Jurnal Teknologi

Full paper

Removal of Etyhl Orange Dye using Waste Eggshell

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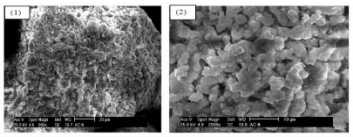
Article history

Received :27 March 2013
Received in revised form :
13 June 2013
Accepted :15 August 2013

Graphical abstract



Abstract

In this study, waste eggshells were used as a low cost raw material to remove ethyl orange dye in aqueous solution. The waste eggshells were calcined at temperatures of 600, 700, 800 and 900°C in the furnace for 2 h. Further, the calcined waste eggshells were treated chemically using 2 M of potassium carbonate. The calcined waste eggshells were characterized using Thermal Gravimetric Analyzer (TGA). The surface morphology of the calcined and uncalcined (i.e. natural) waste eggshell was obtained using Scanning electron microscope (SEM). The dye concentration was determined using UV-Vis spectrometry at wavelength of 474 nm. The results obtained showed that the percentage of dye removal using natural waste eggshell was 47.1%. For the calcined waste eggshell, the removal of dye decreased as the calcined temperature increased. For the pH effect, the acidic solutions give the highest percentage of dye removal which is 54 %. As expected, the higher the dose of waste eggshell used, the higher the dye removed. The highest removal of dye was obtained by using 2.0g of waste eggshell which is 48.2%. For the temperature effect, the adsorption of dye decreased as the temperature increased. The highest removal of dye was achieved at 50°C which is 63.0%. In this study, the adsorption process was found to fit the Freundlich isotherm than of the Langmuir isotherm.

Keywords: Egg shells; etyhl orange; adsorbent; Langmuir; Freundlich

Abstrak

Dalam kajian ini, sisa kulit telur telah digunakan sebagai bahan mentah yang berkos rendah untuk menyingkirkan pewarna etil oren dalam larutan pewarna. Sisa kulit telur telah di panaskan pada suhu 600, 700, 800 dan 900°C di dalam relau selama 2 jam. Kemudian, sisa kulit telur tersebut dirawat secara kimia dengan menggunakan 2 M kalium karbonat. Seterusnya, sisa kulit telur tersebut dicirikan menggunakan Analisis Termal Gravimetrik (TGA). Imej permukaan kulit telur yang dipanaskan dan yang tidak dipanaskan (i.e. natural) diperolehi dengan menggunakan pengimbas mikroskop elektron (SEM). Kepekatan pewarna ditentukan dengan menggunakan spektrometri UV-Vis pada keserapan maksimum iaitu 474 nm. Keputusan yang diperolehi menunjukkan bahawa peratusan penyingkiran pewarna menggunakan sisa kulit telur yang tidak dipanaskan adalah 47.1%. Bagi kulit telur yang dipanaskan, penyingkiran pewarna berkurangan apabila suhu pemanasan semakin tinggi. Bagi kesan pH, larutan berasid memberikan peratusan tertinggi penyingkiran pewarna iaitu 54%. Seperti yang telah dijangka, semakin tinggi dos sisa kulit telur yang digunakan, semakin banyak pewarna disingkirkan. Penyingkiran pewarna yang paling tinggi ialah menggunakan 2.0g sisa kulit telur iaitu 48.2%. Bagi kesan suhu, penyerapan pewarna menurun apabila suhu yang dikenakan dalam rawatan semakin meningkat. Penyingkiran pewarna yang paling tinggi dicapai pada suhu 50°C iaitu 63.0%. Dalam kajian ini, proses penyerapan adalah sesuai diterangkan dengan Freundlich isoterma dan bukannya Langmuir isoterma.

Kata kunci: Kulit telur; etil oren; penjerap; Langmuir; Freundlich

1.0 INTRODUCTION

Dye is one of the hazardous pollutants often found in wastewater of several industries. Dyes are being discharged from many other industries such as textile companies, dye manufacturing industries, paper and pulp mills, tanneries, electroplating factories, distilleries and last but not least, food industries. Based on the previous research, over 7 × 105 tonnes of dyes are produced annually and it is estimated that approximately 2% of the annual dyes production are discharged from manufacturing industries whilst 10% of the annual dyes production are discharged from textile and associated industries [Easton, 1995].

There are a lot of methods that can be used for dye removal such as adsorption, coagulation, precipitation, filtration and oxidation. However, adsorption process appeared to be one of the most effective and low cost methods for the decolourization of wastewater. In this regard, activated carbon has been evaluated extensively for the removal of color resulting from the different

classes of dyes, and is now the most widely used adsorbent for dyes. However, the adsorption using carbon adsorbent still remains an expensive process due to the high cost in the use of activated carbon and the difficulty in the regeneration of spent activated carbon. For this reason, there is growing interest in utilizing biomass wastes/alternatives to activated carbon as low-cost adsorbents [Park, *et al*. 2007].

One of the waste materials that have been widely produced in Malaysia is hen egg shells. Hen egg shell is one of the major by product of the food industry. This by-product eggshell weights approximately 10% of the total mass of hen egg, representing a significant waste from the egg-derived products processor because it was traditionally useless and commonly disposed of in landfills without any pretreatment [Tsai, *et al*. 2008]. Hen eggshell composed of calcium carbonate (94%), magnesium carbonate (1%), calcium phosphate (1%) and organic matter (4%) (Stadelman, 2000). Due to its intrinsic pore structure and the amount in abundance, it is thus feasible to grind the eggshell waste in the preparation of fine powders, which might pave the way for available materials such as porous adsorbents. Park, *et al*. [2007], found out that the waste eggshell adsorbent was able to remove up to 99% of Cd and Cr. In other study, it was reported that the waste eggshell removed anionic dye better than cationic dye [Tsai, *et al*. 2008].

Therefore, in this study, it is aimed to investigate the potential of waste eggshell towards removal of ethyl orange dye. Ethyl orange dye is one of the anionic dyes that commonly used in industries. Ethyl orange is a type of azo dyes which is complex unsaturated aromatic compounds. The effects of calcination temperature on the performance of waste eggshell were investigated.

2.0 METHODOLOGY

2.1 Preparation of Waste Eggshell Adsorbent

The waste eggshell samples were immersed in cold water for four hours to remove impurities and rinsed cleanly. Then, the samples were immersed in ethanoic acid for four days and then rinsed by using distilled water for several times. Before immersing in the acid, the waste eggshells were crashed into small pieces so that the surface area of the samples exposed to the acid are larger. Further the samples were dried at 105°C for 24 hours in the dry oven. Afterwards, the dried sample was blended to become powder and sieved to get the samples smaller than 1mm. The sieved sample was divided to get two types of sample which are calcined and uncalcined waste eggshell samples. For the calcined waste eggshell, the sample was undergoing further calcinations process. Calcinations process in this study was carried out in the furnace at four different temperatures which are 600, 700, 800 and 900°C for 2 hours.

For the next step, both calcined and uncalcined samples were preceded by the chemical treatment. In this study, the samples were treated by using potassium carbonate solution, K_2CO_3 with concentration of 2 M. In the chemical treatment, each sample was mixed with 100 mL of K_2CO_3 solution. The mixture was then stirred and heated by using magnetic stirrer until the mixture was fully dried. The impregnation was carried out at temperature of approximately 80°C. Theoretically in this process, the chemicals were impregnated into the sample. Then, the samples were washed using hot distilled water to lower the pH of the samples. Furthermore, the samples were washed in order to remove any non carbonaceous materials that might stick to the samples. The samples were then dried in an oven at temperature of 110°C for four hours.

2.2 Preparation of Dye Solution

The concentration of ethyl orange used in this experiment was 30 mg/L. 0.03g of dye was weighted and added to 1L of distilled water in 1L beaker. Before starting the experiment, a standard relationship between dye concentration and absorbance was determined. The concentrations used were 5, 10, 30 and 50 mg/L. The calibration graph was used to compare the initial and final concentration of dye solution by using the absorbance obtained after the treatment was done.

2.3 Effect of pH

1.0 g of natural (i.e. uncalcined) waste eggshell was weighted and 100 mL of 30 mg/L of ethyl orange dye was added into 500 mL beaker. The pH of the color solution was adjusted to pH 6. A few drop of HCL was added to the solution to obtain an acidic solution. The pH reading was performed by pH meter. Then, the solution was stirred at high speed for 90 minutes at room temperature (i.e. from the screening test, the adsorption took about 80 minutes to reach an equilibrium). After 90 minutes, the solution was filtered using micro centrifuge and the absorbance was determined using UV spectrophotometer. The experiment was repeated at pH 5,7,8,9. Then this set of experiment was repeated using calcined waste eggshell instead of natural waste eggshell.

2.4 Effect of Dosage of Activated Carbon

0.5, 1.0, 1.5 and 2.0 g of uncalcined waste eggshell were weighted and 100 mL of 30 mg/L of ethyl orange dye was added into 500 mL beaker. The pH of the color solution was adjusted to pH 6. A few drop of HCL solution was added to the solution to obtain acidic solution and NaOH solution was added to maintain the pH and the reading was performed using pH meter. Then, the uncalcined waste eggshell was added into the solution and stirred using the magnetic stirrer at high speed for 90 minutes at room temperature. After 90 minutes, the solution was filtered using micro centrifuge and the absorbance was determined using UV spectrophotometer. The experiment was repeated for calcined waste eggshell.

2.5 Effect of Temperature

1.0 g of uncalcined waste eggshell was weighted and 100 mL of 30 mg/L of orange color was added into 500 mL beaker. The pH of the color solution was adjusted to pH 6. A few drop of HCL was added to the solution to obtain acidic solution and NaOH solution was added to maintain the pH and the reading was performed by using pH meter. Then, the natural waste eggshell was added into the solution and stirred using the magnetic stirrer at high speed for 90 minutes at temperature of 35°C. After 90 minutes, the solution was filtered using micro centrifuge and the absorbance was determined using UV spectrophotometer. The experiment was repeated at different temperature; 40, 50 and 60°C. Then, the experiment was repeated for calcined waste eggshell.

2.6 Adsorption Studies

Adsorption capacities of adsorbent, q, on dye were calculated by a mass balance equation as shown by Equation 2.1.

$$q_i = \frac{(C_{o,i} - C_{f,i})V}{m} \quad (2.1)$$

where, C_0 and and C_f is the initial and final concentration of dye (mg/L), respectively, V is the volume of dye solution used in the experiment (L) and m is the amount of adsorbent (g).

For the percentages of dye removal, Equation 2.2 was used;

$$\text{Percentage of dye removal} = \frac{C_{0,i} - C_{f,i}}{C_{0,i}} \times 100 \quad (2.2)$$

3.0 RESULT AND DISCUSSION

3.1 Calibration Graph

A standard relationship between dye concentration and absorbance was determined. The standard was done by using four different concentrations of dye solution which are 5, 10, 30 and 50 mg/L (refer Figure 1). The equation obtained from the graph was used to calculate the final concentration of the dye solution after the adsorption process.

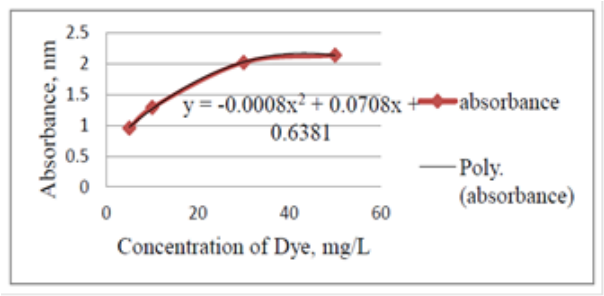


Figure 1 Calibration graph

3.2 Characterization

3.2.1 Thermal Stability of Calcined Samples

The thermal stability of calcined waste eggshell was determined using Thermal Gravimetric Analysis (TGA) with high purity nitrogen gas at a flow rate of 100 cm^3/min as the purge gas to provide an inert environment. The instrument was monitored continuously and recorded the changes of mass of the sample as temperature increased at heating rate of 20°C/min. Figures 2(a), (b), (c), and (d) show the results of the TGA for all the calcined samples. The results show that the weight loss increased with temperature. The observation was consistent with the other research [Kelly, *et al*. 2012]. As can be seen, the highest weight loss was given by Sample B which is about 98 % and the lowest weight loss was given by Sample E with percentage of 97%. The decreasing weight loss might be due to the decomposition of the samples during calcinations process. Nevertheless, the difference in weight loss between these two samples can be considered as insignificant. This indicated that the carbonization temperature ranged from 600 to 900°C did not significantly alter the thermal stability of the samples.

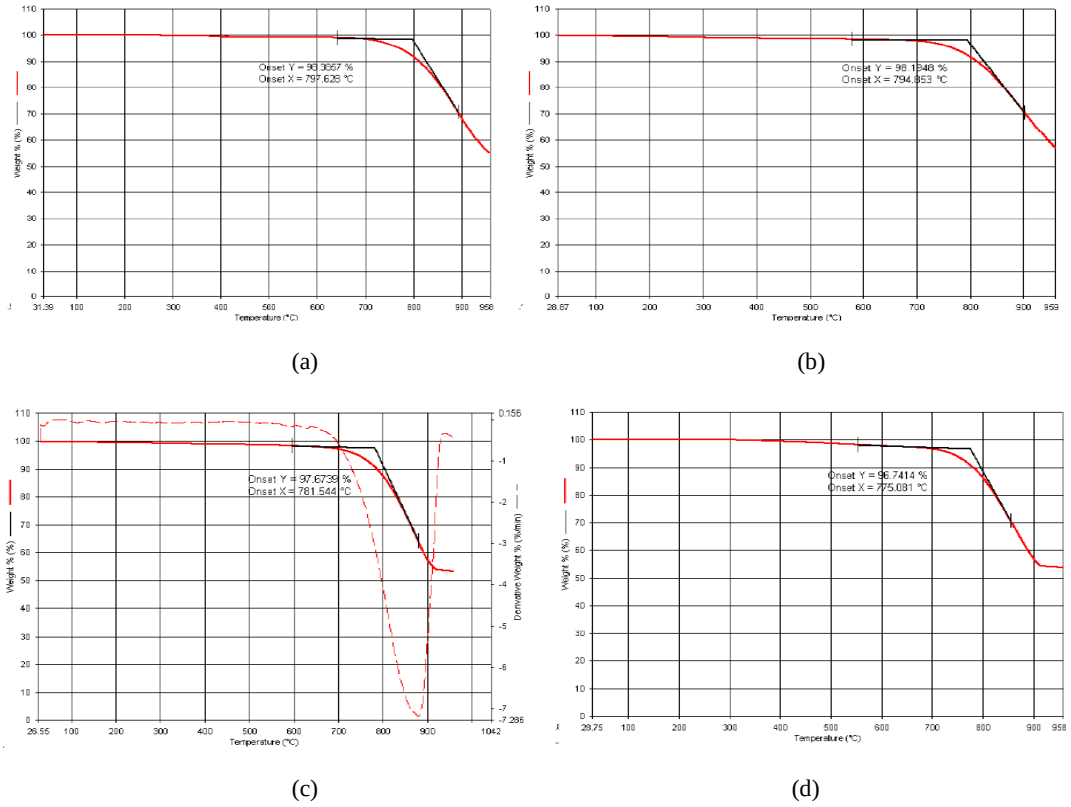


Figure 2 Termogravimetric analysis: (a) Sample B; (b) Sample C; (c) Sample D; (d) Sample E

3.2.2 Surface Morphology Analysis of Calcined Samples

Scanning Electron Microscope (SEM) was used to determine the surface morphology of calcined and uncalcined samples. The results obtained from the experiment are illustrated as shown in Figure 3; Figures 3a, 3b, 3c, 3d and 3e refer to sample A,B,C,D and E, respectively. The image of the sample was determined at 800X and 2000X magnification. As can be seen, the structure of the sample surface had packed surface and showed less number of pores as temperature was increased. Both calcined and uncalcined structures are monocrystalline but the calcined structure is finer [Fenech, *et al*. 2009]. The surface morphology of the sample becomes rougher and more unstructured at the highest temperature.

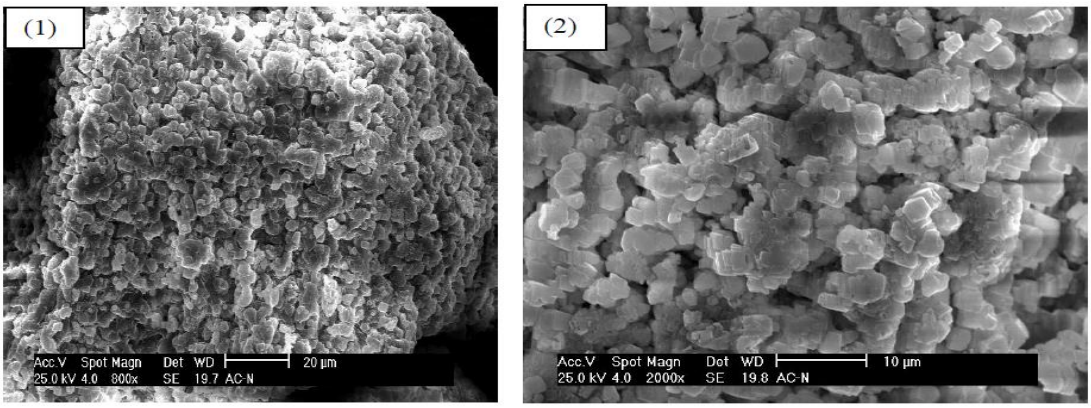


Figure 3a Surface Morphology of Sample A: (1) at 800X Magnification; (2) at 2000X Magnification

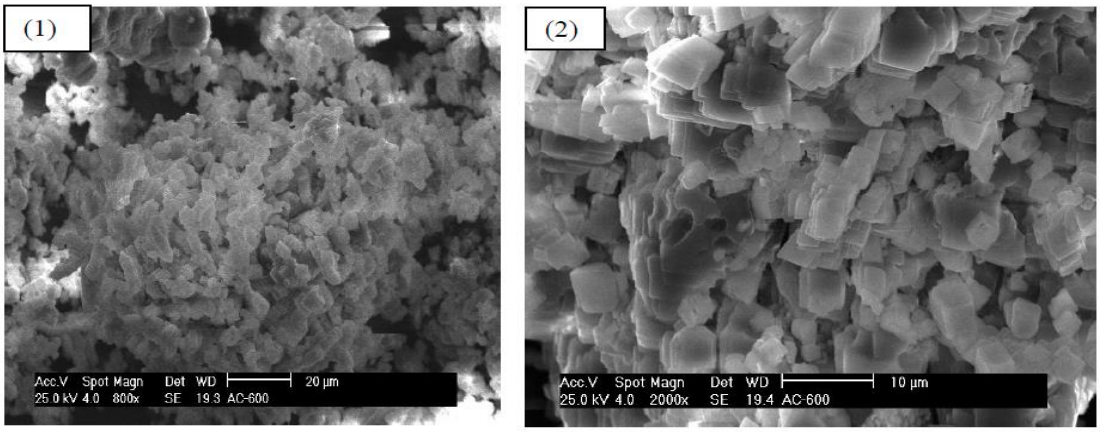


Figure 3b Surface morphology of sample B: (1) at 800X magnification; (2) at 2000X magnification

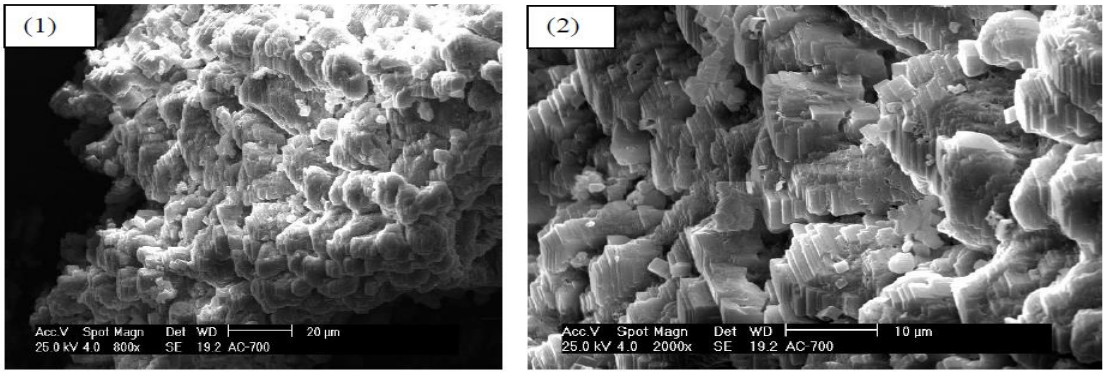


Figure 3c Surface morphology of sample C: (1) at 800X magnification; (2) at 2000X magnification

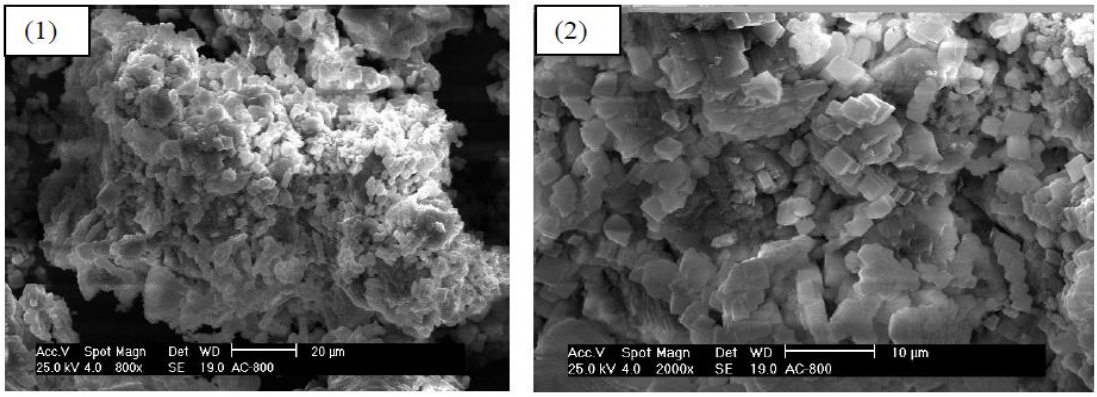


Figure 3d Surface morphology of sample D: (1) at 800X magnification; (2) at 2000X magnification

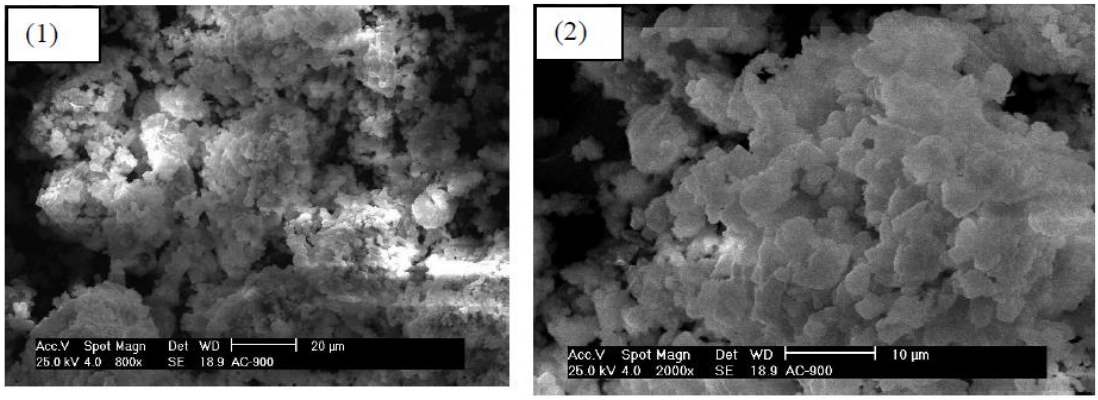


Figure 3e Surface morphology of sample E: (1) at 800X magnification; (2) at 2000X magnification

3.3 Adsorption Study

From the screening test (i.e. the data is not shown), it showed that the highest removal of dye was achieved when sample B was used. Thus, the sample was used in further adsorption study in which the effects of pH, dosage and temperature towards the percentage removal of dye were investigated.

3.3.1 Effect of pH

The effect of pH on dye removal treatment was investigated in the range of pH 5 to 9 as shown in Figure 4. The adsorbent dosage and temperature of the solution was kept constant at 1.0 g and 27°C, respectively. The highest percentage of dye removal was achieved at pH 5, which is 54%. The percentage removal of dye starts to decrease when the pH was increased. This shows that the adsorption was favoured under acidic medium. According to [Bhaumik, *et al.* 2011], pH solution affected the surface charge of the adsorbent material. In addition, it is directly related with competition ability of [H+] with adsorbate ions to active sites on the adsorbent surface. In this case, the adsorbent sample was interacted with the dye molecules via hydrogen bonding. Under acidic solution, the H+ ions were increasing and caused an increase in positive sorption. Therefore, lower pH effectively increases the number of positive surface sites leading to an increase in the amount of dyes been adsorbed and thus removed from the solution.

On the other hand, the slightly increment of dye removal at pH 8 which is slightly basic condition indicated that the dye adsorption system involved an electrostatic interaction. Theoretically, when the electrostatic forces between the adsorbent surface and adsorbate ions were attractive, as in this system, an increase in ionic strength will decrease the adsorption capacity. Conversely, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption process [Yahya, *et al.* 2007]. In this case, ethyl orange has negatively surface charge and the basic condition of the dye solution provide more OH- ions. The repulsion of the ions increased the ionic strength and hence removed dyes in the solution

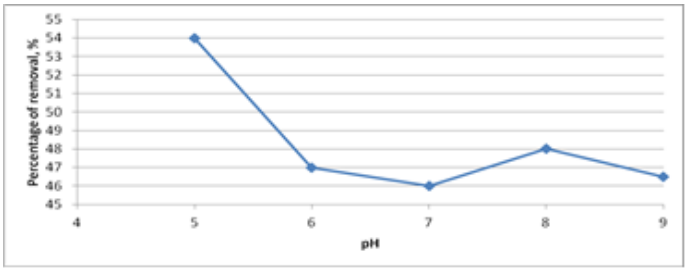


Figure 4 Effects of pH on the percentage of dye removal

3.3.2 Effect of Dosage

Figure 5 illustrates the effect of adsorbent dosage on the percentage removal of dye. The pH and temperature was kept constant at pH 6 and 27°C, respectively. As expected, the percentage removal of dye increased as the dosage of the adsorbent increased. The highest percentage of dye removal of

48% was achieved when 2.0 g of adsorbent was used. Meanwhile, the lowest percentage of dye removal of 46 % was recorded when 0.5g adsorbent was used. The adsorption efficiency increased with adsorbent dosage because there were plenty of surface area and 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].

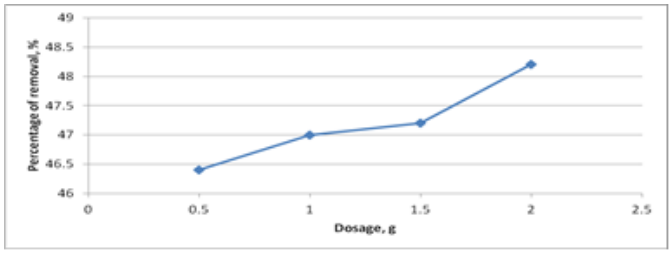


Figure 5 Effects of adsorbent dosage on the percentage of dye removal

3.3.3 Effect of Temperature

Figure 6 shows the effect of temperature on the percentage removal of dye. The adsorbent dosage and pH of the solution was kept constant at 1.0 g and pH 6, respectively. As can be seen, the removal of dye increased from about 46 to 64% as temperature increased from 27 to 50°C respectively. This indicated that the elevation of solution temperature to around 50°C 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. Apart from that, the swelling effect within the internal surface of the eggshell powder due to elevated temperature enabled large amount of dye molecules to penetrate further into the eggshell structure [Denis, *et al*. 2011]. However, increasing the temperature to 60°C resulted to decrement in dye removal. It shows that the adsorption process was an exothermic at high temperature. These might be explained on the basis that the solubility of the dyes was increased at higher temperature and the interaction between adsorbate and adsorbent decreased resulting to the decrement of adsorption [Muhammad, *et al*. 2006]. Moreover, the structure of the adsorbent might be damage at elevated temperature and thus led to the failure of the adsorbent.

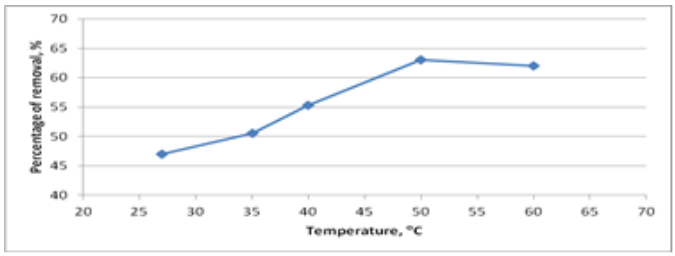


Figure 6 Effects of temperature on the percentage of dye removal

3.4 Langmuir Isotherm

The data of C_e/q_e was plotted against C_e to get the isotherm modelled as shown in Figure 7. Based on the graph, the Langmuir constant and adsorption rate were determined. The value of R^2 for Langmuir isotherm was 0.5008. These result indicated the isotherm was not well fitted to the adsorption process. The isotherm modelled in Figure 8 shows that the maximum adsorption capacity of dye on the adsorbent, q_m, was estimated as -51.02 mg/g and the Langmuir constant, K_L, was estimated at -0.0602 Lg^{-1}. The negative value of q_m and K_L indicates that the adsorption process of dye does not occur because there are no adsorption capacity and adsorption rate for this case. This shows that the Langmuir isotherm did not fir the adsorption.

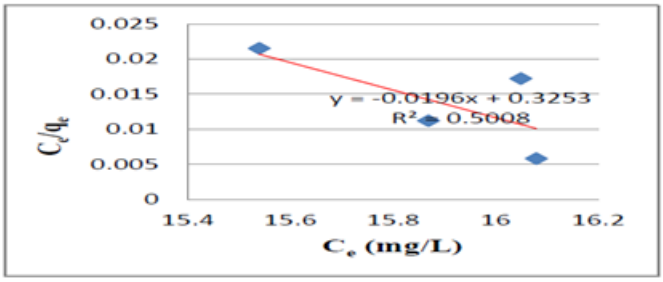


Figure 7 Langmuir isotherm model

3.5 Freundhlich Isotherm

Freundlich parameters indicated whether the adsorption process is either favorable or unfavorable. The intercept and slope are indicators of adsorption capacity and intensity, respectively. Based on Figure 8, the value of Kf was found to be 13.9380. The value of n is larger than 1 which is 55.2486. Larger value of n indicates that adsorption intensity was good and favorable over the adsorption studied. However, the R^2 value obtained from the modeled isotherm was 0.4585 which indicated the process did not fit the isotherm. Nevertheless, the process can be said to follow Freundlich isotherm since there is adsorption capacity when the result was fitted using Freundlich isotherm.

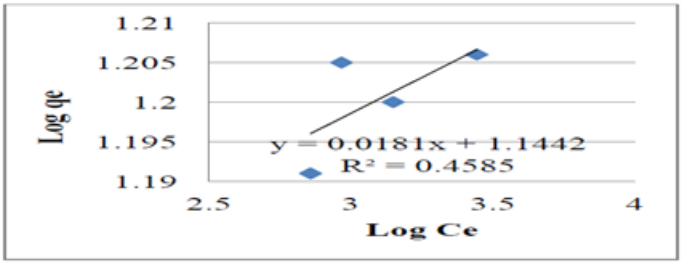


Figure 8 Freundlich Isotherm Model

4.0 CONCLUSION

It can be concluded that waste hen eggshells has potential to be used as a low adsorbent to treat dye in waste water. The result showed that the carbonization temperature ranged from 600 to 900°C did not significantly affect to the performance of the adsorbent. The adsorption was favored under acidic condition (pH 5) than either neutral or alkaline condition and at high temperature (50°C). As the dosage increased, the percentage of dye removal also increased. The highest removal of dye achieved was approximately at 64 % which is not too high. The performance of the adsorbent can be improved by modifying it

with cationic substance such as poly(ethyl imine) (PEI) as the orange dye is an anionic dye.

Acknowledgement

The authors would like to extend their sincere gratitude to the Ministry of Higher Education Malaysia (MOHE) for the financial supports received under University Grant (Vote no. Q.J130000.2544.04H95).

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