Performance of rubber seed shell adsorbents for removal of methylene blue dye in aqueous solution

Thevdarshni Chanderan1, Masitah Hasan1,3, Zulfakar Mokhtar2,3 and Naimah Ibrahim1,3

1Faculty of Civil Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
2Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia
3Water Research Group (WAREG), Universiti Malaysia Perlis (UniMAP), Perlis, Malaysia.

Email: masitah@unimap.edu.my

Abstract. Regeneration of rubber seed shell (RSS) in producing an effective low-cost activated carbon (AC) through chemical activation using H3PO4. Adsorption of methylene blue (MB) by raw, AC1 (impregnation ratio 1:1) and AC2 (impregnation ratio 1:3) carbons were analyzed to discover its adsorption capacity. The effects of various experimental parameters: pH of solution, initial concentration, contact time and adsorbent dosage were analyzed. Characterization of adsorbents produced were performed using SEM, ash content, iodine number and BET. Overall performance of the adsorbents was investigated by employing the optimum values obtained in the batch adsorption studies. This study revealed that the carbon with higher impregnation ratio (AC2) has the highest removal efficiency of MB at 91.4%. Specific surface area, iodine adsorption number and ash content for AC2 are 317.6 m²/g, 676.9 mg/g and 2.6%, respectively. This study revealed the primacy of chemically activated carbons with higher impregnation ratio (AC2) for the removal of MB.

1. Introduction
Water covers around 70 percent of the Earth’s surface making water (freshwater or groundwater) one of the world's most essential resources. Water quality has a remarkable importance as water resources are used for various activities such as household and industrial water supply, hydroelectric power plants, tourism, agriculture (irrigation), and other human or economic ways of using water [1]. However, existing water quality is at high risk due to the high concentration of pollutants in water. The effluent from industries that known as industrial wastewater is indeed the primary contributor to water pollution especially in Malaysia. The most undesirable contaminants that present in water are colours due to the aesthetic values which caused by the dyeing and colouring industries [2].

High concentration dyes like methylene blue in industrial wastewater discharge prone to disturb the light penetration and affects the photosynthesis process [3]. These dyes are mutagenic, carcinogenic and teratogenic and toxic to human and aquatic microorganisms. There are many methods of removing dyes from wastewater including oxidation, membrane separation, coagulation and ozonation. However, these methods are not cost-effective. The most feasible method to remove...
dyes from wastewater is through adsorption using activated carbon [4]. However, commercial activated carbon is too costly. Therefore, in this study is transforming rubber seed shell into AC that will be used as adsorbent to treat dyes. This means that AC produced could be a new substitute for the commercial AC which leads to lower cost of adsorption process yet effective. This indicates that the operation of most of the wastewater treatment industries can lower down their operating cost as AC produced using agricultural waste is much cheaper compared to commercial AC. Characterization of chemically modified AC was performed. Hence, this study aims to evaluate and validate the visible potential of agricultural waste - based AC (chemically activated with different ratio) as an adsorbent for future applications.

2. Materials and methods

2.1. Preparation of adsorbents
The rubber seed shell utilized in this research was collected from rubber plantation located in Rantau, Negeri Sembilan. In this research, three adsorbents are produced (raw activated carbon denoted as raw, activated carbon with impregnation ratio of 1:1 denoted as AC1 and impregnation ratio of 1:3 denoted as AC2). The raw adsorbent go under no chemical activation, it was only being activated in the muffle furnace at 550°C for 90 minutes. The raw adsorbent was pre-dried in the oven at 105°C for 24 hours to remove excess moisture. AC1 and AC2 were prepared by impregnating the pre-dried sample with phosphoric acid (H₃PO₄) in ratio of 1:1 (sample: H₃PO₄) and 1:3 (sample: H₃PO₄) respectively for 24 hours. The resulting samples were than washed with hot distilled water to remove excess activating agent. After that, the samples were dried in the oven at 105°C for 24 hours to remove the moisture. Lastly, the samples were thermally activated in the muffle furnace at 550°C for 90 minutes.

2.2. Preparation of adsorbate
The methylene blue (MB) used in this work was obtained from Sigma–Aldrich, Malaysia and used without further purification. The adsorbate was prepared as stock solution with 1000 mg/L. The methylene blue (MB) dye powder was weighed ± 1.00g and dissolved in 1000 mL of distilled water. The stock solution was stored in a dark area prior usage to avoid degradation of the colour due to the exposure of light.

2.3. Characterization of adsorbents
Surface morphology was conducted using Scanning Electron Microscope (SEM) to identify the pore distribution of the adsorbents. Brunauer-Emmett-Teller (BET) analysis was performed to identify the specific surface area and pore size of adsorbents and functional group on the adsorbents was identified using the Fourier Transform Infrared Spectroscopy (FTIR). Total ash content was performed using ASTM D2866 AC (were burned in furnace at 650 °C for 16 hours) and was calculated using equation (1) as follows:

\[ A = \frac{(D - B)(C - B)}{100} \]  \hspace{1cm} (1)

where \( A \) is the ash percentage (%), \( B \) is the mass of crucible (g), \( C \) is the mass of crucible + pre-dried sample (g) and \( D \) is the mass of crucible + ash (g). Iodine adsorption number (ASTM D 4607 − 14) of adsorbents was calculated using equation (2) as follows:

\[ \frac{X}{M} = \frac{(A - (DF \times B \times S))}{M} \]  \hspace{1cm} (2)

where \( X/M \) is the iodine absorbed per gram of carbon (mg/g), \( S \) is the volume of sodium thiosulphate (mL) and \( M \) is the mass of carbon (g).
2.4. Batch adsorption studies
Adsorption of methylene blue by raw, AC1 and AC2 adsorbents were performed in a set of Erlenmeyer flasks (250 mL), where solutions of methylene blue dye (150 mL) with different initial concentrations ranging from 50 to 250 mg/L were placed in these flasks. The contact time were taken for the first 6 hours with 20 minutes interval and the final reading was taken after 24 hours. The amount of adsorbent dosage use in this experiment was 0.6 g and the pH of solution was constant at 7. The final concentration of samples were filtered prior analysis and analyzed using UV-vis spectrophotometer (Hitachi U-2810) and the solution was measured at 664 nm. The removal efficiencies of the carbon prepared (raw, AC1, AC2) were calculated using equation (3) as follow:
\[
\text{Removal Efficiency} = \frac{(C_0 - C_t)}{C_0} \times 100\%
\]
where \(C_0\) is initial concentration of the solution (mg/L) and \(C_t\) is concentration of the solution after adsorption at time, \(t\) (mg/L).

3. Results and discussion
3.1. Characterization of adsorbent
SEM was conducted to observe the surface and porosity of the activated carbons. The magnification of 1000 times were used for this study. Figure 1(a), 1(b) and 1(c) illustrated the SEM images of raw, AC1 and AC2 respectively in the magnification of 1000×.

Figure 1. SEM micrograph of raw (a), AC1 (b) and AC2 (c) respectively in the magnification of 1000×.

Figure 1(a) clearly shows the canal structure proving that it is a good surface texture for preparing effective adsorbents. This is because activating agents like \(\text{H}_3\text{PO}_4\) can easily penetrate to inner surfaces of the rubber seed shell which can increase the porosity of the adsorbents through chemical activation process. Figure 1(b) and 1(c) demonstrated that the AC developed heterogeneous hollow and porous structure after being activated by \(\text{H}_3\text{PO}_4\). However, figure 1(c) illustrated that the pores sizes were larger compared figure 1(b) due to more amount of \(\text{H}_3\text{PO}_4\) acid is used during the activation process. Adsorbents with larger pore size results in better efficiency of adsorption process [5]. Thus, making AC2 as the potential adsorbents followed by AC1 and raw respectively. The results of specific surface area and average pore size from BET analysis, ash content and iodine adsorption number of the raw, AC1 and AC2 adsorbents were tabulated as shown in table 1.

From table 1, the specific surface area for raw, AC1 and AC2 are 136.11 m²/g, 214.10 m²/g and 317.69 m²/g, respectively. All three adsorbents can be classified as mesopores as all the three carbon’s average pore size are within the range of 2 to 50 nm as stated by International Union of Pure and Applied Chemistry (IUPAC). Mesoporous carbons are more effective in the removal of the contaminants in aqueous solution due to the molecular structures of the contaminants are larger than the contaminants in the air [6]. This shows that AC2 has the highest specific surface area.

The ash content of the AC2 is relatively the lowest at 2.61% compared to the raw and AC1 at 9.68% and 4.68% respectively. A good adsorbent has the characteristics of low ash content [7]. The iodine
adsorption number for raw, AC1 and AC2 adsorbents are 616.7 mg/g, 642.5 mg/g and 676.9 mg/g respectively. Higher iodine adsorption number, the better its performance during the adsorption process [8]. From those analysis, it can be concluded that AC2 disclosed the better results in all the analysis thus making AC2 as the most potential alternative adsorbents that can be replaced with commercial AC followed by AC1 and raw respectively.

| Adsorbent samples | Specific surface area (m²/g) | Average pore size (nm) | Ash content (%) | Iodine adsorption number (mg/g) |
|-------------------|-----------------------------|------------------------|-----------------|-------------------------------|
| Raw              | 136.11                      | 3.96                   | 9.68            | 616.70                        |
| AC1              | 214.10                      | 3.14                   | 4.68            | 642.50                        |
| AC2              | 317.69                      | 2.55                   | 2.61            | 676.90                        |

3.2 Overall performance of adsorbents
The overall performance of adsorbents on the adsorption process of the MB was analysed by taking the optimum values of pH (7), initial concentration (50 mg/L), contact time (6 hours) and adsorbent dosage (0.6 g) after the adsorption studies for each parameter. The agitation speed remains constant throughout this study at 150 rpm. Figure 2 illustrated the overall performance of the activated carbons produced through chemical activation (H₃PO₄) using rubber seed shell as the raw material.

Based from figure 2, it is clearly demonstrated that AC2 achieved the highest percentage removal of methylene blue from aqueous solution at 91.4% followed by AC1 and raw with 85.1% and 78.9% respectively. It can be summarized that all three adsorbent experiences gradual increment in the removal efficiency. It is proven that by initiating proper pH value, initial concentration, contact time and adsorbent dosage can enhance the performance of adsorbents for the removal of methylene blue dye from the aqueous solution. Conducting batch adsorption studies for this research had helped in identifying the potential adsorbent (AC2). Thus, making rubber seed shell as the potential alternative raw material to be used in producing activated carbons for adsorption process.
4. Conclusion
Rubber seed shell is an agricultural waste which is abundantly available in Malaysia. The production cost of transforming rubber seed shell into AC is subsequently low as the cost of raw material are low compared to the cost in producing commercial AC. This study revealed that chemically activated carbon produced using rubber seed shell performed well in removing methylene blue as it records a better removal efficiency which is more than 80 % for both chemically activated carbons (AC1 and AC2). These chemically activated carbons developed larger pore size after the activation process which had enhanced its adsorption capacity. This study also had manifest that proper activation process can seed a higher adsorption capacity of adsorbents.

References
[1] Venkatramanan S, Chung S Y, Lee S Y, Park N 2014 J. Earth and Environ. Sci. 9(2) 125-132
[2] Li D and Liu S 2018 Water Quality Monitoring and Management: Basis, Technology and Case Studies. Academic Press
[3] Hameed K S, Muthirulan P, Meenakshi S M 2017 Arabian J. Chem. 10 S2225-S2233
[4] Liew R K, Azwar E, Yek P N Y, Lim X Y, Cheng C K, Ng J H, ... & Lam, S. S. 2018 Bioresour. Technol. 266 1-10
[5] Kumar A and Jena H M 2016 J. Clean. Prod. 137 1246-1259.
[6] Nasrullah A, Bhat A H, Naeem A, Isa M H, Danish M 2018 Int. J. Biol. Macromol. 107 1792-1799.
[7] Zawawi N M, Hamzah F, Nasarudin N A, Azman N N 2017 Adv Sci Lett. 23(5) 3921-3925.
[8] Şahin Ö, Saka C, Ceyhan A A, & Baytar O. 2015 Sep Sci Technol 50(6) 886-891.