Removal of Ethyl Orange Dye Using Hybrid Chitosan and Zinc Oxide

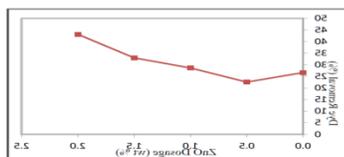Norzita Ngadi[a]*, Mohamad Akmal Mahmud[a], Mazura Jusoh[a], Roshanida Abd Rahman[a], Hajar Alias[a]

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Graphical abstract

Abstract

Ethyl Orange is a type of water-soluble azo dye, which is widely used in the textile, printing, paper manufacturing, pharmaceutical and food industries. Due to a large-scale production and extensive application of azo dyes, it can cause considerable amount of polluted wastewater and can generate serious health-risk factors. Chitosan, a low cost adsorbent has been widely used to treat azo dye. Recent studies had discovered heterogeneous photocatalysis using semiconductors such as zinc oxide is quite applicable because of its ability to decolorize dye-containing wastewater more effectively. The purpose of this research is to hybridize the low-cost adsorbent chitosan and semiconductor zinc oxide to produce an adsorbent which has high efficiency for removing azo dye. The parameters that were used in this study are pH values (pH 5.0 to 9.0), temperature (25 to 60◦C) and the initial dye concentration (0.10 to 1.00 mg/L). The results obtained showed that hybrid chitosan and zinc oxide adsorbent had successfully decolorized ethyl orange dye in water. The optimum conditions for the highest removal of ethyl orange (85%) were achieved at following conditions; temperature of 60°C, using adsorbent containing 1 g of chitosan and 2.0wt % of zinc oxide, 1.0 mg/L of dye concentration, at pH 7 and 2 hours of mixing time with 130 rpm of mixing rate. In this study, the adsorption process was found to fit the Freundlich isotherm than of the Langmuir isotherm.

Keywords: Adsorption; chitosan; ethyl orange; zinc oxide; hybrid

Abstrak

Etil Oren adalah sejenis pewarna azo yang larut air yang digunakan secara meluas dalam industri tekstil, percetakan, pembuatan kertas, farmaseutikal dan makanan. Oleh kerana pengeluaran pewarna azo yang besar dan penggunaan yang meluas, ia menyebabkan pencemaran kepada air dan menyumbang kepada risiko kesihatan manusia yang serius. Kitosan, bahan penjerap yang murah telah digunakan secara meluas untuk merawat pewarna azo. Kajian terbaru telah menemui fotopemangkinan heterogenes yang menggunakan semikonduktor seperti zink oksida juga berkesan kerana keupayaannya yang tinggi untuk melunturkan warna pewarna azo dalam air yang tercemar. Objektif kajian ini adalah untuk menghibridkan kitosan dan zink oksida semikonduktor untuk menghasilkan bahan penjerap yang mempunyai kecekapan yang tinggi untuk meluntur pewarna azo dalam air. Parameter-parameter yang digunakan dalam eksperimen ini ialah pH (pH 5.0-9.0), suhu (25 hingga 60˚C) dan kepekatan pewarna awal (0.10 hingga 1.00 mg/L). Keputusan yang diperolehi menunjukkan bahawa hibrid penjerap kitosan dan zink oksida telah berjaya menyahwarna etil oren dalam air. Keadaan optimum untuk penyingkiran pewarna etil oren yang tertinggi (85%) telah dicapai pada keadaan berikut; suhu 60°C, dengan menggunakan bahan penjerap yang mengandungi 1 g kitosan dan 2.0 wt% zink oksida, 1.0 mg/L kepekatan pewarna, pada pH 7 dan 2 jam masa pencampuran dengan 130 rpm kadar pencampuran. Dalam kajian ini, proses penjerapan adalah sesuai diterangkan dengan Freundlich isoterma dan bukannya Langmuir isoterma.

Kata kunci: Penjerapan; kitosan; etil oren; zink oksida;hibrid

■1.0 INTRODUCTION

One of the major problems concerning environmental pollutants is wastewater problem. Their toxic effluents are a major source of aquatic pollution and will cause considerable damage to the receiving waters if discharged untreatedly [Mahmoodi *et al.*, 2009]. The main problem found in the decontamination of wastewater is the removal of colour. Wastewaters containing dyes are the most difficult to remove because of their inert properties and the low concentration of dye molecules in wastewater [Wan Ngah *et al.* 2010].

Adsorption method is a prominent method of treating aqueous effluent in industrial processes [Benkli *et al.*, 2005] for a variety of separation and purification purpose. This technique also was found to be highly efficient for the removal of colour in terms of initial cost, simplicity of design, ease of operation and

insensitivity to toxic substances [Ilhan *et al.,* 2004]. Adsorption is undoubtedly the most important of the physicochemical processes responsible for the uptake of inorganic and organic substances in the aqueous environment. Factors such as pH, nature and concentration of substrate and adsorbing ion, ionic strength, and the presence of competing and complex ions affect the extent of adsorption. Chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity and adsorption properties [Kumar, 2000]. Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites [Wu *et al.*, 2001]. Recently, hybrid materials based on chitosan have been developed, including conducting polymers, metal nanoparticles and oxide agents, due to its excellent properties of individual components and outstanding synergistic effects simultaneously. For example, Repo *et al.* [2011] had used EDTA-modified chitosan–silica hybrid adsorbent to remove Co(II), Ni(II), Cd(II), and Pb(II). They found out that, the adsorbent with the highest chitosan content showed the best adsorption efficiency. The synthesized adsorbents combined successfully the beneficial properties of silica-gel and chitosan; porous and rigid like silica gel and had high coverage of functionalities due to the chitosan groups [Repo *et al*., 2011]. Alumina-chitosan hybrid adsorbent was also been used for removal of Cu (II) from aqueous solution by [Guijuan *et al.*, 2012]. They noticed that chitosan coated alumina adsorbent not only have high adsorption activity, but also had good stability in the wastewater treatment process. In another study, chitosan hydrogel/SiO2 had been prepared to treat Remazol Black B, Erythrosine B, Neutral Red and Gentian Violet dyes [Copello *et al*., 2011]. The main mechanism of dye adsorption was found to be a spontaneous charge associated interaction.

Based on the previous research, TiO$_2$ is the most widely used effective photocatalyst for its high efficiency, photochemical stability and non-toxic nature [Jain and Sikarwar, 2008, Han *et al*., 2012, Norzita and Aisyah, 2012, Adam *et al*., 2013]. However, research nowadays has been focused on ZnO as an alternative of TiO$_2$ since it has the similar band gap as TiO$_2$. In addition, ZnO has more functions than TiO$_2$ and recent researches have pointed out that ZnO can also be used in the acidic or alkaline conditions through the proper treatment [Najafi and Mahmoodi, 2012].

Thus, in this study, it is aimed to prepare hybrid chitosan and zinc oxide and to study its ability as an adsorbent for removal of ethyl orange dye. The effects of adsorbent dosage, settling time, pH, initial dye concentration and temperature on the performance of hybridized adsorbent towards removal of azo dye in wastewater were also been investigated in this study.

■2.0 MATERIALS AND METHODOLOGY

2.1 Materials

Chitosan was purchased in the form of white fine powder from Agros. Zinc oxide powder was purchased in the form of nanoparticles from Sigma-Aldrich with concentration of 50 wt. % in H$_2$O. Ethyl orange dye was purchased from Sigma-Aldrich with pH range between 3.0 to 4.4 and has 85% dye concentration. The sample of wastewater was prepared by adding ethyl orange dye with different concentrations (0.1 mg/L – 1.0 mg/L) into 1 L of distilled water.

2.2 Preparation of Hybrid Chitosan-Zinc Oxide

The appropriate amount of ZnO powder (0.5 wt% - 2.0 wt %) was dissolved in100 mL of 1% (v/v) acetic acid. ZnO reacts with acetic acid and changed to zinc cations. Takahashi *et al*., (2005) proved that the solubility of chitosan decreases as the pH varies towards the basic condition, which is why chitosan and zinc oxide adsorbent were dissolved in acetic acid solution at pH less than 6.0. Over pH 6.0, it becomes insoluble in solution and exists as solid particles.

Then 1.0 g of chitosan was added to the mixture solution. The mixture was sonicated for 30 min in sonicator bath. After magnetic stirring, 0.10 M NaOH was added drop by drop until the solution attained pH 7. The solution was heated in water bath at 75 - 80°C for about 3 hours. Next, the solution was filtered and washed with distilled water for several times before being dried in an oven at 50°C for 1 hour.

2.3 Batch Adsorption Experiments

In a batch adsorption process, the feed solution and the adsorbent particles were brought into contact until equilibrium was achieved. Batch adsorption occurs when the adsorbent was added to the solution to remove a contaminant which also sometimes called admixing. After the process, the solution which also contains impurities was then separated from the adsorbent by using an appropriate solid-liquid separation technique e.g. filtration or centrifugation.

Batch adsorption experiments of ethyl orange dye were carried out in a 100mL beaker using a shaking thermostat machine or magnetic stirrer at a speed of 130 rpm. The experiment was started first by conducting an adsorption process by using adsorbent containing hybrid of chitosan and zinc oxide by considering three parameters. The parameters are:
(a) Effect of pH (5.0-9.0). The pH was varied to form acidic, neutral and alkaline medium.
(b) Effect of chitosan dosage (0.10 mg/L – 1.00 mg/L)
(c) Effect of temperature (25^{0}C - 60^{0}C). The ranged was used as the adsorption process normally occurs in that range.

After adsorption process was done, the samples were centrifuged using a microcentrifuge machine (Kubota KIM-15200) at a speed of 10000 rpm for about 5 minutes. The concentrations of ethyl orange dye in the supernatant liquor were determined by using a standard curve. The absorbance of ethyl orange in aqueous solutions was measured with a Shimadzu UV-1601PC spectrophotometer at 474 nm, equipped with an electronically thermostatic cell holder (Shimadzu); the quartz cell had a path length of 1.0 cm. Before each measurement, the base line of spectrophotometer was calibrated against solvent. The standard curve was obtained by plotting absorbance versus concentration of ethyl orange. The amount of ethyl orange adsorbed (*q*e) was determined by using Equation 1:

$$q_e = \frac{V(C_0 - C_e)}{m} \qquad (1)$$

where *C*0 and *C*e represent the initial and equilibrium ethyl orange concentrations (mg/L), respectively; *V* is the volume of the ethyl orange solution (L) and *m* is the amount of adsorbent used (g).

■3.0 RESULTS AND DISCUSSION

3.1 Effect of Adsorbent Dosage on Removal of Dye

Adsorbent dose is an important parameter in the determination of adsorption capacity. Theoretically, insufficient amount of adsorbent or overdosing would result in poor performance of sorption capacity of the adsorbent. Therefore, it was crucial to determine the optimum dosage for the adsorption process of adsorbent onto the dye water as such to obtain the optimum performance in the treatment process as well as minimizing the dosing cost. In this experiment, the effect of the adsorbent dose was investigated by the addition of constant amount of chitosan (1 g) with varied amount of zinc oxide from 0.5 wt% up until 2.0 wt%. The experiment was conducted in a 100mL with 1.0 mg/L

of ethyl orange dye solution at ambient temperature which is around 25°C for about 2 hours.

The result is shown in Figure 1. It is observed that the removal efficiency increased from about 27 to 43% with the increment of zinc oxide dose from 0 to 2 wt%. This can be attributed to the increase in the adsorbent specific surface area and availability of more adsorption sites available to interact with the dye molecules provided by the increased adsorbent dosage. In contrast, the low adsorption capability might due to the saturation of adsorption sites and hence cannot further adsorb the dye molecules. The observation was consistent with the other works [Nevine, 2008]. Therefore, the optimum adsorbent value set for the next experiment was chitosan with zinc oxide (2.0 wt %).
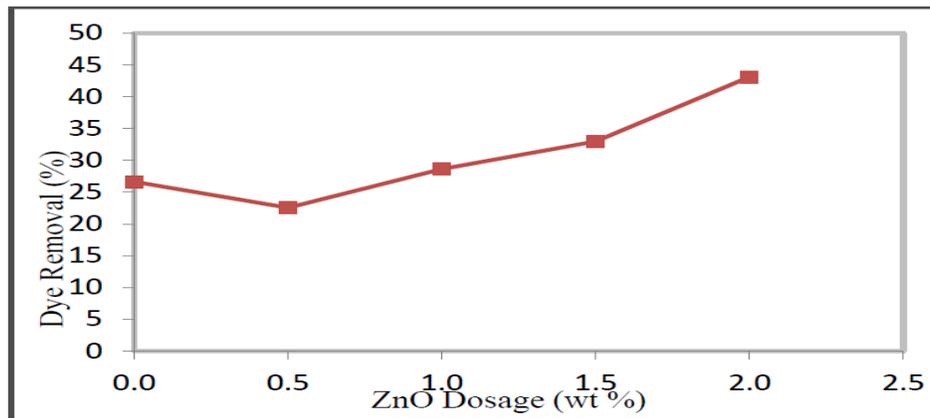

Figure 1 Effects of ZnO dosage on the percentage removal of dye

3.2 Effect of pH on Removal of Dye

The effect of pH on dye removal treatment was investigated in the range of pH 5 to 9 as shown in Figure 2. The adsorbent dosage, initial dye concentration and temperature were kept constant at 2 wt% of ZnO, 1.0 mg/L, and 25°C, respectively. The pH was adjusted using 0.01M HCl or 0.01M NaOH solutions. As can be seen, the percentage removal seems were fluctuated with the pH. It might be due some error where the supernatant liquid may have mixed with the precipitate formed after centrifuge process and thus eventually affected the results. However, from overall plotted distribution, the percentage removal was

decreased as the pH increased. This may be attributed to the protonation of functional groups such as amino groups and hydroxyl groups, which increases the electrostatic interaction between the positively charged adsorbent surface and the negatively charged dye molecules. According to Kumar [2000], at lower pH, more protons will be available to protonate amino groups of chitosan molecules to form groups NH_3^+, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites and thus causing an increase in dye adsorption.
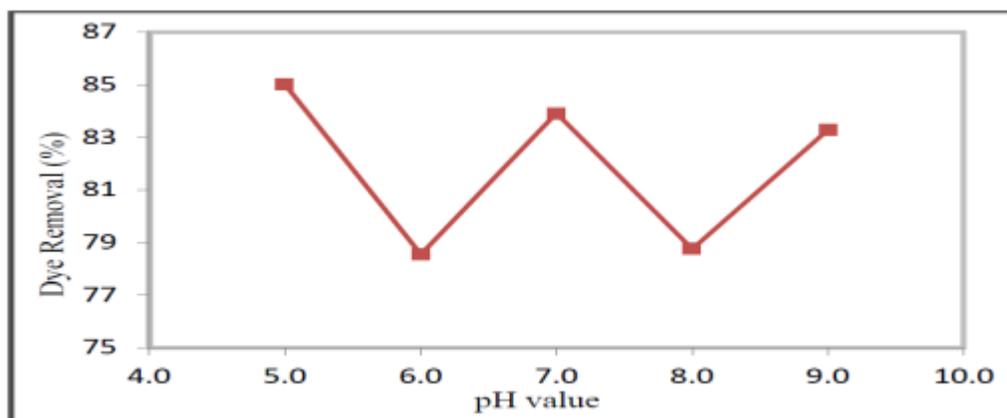

Figure 2 Effects of pH on the percentage removal of dye

3.3 Effect of Initial Dye Concentration on Removal of Dye

To investigate the effect of initial dye concentration on the adsorption of ethyl orange solution, experiments were conducted at different initial dye concentration (0.1–1.0 mg/L) with 100mL ethyl orange solution and adsorbent of chitosan and zinc oxide (2.0 wt %) at 25°C for 2 hours. An increase in the initial dye concentration leads to an increase in the adsorption capacity of the dye on chitosan. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial dye concentration.

Figure 3 shows the effect of initial dye concentration on remocal of ethyl orange dye. It is clearly shows that from the graph the removal efficiency decreased gradually from about 68 to 6% as the concentration of ethyl orange dye increased from 0.10 to 1.00 mg/L. The overall pattern of the graph plotting was reliable as it follows the theory that the percentage removal value was inversely proportional to the initial dye concentration. Basically, the greater the amount of initial dye concentration, the lower the absorbance value, thus reduced the removal percentage of ethyl orange dye. An increase in the initial dye concentration leads to an increase in the adsorption capacity of the dye on the adsorbent. This is due to the increase in the driving force of the concentration gradient, as an increase in the initial dye concentration [Chiou *et al.,* 2002].
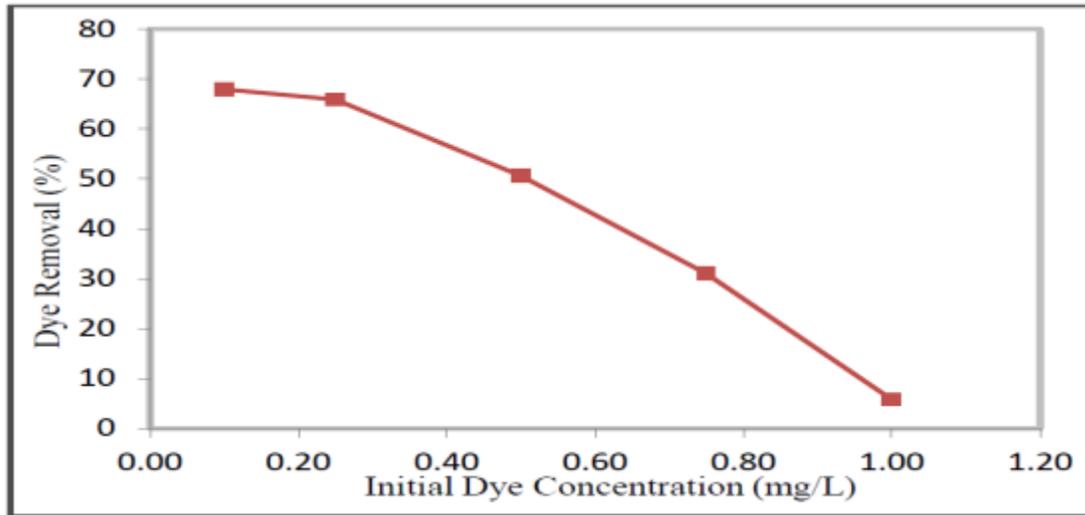

Figure 3 Effects of initial dye concentration on the percentage removal of dye

3.4 Effect of Temperature on Removal of Dye

Figure 4 shows the percentage removal of ethyl orange dye at different temperatures. The effect of temperature was studied with different temperature of ethyl orange solution ranging from 25 to 60°C and using adsorbent of chitosan and zinc oxide (2.0 wt %) for 2 hours at continuous mixing condition. As can be seen, the temperature effects in removal of dye are significant. It can be concluded that the temperature of dye solution does significantly affect the overall decolourization performance. This indicated that the elevation of solution temperature can provide suitable driving force to raise the mobility of dye molecules. As a result, more dye molecules number get enough of energy to move towards the adsorbent and undergone an interaction with its structure. The observation indicates that the reaction is a controlling process [Kumar *et al.,* 2010].
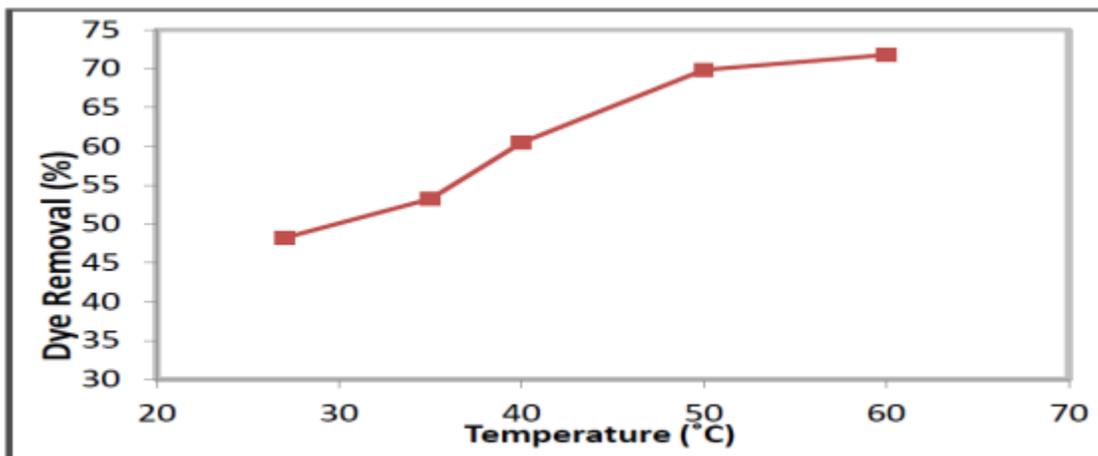

Figure 4 Effects of temperature on the percentage removal of dye

3.5 Adsorption Isotherm

The purpose of the adsorption isotherms is to relate the adsorbent concentration in the bulk and the adsorbed amount at the interface [Eastoe *et al.*, 2000].

Adsorption data are usually described by adsorption isotherms, such as Langmuir, Freundlich and Tempkin isotherms. These isotherms relate adsorbate uptake per unit mass of adsorbent, qe, to the equilibrium adsorbate concentration in the bulk fluid phase Ce. In this study, Langmuir and Freundlich isotherms were applied to fit the experimental data. The expression of Langmuir model is given by Equation 2.

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{2}$$

where qe (mg/g) and Ce (mg/L) are the amount of adsorbed dye per unit mass of sorbent and unadsorbed dye concentration in solution at equilibrium, respectively. The Langmuir equation can be described by the linearized form as stated in the Equation 3.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{q_L}{K_L}\right) C_e \tag{3}$$

The saturation can be representing by plotting of Ce/qe versus Ce in linear graphical relation. The value of qL and KL were determined for all adsorbents from interception and slope.

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The Freundlich equation is expressed by Equation 4.

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

where KF and n are Freundlich constants with KF is the adsorption capacity of the adsorbent and giving an indication of how favourable the adsorption process.

To determine the constants KF and n, the linear form of the equation was be used to produce a graph of log (qe) against log (Ce):

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{5}$$

The values of KF and n were calculated from the intercept and slope of the plot.

Figure 5 shows the Langmuir isotherm model obtained in this study. As can be seen, the data fits the Langmuir equation well at $R^2 = 0.9566$. The values of qL and KL were determined and calculated from the figure and were found to be 2.2499 mg/g and 0.0069 L/mg, respectively.
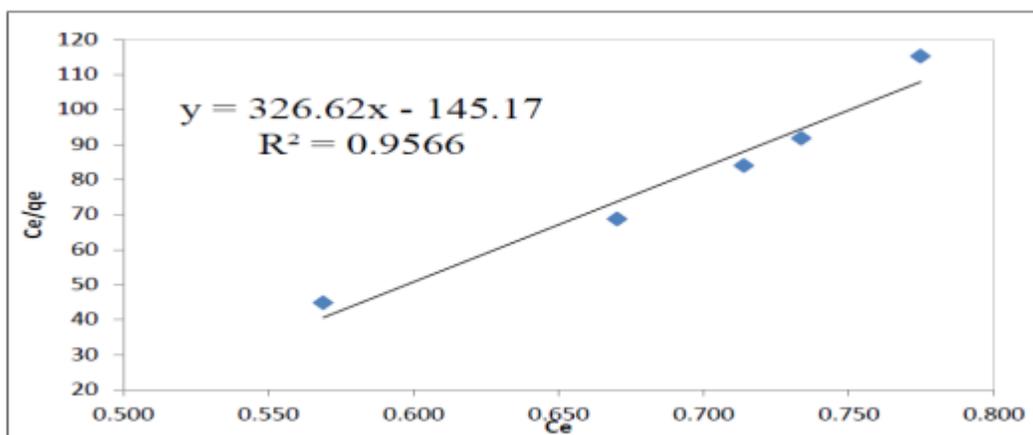

Figure 5 Langmuir isotherm model

Figure 6 shows the Freundlich isotherm model obtained in this study. From the figure, the Freundlich constants K_F and n were found to be 0.0045 L/mg and 0.5054, respectively. The magnitudes of K_F and showed an easy separation of ethyl orange from the aqueous solution and indicate favourable adsorption. The intercept K_F value is an indication of the adsorption capacity of the adsorbent; the slope 1/n indicates the effect of concentration on the adsorption capacity and represents adsorption intensity. Freundlich isotherm fitted well with the correlation coefficient of 0.9774.

Table 6 shows the calculated constants for both Langmuir and Freundlich isotherms. Based on the result showed, it can be seen that both of the isotherms showed the best fitting to give the correlation coefficients, R^2 approximate to 1. Although both isotherms describe the adsorption process very well, Freundlich

isotherm fitted the behaviour better with higher correlation coefficient recorded for each sample compared to Langmuir. This indicates that the data follows Freundlich isotherm which suggest multiple layers coverage of ethyl orange dye on the chitosan-ZnO adsorbent.
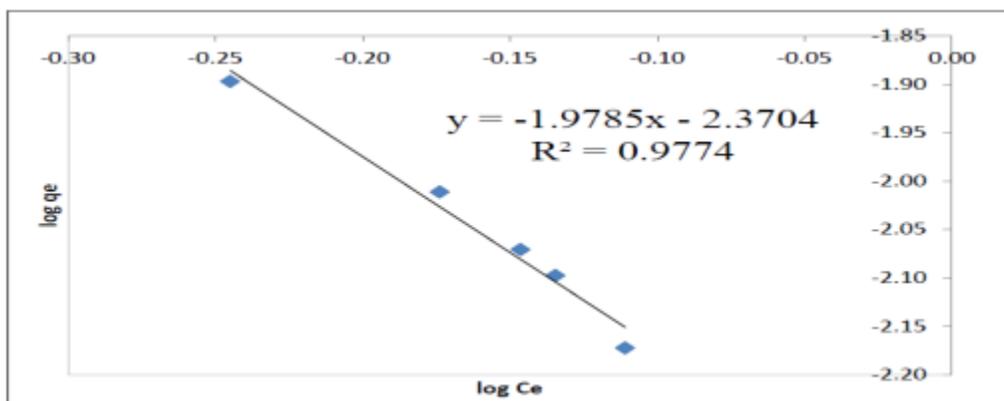
$$y = -1.9785x - 2.3704$$
$$R^2 = 0.9774$$

Figure 6 Freundlich isotherm model

Table 6 Langmuir and Freundlich isotherms constants

Langmuir's Constant			Freundlich's Constant		
q_L (mg/g)	K_L (L/mg)	R^2	n	K_F (L/mg)	R^2
2.2499	0.0069	0.9566	0.5054	0.0045	0.9774

■4.0 CONCLUSION

Batch experiments showed that the initial dye concentration, the pH and the temperature of aqueous solutions significantly affect the adsorption capacity of ethyl orange dye on the hybridized chitosan-ZnO. From the result obtained, the optimum removal of ethyl orange dye was achieved at pH 7 with 2.0 wt% of ZnO dosage and 120 minutes of mixing time at temperature 60˚C. Under this condition, about 85 % of ethyl orange dye was successfully removed (i.e. adsorption capacity of 0.014 mg/g).

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