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ADSORPTION ISOTHERM STUDY OF ADSORPTION METHYLENE BLUE ONTO OIL PALM KERNEL SHELL ACTIVATED CARBON

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ABSTRACT

Industrial palm kernel abundance of waste can be converted into useful activated carbon through chemical activation. This study is focusing on analyzing adsorption isotherm of methylene blue dye onto oil palm kernel shell activated carbon (OPKS-AC) and to analyze the equilibrium data using Langmuir and Freundlich isotherm. OPKS was impregnated with phosphoric acid (H_3PO_4) at 2 impregnation ratio by weight (0.5:1 and 2.5:1) and later carbonized under high temperature (700 °C) for 3 hours. Batch adsorption experiment of methylene blue solution was conducted by adding prepared activated carbon to study the adsorption behavior using adsorption isotherm analysis. Batch adsorption experiment of methylene blue onto OPKS shows more uptake of methylene blue occurred onto higher impregnation ratio of OPKS-AC. Batch adsorption data at equilibrium shows Langmuir isotherm fits the data better which indicated the adsorption occurs at monolayer of the OPKS-AC. Correlation coefficient (R^2) value of adsorption isotherm was calculated to show suitable fit of the data. R^2 value of Langmuir isotherm was calculated at 0.8091 and 0.996 for impregnation ratio 0.5:1 and 2.5:1 respectively. Results from this study showed that the adsorption of methylene blue onto OPKS-AC prepared at a higher impregnation ratio fit better on Langmuir adsorption isotherm. The adsorption is concluded occurs at monolayer of the activated carbon.

Keywords: oil palm waste, cationic dye, langmuir adsorption isotherm, freundlich adsorption isotherm.

INTRODUCTION

It was reported that more than 100 000 types of dyes are produced annually in an amount up to 7 x 10^5 metric tonnes per year [1]. Dye either natural or synthetic widely uses in various industries especially textile, paper and plastic industry. Effluent water forms these industries are normally being channeled down into water resource.

Methyelene blue is a cationic dye which is not very harmful, but still may cause various effects if its concentration is high in the water stream. In [2] had mentioned that colored waste water may also cause great damages to the human body, the functions of kidneys, reproductive system, liver, brain and nervous system. There are may ways of treating waste water containing dye from industrial sources. One of the most favorable method is adsorption due to its effectiveness. However, adsorbent are not always cheap and easy to be prepared.

As Malaysia reported being the largest palm oil producer which contributes to 47% of the world production [3], waste from this kind of plantation are creating an environmental problem to another extend. Currently, this high density of waste are underutilized especially oil palm kernel shell (OPKS). It may due to its hard surface structure, which very feasible to be converted into fertilizer.

Since the source of hardwood is expensive and narrowing, OPKS seems to be a good source as adsorbent for adsorption process. OPKS is a good precursor for activated carbon due to its high carbon content and environmentally desirable. Activated carbon was reported as a very good adsorbent for adsorption process [4]. Due to its nature as carbonaceous material in OPKS makes it possible to be developed into higher porosity adsorbent [5], either through physical or chemical treatment.

As of current research, only few studies are focusing on the converting OPKS into activated carbon as an adsorbent for adsorption of wastewater effluent containing dyes contaminant. So, this study is focusing on the adsorption of methylene blue using activated carbon prepared from OPKS through chemical activation impregnated with phosphoric acid before carbonized at high temperature. The adsorption was conducted under batch process and different initial dye concentration and adsorbent dosage.

METHODOLOGY

Preparation of adsorbent

OPKS was collected directly from palm oil factory before it was washed several times to remove the unwanted residue of fiber. The OPKS then dried in the oven at 105 ºC for 24 hours to remove the moisture. The dried OPKS then impregnated with phosphoric acid at 2 different impregnation ratio (0.5:1 and 2.5:1) by weight to give 2 different types of activated carbon namely type I and type II respectively. Impregnated OPKS later carbonized in the furnace at 700 °C for 3 hours to develop its surface porosity and internal surface area. Upon activation process, OPKS activated carbon was washed with distlled water until the pH of the effluent approaching 7.0.

Batch adsorption of methylene blue

Methylene blue dye solution at different initial concentration (15, 20 and 25 ppm) was prepared. Then, 0.3g of 2 different types of activated carbon added into the dye solution prepared. The mixture was then run in orbital shaker at agitation speed of 120 rpm for 3 hours. A sample

from each flask was then collected 20 minutes to measure its dye concentration using UV-VIS spectrophotometer.

Adsorption isotherm study

The adsorption capacity of the adsorbent, the solute-solution interaction and the degree of accumulation of adsorbed materials on the surface of the adsorbent can be explained from adsorption isotherm. Data from a batch adsorption experiment which conducted under constant pH and temperature were collected and analyzed using Langmuir and Freundlich adsorption isotherm.

The following Langmuir isotherm is used to predict the sorption of compound in aqueous solution onto a solid phase at constant temperature [6]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (1)$$

where q_e (mg/g) is the amount of adsorbed materials per unit weight of the adsorbent at equilibrium concentration, C_e (mg/L).The Q_0 (mg/g) and b (L/mg) are the Langmuir constants related to the maximum monolayer capacity and energy of adsorption respectively [7].

Freundlich isotherm is assuming that the adsorption process takes place on a heterogeneous surface [8]. The Freundlich exponential equation is shown in Equation. (2):

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

K_F (L/mg) value in Equation. (2) is an indicator of the adsorption capacity, and 1/n is the adsorption intensity and indicates both the relative distribution of energy and the heterogeneity of the adsorbent sites. The linear form is derived by taking the natural log of the term to give Equation. (3).

$$ln\, q_e = ln\ K_F + \frac{1}{n} ln\, C_e \quad (3)$$

Langmuir isotherm assumes a monolayer adsorption surface without any lateral interaction between adsorbed molecules, while Freundlich model is suitable for describing a multilayer adsorption with interaction between adsorbed molecules.

RESULTS AND DISCUSSION

Effect of contact time

The effect of contact time on the adsorption of methylene blue by OPKS-AC was studied at fixed adsorbent dosage, fixed initial concentration and contact time, which is at 0.3 g, 15 ppm and 3 hours respectively. The experiment was conducted for both types of activated carbon.

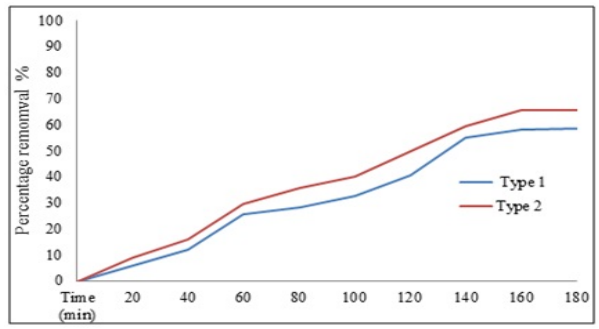

Figure-1. Effect of contact time on percentage removal of dye.

Figure-1 shows the trend of percentage removal of methylene blue for 3 hours duration which analyzed at 20 mins interval. The dye was rapidly adsorbed in the first 60 minutes for both types of adsorbent and then adsorption rate decreased gradually and reached equilibrium in after almost 150 minutes. Optimum contact time recorded for color removal by activated carbon prepared from mangoseed shell was within 40 minutes [9]. At the beginning, the surface area of activated carbon has not yet occupied. The dye ions were adsorbed by the exterior surface of the activated carbons causes the rate of adsorption was fast initially. Once the exterior surface occupied by the dye ions and saturated, the dye ions entered into the pores of the adsorbent particles and were adsorbed by the interior surface of the particle.

This phenomenon takes a relatively long contact time until the interior surface also saturated and cause the equilibrium rate attained in the adsorption. In [10] suggest that the rapid adsorption at the initial contact time can be attributed to the availability of positively charged surface of active carbon.

Effect of adsorbent dosage

The effect of the adsorbent dosage adsorption experiment was conducted at 3 different dosages which were 0.1g, 0.3g and 0.6g.Batch experiment was conducted at constant pH, temperature and initial concentration that is 15 ppm. The mixture was then run on the orbital shaker at agitation speed of 120 rpm for 3 hours to ensure the adsorption process reach the equilibrium stage.

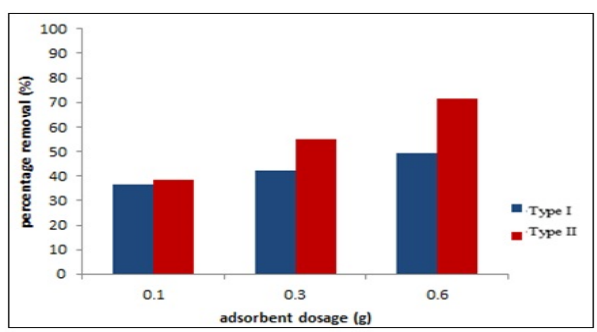

Figure-2. Effect of absorbent dosage on percentage removal of methylene blue solution.

Figure-2 shows the increment of the removal percentage as the amount of adsorbent increased. Type I adsorbent adsorb less methylene blue molecules compared to type II adsorbent for all weights of adsorbent. The increased removal at high dosages is expected due to the increasement of an adsorbent surface area and availability of more adsorption sites. Higher adsorbent dosage provides a larger surface area available, thus more binding site present on the surface of the adsorbent. Generally, the higher adsorbent dosage the higher the percentage removal of dye wastewater.

Langmuir isotherm

The Langmuir model describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, thus no further adsorption takes place [11]. It represents the adsorbate uptake that occurs on a homogeneous monolayer with no interaction between the adsorbed ions. Figure-3 and Figure-4 show Langmuir model fitted for adsorption of methylene blue onto 2 different types of adsorbent.

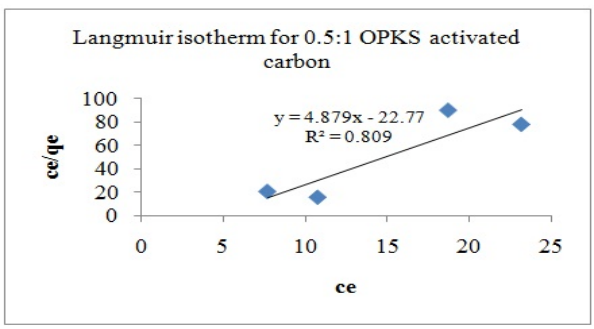

Figure-3. Langmuir isotherm for type I adsorbent (impregnation ratio; 0.5:1).

Langmuir model for adsorption of methylene blue onto type I and type II adsorbent shows in Figure-3 and Figure-4. The linear plots of Qe/qe versus Ce show that the adsorption obeys Langmuir isotherm. The values of Q_0 and b were determined for all types of activated carbon from the intercept and slopes of the linear plots of Langmuir isotherm. The values are tabulated in the Table-1.

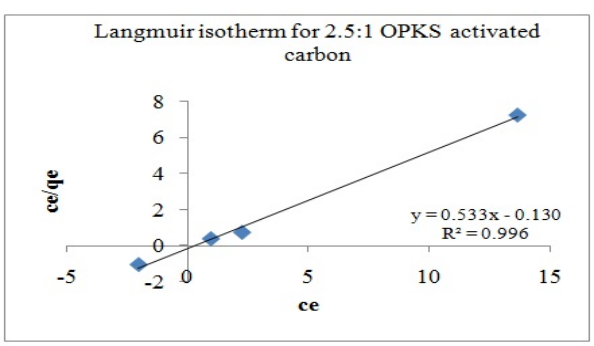

Figure-4. Langmuir isotherm for type II adsorbent (impregnation ratio; 2.5:1).

Table-1. Equilibrium constant for langmuir isotherm.

Constant	Type I	Type II
K_L (L/mg)	-0.2143	-4.1029
q_{max} (mg/g)	0.2049	1.8734
R^2	0.8091	0.9964

Correlation coefficient (R^2) calculated below 0.89 for type 1 adsorbent indicates less applicability for Langmuir isotherm. Type II correlation coefficient shows higher value which is 0.9964.

Freundlich isotherm

The Freundlich adsorption model is one model in describing sorption related to heterogeneous systems. It is known to be fairly satisfactory empirical isotherm that can be used for non-ideal sorption for heterogeneous system.

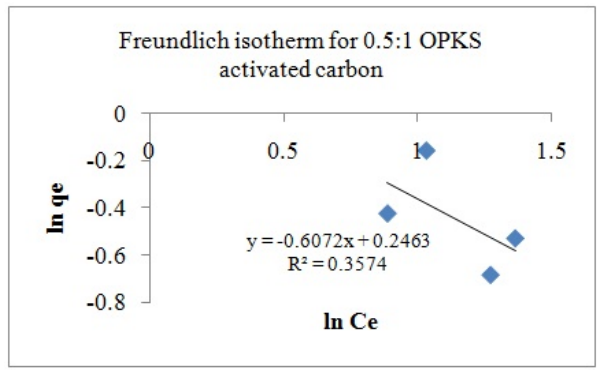

Figure-5. Freundlich isotherm for type I adsorbent (impregnation ratio; 0.5:1).

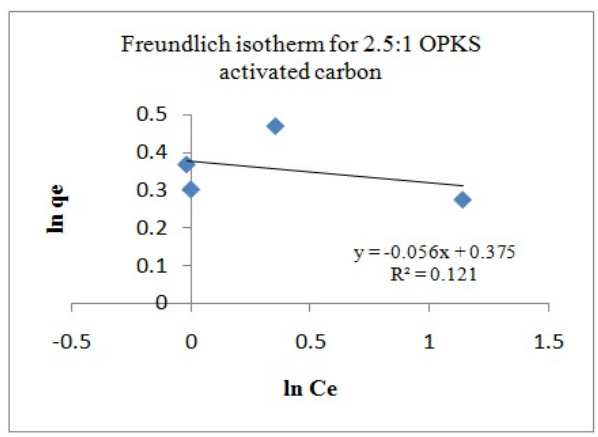

Figure-6. Freundlich isotherm for type II adsorbent (impregnation ratio; 2.5:1).

Freundlich isotherm equilibrium constant for adsorption of type I and type II adsorbent are tabulated in Table-2.

Table-2. Equilibrium constant for Freundlich isotherm.

Constant	Type I	Type II
K_F (mg/g(L/mg))	1.2793	1.4553
n_F	-1.6469	-17.8571
R^2	0.3574	0.1212

Correlation coefficient (R^2) calculated from Freundlich isotherm for both types of adsobent are below 0.89, which indicate less applicability for Frendlich isotherm.

From both isotherm plotted, adsorption of methylene blue best model with Langmuir isotherm. The characteristic of the Langmuir model best described by separation factor or equilibrium parameters R_L. The R_L value of 0.5:1 OPKS activated carbon ranging from -0.8749 to -0.2295, while for 2.5:1 OPKS activated carbon is -0.02498 to -0.00985. Their maximum adsorption capacity are 1.8734 mg/g and 0.2049 mg/g for both ratios.

CONCLUSIONS

From batch adsorption experiment done on both types of adsorbent, type II adsorbent shows higher removal percentage. Experimental data in the adsorption studies fitted into Langmuir and Freundlich isotherm show favorable homogenous adsorption process and occur on the first later interface between adsorbate and adsorbent, with a high regression value of 0.9964 and 0.8091 for type I and type II respectively. Their maximum adsorption capacity are 1.8734 mg/g and 0.2049 mg/g for both ratios. This described that the adsorption process occurs at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes.

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