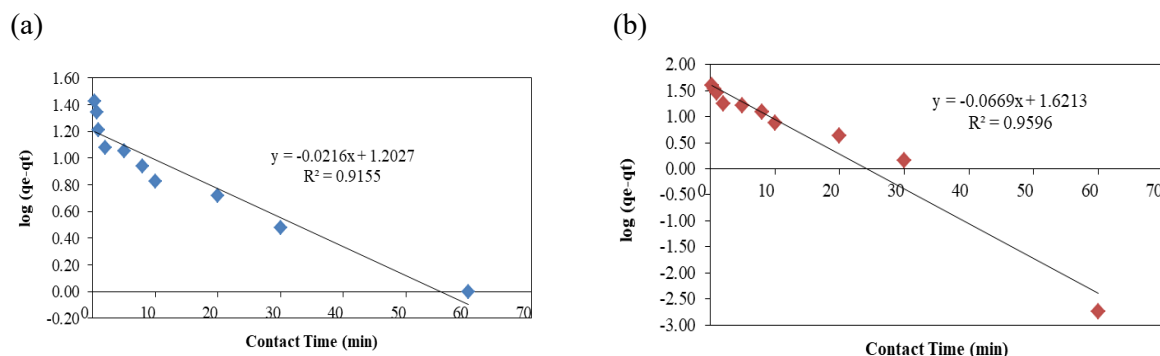


Figure 11. Pseudo-first-order kinetic model for the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 75 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20).

Figures 12(a) and 12(b) show the pseudo-second-order kinetic model for the adsorption of AG 25 adsorption on KM 20 and KM 40, respectively. The R^2 values obtained from this model were 0.9971 and 0.9991 for KM 20 and KM 40, respectively.

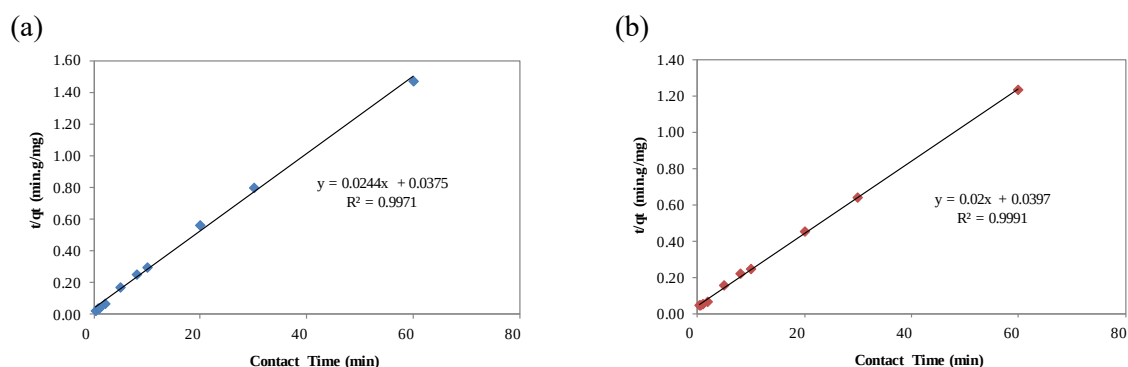


Figure 12. Pseudo-second-order kinetic model for the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 75 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20).

Figures 13(a) and 13(b) show the Elovich model for the adsorption of AG 25 on KM 20 and KM 40, respectively. The R^2 values obtained for KM 20 and KM 40 were 0.9519 and 0.9634, respectively.

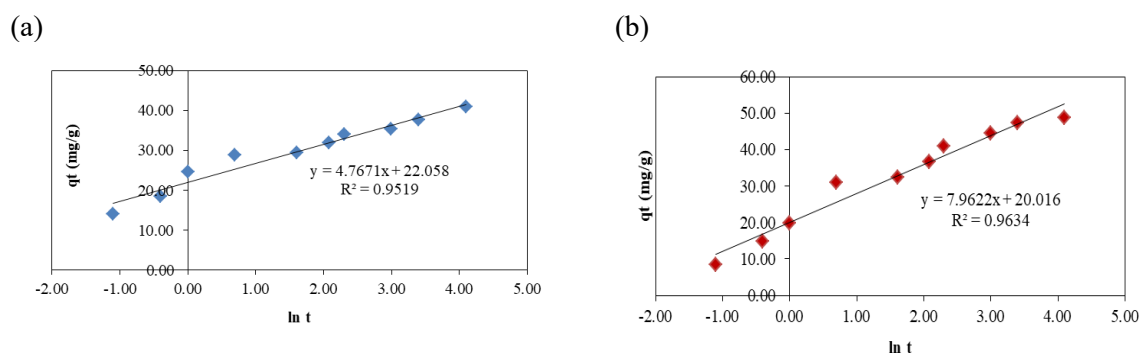


Figure 13. Elovich model of the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 75 mg/L, dosage of adsorbent : 0.6 g/L, solution pH: 6.80 ± 0.20).

Table 4. Adsorption kinetic parameters for different adsorption kinetic models for the adsorption of AG 25 on KM 20 and KM 40.

Adsorbent	Parameters								
	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model			Elovich model		
	q_e (mg/g)	k_1 (1/min)	R^2	q_e (mg/g)	k_2 (g/mg.min)	R^2	α (mg/g.min)	β (g/mg)	R^2
KM 20	15.95	0.050	0.9155	40.98	0.016	0.9971	487.30	0.210	0.9519
KM 40	41.81	0.154	0.9596	50.00	0.010	0.9991	98.36	0.126	0.9634

Table 4 shows the adsorption parameters for different adsorption kinetic models for the adsorption of AG 25 on KM 20 and KM 40. For pseudo-first-order kinetics, the values achieved by KM 20 for the q_e (15.95 mg/g) and k_1 (0.050/min) were lower compared to KM 40, which had q_e of 41.81 mg/g and k_1 of 0.154/min. For pseudo-second-order kinetics, the adsorption of AG 25 on KM 40 achieved a higher value of q_e which was 50.00 mg/g as compared to KM 20, which had q_e of 40.98 mg/g. For Elovich kinetics, the constants α and β obtained for adsorption of AG 25 on KM 20 were higher than that of KM 40. By overall comparison, pseudo-second-order kinetic model was best fitted for both KM 20 and KM 40. Our results are in agreement with the other researchers [16,21] who had reported that pseudo-second-order kinetic model was best fitted to represent the adsorption kinetic of anionic dyes on kaolin.

3.5. Adsorption isotherms of AG 25

Figures 14(a) and 14(b) show the Langmuir isotherm model for the adsorption of AG 25 on KM 20 and KM 40, respectively. The R^2 values obtained from this model were 0.9986 and 0.9996 for KM 20 and KM 40, respectively.

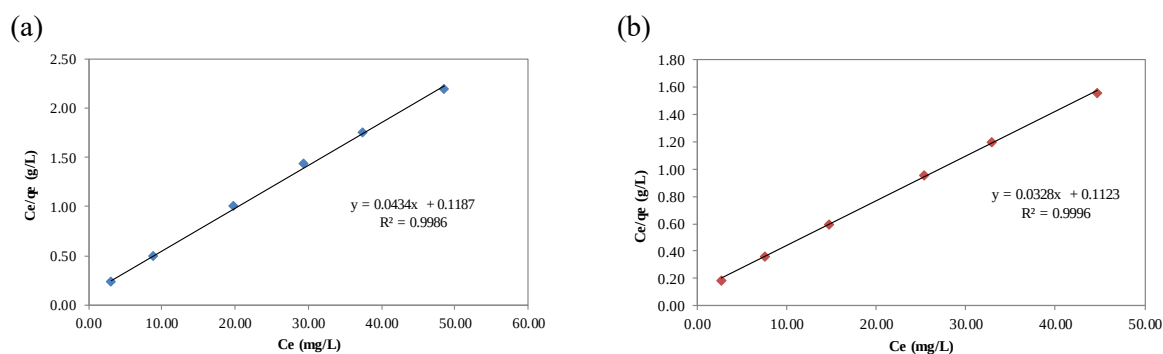


Figure 14. Langmuir isotherm model for the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , contact time: 3 hours).

Figures 15(a) and 15(b) show the Freundlich isotherm model for the adsorption of AG 25 on KM 20 and KM 40, respectively. The R^2 values obtained from this model were 0.9479 and 0.9483 for KM 20 and KM 40, respectively.

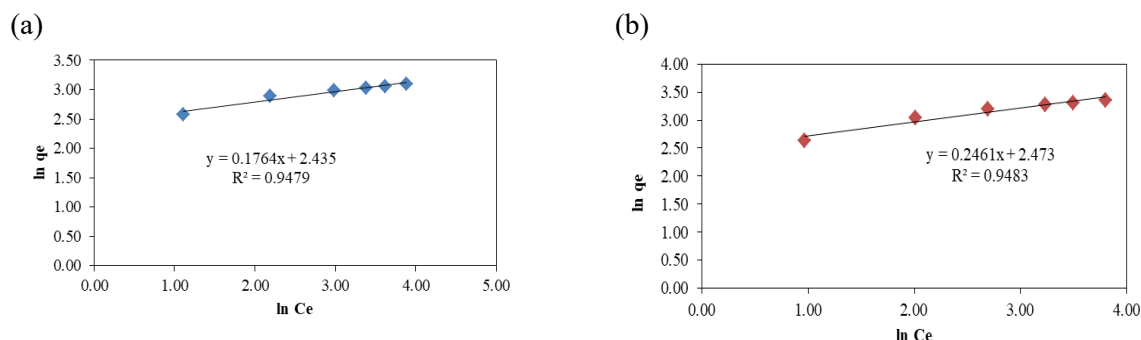


Figure 15. Freundlich isotherm model for the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , contact time: 3 hours).

Figures 16(a) and 16(b) show the Temkin isotherm model for the adsorption AG 25 on KM 20 and KM 40, respectively. The R^2 values obtained from this model were 0.9717 and 0.9812 for KM 20 and KM 40, respectively.

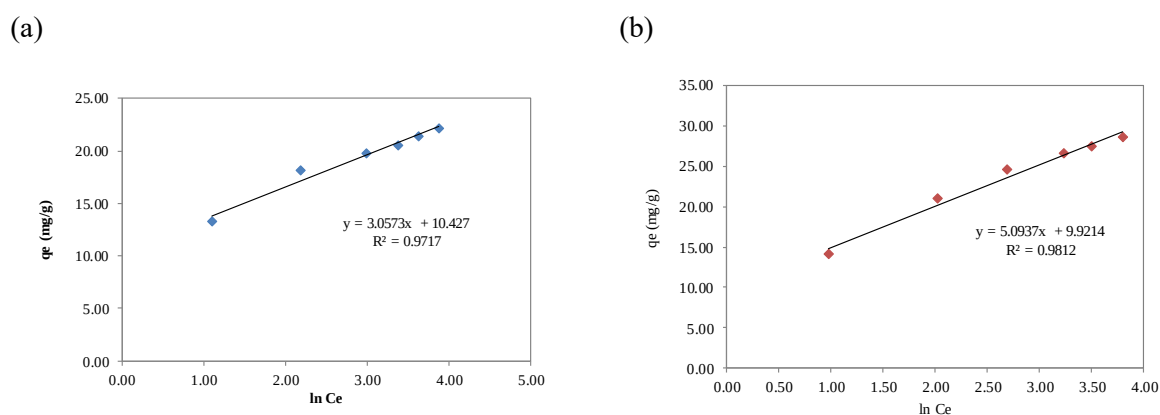


Figure 16. Temkin isotherm model for the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , contact time: 3 hours).

Figures 17(a) and 17(b) show the Dubinin-Radushkevich isotherm model for the adsorption of AG 25 on KM 20 and KM 40, respectively. The R^2 values obtained were 0.9767 and 0.9748 for KM 20 and KM 40, respectively.

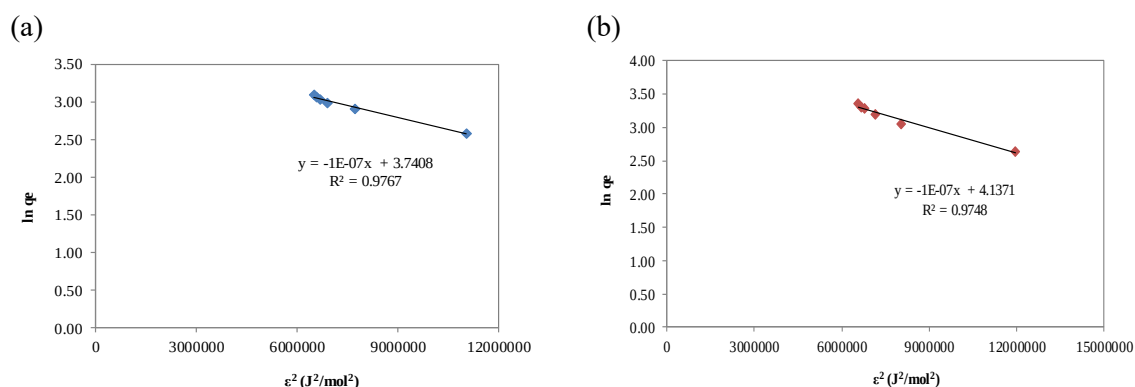


Figure 17. Dubinin-Radushkevich isotherm model for the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 6.80 ± 0.20 , contact time: 3 hours).

Table 5: Adsorption isotherm parameters for different adsorption isotherm models for the adsorption of AG 25 on KM 20 and KM 40.

Adsorbent	Parameters									
	Langmuir isotherm model			Freundlich isotherm model			Temkin isotherm model			Dubinin-Radushkevich isotherm model
	q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F (mg/g)(L/mg) ^{1/n}	R^2	A_T (L/g)	B (J/mol)	R^2	
KM 20	23.26	0.362	0.9986	5.67	11.42	0.9479	30.28	816.361	0.9717	1×10^{-7}
KM 40	30.49	0.292	0.9996	4.06	11.86	0.9483	7.01	491.622	0.9812	1×10^{-7}

Table 5 shows the adsorption isotherm parameters for different adsorption isotherm models for the adsorption of AG 25 on KM 20 and KM 40. For Langmuir isotherm, the q_{max} values were 23.26 mg/g and 30.49 mg/g for KM 20 and KM 40, respectively. For Freundlich isotherm, the K_F values were quite similar for KM 20 and KM 40. For Temkin isotherm, constants A_T and B for KM 20 were markedly higher than that of KM 40. For Dubinin-Radushkevich isotherm, the constant K_{DR} was the same for KM 20 and KM 40. By overall comparison, Langmuir model was best correlated due to highest R^2 value for KM 20 and KM 40. Therefore, it is concluded that monolayer adsorption has occurred. Other researchers who had conducted study on the adsorption of anionic dyes on kaolin had also reported that Langmuir model was best fitted for adsorption isotherm [16,22].

Meanwhile, adsorbent KM 40 demonstrated higher adsorption capacity for the dye. Particle size factor could be one of the governing factors. KM 40 has a smaller particle size compared to KM 20 (refer Appendix). Smaller particle size provides larger surface area for the dye molecules to be adsorbed and thus, resulting in greater removal efficiency of the dye.

3.6. Effect of solution pH of AG 25

Figures 18(a) and 18(b) show the effect of solution pH on the adsorption of AG 25 on KM 20 and KM 40 at pH 3, 7, and 11.

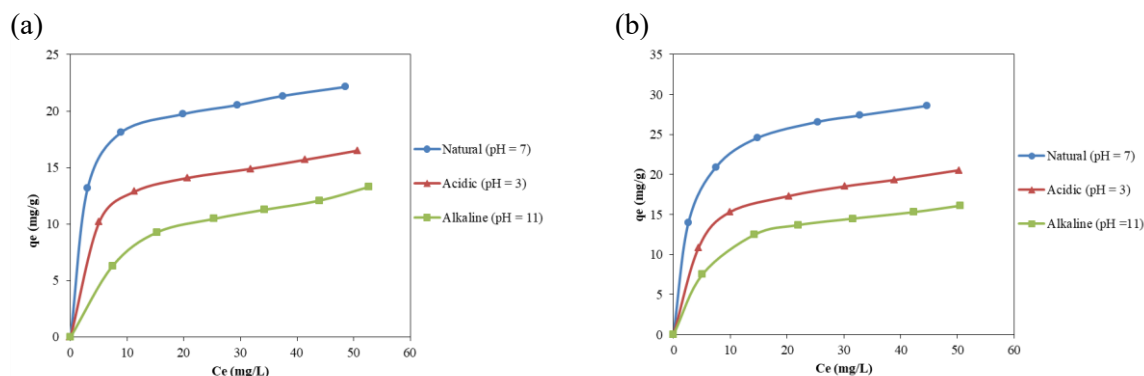


Figure 18. Effect of solution pH on the adsorption of AG 25 on (a) KM 20 and (b) KM 40 (Experimental conditions: C_o : 10, 20, 30, 40, 50, 60 mg/L, dosage of adsorbent: 0.6 g/L, solution pH: 3, 7, 11, contact time: 3 hours).

Table 6. The $q_{\max}$ values for the adsorption of AG 25 on KM 20 and KM 40 at different solution pH.

Adsorbent	$q_{\max}$ (mg/g)		
	pH 3	pH 7	pH 11
KM 20	17.54	23.26	15.63
KM 40	22.12	30.49	18.08

Table 6 shows the $q_{\max}$ values for the adsorption of AG 25 on KM 20 and KM 40 at three different solution pH. The experimental results indicate that the removal of AG 25 was strongly dependent on the solution pH. At solution pH of 3 (acidic), the interaction between AG 25 and positively charged edges of KM 20 and KM 40 causes a great electrostatic attraction to occur. This is basically because of ionization of functional groups of KM 20 and KM 40. At solution pH of 11 (alkaline), the presence of negative edge charges of KM 20 and KM 40 has increased. This causes electrostatic repulsion to occur since both AG 25 and adsorbents (KM 20 and KM 40) are negatively charged. This leads to a reduction in the adsorption capacity. The removal efficiency of AG 25 was higher in acidic solution as compared to in alkaline solution. At solution pH of 7, the $q_{\max}$ values were 23.26 mg/g and 30.49 mg/g for KM 20 and KM 40, respectively. This may possibly be due to the fact that the AG 25 used contained impurities (dye content $\geq 60\%$). Thus, it is anticipated that there could be some underlying adsorption mechanism which had occurred. More study will be conducted in the future to understand the effects of the impurities present in the AG 25.

4. Conclusion

In this study, two types of kaolin (KM 20 and KM 40) were used as adsorbents for the removal of CV and AG 25 from water. Adsorption kinetic and isotherms models were fitted based on the experimental results obtained. For kinetic study, pseudo-second-order kinetic model was best fitted for both CV and AG 25 dyes. It was found that 60 min was the minimum equilibrium time. For isotherm study, Langmuir isotherm model was best correlated for both CV and AG 25 dyes, thus indicating monolayer adsorption had occurred. The optimum solution pH for the adsorption of CV on KM 20 and KM 40 was at pH 11. Maximum adsorption capacity was observed at pH 7 for the adsorption of AG 25 on KM 20 and KM 40.

Appendix

Technical data of different types of kaolin provided by Kaolin (Malaysia) Sdn. Bhd.

Technical data	KM 20	KM 40
Moisture content	Below 2.0%	Below 2.0%
pH (30% solid)	3.5 - 5.5	3.5 - 5.5
Viscosity (30% solid)	Below 100 cp	-
325 mesh residue	Below 2.0%	Below 0.2%
Average particle size	7.0 - 11.0 μm	2.5 - 4.5 μm
Brightness	-	76.0 - 80.0%

Acknowledgement

Kaolin (Malaysia) Sdn. Bhd. is thanked for the generous provision of the kaolin samples KM 20 and KM 40.

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