

ISOTHERM, KINETICS AND THERMODYNAMICS ADSORPTION STUDIES OF DYE ONTO Fe₃O₄-WASTE PAPER ACTIVATED CARBON COMPOSITES

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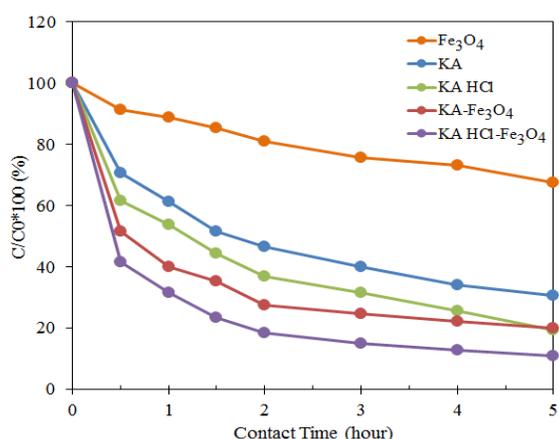
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Graphical abstract



Abstract

This paper focused on the studying of adsorption properties of Fe₃O₄-waste paper activated carbon composites for the removal of methylene blue dyes from water. The various parameters were carried out for the adsorption test of the composites, namely; contact time, adsorbent dose, initial MB concentration, pH solution, and temperature. The adsorption of isotherm, thermodynamics and kinetic was used to determine the characteristics of methylene blue adsorption onto the prepared adsorbent. The result indicates that the optimum adsorption capacity has occurred at pH = 6 in water solution. The adsorption capacity increase as the temperature increase until at 315K (45°C). The Langmuir isotherm is more appropriate to be applied as the adsorption model with the maximum adsorption capacity (q_m) value of 101 and 93 mg/g for KA HCl-Fe₃O₄ and KA-Fe₃O₄ composites, respectively. The value of adsorption thermodynamic parameters was positive for ΔH , negative for ΔG° and positive for ΔS° , meaning the process adsorptions were endothermic, feasibility and spontaneity and randomness, respectively. The pseudo-second-order model was appropriate to predict the kinetic models for methylene blue adsorption onto the composites. The obtained adsorbent composites possess high adsorption efficiency and rapid magnetic separation. They were a promising for practical wastewater treatment for dyes removal from water.

Keywords: Activated carbon, waste paper, magnetite (Fe₃O₄), dyes, adsorption

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1.0 INTRODUCTION

Dyes have been commercialized in more than 100,000 species and are produced for more than 7x10⁵ metric tons/year. Dyes are used in the coloring process of

various industrial materials such as dyestuffs, textiles, plastics, cosmetics, paper, leather and so forth [1]. The industry uses dye in their product for its ornamental or decorative quality. Most industry such as the textile industry consumes a large volume of water in the

coloring process. Nevertheless, most dyes are not absorbed by the textiles material and 50% of the dye still remains in the liquid. Thus, large volumes of colored wastewater are produced containing a strong colored organic compound [2]. Dyes contaminated water is very easily visible to the naked eyes. The presence of just a very small amount of dyes (less than 1 ppm) can be seen in natural water. The presence of the dye-contaminants in water causes the reduction of sunlight transmission, the retardation of photosynthetic activity, the inhibition of the growth of biota and damages the aesthetic nature of the water surface [1], [3]. In addition, most of these dyes are toxic, mutagenic, carcinogenic and teratogenic. Therefore, the presence of dyes in water is not only unpleasant for the eyes and decreases the water quality but may also cause severe damage to the health of human beings, such as dysfunction of the kidneys, reproductive system, liver, brain, and central nervous system [4].

Methylene blue (MB) is one of the most important dyes in the decorative materials industry. It is generally used in the coloring process of cotton fiber, silk, and wood fabrics [5]. However, methylene blue is chemically very dangerous. When contacted to eyes, it can cause a permanent injury to both human and animals. If by an accidental oral intake the dye manages to reach the digestive system, it could cause the person to suffer from nausea, vomiting, excessive sweating, metal confusion and methemoglobinemia [6]. Therefore, the treatment of effluents containing dyes is quite interesting to study and requires more attention [7].

During the past three decades, numerous methods relating to the removal of methylene blue in wastewater have been well documented, such as; biodegradation [8], photocatalysis [9], chemical oxidation [10], electrochemical oxidation [11], emulsion liquid membrane [12], froth flotation [13], electro-coagulation [14] and adsorption [6]. Among of them, the adsorption technique is the most widely applied method in the treatment of dyestuff wastewater due to it being a simple and in addition, also a most effective and economical method, to date. This technique produces a high-quality treated effluent and is easy to apply.

Many approaches have been studied to find cheaper and more effective adsorbents [15]. Currently, it appears that activated carbon is still the the best and the most widely used in the industry due to its excellent adsorption ability and its low price. Activated carbon possesses high adsorption capacity which is related to its physical properties, namely; surface area, pore volume and porosity [16]. Activated carbon has been shown to be effective in the removal of the various pollutants from organic compounds (dyes, pigments) [2] and inorganic pollutants [17].

Activated carbon was produced from various natural material which contains carbon. Activated carbon can be prepared via the direct activation of dry raw material or two step process including initial

carbonisation and then activation. In the two-stage process, carbonisation was done through a pyrolytic process under open or less atmosphere. While, activation process can be done including physical activation in atmosphere oxidising gases or chemical activation using wet chemical agent [18]. Treated chemical of activated carbon plays an important role in its adsorption properties. Various chemical agents have been used for activation of activated carbon, including acids, alkaline and salt. Acidic treatment of activated carbon can increase the surface acidic property, and also removes the mineral's impurities, therefore improving the hydrophilic nature of carbon surface [19] and producing well-developed pores on the surface of the activated carbon [20]. HCl treatment enhances the adsorption of larger molecules on activated carbon [21] and affects an increase in the amount of single-bonded oxygen functional groups such as phenols, ethers, and lactones [22].

Paper consumptions increase with increasing industrialization and cultural activities. Most of the times papers are used in the packaging and the printing or publishing industries. Thus, along with the increasing consumption of paper, the paper waste constituent in municipal solid waste disposal also increases [23]. The waste paper is the main component in the disposal of municipal solid waste [24]. There are around 7.60-12.36 % of the paper content in the disposal of municipal solid waste (MSW) in Indonesia [25]. Recycling paper can be considered useful from the perspective of resources and the environment and must be promoted as much as possible [26].

Over the past few years, a considerable number of studies have been done on activated carbon preparation from paper. Activated carbon has been successfully prepared from waste newspaper paper with chemical and physical activation, resulting in the adsorption capacity of 390 mg/g for MB [27]. Shimada, et al. [28] reported that activated carbon from waste newsprint paper through physical activation has obtained a high methylene blue adsorption capacity (325 mg/g). Baghapour et al. [5] reported that the activated carbon has been prepared from waste paper through the chemical activation process by KOH, obtained a moderate maximum adsorption capacity (68.03 mg/g) for methylene blue adsorption. Activated carbon fibers has been obtained from the paper by chemical activation with KOH, and the fibers have an excellent maximum adsorption capacity of 520 mg/g [29]. However, the main problem of the activated carbon from paper is the side product of fine particles. The main drawback is the fact that it is very difficult to separate the particles from liquids after the adsorption process is completed. Certainly, this will be even more complicated for the large waste volumes.

Magnetic technology can be applied in environmental applications to assist in the separation process. The advantages of magnetic separation are that it is cheaper, simpler, faster and effective in the

recovery of the adsorbents from wastewater [4]. In the previous study, the incorporation of adsorbents with magnetic particles has been reported in the literature, such as Fe_3O_4 /bentonite [30], $\text{Fe}_3\text{O}_4/\text{SiO}_2$ [31], Fe_3O_4 /CTAB [32], Zeolit/ Fe_3O_4 [33] and graphene oxide- Fe_3O_4 [34], Fe_3O_4 -Chitosan [35]. A number of studies on activated carbon/ Fe_3O_4 composite have been reported [36][37][38], however the most of them used commercial activated carbon as the precursor.

In the authors' previous work, the Fe_3O_4 -waste paper active carbon composites has been successfully synthesized. The characteristics of the prepared sample has shown that the presence of Fe_3O_4 magnetic nanoparticles on the structure of activated carbon has led to the formation of a new mesopore system, magnetic properties and the performance of cation exchange properties [39]. In this work, as a continuation of the previous work, the authors' objective is the investigation into the ability of Fe_3O_4 -active carbon from waste paper to adsorb the dyes (methylene blue) in water. Several adsorption parameters were investigated, namely; effect of contact time, adsorbent dose, dye concentration, pH values and temperature. The analysis and interpretation of adsorption data are accomplished using the equations of equilibrium, kinetics, and thermodynamic adsorption so that the adsorption properties of prepared adsorbent to adsorb dyes can be understood.

2.0 METHODOLOGY

2.1 Preparation Composites

The Fe_3O_4 /activated carbon composites were prepared according to previous work [39]. Briefly, carbonisation of waste paper was carried out by pyrolysis process via the burned waste paper in laminar airflow and the activation of carbon was done by soaking into HCl concentrate. The Fe_3O_4 /activated carbone was prepared via the mixture the iron salt solution (Fe(III)/Fe(II), mole ratio = 2:1) and active carbon suspension and added dropwise NaOH solution under temperature of 70°C . The formed magnetic solid was washed and dried in an oven. Five prepared samples were used for adsorption test each with its own code, as follows; magnetite pure (Fe_3O_4),

non-acid treated active carbon (KA), acid treated active carbon (KA HCl), non-acid treated active carbon- Fe_3O_4 composite (KA- Fe_3O_4) and acid treated active carbon- Fe_3O_4 composite (KA HCl- Fe_3O_4).

2.2 The Evaluation of Adsorption Test

MB (molecular formula of $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+\text{Cl}^-$ with a molecular weight of 319.85 g/mol, Merck) was used as dyes for the adsorption test of the adsorbent. The molecular structure of methylene blue is shown in Figure 1. Stock solution methylene blue was prepared by dissolving the required amount of methylene blue in demineralized water. The test solutions were prepared by diluting the stock solution to the desired concentration.

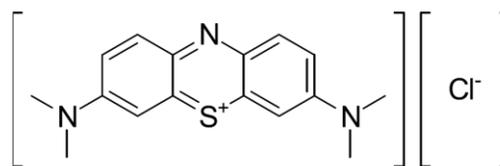


Figure 1 Molecular structure of methylene blue dyes

Batch experiments were carried out to test for the sorption of MB onto adsorbents. The amount of Fe_3O_4 /activated carbon composite adsorbent was added to the solution containing MB. The effects on contact time, adsorbent dose, MB concentration, pH, and temperature were investigated. The various and constant parameters of the batch adsorption experiment were shown in Table 1. The NaOH solution was used to shift the pH solution towards the base. The HCl solution was used to shift the pH solution towards the acid. The apparatus shaker in which the sample has been placed was run at a constant stirring rate of 50 rpm. After the adsorption process is completed, the sample is placed on a permanent magnet bar. It was seen that the magnetic adsorbent particles in the solution move and attached themselves to the magnetic bar. The obtained clear solution was sampled in the amount of as much as 5 ml to determine the MB concentration residual using UV/Vis Lamda 25 Perkin Elmer spectrophotometer at a wavelength of 661 nm.

Table 1 The varied and constant parameter of batch adsorption experiment

Trial	Contact time (hours)	Dose adsorbent (g/L)	MB concentration (mg/L)	pH	Temperature (oK)
1	0; 0.5; 1; 1.5; 2; 3; 4; 5	1	60	not-adjust	ambient
2	5	0.5; 1; 1.5; 2; 2.5; 3	60	not-adjust	ambient
3	5	1	100; 150; 200; 250; 300; 350	not-adjust	ambient
4	5	1	150	2; 4; 6; 8; 10	ambient
5	5	1	150	not-adjust	300; 306; 312; 318

3.0 RESULTS AND DISCUSSION

The Effect of Contact Time

Figure 2 shows the effect of contact time of MB dye on various adsorbents. The adsorption data were evaluated to obtain a relationship between contact time (hours) and the percentage of residual MB in the solution. As Figure 4 reveals, the percentage of MB in the solution decreases with the longer the contact time for all samples due to the higher amount of MB being absorbed on the adsorbent. Fe₃O₄ nanoparticles were able to adsorb MB in water even though its concentration was low. Which then left 67.7% of the MB in the solution for a 5 hours contact time. The surface of Fe₃O₄ nanoparticles has active sides which can adsorb various contaminants of inorganic and organic ions in water [40]. Activated carbon (KA) and chemical activation of activated carbon (KA HCl) from waste paper could adsorb more MB than Fe₃O₄ nanoparticles with 30.7% and 19.8% of residual MB in solution, respectively. Activated carbon contains the kind of surface functional groups, such as aromatic compounds, aliphatic compounds, hydroxyl group, carbonyl group, and a carboxyl group. These groups play an important role in terms of chemical adsorption and electrostatic interaction with chemicals [41]. Chemical treatment of activated carbon (KA HCl) activation has a higher adsorption ability than activated carbon with a non-chemical treatment (KA). Activated carbon naturally provides relative low surface area and pore volume. The acid treatment of activated carbon would increase the surface area, volume pore and site active expose [39], consequently its adsorption ability increases.

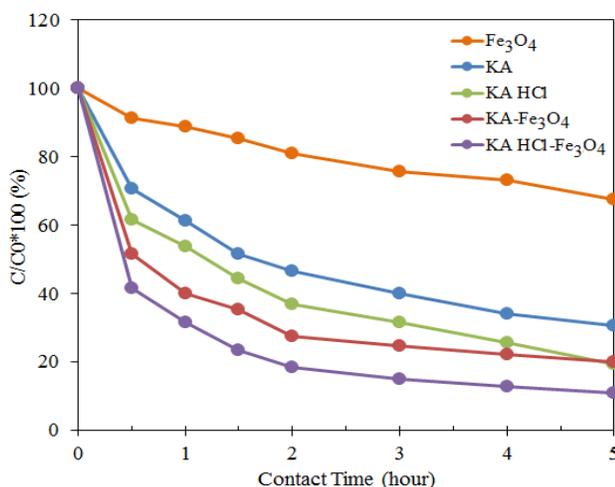


Figure 2 The effect of contact time on the percentage of residual MB

Other literature mentions that the change of surface functional group and pore structure of activated carbon depend on the type of the acid used, therefore the resulting texture structure varies [37]. The presence of Fe₃O₄ nanoparticles on the

active carbon structure increases its adsorption capacity which would then left 19.8% and 10.7% of MB in the solution for KA+Fe₃O₄ and KA HCl+Fe₃O₄, respectively. Thus, the incorporation of Fe₃O₄ nanoparticles with activated carbon possesses a double advantage, not only for the magnetic properties but also for increasing the adsorption capacity. Previous research mentioned that the presence of Fe₃O₄ nanoparticles in the activated carbon structure forms a new pore meso-system and the pore volume of the material increases highly [39]. It is observed that the increase of pore volume has played an important role to increase in the adsorption capacity of composites.

The Effect of Adsorbent Dose

Figure 3 shows the effect of adsorbent dose on MB adsorption efficiency. The efficiency of MB adsorption on the composite is calculated using the following formula:

$$\text{Adsorption efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where C_0 and C_e are the initial and the equilibrium concentration of MB (mg/L) in the solution for 5 hours of the contact time. It is seen that the higher the adsorbent dose concentration in the solution, the higher the adsorption efficiency value of MB. In the range of adsorbent doses from 0.5 to 2.5 g/L, the efficiency adsorption of MB increased from 19.1% to 90.8% and from 20.2% to 98% for KA-Fe₃O₄ and KA HCl-Fe₃O₄, respectively. The increase of adsorption efficiency due to the increasing availability of surface area of adsorbent in the solution [39].

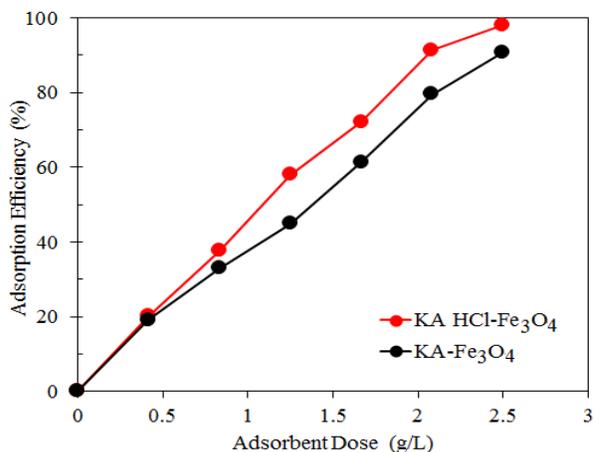


Figure 3 The effect of adsorbent dose on adsorption efficiency

The Effect of pH

The pH of the solution significantly effects on absorbing dyes. It is related to the surface charge of the

adsorbent, the degree of ionization and species of the adsorbate in solution. Figure 4 shows the effect of the pH of the solution on the adsorption capacity of the prepared sample. The adsorption capacity is calculated using the following formula;

$$q = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where q (mg/g) is the adsorption capacity, C_0 and C_e are the initial and equilibrium of MB concentration (mg/L) in solution, V is the volume of solution and W is the weight of adsorbent (g). The figure shows that adsorption capacity increases with increasing pH level from 2 to 6 and then tends to decline slightly in higher pH levels. The maximum value of adsorption capacity was obtained at pH level 6 with the value of 108 mg/g for KA HCl-Fe₃O₄ and 83 mg/g for KA-Fe₃O₄. While, the lowest of adsorption capacity was found in the lowest pH (pH=2) with the value of 35 mg/g and 19 mg/g for KA HCl-Fe₃O₄ and KA-Fe₃O₄ in pH=2, respectively. MB was poorly adsorbed on the composite surface at the lowest pH level due to electrostatic repulsion between protons and MB in solution to be adsorbed on the adsorbent surface. In other words, H⁺ and MB⁺ ion in solution which possess the same charge compete to be adsorbed on the adsorbent surface. With the increase of the pH value, the H⁺ concentration in the solution decreases, so, the amount of MB was more adsorbed on the adsorbent surface. Furthermore, at pH level above 6, MB tends to be adsorbed relatively less due to alkaline conditions, where an excess of OH⁻ ions causes the blocking MB to be adsorbed on the adsorbent surface.

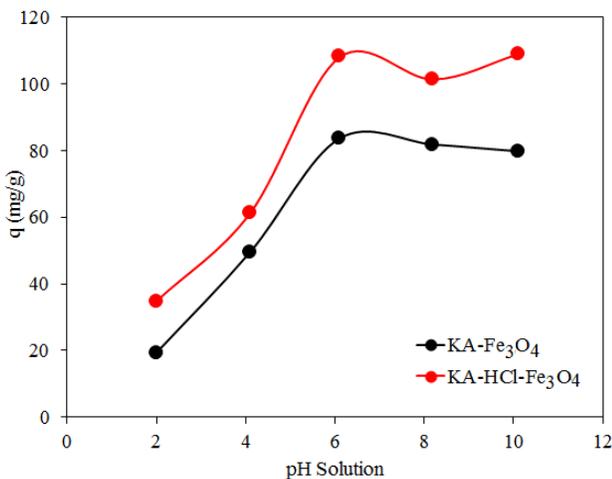


Figure 4 Effect of pH of the solution on the adsorption capacity

The Effect of Temperature

The temperature plays an important role in determining the adsorption process. The capacity and rate of adsorption changes with the shift in

temperature of the solution. It is related to both the physicochemical properties of the adsorbent and the diffusion rate of the adsorbate molecules [12]. Figure 5 shows that the adsorption capacity increases with the increasing temperature of the solution. The adsorption capacity reach 95; 103; 110 and 115 mg/g for KA HCl-Fe₃O₄ and 83; 94; 95 and 98 mg/g for KA-Fe₃O₄ in solution temperature of 300°K, 306°K, 312°K, 318°K, respectively. With the increasing temperature of the solution, the MB kinetic energy also increases, whereas the solution viscosity decreases. This condition would then increase the rate of diffusion of MB molecules into the composite internal pore system, which in turn also increases the absorption capacity [42].

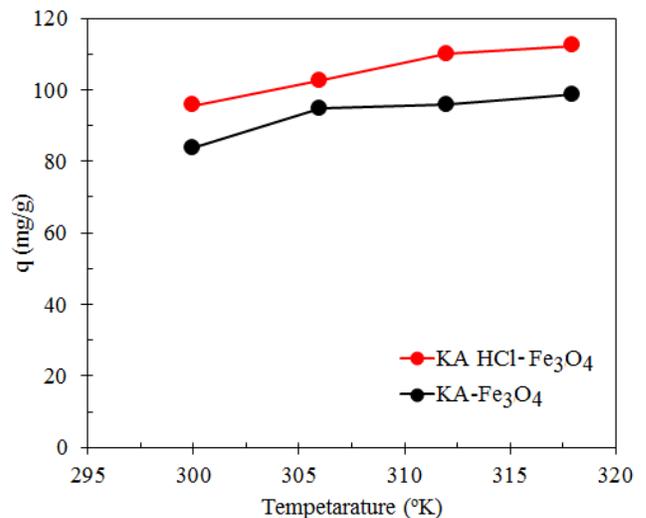


Figure 5 The effect of temperature on adsorption capacity

Adsorption Isotherm. The adsorption isotherm can be explained by the a class of equations models. However, this study only focused on the Langmuir and Freundlich isotherm models. Langmuir isotherm is based on the assumption that the adsorption process takes place on a uniform adsorbent surface, a constant energy level and the adsorbate covering monolayer. The linear form of the Langmuir isotherm equation is shown in the following formula;

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (3)$$

where C_e is the equilibrium concentration of MB solution (mg.L⁻¹), q_e is the amount of MB adsorbed per unit mass of adsorbent (mg.g⁻¹), q_m (mg.g⁻¹) and b (L.mg⁻¹) are the Langmuir constants related to the maximum adsorption capacity and the rate of adsorption, respectively. The plot of C_e/q_e versus C_e for the adsorption of MB onto composites give a straight line, with a slope given by $(1/q_m)$ and with an intercept given by $(1/q_m.b)$ as shown in Figure 6a.

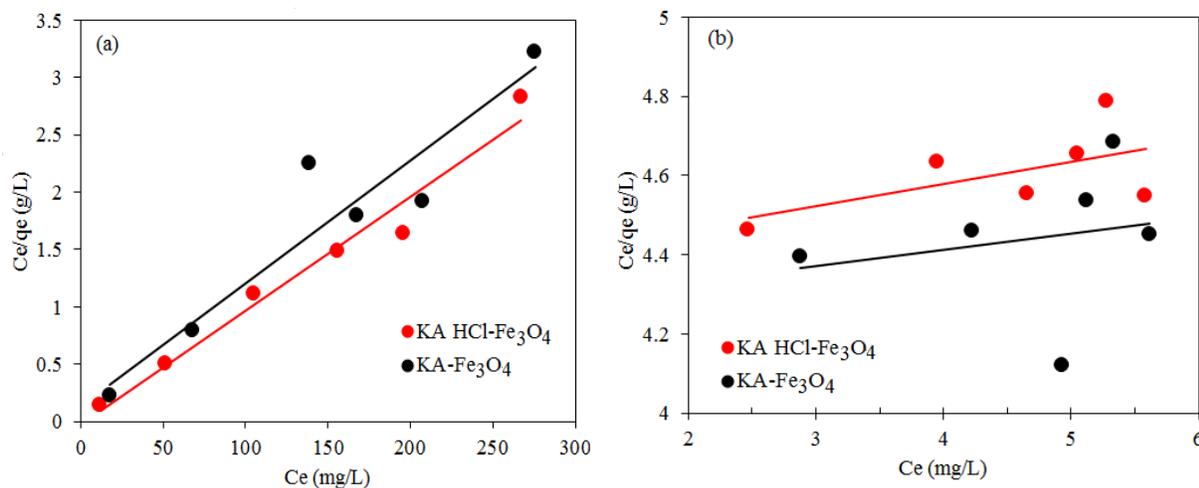


Figure 6 Plot (a) Langmuir dan (b) Freundlich isotherm of KA HCl-Fe₃O₄ and KA-Fe₃O₄ for methylene blue adsorption

The core characteristics of the Langmuir isotherm is to obtain the dimensionless equilibrium parameter (R_L) value, which is obtained in the following equation:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is the Langmuir constant and C_0 is the initial concentration of MB (mg.L⁻¹). R_L value indicates the type of the isotherm, namely unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$) [44]. Whereas, the Freundlich's Isotherm assumes that the adsorption process occurs on heterogeneous surfaces with a non-uniform distribution of adsorption. Freundlich's isotherm is expressed in the following equation:

$$q_e = kC_e^{1/n} \quad (5)$$

with the linear form as follows;

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (6)$$

Where, C_e is the equilibrium concentration of MB solution (mg.L⁻¹), q_e is the amount of MB adsorbed per unit mass of adsorbent (mg.g⁻¹), K_F ((mg/g)(L/mg)^{1/n}) and $1/n$ (no unit) Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively. The plot of $\ln q_e$ versus $\ln C_e$

gives a straight line of slope ($1/n$) and intercept ($\ln K_F$), as expressed in Figure 6b. If the obtained value of the slope $1/n$ is between 0 and 1, it indicates the surface heterogeneity. The closer this number is to zero value, the more heterogeneous is the surface. The n value indicates the type of adsorption, i.e; favorable (in the range of 2-10), moderately difficult (in the range of 1-2) and poor adsorption ($n < 1$) [45].

It is seen in Table 2 that the obtained correlation coefficient values in the Langmuir model were 0,967 and 0,8869 for KA HCl-Fe₃O₄ and KA-Fe₃O₄, respectively. It is also observed that the value of the dimensionless equilibrium (R_L) is in the range of 0,003-0,011 and 0,032-0,110 for KA-HCl/Fe₃O₄ and KA-Fe₃O₄, respectively. This value between 0 and 1 reflects that the methylene blue is favorably adsorbed onto both composites. However, the regression coefficients value of Freundlich's model indicates a weak linear relationship for both KA HCl-Fe₃O₄ and KA-Fe₃O₄. Thus, according to the regression coefficients, the description of the adsorption process' of MB using the Langmuir model provides better results than the one using the Freundlich's model. The Langmuir model was appropriately applied to describe the adsorption equilibrium of MB on composites with the maximum adsorption capacity value of 101 and 93 mg/g for KA HCl-Fe₃O₄ dan KA-Fe₃O₄, respectively.

Table 2 Isotherm parameter values of KA HCl-Fe₃O₄ and KA-Fe₃O₄ for methylene blue adsorption

Sampel	Isotherm Langmuir				Isotherms Freundlich
	R2	qm	b	RL	R2
KA-HCl/Fe ₃ O ₄	0,9672	101	0,92	0,003-0,011	0,3353
KA/Fe ₃ O ₄	0,8869	93	0,08	0,032-0,110	0,0496

The Comparison of Various Adsorbents

The removal of MB by the various types of Fe₃O₄-based magnetic adsorbents has been mentioned extensively in literatures. Table 3 shows a comparison of the obtained adsorption capacity values of magnetic composites of this study with the different adsorbents which have been previously utilized for MB removal. It could be seen in this table that the values of the adsorption capacity of different Fe₃O₄-based composites is varied. Some of them are much lower than those of the synthesized composites. This result indicates that both KA HCl-Fe₃O₄ and KA-Fe₃O₄ composites have great potential applications in the dye removal from contaminant water.

Table 3 Comparison of adsorption of some magnetic composites for MB removal

Adsorbent	q _m (mg.g ⁻¹)	Reference
KA HCl-Fe ₃ O ₄	101	This work
KA-Fe ₃ O ₄	93	
Montmorillonite/CoFe ₂ O ₄	98	[46]
Chitosan/activated chrcoal/Fe ₃ O ₄	200	[47]
Fe ₃ O ₄ /Montmorillonite	106	[48]
Chitosan/Fe ₃ O ₄ /Silica	43	[49]
Fe ₃ O ₄ /Chitosan/graphene	262	[50]
Gum arabic/Fe ₃ O ₄	14,3	[51]

Adsorption Thermodynamics

Thermodynamic parameters are used to better understand the temperature effect of dye adsorption on adsorbents. There are several thermodynamic parameters to be determined in this study, namely; the change of free energy, enthalpy, and entropy. They were determined experimentally from temperature variation data using the following equation:

$$K_d = \frac{q_e}{c_e} \quad (7)$$

$$\Delta G^\circ = -RT \ln K_d \quad (8)$$

Table 4 The thermodynamic parameter values of methylene blue adsorption on composites

Sample	ΔH°	ΔS°	ΔG° (kJ.mol ⁻¹)			
	(kJ.mol ⁻¹)	(kJ.mol ⁻¹ .K ⁻¹)	300K	306K	312K	318K
KA-HCl/Fe ₃ O ₄	24.66	0.08716	-1.444	-2.005	-2.678	-2.956
KA/Fe ₃ O ₄	16.06	0.05548	-0.424	-1.156	-1.253	-1.489

Adsorption Kinetics

Two kinetic models are used to investigate the adsorption mechanism of MB onto the composites,

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

where K_d (L/g) is the distribution coefficient, ΔS° is the change of entropy, ΔH° is the change of enthalpy, ΔG° is the change of Gibbs free energy, T (K) is the temperature, R (8,3145 J.mol⁻¹.K⁻¹) is the gas constant, C_e (mgL⁻¹) is the equilibrium concentration in solution and q_e (mg.g⁻¹) is the amount of MB adsorbed per unit mass of adsorbent. The ΔH° and ΔS° were obtained from the intercept of Von't Hoff plots of K_d versus $1/T$ (Figure 7). The thermodynamic parameters of adsorption are shown in Table 4. The positive value of ΔH° indicates that the adsorption of MB on the adsorbent surface is endothermic. ΔG° is the a negative, assumption that the adsorption process is exergonic (feasibility) and will proceed spontaneously.

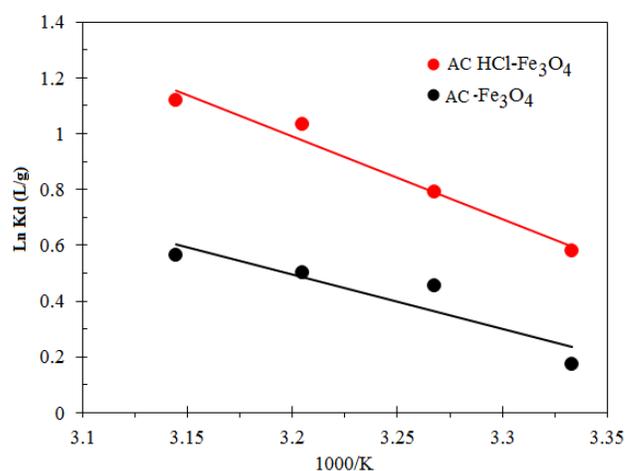


Figure 7 Van't Hoff plot Ln K_d versus 1/T

With increasing temperature, the ΔG° value decreases, consequently the reaction extant decrease. Thus, the process is becoming more feasible at elevated temperature. The ΔS° is positive, indicating that the randomness at the solid/solution interface increases during MB adsorption onto the adsorbent [46].

such as the kinetic model of pseudo-first-order and pseudo-second-order [17]. The kinetic model of pseudo-first-order is expressed by the following equation;

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (10)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}), q_e and q_t are the amounts of MB adsorbed per unit mass of adsorbent at equilibrium and at time t (min), respectively. The k_1 value was found from the intercept of Lagergren plot of $\log(q_e - q_t)$ versus t .

The kinetic model of the pseudo-second-order model can be given the following equation;

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where k_2 ($\text{g mg}^{-1}\text{min}^{-1}$) is the rate constant of the pseudo-second-order adsorption. The value of k_2 was determined from the slope of Ho-Mackay plot of t/qt versus t .

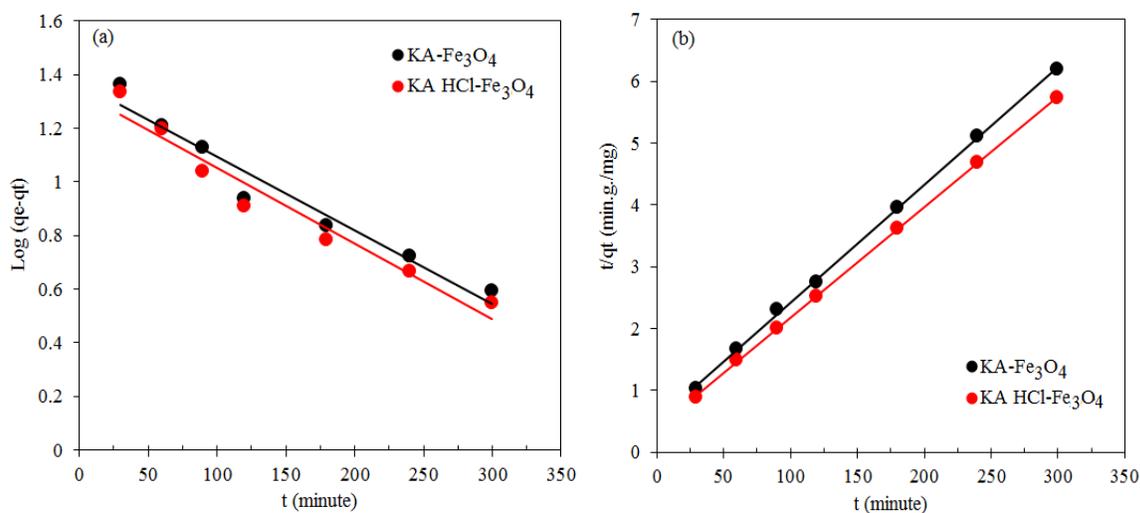


Figure 8 The linear regression of (a) pseudo-first-order kinetic model and (b) pseudo-second-order kinetic model of KA-Fe₃O₄ and KA HCl-Fe₃O₄

Table 5 The kinetic constant values for both pseudo-first-order and pseudo-second-order model of prepared composites

Sampel	$q_{e,exp}$ (mg.g^{-1})	Pseudo-first-order (Lagergren)			Pseudo-second-order (Ho-Mackay)		
		$q_{e,cal}$ (mg.g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg.g^{-1})	k_2 ($\text{g.mg}^{-1}\text{min}^{-1}$)	R^2
KA/Fe ₃ O ₄	48.44	23.33	0.0046	0.954	52.36	0.00072	0.9993
KA-HCl/Fe ₃ O ₄	52.34	21.62	0.0046	0.952	55.86	0.00084	0.9991

Adsorption Mechanism

On a wide range of activated carbon, the adsorption process of MB occurs rapidly in the initial period of the contact time and then slows down and finally becomes stagnant with increasing contact time. Kanaan *et al.* [52] reveal that the MB adsorption mechanism consists of four steps, including (1) migration of MB from bulk of the solution to the surface of the activated carbon, (2) diffusion of dye through the boundary layer to the surface of the adsorbent (3)

The linear regression and the kinetic constant for both the pseudo-first-order and pseudo-second-order model of composites can be seen in Figure 8 and Table 5, respectively. The correlation coefficients (R^2) of both KA/Fe₃O₄ and KA-HCl are relatively low for the pseudo-first-order kinetic model. In addition, the value of calculated q_e ($q_{e,cal}$) from the pseudo-first-order kinetic model is very different from the experimental q_e ($q_{e,exp}$), suggesting that the pseudo-first-order kinetic model provides a poor result when applied to the adsorption of MB onto the composite. The correlation coefficients (R^2) for the pseudo-second-order kinetic model are close to 1 (0.999 for both composite) as well as the value of $q_{e,cal}$ approached the $q_{e,exp}$ values. It could be concluded that the pseudo-second-order model provides an appropriate analysis when applied to the adsorption process of MB onto composites.

adsorption of dye at an active site on the surface of activated carbon and (4) intra-particle diffusion of dye into the interior pores of the activated carbon particle. MB is cationic (MB^+) in nature and possesses the chemical structure of rich aromatic ring. On the other hand, activated carbon surface has the main functional group including carboxylic acid, lactone and phenol. Ionic interaction, electrostatic interaction and $\pi - \pi$ stacking interaction were involved in MB adsorption to activate carbon via a site-to site

hopping mechanism between functional groups [53], [54].

4.0 CONCLUSION

The adsorption properties of Fe₃O₄/waste paper activated carbon composites has been successfully studied. The presence of magnetic (Fe₃O₄) in the activated carbon structure increases the removal of MB compared to non-magnetic sample. The adsorption capacity increases with the increasing temperature (in range of 300-318°K) of the solution. The maximum adsorption capacity is obtained at a solution pH level of 6. The adsorption equilibrium of MB on composites trend to follow the rules of Langmuir model with the maximum adsorption capacity value of 101 and 93 mg/g for KA HCl-Fe₃O₄ dan KA-Fe₃O₄, respectively. The adsorption process is found to be pseudo-second-order. The prepared magnetic adsorbents have shown a highly promising potential of utilization in the adsorption field for the removal of dye in wastewater treatment. They are becoming very attractive and are able to provide a simple method to recover the adsorbent from water with the assistance of an external magnetic device.

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