Removal of Azo Dye from aqueous solution by activated carbon derived from *Moringa oleifera* seeds

Tan Shouzheng¹, Zulfakar Mokhtar¹,³ and Masitah Hasan²,³

¹Fakulti Teknologi Kejuruteraan Kimia, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Malaysia
²Fakulti Teknologi Kejuruteraan Awam, Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Malaysia
³Water Research Group (WAREG), Universiti Malaysia Perlis, Kompleks Pusat Pengajian Jejawi 3, 02600 Arau, Malaysia

Email: zulfakar@unimap.edu.my

Abstract. The aim of this work is to utilize activated carbon derived from *M. oleifera* seeds that is treated with zinc chloride to remove the Remazol Brilliant Pink solution in aqueous solution. The acid-treated activated carbon was characterized using Scanning Electron Microscope (SEM) and Fourier Transform Infra-Red (FTIR) to determine the adsorbent surface morphology and functional groups, respectively. Three experiment parameters including pH, adsorbent dosage and initial dye concentration were carried out in a batch adsorption process. From the study, pH 3, 0.20 grams of adsorbent dosage, and initial dye concentration of 150 mg/L were the best operating parameter. The adsorption data was then undergone further analysis using Langmuir adsorption isotherm and Freundlich adsorption isotherm. Langmuir adsorption isotherm has a superior $R^2$ value of 0.9784 when compared to the latter. The adsorption kinetics follows pseudo-second-order kinetic model was, indicating that the adsorption process is a chemisorption and monolayer formed at the surface of activated carbon. Thus, activated carbon derived from *M. oleifera* seeds deemed to be effective in removing Remazol Brilliant Pink from aqueous solution.

1. Introduction
With whopping surge of businesses in the dye industries, by-products released by those operating factories have turned out to be a great concern for the human beings. The largest demand of the colorants come from Asia Pacific with countries such as People’s Republic of China and India. Dyes does not only originate from textile industries, it also comes from leather and paper industries [1].

In Malaysia, azo dyes from textile industries are released into the environment daily. In the year of billion in sales, taking up to 1.8% of the total exports in the country [2]. Dyes flow into the seas, lakes and rivers have become a health concern for the public. Those dyes increased the Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) in the wastewater [3]. Along with the dyes, the wastewater consists of substantial amount of heavy metals, oxidizing and reducing agents, and suspended materials, rendering the water unsuitable for human consumptions, affecting aquatic and marine lives.

There are 31.7 million population in Malaysia as of September 2017 [4]. An estimated of 98% of the country’s residents have access to refined water sources [5]. Industrial effluent is the wastewater discharged by any operating facilities. Department of Environment (DOE) is responsible for the quantity
of the industrial effluent released into the water, by complying with the Environmental Quality Act 1974 and Malaysia Environmental Quality (Sewage and Industrial Effluents) Regulations 2000 [6].

According to Indah Water Konsortium, currently Malaysia relies on preliminary, primary and secondary wastewater treatment. Malaysia does not have the technologies to develop tertiary wastewater management [5]. Biological treatment of wastewater is designated as the secondary treatment. Coping with high performance and maintenance fees [7], technologies have been developed from biological materials to treat the dyes and colorants found in industrial effluents as they were found to be cost effective.

For the past few years, many biological materials are used to treat the dyes in the wastewater. Those biological materials are generally derived from plants. Some examples of the plants include rice husk [8], oil palm empty fruit bunch [9], Mangifera indica [10] and papaya seeds [11]. The biosorbents are economical and the adsorption processes can be easily carried out. Activated carbon derived from M. oleifera seeds are used in this study as the seeds are cheap and they can act as a powerful sorbent in the wastewater treatment [12].

2. Materials and methods

2.1. Chemicals
Remazol Brilliant Pink was purchased from A.R. Alatan Sains (K) Sdn. Bhd. Zinc chloride was purchased from HmbG® Chemicals. Hydrochloric acid was bought from Fisher Chemicals whereas sodium hydroxide was purchased from a company called ALPHA.

2.2. Raw materials
M. oleifera seeds were collected in front of Puspakom, Arau, Perlis. Fresh M. oleifera seeds were dried in the oven at 100°C for 24 hours. The part of the dried samples then undergone carbonization process. Both pure M. oleifera seeds and activated carbon were then blended and sieved at 1 mm to produce fine powder.

2.3. Preparation of activated carbon
The seeds were cut into small pieces, around 2 cm, and then cleaned with distilled water and placed in an oven. The seeds were dried at 100°C for 24 hours [13]. Activated carbon derived from M. oleifera seeds was carried out through chemical activation process. One chemical was involved in the chemical activation process, which was zinc chloride, ZnCl₂. First, 80 g of dried M. oleifera seeds was weighted using an electronic balance. The ratio of the raw materials used to the distilled water was 1:10. The seeds were placed inside a 1000 ml conical flask and impregnated with 800 ml of distilled water and 10% of ZnCl₂ (w/v), which was equivalent to 80 g of ZnCl₂. The sample was impregnated for 24 hours with shaking using an incubator shaker. After that, the sample was taken out and placed inside the oven for another 24 hours, dried at 100°C.

The sample was taken into a furnace where it undergoes carbonization and activation process. The process was carried out at 600°C. The process took place for around 45 minutes. The activated carbon produced was washed with distilled water and dried in the oven at 100°C for a day. The sample was then blended and sieved at 1 mm [14].

2.4. Characterization of activated carbon
2.4.1. Scanning Electron Microscope (SEM). Scanning Electron Microscope (SEM) was used to study the surface morphology of the M. oleifera seeds and the activated carbon derived from M. oleifera seeds. The microscope utilized the emission of electron rather than the light, making the resolution and the magnification of the images better and higher. The SEM that was available was with the model of ZEISS Sigma 300 (Carl Zeiss Microscopy GmbH, Jena, Germany), situated in the laboratory of School of Material Engineering, UniMAP. The SEM was used twice, before and after the preparation of activated carbon. The adsorbent was observed using enlargement of 500×, 1000×, and 8000×.
2.4.2. **Fourier-Transform Infrared Spectroscopy (FTIR).** Fourier-Transform Infrared Spectroscopy (FTIR) was used to measure the functional groups that were present in *M. oleifera* seeds itself and the activated carbon derived from *M. oleifera* seeds. The model of the FTIR was Perkin Elmer located at laboratory of School of Material Engineering, UniMAP.

2.5. **Process study**

2.5.1. **Effect of pH.** To study the effect of pH, different pH was used throughout the experiment. The pH ranging from acid to alkali. The pH value that was used include pH 3, pH 4, pH 5, pH 7, pH 9 and pH 11. The pH of the solution was adjusted using 0.1 M of HCl and 0.1 M of NaOH. Throughout the experiment, temperature was kept constant at room temperature of 25°C and the amount of adsorbent added into each flask was the same, which is at 0.2 g. 100 ml of 100 mg/L of the Remazol Brilliant Pink solution at different pH was transferred into 6 conical flasks. The solution was mixed well to obtain a uniform solution. After that, 0.2 g of activated carbon was added into each flask and the flasks were placed in the shaking incubator for 180 minutes, at 200 rpm [15]. For every 30 minutes, small number of samples were filtered using filter paper and transferred into the cuvettes using a dropper. The cuvettes were placed in the UV-spectrophotometer at the wavelength of 540 nm to test the concentration of the Remazol Brilliant Pink solution. The results were recorded.

2.5.2. **Effect of initial dye concentration.** Different concentration of Remazol Brilliant Pink solutions was prepared from the stock solution, with concentration of 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 120 mg/L and 150 mg/L. The solutions were placed in 250 ml conical flasks. The pH of the solution was adjusted to pH 3 using a pH meter. 0.2 g of activated carbon was measured using analytical balance and transferred into Erlenmeyer flasks. The flasks were placed in the shaking incubator for 180 minutes, shaking at 200 rpm [15]. For every 30 minutes, sample was taken out from the flask, filtered with a filter paper and then transferred into the cuvettes. The concentration of Remazol Brilliant Pink was measured using UV-Spectrophotometer at the wavelength of 540 nm. The experiment was conducted at room temperature of 25°C.

2.5.3. **Effect of adsorbent dosage.** In order to study the adsorbent dosage, different amount of activated carbon was used throughout the experiment. The weight of the adsorbent used were 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g. In this experiment, the temperature was kept constant throughout as it is in room temperature of 25°C. The pH was at 3 for all the samples. 100 ml of 100 mg/L of the Remazol Brilliant Pink solution was transferred into 5 conical flasks. The flasks were mixed well to obtain a uniform solution. Different amount of the activated carbon was added into the flasks. After that, the flasks were placed in the shaking incubator for 180 minutes, at 200 rpm [15]. For every 30 minutes, small number of samples were filtered using filter paper and transferred into the cuvettes using a dropper. The cuvettes were then placed in the UV-spectrophotometer at the wavelength of 540 nm to test the concentration of the Remazol Brilliant Pink solution. The results were recorded.

3. **Results and discussion**

3.1. **Characterization of adsorbent**

3.1.1. **Scanning Electron Microscope (SEM).** Surface morphology of *M. oleifera* was examined using Scanning Electron Microscope (SEM). The emergence of pores as well as the alteration to the outer layer structure, were clearly observed using SEM. Based on figure 1, the pore-free surface of the *M. oleifera* seeds powder is noticeable using the magnification of ×8000. Unwrinkled and smooth fiber surface is well-detected too.
3.1.2. Fourier-Transform Infrared Spectroscopy (FTIR). The FTIR spectrum for *M. oleifera* seeds powder has a range from 3289.70 cm\(^{-1}\) to 782.24 cm\(^{-1}\) whereas the spectrum for activated carbon derived from *M. oleifera* seeds are ranging from 3187.15 cm\(^{-1}\) to 725.21 cm\(^{-1}\).

| I.R. Peaks | *M. oleifera* Seeds (Powder) | *M. oleifera* Seeds (Activated Carbon) | Band Assignments          |
|------------|-------------------------------|----------------------------------------|---------------------------|
| 1          | 3289.70                       | 3187.15                                | O-H stretching of alcohols |
| 2          | 2919.86                       | 2915.62                                | C-H stretching of alkanes |
| 3          | 2167.61                       | 2194.47                                | C\(=\)C stretching of alkynes |
| 4          | 1639.43                       | 1596.79                                | N-H bending of amides     |
| 5          | 1039.56                       | 1154.36                                | C-O stretching of alcohol |
| 6          | 782.24                        | 725.21                                 | C-Cl stretching of alkyl halide |
Based on table 1, peak 1 (3289.70 cm\(^{-1}\) & 3289.70 cm\(^{-1}\)) has a band wavelength that shows the O-H stretching of alcohols, which indicates that the existence of cellulose content in the material as *M. oleifera* seeds is part of the plan, which has the similar discovery as Hussin [14]. A sharp peak arises in Peak 2 (2919.86 cm\(^{-1}\) & 2915.62 cm\(^{-1}\)). It shows the C-H stretching of alkanes [16] whereas peak 3 (2167.61 cm\(^{-1}\) & 2194.47 cm\(^{-1}\)) displays the CΞC stretching of alkyne [14]. N-H bending of amides and C-O stretching of alcohols are prominently shown in peak 4 (1639.43 cm\(^{-1}\) & 1596.79 cm\(^{-1}\)) and peak 5 (1039.56 cm\(^{-1}\) & 1154.36 cm\(^{-1}\)) respectively, which has the same result obtained by Bello [16]. Finally, peak 6 (782.24 cm\(^{-1}\) & 725.21 cm\(^{-1}\)) has a C-Cl stretching of alkyl halide [16]. The analysis of FTIR spectra demonstrate the presence of functional groups such as alcohols, alkanes, alkyne, amides and alkyl halide in *M. oleifera* seeds.

3.2. *Effect of pH*

The effect of pH on the uptake of dye treated with activated carbon derived from *M. oleifera* seeds was investigated. In order to eliminate the Brilliant Pink dye from the solution, acidic, neutral, and alkali pH were set as the variables to determine the quantity of dye removal. The pH aforementioned comprised of pH 3, pH 4, pH 5, pH 7, pH 9, and pH 11, with the adsorbent dosage controlled at 0.2g and the dye concentration of 100 mg/L. Based on figure 3, it is shown that acidic pH has a superior dye removal quality than those in alkali pH. When the pH is at 3, percentage removal of dye is peaked at 24.20%, whereas when the pH is at 11, colorant removal percentage is at its lowest point of 2.22%.

![Percentage of Dye Removal vs. pH](image)

**Figure 3.** Graph of percentage of dye removal vs. pH.

At low pH, Brilliant Pink acts as an anionic dye, bearing a negative charge. The surface of the absorbent is positively charged. Thus, strong electrostatic forces of attraction between the dye and adsorbent allows the negatively charged dye to adhere on the positively charged surface of the activated carbon. When the pH of the solution increases, the positive charge of the dye will increase, making the solution cationic. Surface of the activated carbon has less positively charged active sites, and the OH-molecules will compete with one another to stick onto the porous structure of the absorbent [16]. This condition causes the decrease in the adsorptive properties of the dye, leading to a lower percentage of colorant removal. As a result, pH 3 was chosen as the optimum pH for further experimentation, as well as the standard pH used in the generation of the standard curve. This finding was the identical to the one conducted by Bello [16].

3.3. *Effect of adsorbent dosage*

To understand the end result of absorbent dosage on Brilliant Pink dye elimination, various amount of activated carbon derived from *M. oleifera* seeds is used in this analysis. The range of the adsorbent used
comprised of 0.2g, 0.4g, 0.6g, 0.8g and 1.0g, with the pH controlled at 3 and colorant concentration of 100 mg/L. Based on figure 4, it displayed that percentage of colorant removal peaked at 24.3% when 0.2g of activated carbon is used. This indicates that the optimum adsorbent to use is 0.2g. On the other hand, the removal of the pigment was minimum at 1.0g, showing only a 12.26% removal.

This condition occurs due to the overlapping of active sites of the activated carbon, resulting in a decline of total surface region that are accessible to the colorant. Almost identical outcome was described by Rapeia [8]. A slight peaked at 0.8g of absorbent occurred might cause by the incomplete shaking of the activated carbon inside the flask, as some of the activated carbon is adhered onto the walls of the glassware. Based on the analysis, adsorbent dosage at 0.2g is chosen and will be used for further assessment.

3.4. Effect of initial dye concentration
Efficiency Activated carbon produced from *M. oleifera* seeds was evaluated using different initial dye concentration. During the entire research, three constant variables associated with the parameter are the adsorbent dosage that was kept constant at 0.2g and the temperature and incubator shaker speed that were placed at 25°C and 200 rpm, respectively. The initial dye concentration used for this procedure were 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L, 120 mg/L, and 150 mg/L. The experiment was run for 2 hours. Figure 5 shows the graph of initial dye concentration vs. time. From the graph, it can be seen that the colorant concentration decreases gradually for the first hour. On the second hour, the colorant concentration decreases until it reaches equilibrium.

Based on the data obtained, it can be interpreted that when the activated carbon is added into the dye, the adsorbent has readily-available porous surface structure that allow the colorant to adsorb onto the surface of the adsorbent. When this phenomenon take place, the colorant molecules initiate a powerful driving energy to overpower the mass transfer resistance between both phases inside the solution. After an hour, the reaction began to decelerate due to the powerful electrostatic forces between the molecules. This causes the colorant in the solution hard to bind with the active sites of the adsorbent. Soon after, equilibrium in the solution will reach. When the equilibrium reached, it also shown that the dye has reached its maximum adsorption ability. Similar results was also observed by Bello [16].

Based on figure 5, it can also be concluded that the different initial pigment concentration has effect on the amount of pigment that being adsorbed at equilibrium. Higher initial pigment concentration has a higher concentration gradient when compared to those pigments with lower initial pigment concentration. For instance, the maximum adsorption uptake for the dye with 148.42 mg/L has an equilibrium of 120.10 mg/L, showing that 28.32 mg/L of the pigment has been adsorbed onto the surface of the activated carbon. On the other hand, the maximum adsorption uptake for pigment with 19.66 mg/L
has an equilibrium of 6.18 mg/L, showing that only 13.48 mg/L of the pigment has been absorbed, even though for both sets of the experiment, same adsorbent dosage is being used. This is because higher initial dye concentration has a stronger driving force that allow the adsorption process to take place [16].

![Graph of Initial Dye Concentration vs. Time](image)

**Figure 5.** Graph of initial dye concentration vs. time.

### 3.5. Adsorption isotherm analysis

Based on table 2, it can be seen that the R² value in Langmuir isotherm is slightly higher than the R² value in Freundlich isotherm. The final result was the same as Bello [16]. Therefore, the removal of azo dye using activated carbon derived from *M. oleifera* seeds favour towards Langmuir isotherm.

|                     | Langmuir Isotherm | Freundlich Isotherm |
|---------------------|-------------------|---------------------|
| **q_m (mg/g)**      | 37.3134           | K_f                 |
| **K_L (L/mg)**      | 0.0696            | n                   |
| **R_L**             | 0.08826           | 1/n                 |
| **R²**              | 0.9784            | R²                  |

### Table 2. Summary of Langmuir isotherm and Freundlich isotherm values.

### 3.6. Kinetics analysis

In order to explore the adsorption kinetics of the dye onto activated carbon, two adsorption kinetic study were focused, which are the pseudo-first order kinetic model and pseudo-second order kinetic model. Two graphs will be generated and the R² value will be extracted from the graphs. It is known that the kinetic model that has a better R² value will best fit the experimentation. Table 3 shows the K_1, K_2 and R² values from pseudo-first order kinetic model and pseudo-second order kinetic model, respectively.

It can be seen that the R² values in pseudo-second order kinetic model is better than those in the pseudo-first order kinetic model. Similar findings were observed by both Agbahoungbata [17] and Bello [16]. This concludes that the adsorption of the dye onto the activated carbon best fitted with the pseudo-second order kinetic model.
Table 3. Parameters in pseudo-first order and pseudo-second order kinetic models.

| Concentration (mg/L) | Pseudo-first order kinetic model | Pseudo-second order kinetic model |
|----------------------|----------------------------------|----------------------------------|
|                      | \( K_1 \)  \( \text{min}^{-1} \) | \( K_2 \) \( \text{min}^{-1} \) |
| 20 mg/L              | 0.0297                           | 3.65 \times 10^{-5}             |
| 40 mg/L              | 0.0286                           | 1.23 \times 10^{-4}             |
| 60 mg/L              | 0.027                            | 2.02 \times 10^{-4}             |
| 80 mg/L              | 0.0212                           | 8.01 \times 10^{-4}             |
| 100 mg/L             | 0.0209                           | 7.5 \times 10^{-4}              |
| 120 mg/L             | 0.0216                           | 2.82 \times 10^{-4}             |
| 150 mg/L             | 0.0353                           | 6.21 \times 10^{-4}             |

|          | \( R^2 \)                           | \( R^2 \)                           |
|----------------------|----------------------------------|----------------------------------|
| 20 mg/L              | 0.9313                           | 0.9688                           |
| 40 mg/L              | 0.9629                           | 0.9662                           |
| 60 mg/L              | 0.9793                           | 0.9827                           |
| 80 mg/L              | 0.989                            | 0.9872                           |
| 100 mg/L             | 0.9705                           | 0.9727                           |
| 120 mg/L             | 0.9742                           | 0.9928                           |
| 150 mg/L             | 0.9826                           | 0.9934                           |

The difference between the two models is that pseudo-first order model is closely associated with chemisorption, whereas in pseudo-second order model is related to physisorption. In chemisorption, it is characterized by chemicals. The electrostatic forces between the molecules will adsorb the dye onto the surface of the activated carbon, and only one layer of molecule will be formed. Hence, it is related to Langmuir isotherm model. On the other hand, during physisorption, the equilibrium is reached between the adsorbate and the fluid. Multilayer of adsorption will occur to fill the porous structure of the materials [18].

4. Conclusion
As a whole, to remove the azo dye from aqueous solution using activated carbon derived from \( M. \) oleifera seeds, activated carbon that has a more porous structure will help in the adsorption process. The optimum pH to remove the dye is using pH 3, whereas the suitable adsorbent dosage is 0.2g. Langmuir isotherm best fits with this dye removal process. The kinetic model that best describe the adsorption process is pseudo-second order kinetic model.

References
[1] Dye Stuff Market Research Report 2017 Retrieved September 22, 2017, from https://www.marketresearchfuture.com/reports/dye-stuff-market-3235
[2] Textiles and Textile Products 2017 Retrieved September 22, 2017, from http://www.mida.gov.my/home/textiles-and-textile-products/posts/
[3] Haque M 2008 Treatment of Textile Wastewater. Retrieved September 22, 2017, from http://www.cottonbangladesh.com/April2008/Wastewater.htm
[4] Malaysia Population 2017 Retrieved September 22, 2017, from http://www.worldometers.info/world-population/malaysia-population/
[5] Environmental Technologies Top Markets Report 2016 Retrieved from http://www.trade.gov/topmarkets/pdf/Environmental_Technologies_Southeast_Asia.pdf
[6] Environmental Requirements 2010 Retrieved from http://www.doe.gov.my/eia/wp-content/uploads/2012/03/A-Guide-For-Investors1.pdf
[7] Azman E, Mat T, Shaari J and How V K 2009 Wastewater Production, Treatment, and Use in Malaysia Retrieved from http://www.ais.unwater.org/ais/pluginfile.php/501/mod_page/content/87/report_malaysia.pdf
[8] Rapeia N S B M 2012 Basic Red 46 removal by a potentially low cost biosorbent (Perlis: Universiti Malaysia Perlis)
[9] Lim C H 2013 Optimization of phenolic removal using oil palm empty fruit bunch (OPEFB) biosorbent. (Perlis: Universiti Malaysia Perlis)
[10] Yusoff N H B M 2016 Application of mangifera indica (Mango) seed as a biosorbent for the removal of methyl red (Perlis:Universiti Malaysia Perlis).
[11] Cheong X Z 2016 Removal of copper ions from aqueous solution by papaya seeds (Perlis:...
Azhar Abd Wahid M, Hara H and Johari Megat Mohd Noor M 2016 A Review on Genetically Engineered Natural Coagulant Based on Moringa oleifera for Turbidity Removal Malaysian J. Civil Eng. 28 Special Issue(1) 26–34.

Moravec C M, Bradford K J and Laca E A 2008 Water relations of drumstick tree seed (Moringa oleifera): Imbibition, desiccation, and sorption isotherms Seed Sci. Technol 36(2) 311–24.

Hussin H, Abdullah S and Sharifuddin S 2017 Preparation and Characterization of Activated Carbon From Moringa Oleifera Seed Pod Cellulose 28 50–4.

Santhi T, Manonmani S and Smitha T 2010 Removal of methyl red from aqueous solution by activated carbon prepared from the Annona squamosa seed by adsorption Chem. Eng. Res. Bull. 14 11–8.

Bello O, Lasisi B, Adigun O and Ephraim V 2017 Scavenging Rhodamine B dye Using Moringa oleifera seed Chem. Speciat. Bioavail. 29(1) 120–34.

Agbahoungbata M Y, Fatombi J K, Ayedoun M A, Idohou E, Sagbo E V, Osseni S A and Aminou T 2015 Removal of reactive dyes from their aqueous solutions using Moringa oleifera seeds and Grewia venusta peel Desalination Water Treat 3994(January 2016) 1–9.

Hameed B H, Mahmoud D K and Ahmad A L 2008 Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste J. Hazard. Mater. 158(2–3) 499–506.