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Methylene Blue Dye Adsorption to Durian Shell Activated Carbon

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Abstract. A low cost adsorbent for waste water treatment can be achieved by producing an activated carbon from agriculture waste. In this research work, the activated carbons were prepared from durian shell using the physical and chemical activation at different concentrations of hydrogen peroxide followed by carbonization at high temperature under the flow of nitrogen gas. The produced activated carbon was characterized to obtain the physical and chemical properties. The adsorption of methylene blue dye has been studied in this experiment and the results showed that the efficiency of dye removal was increased for the treated durian shell as compare to the untreated one. It is found that 99% of methylene blue has been removed using durian shell activated carbon (DShAC) that treated at the conditions 0.6M H_2O_2 at 700°C for 30 minutes.

Introduction

Dye can be generally described as the colored substance that has an affinity to the substrate to which it is being applied. It is a coloring agent that is widely used in industries such as textiles, rubber, paper, plastic and cosmetic. Color is the first contaminant to be recognized in water and has to be removed from wastewater before discharging it into water bodies [1]. Spent dye solutions from textile dyeing operations have undergone wastewater treatment before discharging tp stream/river but the dye are not effectively removed from wastewater. This may result in environmental and human exposure. Since, color impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has tendency to chelate metal ions which produce micro-toxicity to fish and other organisms [2, 3]. Methylene blue is a basic dye that commonly used for dying cotton and silk. However, it can cause eye burn, and if swallowed, its causes irritation to the gastrointestinal tract with symptoms of nausea, vomiting and diarrhea. It may also cause methemoglobinemia, cyanosis, convulsions and dyspnea if inhaled [4]. Generally, dyes containing wastewaters can be treated in two ways, which are physical and chemical. As for that, various chemical and physical methods have been proposed for the removal of dye from the effluent water such as nanofiltration, electrokinetics coagulation, liquid-liquid extraction, ozonation, biological process and adsorption. Among these, adsorption has been found to be the most sufficient as compared to the others techniques. This is due to its capability for efficiently adsorbing a broad range of adsorbates and its simplicity of design.

Activated carbons are known to be effective adsorbents due to highly developed porosity, large surface area, variable characteristic of surface chemistry, and high degree of surface reactivity [5]. However, the uses of activated carbon as the adsorbent are still considered as an expensive material. Therefore, there is a need to find out much economical, effective, viable alternative adsorbent. As for that, natural materials, waste materials from industry or domestic uses and agricultural and biosorbent can be obtained and employed as inexpensive adsorbents. One of the abundance agriculture wastes in Malaysia is durian shell. Ministry of Agricultural and Agro Based Industry Malaysia has reported that approximately 255,353 MT of durian shell are produced in year 2011 in Malaysia [6]. Therefore it has been chosen as a raw material in producing activated carbon for this present study. Another considerations that need to be taken into account is the problems associated with activated carbons such as the combustion at high temperature, pore blocking, and hygroscopicity [7]. To overcome these problems, various modifications must be developed to prepare the activated carbons that achieve the requirement for better abatement of organic pollutant but with the low cost production.

Thus, the objective of the study is to develop activated carbon from durian shell and to test the develop materials by removing methylene blue through adsorption process.

Methodology

Preparation of adsorbent. Durian shells were used as a raw material in this experiment by purchasing it from commercial market in Perak. The shells were cleaned by washing with water and dried under the sun for 1 day in order to remove any dust or inorganic impurities. Next, the drying process was continued in the oven at 80°C for 24 hours. Then, durian shells were ground and sieved to a desired geometric particle size. For treated samples, the durian shells were further activated by chemical and physical activation. Five grams of durian shell was immersed in the 100mL hydrogen peroxide at different concentrations. After the impregnation process, the durian shell was washed with distilled water until it reached approximately pH 6-7. The shell was then dried at 80°C for overnight. Later, the samples were carbonized in a tube-furnace at different conditions. The flow of nitrogen gas at 500ml/min volumetric flow rate is maintained throughout the heating process.

Adsorption studies. The methylene blue (MB) was used as an adsorbate in this experiment with the chemical formula of $C_{16}H_{18}ClN_3S$, MW of 319.85g/mol and λ_{max} of 665nm. The stock solution was prepared by dissolving 1.0 g of dye in 1000ml distilled water to make a stock solution of 1000mg/l. Then, it was diluted with specific volume to get the desired concentration. To study the effect of initial concentration, a batch experiment was carried out by adding 0.2 g of adsorbent for treated and untreated durian shell into each 200 mL methylene blue solution at different initial concentrations (5, 10, and 15ppm) in room temperature (approximately 27°C). The flasks were shaken for 5 hours and the MB concentration in the solution was analyzed at various predetermined intervals time. To study the effect of adsorbent dosage on adsorption, different amount of treated and untreated durian shell in the range from 0.2 g to 0.6 g was added into 200 mL methylene blue solution with the concentration of 5ppm. The samples were separated by filtration and the concentrations of methylene blue were determined using a UV-vis spectrometer at wavelength of 665nm. The adsorption performances of untreated and treated durian shell were studied by evaluating the removal efficiency of methylene blue.

Properties of activated carbon. The comparison of pore structure characteristic for durian shell before and after activation processes were observed by using Field Emission Scanning Electron Microscopy (FESEM) Model Veiss SUPRA 55VP at accelerating voltage of 0.02 to 30 kV. For elemental analysis, CHNS analyzer LECO CHNS-932 USA was used to determine the percentage of C, H, N and S present in the raw material and activated carbon in order to analysis the potential of durian shell as activated carbon.

Results and discussion

Characterization of durian shell

Several aspects should be considered as they may influence the quality of activated carbon productions such as the activation temperature, the duration time in activation reagent solution as well as the amount and type of activating agent uses since different conditions would give different quality of activated carbon [8]. This can be shown in Figure 1(b), (c) and (d). Before the activation process, the raw durian shell surface was smooth with no pores (refer to Figure 1(a)). However, after the activation process, the surface has been developed into porous structure [9]. The activation step could increase the pore diameter and also create new pores. As a result, higher adsorption uptake could be achieved [10]. The durian shell that was treated in 0.6 M of H_2O_2 at 700°C for 30 minutes had developed uniform pores (refer to Figure 1(d)) as compare to the durian shell that treated in 0.6 M H_2O_2 at 500°C for 2 hours and in 0.4 M of H_2O_2 at 500°C for one hour (refer Figure 1(b) and (c)). This is due to the insufficient heating temperature where the process of pore development was not completed at the low temperature. The result is in good agreement with Yang J. et al. that the performance of activated carbon not only depends on the properties of raw material but also influenced by the activation method used [11]. It is observed that there is a combination of mesoporous and microporous in the pore structure of durian shell activated carbon. In this study, the yields were obtained in the range of 21–24%. Different activating agent will influence the yield production as compared to the production of yield by durian shell that activated by KOH solution is between 21.50% to 52.74% [12]. According to Tham Y. et al., the elemental content of durian shell contains 37.84% of C, 54.08% of O, 60.29% of K and 1.78% of Ca [13]. In this study, after the activation the weight percentage of fixed C has increased to 62.58%. This proved that hydrogen peroxide can be considered as one of good activating agents.

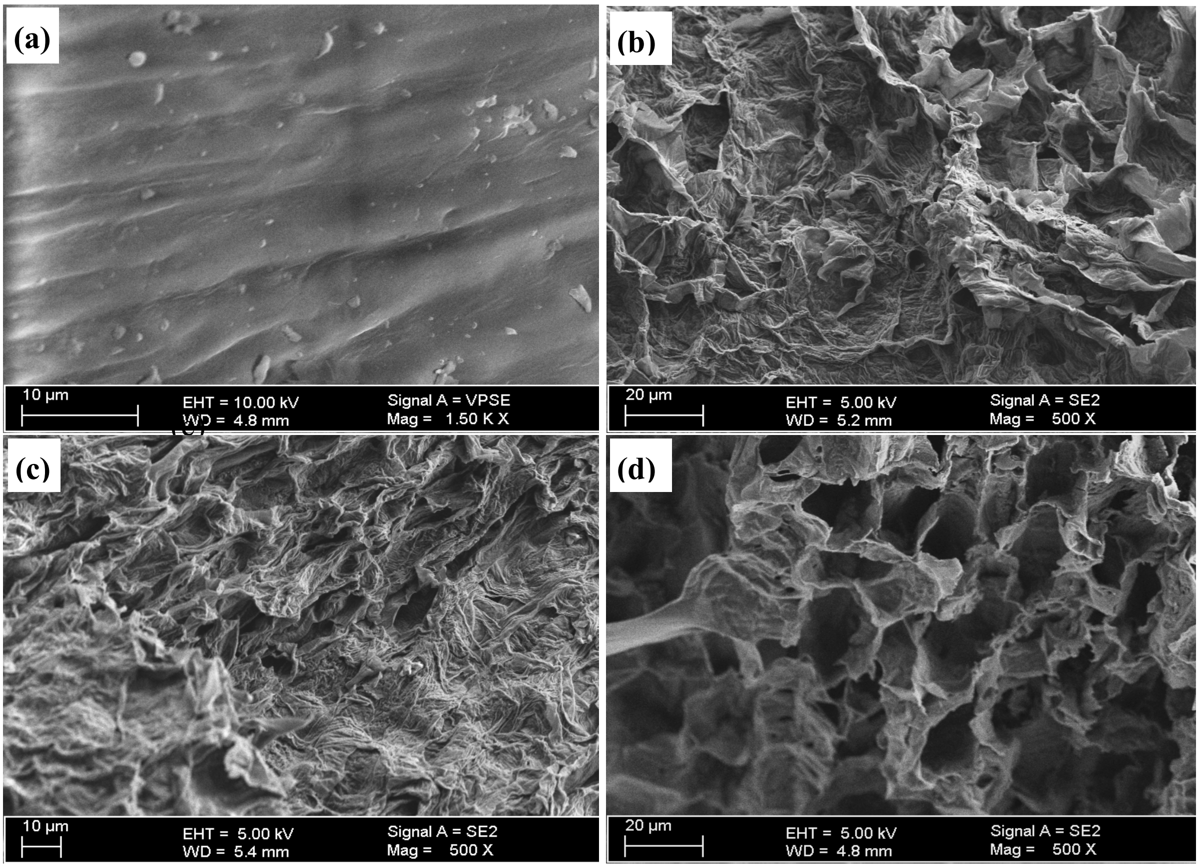

Figure 1 : FESEM image for (a) untreated durian shell and treated durian shell at (b) 0.6 M H_2O_2 at 500°C for 2 hours, (c) 0.4 M H_2O_2 at 500°C for one hour, (d) 0.6 M H_2O_2 at 700°C for 30 minutes

Adsorption study

Effect of initial dye concentration. At the initial stage the untreated durian shell adsorbed methylene blue more than 50% as compared with the treated durian shell (refer to Figure 2). After 50 mins, the adsorption process using untreated durian shell gradually slowed down until it reached equilibrium. This phenomenon is due to the instantaneously solute adsorption as a result of open sites for dye adsorption. More over, the development of a thin film on the surface of the material would minimize the diffusion process. According to Marsh, H. et al., the adsorption capacity depend on the availibility and accessibility of the organic molecules to the microporosity which is dependent on their size [14]. At this stage, the amount of dye desorbing from the adsorbent is in a state of dynamic equilibrium and the time needed to reach this state of equilibrium is known as equilibrium time [6, 15]. The efficiency of the dye removal was decreased with the increasing initial dye concentration although the actual amount of dye adsorbed per unit mass of adsorbent increased with the increasing of dye concentration. For untreated durian shell, the unit adsorption was increased from 3.15 to 8.45 ppm as the initial concentration of methylene blue dye solution from 5 to 15 ppm respectively. For treated durian shell, the unit adsorption was increased from 1.78 to 5.14 ppm. This is because higher initial concentration will increase the driving force for adsorption process to occur based on concentration gradient [16]. A similar trend was shown for removal the methylene blue by using rice hulls [17]. The performanc of dye removal using the treated durian shell is better as compared to the untreated durian shell where approximately 99% of dye was successfully removed from the solution.

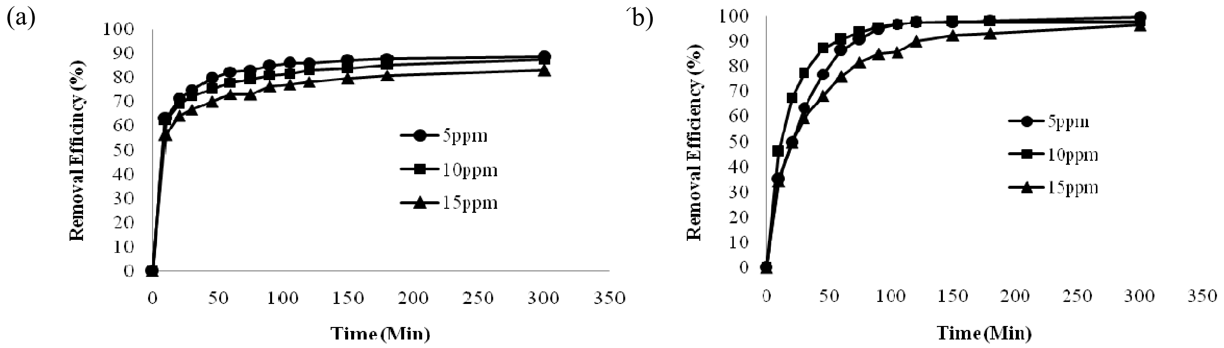

Figure 2 : The effect of initial concentration on dye removal by (a) untreated and (b) treated durian shells

Effect of adsorbent mass. As shown in Figure 3(a), by increasing the mass of untreated durian shell, the initial removal efficiency capacity was also increased from 62% for 0.2 g adsorbent to 85% for 0.4 g and 86% for 0.6 g. For treated activated carbon, the removal efficiency was increased from 35% (0.2 g) to 96% (0.4 g) and 95% (0.6 g) as shown in Figure 3(b). The dye removal percentage increases with the amount of adsorbent since more adsorption sites are available at larger surface area. The dye removal process can be considered effective because almost 70% of dye was completely removed from the solution within 20minutes.

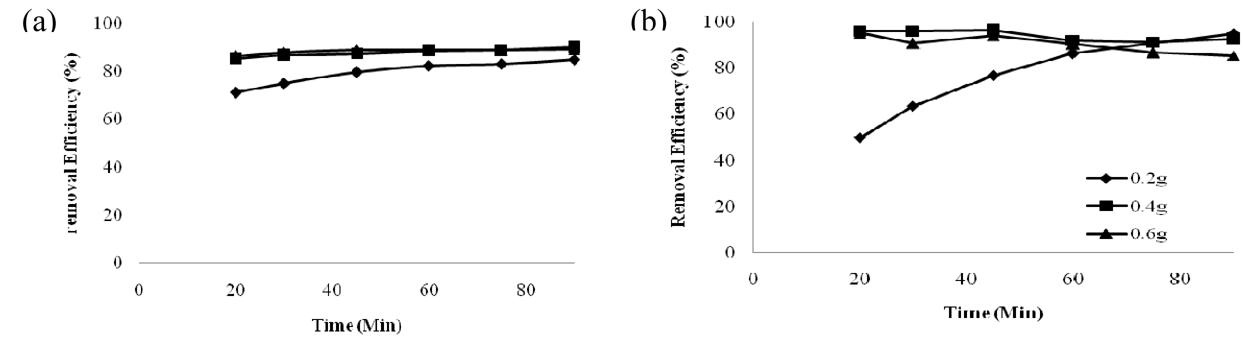

Figure 3 : The effect of adsorbent mass on the removal of dye by (a) untreated and (b) treated durian shells

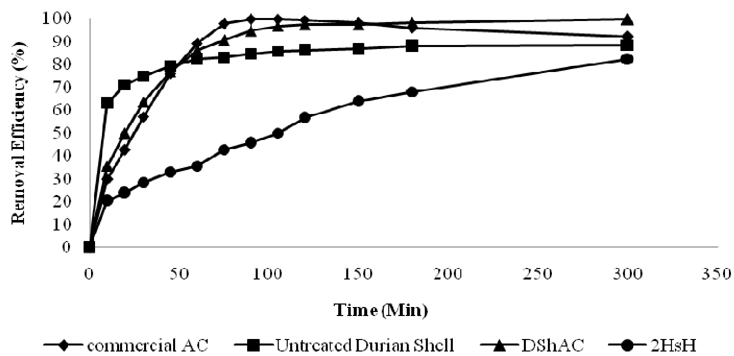

Figure 4 : Comparison between commercial activated carbon, untreated and treated durian shells

Comparison between untreated, treated durian shells and commercial activated carbon.
The adsorption results have been compared with the commercial activated carbon as in Figure 4. It can be seen that the removal of dye using commercial activated carbon is higher at the first 60 minutes of adsorption before it achieved aquilibrium with uptake at 97%. On the other hand, for untreated durian shell and treated durian shell with uniform pore structure (DShAC), the adsorption is slower than that of commercial activated carbon. However, at t=50minutes, both materials adsorbed dye more in which at equilibrium the adsorption uptake reached 99%. For treated durian shell with uneven and collapse pores (2HsH) the adsorption rate is very slow and the adsorption uptake is 82%. This is due to undeveloped pores at the surface. Therefore the dye molecules had a difficullty to diffuse from the external surface into the pores of the activated carbon. Thus, a long contact time is needed to reach a complete diffusion.

Conclusion

The optimum conditions to produce durian shell activated carbon are 0.6M H_2O_2 at 700°C for 30 minutes. From the adsorption study, 99% of methyelene blue has been removed. This results prove that treated durian shell has the capability for dye removal and it is compatible with the commercial activated carbon.

Acknowledgement

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