Methylene blue adsorption by using copper pyrophosphate

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Abstract

This project aimed to study a preparation and characterization of copper pyrophosphate ($Cu_2P_2O_7$) that was prepared using the solid combustion method in order to study adsorption of methylene blue. The copper pyrophosphate was prepared from mixture of cupric carbonate ($CuCO_3{\cdot}Cu(OH)_2$) and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) and calcined at 550 ^{O}C for 3 hrs. Then, it was characterized by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). After that, methylene blue was adsorbed by $Cu_2P_2O_7$ showed that it was a monolayer adsorption and the data conformed well to the Langmuir isotherm model.

Keywords: Adsorption, Methylene blue, Copper pyrophosphate

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บทคัดย่อ

งานวิจัยนี้ศึกษาการเตรียมและตรวจสอบเอกลักษณ์ของคอปเปอร์ไพโรฟอสเฟต ($Cu_2P_2O_7$) ที่เตรียมได้จากวิธีเผาไหม้ของแข็ง เพื่อนำไปศึกษาการดูดซับของสารละลายเมทินลีนบลู โดยนำของผสมระหว่างคิวปริกคาร์บอเนต ($CuCO_3{\cdot}Cu(OH)_2$) กับไดแอมโมเนียมไฮโดรเจนฟอสเฟต ($(NH_4)_2HPO_4$) มาเผาที่ 550 องศาเซลเซียส เป็นเวลา 3 ชั่วโมง จากนั้นนำสารที่เตรียมได้มาตรวจสอบเอกลักษณ์ ได้แก่ พฤติกรรมทางความร้อนด้วยเทคนิคเทอร์โมกราวิเมทริก (TGA) การวิเคราะห์การเลี้ยวเบนของรังสีเอกซ์ (XRD) และกล้องจุลทรรศน์แบบส่องกราด (SEM) เมื่อนำคอปเปอร์ไพโรฟอสเฟตที่เตรียมได้มาทดสอบการดูดซับสารละลายเมทินลีนบลู พบว่าเป็นการดูดซับแบบชั้นเดียวซึ่งสอดคล้องกับไอโซเทอร์มการดูดซับของแลงเมียร์

คำสำคัญ: การดูดซับ เมทิลีนบลู คอปเปอร์ไพโรฟอสเฟต

1. Introduction

The world population is currently increasing which directly affects the demand for consumer goods. In addition, technological advancement also favors emerging of many factories which add pollution, whether it is solid, liquid, and gas wastes, to the environment (John, and *et al*., 2010). These pollutants accumulate and contaminate water sources, air and sediments and adversely affect humans in the long run. For example, bleaching and dyeing industries use large volumes of water and chemicals: the main problem in this industry is disposal of factory wastewater, which consists of pigments, organic substances, suspended solids, acid-base suspensions and heat. Dye factory wastewater mainly originates from dyeing and washing. This polluted water not only damages natural water sources but also obstructs oxygen transfer to the water and blocks sunlight passing through the water, which in turn hinders photosynthesis in aquatic plants. Further, once oxygen level in the water drops, aquatic animals may die from lack of oxygen.

Dyes can be classified by pH: acid dyes are water soluble and negatively charged and basic ones are water soluble but positively charged. Dye are also be categorized by durability i.e. permanently or temporarily soluble. Methylene blue (MB) is a popular basic dye, used in dyeing textiles, paper, fiber, etc. Wastewater treatment in the dyeing industry can be managed by use of biodegradable with bacteria, chemicals to consolidate and precipitate membranes and ion exchange, etc. These methods have some limitations, time required, implementation difficulty, amount of chemicals and budget. Adsorption is also used for wastewater treatment in the textile industry: many types of adsorbents are available, including cotton textile, bark, hair, coal, olive waste, peanut shell waste, hazel, sawdust and ash (Ferrero, 2007; Han, and *et. al.,* 2007). In recent years, researchers have developed many adsorbents; sometimes the adsorbent is used as it is or impregnated or modified to improve the capacity of the adsorption. Several types of adsorbents are developed to get enhanced adsorption capacity in an inexpensive way (Ajemba, 2014).

Metal phosphates are versatile and have many uses such as coating, ceramics, catalysts, anti-corrosion coating and slow release fertilizers and are environmentally friendly. Metal phosphates have two main sources: natural and synthetic. The common anions are: orthophosphate (PO_4^{3-}), hydrogenphosphate (HPO_4^{2-}), dihydrogenphosphate ($H_2PO_4^{-}$), pyrophosphate ($P_2O_7^{4-}$) and cyclotetraphosphate ($P_4O_{12}^{4-}$). Natural phosphate ore usually undergoes ferrolysis through a reduction reaction at appropriate pH, duration and temperature. Most metal phosphate sediments are water insoluble, e.g. $MnPO_4.H_2O$, $AlPO_4.2H_2O$, $MgHPO_4.2H_2O$, $MnHPO_4.3H_2O$, $CaHPO_4.2H_2O$, $Mn_3(PO_4).3H_2O$, $Fe_3(PO_4).8H_2O$ and $Mg_3(PO_4)_2.8H_2O$ (Banjong, 2013).

In this research study, focused on to describe adsorption of copper pyrophosphate ($Cu_2P_2O_7$) by solid combustion for use as adsorbent to remove methylene blue from aqueous solution was designed. This adsorbent is easily prepared at minimal cost. Importantly, the process is environmentally friendly because it has phosphorus as the main component, which is essential for plant growth and key fertilizers. It is also naturally biodegradable and thus not toxic to living organisms. We describe a batch system to characterize and determine the applicability of two isotherm models (Langmuir and Freundlich) to find the best fit isotherm equation and to determine adsorption kinetics.

2. Research methodology

2.1 Methylene blue solution

Methylene Blue ($C_3H_{18}ClN_3S$) is a monovalent cationic dye, molecular weight 373.9. MB is a basic dye, commonly used for dyeing silk, leather, paper and cotton, as well as production of ink. MB supplied in powder form by Merck, was used without further purification for the preparation of synthetic aqueous solution. The measuring light absorption using an UV-VIS spectrophotometer (Hitachi U-2000) at 668 nm, using distilled water as a reference.

2.2 Preparation of copper pyrophosphate

Normally, copper pyrophosphate appears as light green powder soluble in acid and not soluble in water. It is mainly used in non-cyanide plating, supplying copper ions in the plating bath, used in the copper base of decorative maskant and carburization, used as analytical reagent, and used in the preparation of phosphate pigments. To administer with the weighed cupric carbonate and diammonium hydrogen phosphate in 1:2 molar and ground and mixed them. Then they were heated at 550 °C for 3 hours. The reaction was:

$$CuCO_3.Cu(OH)_2\ (s) + 2(NH_4)_2HPO_4\ (s) \longrightarrow Cu_2P_2O_7\ (s) + CO_2\ (g) + 4NH_3\ (g) + 4H_2O(g) \qquad (1)$$

2.3 Characterization of copper pyrophosphate

The thermal stability of copper pyrophosphate was evaluated by TGA (PerkinElmer STA 6000) from room temperature to 800 °C in a nitrogen atmosphere. XRD patterns of copper pyrophosphate were captured with an X-ray diffractometer (Bruker D8) with Cu-K_α radiation and 30 kV tube voltage and 30 mA current. Surface morphology was observed by Scanning Electron Microscope (Leo 1455 VP, UK), set at 15 kV.

2.4 Adsorption studies

This research procedure refers that this study of Ajemba (2014). In this research study, using 50 ml of MB solution was placed in a conical flask; 0.1 g copper pyrophosphate was added and shaken at 150 rpm and room temperature. The experiment was repeated for 0.1 g of copper pyrophosphate. After 90 minutes, the suspension was filtered and the final concentration of MB in solution was measured by absorbance at 668 nm. The amount of MB adsorbed onto the copper pyrophosphate was calculated as

$$q_e = \left(\frac{C_o - C_e}{w}\right) x\ V \qquad (2)$$

Whereas C_0 and C_e (mg/L) are the liquid-phase concentrations of MB initially and at equilibrium, respectively, V (L) is the volume of the solution and w (g) is the mass of dry prepared sorbent used (Ajemba, 2014). Note that, in this and all following, equations and plots, SI units were used. Batch kinetic studies by procedures of kinetic experiments were basically identical to those of the equilibrium tests. The aqueous samples were taken at preset time intervals, temperature and the initial concentrations of MB were similarly measured. Each experiment was performed in triplicate.

2.4.1 Adsorption isotherm

Experimental isotherm data collected for the adsorption of copper pyrophosphate was fitted with the Langmuir and Freundlich adsorption isotherm models.

Langmuir model

The Langmuir isotherm assumes the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. This model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface, sufficient available adsorption sites, monolayer surface coverage and no interaction between adsorbed species. If MB adsorption follows the Langmuir model, adsorption can be computed from Ajemba (2014).

$$\frac{1}{q_e} = \frac{1}{q_o} + \frac{1}{K_L q_o}\frac{1}{C_e} \qquad (3)$$

Meanwhile q_o is the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L), q_e is the amount of MB adsorbed (mg/g) and K_L is sorption equilibrium constant (L/g).

Freundlich Model

This phase study was designed from the Freundlich equation or Freundlich adsorption isotherm, an adsorption, is an empirical relation between the concentration of a solute on the surface of an adsorbent to the concentration of the solute in the liquid with which it is in contact. In 1909, Herbert Freundlich gave an expression representing the isothermal variation of adsorption of a quantity of gas adsorbed by unit mass of solid adsorbent with pressure (Jaroniec, 1975). As this relationship is entirely empirical, in the case where adsorption behavior can be properly fit by isotherms with a theoretical basis, it is usually appropriate to use such isotherms instead of this equation is obtainable by statistical thermodynamics methods. In Freundlich adsorption isotherms from the exponential isotherm, The energy distribution function corresponding to the exponential adsorption isotherm can be calculated in the way analogous to equation 4.

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad (4)$$

Whereas K_F and n are the constants of the Freundlich adsorption isotherm is evaluated. K_F represents the adsorption capacity and n the adsorption intensity. When $1/n > 1.0$, the change in adsorbed MB concentration is greater than the change in the MB concentration in solution was calculated (Ajemba, 2014).

2.4.2 Adsorption kinetics

To investigate the mechanism of MB adsorption by copper pyrophosphate, pseudo-first order and pseudo-second order kinetic models were considered.

Pseudo-first order kinetic model

A pseudo-first order model is the simplest model describing the kinetics of a liquid-solid phase, based on the adsorption capacity. The pseudo-first-order rate expression is given as (Ho & McKay, 1999):

$$\ln (q_e - q_t) = \ln q_e - k_1 t \qquad (5)$$

Whereas, k_1 is the rate constant of pseudo-first-order adsorption, the sorption of lead ions from aqueous solution onto peat has been studied. Kinetic studies have been carried out using an agitated batch and the effect of varying process parameters has been investigated; these include initial lead ion concentration, peat particle size, solution temperature and agitation speed (Ho & McKay, 1999). The values of q_e and q_t are the amount of MB adsorbed at equilibrium and at time (min), respectively, and k_1 is the rate constant of the pseudo-first order adsorption process. The values of q_e and k_1 were determined from the intercept and slope of the linear plot of log (q_e- q_t) versus t.

Pseudo-second order kinetic model

The corresponding pseudo-second order rate equation, the feasibility for the removal of methylene blue (MB) dye from aqueous solution using copper pyrophosphate. Batch adsorption experiments were carried out as a function of pH, contact time, adsorbate concentration, adsorbent dosage and temperature. The commonly applicable isotherms namely Freundlich and Langmuir equations are used for the prediction of isotherm parameters. A comparison of linear least-square method and a trial-and-error non-linear method are examined in Freundlich and Langmuir (Four forms) isotherms (Kumar & Tamilarasan, 2013) are given as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

Meanwhile, k_2 is the rate constant for pseudo-second-order adsorption process (g/mg-min). The plot of t/q_t versus t.

2.4.3 Adsorption thermodynamics

We determined the thermochemical parameters, including adsorption enthalpy (ΔH^O), adsorption entropy (ΔS^O) and Gibbs' independent energy change (ΔG^O). The enthalpy, entropy, and Gibbs independent energy changes can be calculated from equations 7 and 8. This result refers to research studied by Lin, Zhan, Fang, Qian, & Yang (2008); a low-cost adsorbent for the removal of a typical dye, methylene blue, from aqueous solution. An increase in the specific surface area and dye-adsorption capacity was observed after the acid treatment, and the Freundlich isotherm is better in describing the adsorption process. Two kinetic models, pseudo-first order and pseudo-second order, were employed to analyze the kinetic data.

$$log\frac{q_e}{C_e} = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303TR} \qquad (7)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (8)$$

3. Results and discussion

3.1 Characterization of copper pyrophosphate

Figure 1 shows total weight loss in four phases. Phase 1 between 50 and 160 °C accounted for 12.65% loss as the result of diammonium hydrogen phosphate decomposition in equations 9 and 10.

$$2(NH_4)_2HPO_4 \rightarrow 2NH_4H_2PO_4 + 2NH_3 \qquad (9)$$

$$2NH_4H_2PO_4 \rightarrow 2H_3PO_4 + 2NH_3 \qquad (10)$$

Phase 2 between 210 and 250 °C accounted for a further 9.28% loss as the result of cupric carbonate decomposition in equation 11.

$$CuCO_3{\cdot}Cu(OH)_2 \rightarrow 2CuO + CO_2 + H_2O \qquad (11)$$

Phase 3 between 250 and 340 ^{O}C was the result of the reaction between phosphoric acid and copper oxide, which products were from equations 10 and 11. This accounted for 8.93% in equation 12.

$$2CuO + 2H_3PO_4 \rightarrow 2CuHPO_4 + 2H_2O \qquad (12)$$

Phase 4 between 340 and 800 ^{O}C accounted for a further 4.13% from forming copper pyrophosphate as in equation 13 (Abba, Musa, Kogo, & Salisu, 2012; House, 2010; Khemthong, Daorattanachai, Laosiripojana, & Faungnawakij, 2012).

$$2CuHPO_4 \rightarrow Cu_2P_2O_7 + H_2O \qquad (13)$$

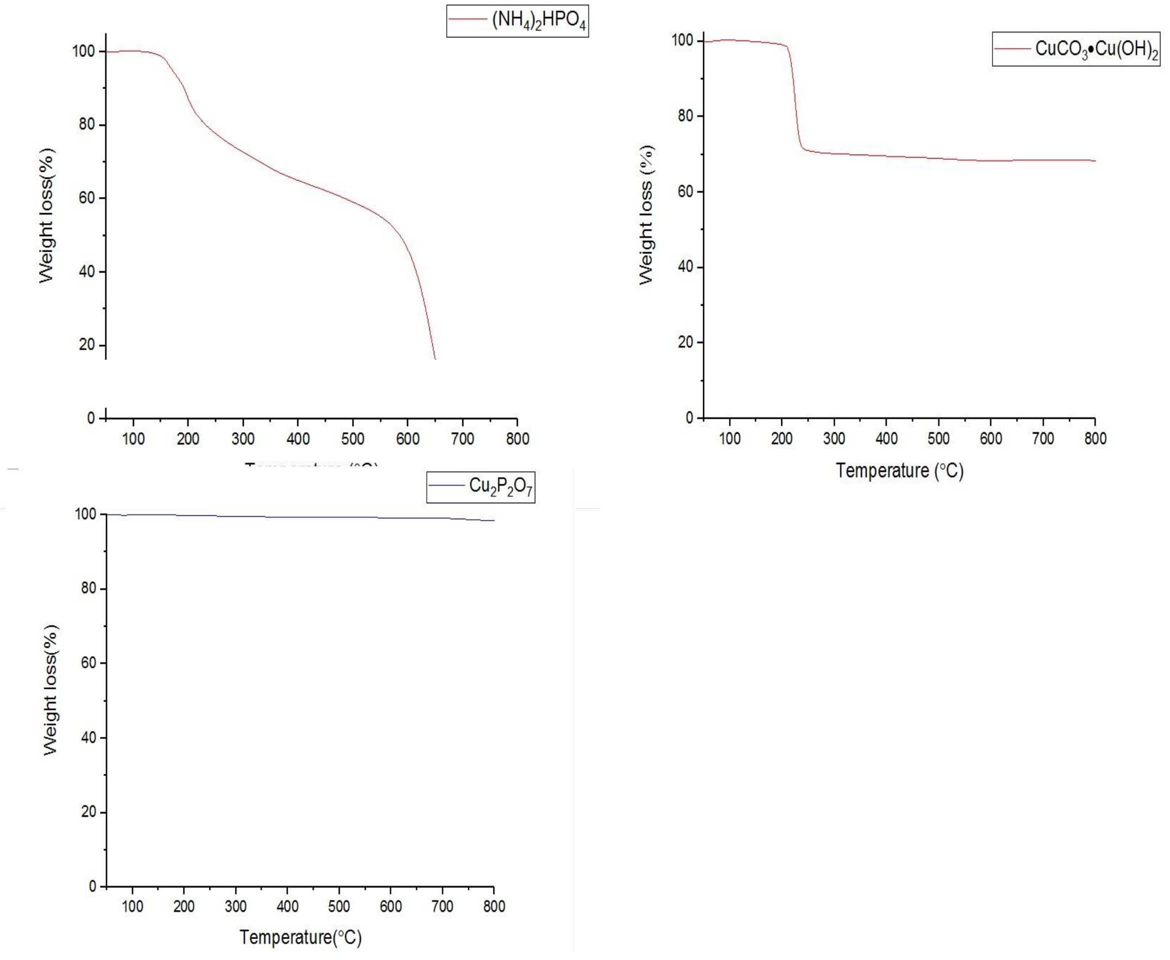


Figure 1 TGA of samples

X-Ray Diffraction (XRD) in Figure 2 showed main 2θ peaks at 16.24, 21.84, 26.80, 30.84 and 32.68 close to those found in JCPDS standard No. 44-0182, which indicated that copper pyrophosphate was prepared from the solid combustion method.

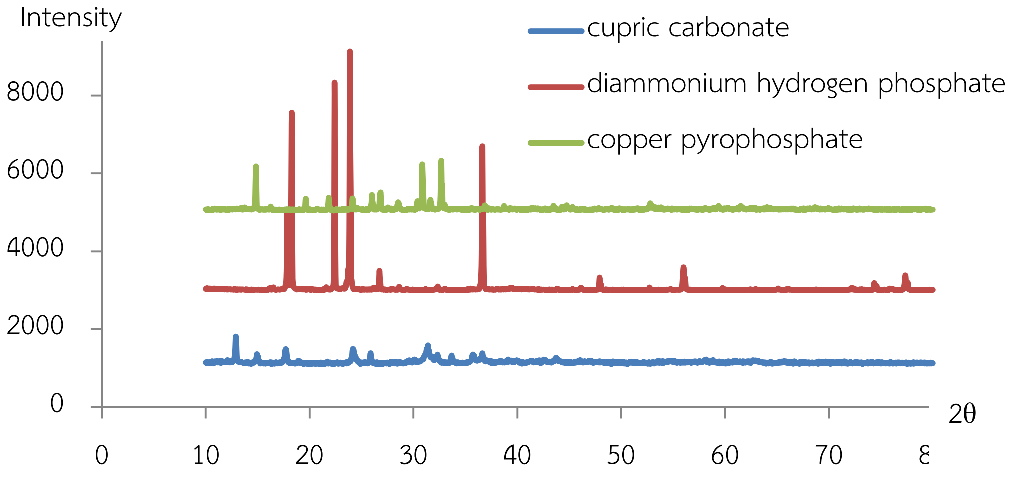
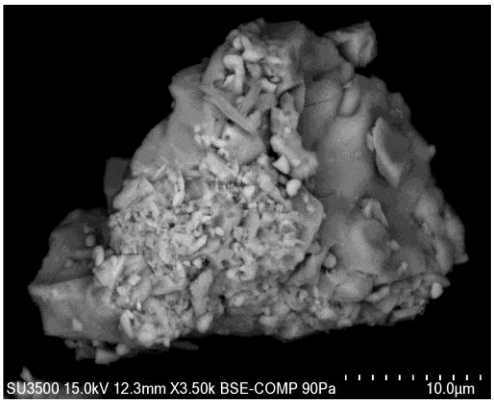


Figure 2 Powder XRD patterns of copper pyrophosphate



SEM images revealed the morphology of the prepared copper pyrophosphate: they showed a random collection of small to large rectangular bars.

Figure 3 SEM image of copper pyrophosphate

3.2 Adsorption studies

The percentage of MB removal was rapid due to adsorption of the MB molecules on the upper surface of the adsorbent. Then it became slow due to slow passing of molecules into the inner structure of the adsorbent (Ahmad, Hameed, & Aziz, 2007). The adsorption capacity of MB by copper pyrophosphate reached the equilibrium at around 90 minutes for concentrations from 1.0 to 5.0 mg/L. In this range, MB uptake increased from 0.37 to 1.19 mg/g - see Figure 4. The adsorption capacity increased with the increasing MB concentration, the MB molecules were adsorbed externally and the percentage of MB removal increased rapidly. When the external surface became saturated, the MB molecules were adsorbed onto the porous structure of the adsorbent (Safa & Bhatti, 2011). The initial MB concentration provides an important driving force to overcome the mass transfer resistance of all molecules between the aqueous and solid phases (Onuma & Thodsaphon, 2017).

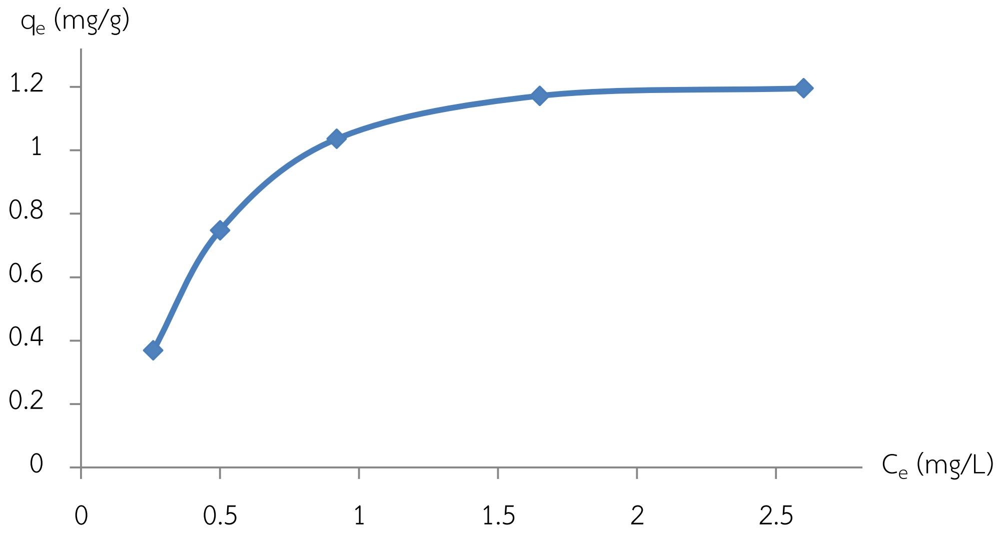


Figure 4 Equilibrium capacity (q_e) *vs* initial MB concentration (C_e)

3.2.1 Adsorption isotherms

Parameters obtained from Langmuir and Freundlich models are shown in Table 1. The Langmuir model (R^2 = 0.9476) clearly fits better than the Freundlich model (R^2 = 0.7998). Thus we conclude that the adsorption is monolayer in nature and that available sites on the copper pyrophosphate adsorbent are not fully occupied (Saechiam & Sripongpun, 2017).

Table 1 Parameters obtained from the Langmuir and Freundlich models

Material	Langmuir			Freundlich			Reference
	q_o	K_L	R^2	K_F	1/n	R^2	
Copper pyrophosphate	1.98	0.937	0.9476	1.25	1.747	0.7998	This research
Banana peels	68.03	0.574	0.992	19.31	0.449	0.769	Saechiam & Sripongpun (2017)

3.2.2 Adsorption kinetics

The k_2 and q_e values from the regression are in Table 2. This procedure is more likely to predict the behavior over the whole range of adsorption. Fitting the data to the second-order model leads to $R^2 = 0.9974$, showing that the second order mechanism dominates, meaning that chemical sorption takes part in the adsorption process. Once the sorptive sites are exhausted, the uptake rate is controlled by the rate of intra particle diffusion (Kumar, *and et al*., 2011).

Table 2 Kinetic parameters for the adsorption of methylene blue by copper pyrophosphate.

Pseudo-first order			Pseudo-second order		
q_e	k_1	R^2	q_e	k_2	R^2
0.3556	0.0297	0.9736	0.8509	0.1231	0.9974

3.2.3 Adsorption thermodynamics

Thermochemical parameters shown in Table 3 revealed that enthalpy change was negative which meant that the adsorption was exothermic reaction. However, entropy change was positive and Gibbs' independent energy change was negative which meant that adsorption reaction was self-initiated.

Table 3 Thermal parameters of methylene blue adsorption using copper pyrophosphate

ΔH^O (kJ/mol)	ΔS^O (J/mol-K)	ΔG^O (kJ/mol)			
		26 °C	45 °C	53 °C	68 °C
11.3	41.0	-0.93	-1.71	-2.04	-2.66

In Table 3 reports of the pseudo-second-order model is the better choice to describe the adsorption behavior. The thermodynamic study reveals that the enthalpy (ΔH^0) value is positive (11.3 kJ/mol), and ΔS^O (41.0 kJ/mol, suggesting an endothermic nature of the adsorption).

In Figure 5, batch experiments were carried out to determine the influence of parameters like initial relationship between 1/T and log (q_e/C_e) of MB adsorption. The pseudo-second-order kinetic model represented the adsorption kinetics equilibrium isotherms were analyzed by Langmuir and Freundlich models using a non-linear regression technique. Adsorption of MB adsorption was favorably influenced by an increase in the temperature of the operation. The positive values of the change in entropy (ΔS^{O}) and heat of adsorption (ΔH^{O}); and the negative value of change in Gibbs free energy (ΔG^{O}) indicate feasible and spontaneous adsorption of MB adsorption (Lakshmi, Srivastava, Mall, & Lataye, 2009).

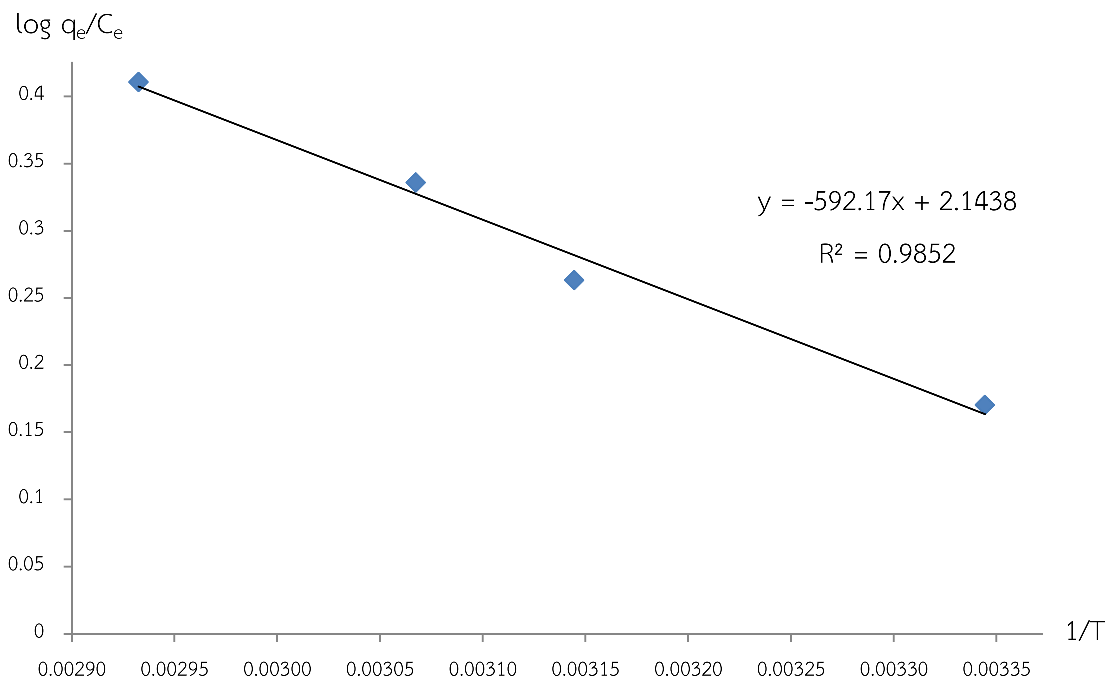


Figure 5 The relationship between 1/T and log (q_e/C_e) of MB adsorption

4. Conclusion

In this study, the copper pyrophosphate prepared from solid combustion method. The Langmuir and Freudlich adsorption isotherm models were used for the description of the adsorption equilibrium of methylene blue onto the adsorbent. Langmuir adsorption isotherm model was found to be had the highest regression value and best described equilibrium data. The adsorption kinetics of methylene blue onto copper pyrophosphate can be successfully fitted to pseudo-second order kinetic model.

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