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ORGANIC POLLUTANTS ADSORPTION BY USING RICE HUSK ACTIVATED CARBON

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Abstract

Ammonium and malachite green dyes were selected as organic pollutants used, representing common agricultural and industrial wastes, respectively. In this research, rice husk was utilized into activated carbon using HCl chemical activation and then undergone a slow pyrolysis process known as HCl pre-treated rice husk activated carbon (RHAC) to treat ammonium and malachite green dyes pollution. The HCl pre-treated rice husk activated carbon was generated at different temperature ranges such as 350℃, 450℃, 550℃, and 650℃. There were 5 types of characterization analyses: moisture content analysis, ash content analysis, percentage yield of activated carbon, pH Zero Point Charge, and Fourier Transform Infrared Spectroscopy (FTIR). Based on the result, when the pyrolysis temperature increased, the moisture content of RHAC decreased while the ash content increased. FTIR spectra of RHAC showed various functional groups such as carboxylic acid, alcohol, ethers, esters, and others for adsorption of organic pollutants. pH 7.0 was the optimum in the pH Zero Charge analysis. Based on the characterization analysis, it could be concluded that RHAC550 was chosen as the most effective activated carbon. In addition, the optimum adsorbent dosage was 0.05 g, while the optimum contact time was 120 minutes. Besides, 2.5 ppm initial concentration and pH 7 were ideal conditions for both pollutants' adsorption processes. Lastly, kinetic analysis (pseudo-second-order) and isotherm analysis (Langmuir) was proved to be a better fit which depicted that it was a monolayer chemisorption process.

INTRODUCTION

Ammonium is an organic compound that includes a positively charged tetrahedral nitrogen as a part of its structure with the chemical formula NH^{4+}. Malachite green (MG) is widely used, especially in aquaculture, as a cationic dye. In the aquaculture industries (leather, cotton, wool and cotton), MG is a therapeutic agent to treat parasites, fungal and bacterial infections in fish and fish eggs, and antiseptic for external application on wounds and ulcers. Agricultural, commercial, domestic and industrial effluent and drainage significantly contribute to the contamination of surface and groundwater bodies by ammonium and MG dyes currently. A high level of ammonium ions in an aqueous solution will release unpleasant taste and odour problems, which can interfere with the life of aquatics and human beings when discharged. Meanwhile, MG has several toxic properties that can cause respiratory toxicity, teratogenesis, mutagenesis, and carcinogenesis. Furthermore, it is essential for humans and other beings to have clean potable water. The quality of raw and treated water is regulated under two standards in Malaysia. For example, in both raw and treated water, the acceptable limit for ammonium in drinking water is below

1.5 mg/L [1]. Therefore, it is important to remove the ammonium ions and malachite green dyes.

Several methods are used to remove the ammonium and MG dyes, such as ion exchange, biosorption, reverse osmosis, conventional nitrification and denitrification, adsorption and many others [29]. Adsorption technique is one of the efficient methods to treat them. This is because it is low cost, environmentally friendly, and has high removal efficiency for ammonium and MG dyes. It is commonly used on a large scale for commercial and water purification [2].

The major by-product of paddy residue is rice husk. The hard protective covering of the rice grain is a rice husk that can be separated from grains during the milling process. In addition, cellulose, hemicellulose and lignin are the main organic compounds of rice husk make it possible to be regarded as an adsorbent. It is an efficient, cost-effective, and easily available adsorbent for removing a wide range of organic pollutants such as ammonium and dyes [3]. Rice husk needs to undergo appropriate activation treatment to eliminate lignin, metal impurities, and other easily accessible functional groups to overcome the associated problems [4]. The HCl-activated rice husk has higher adsorption capacities than the natural rice husk. This chemical activation method is useful for modifying the surface of rice husk biochar to improve the adsorption efficiency [5].

In this research, the objective was to prepare and characterize HCl pre-treated rice husk-activated carbon. After that, it was used to evaluate the adsorption study of ammonium and MG dyes by using HCl pre-treated rice husk-activated carbon. Lastly, it was used to deduce the kinetic and isotherm analysis of ammonium and MG dyes adsorption by HCl pre-treated rice husk activated carbon.

MATERIALS AND METHODS

Preparation of Raw Material

Rice husk was collected from a rice mill factory and washed thoroughly with tap water to remove mud and water-soluble impurities. Next, it was dried in an oven at 105℃ for 24 hours to remove the moisture inside the rice husk [6]. The dried rice husk was then ground and sieved by using a 500 µm size sieve shaker to increase the rice husk's surface area. It was then kept in an air-tight container before undergoing the pyrolysis process to prevent further absorption of moisture.

Chemical Activation

Rice husk was impregnated into 0.1 M of hydrochloric acid for about 6 hours. It was then washed with distilled water three times to remove excess HCl. After that, the sample was dried again in an oven at 105°C for 24 hours. The dried chemically activated carbon was placed in an airtight container to prevent further moisture absorption.

Pyrolysis Process

Slow pyrolysis was chosen to produce rice husk-activated carbon. The chemically activated rice husk was pyrolyzed under oxygen-limited conditions in a muffle furnace at different temperature ranges, which were 350°C, 450°C, 550°C and 650°C. The heating rate was about 10°C per minute during the process and the HCl treated rice husk was carbonized for 1 hour for each temperature [7]. Approximately 100 g of dried chemically activated rice husk was weighed using an electronic mass balance before undergoing a slow pyrolysis process.

Characterization of Activated Carbon

Several methods of activated carbon characterizations were used in the study. They were moisture analysis, ash content analysis, percentage yield of activated carbon, pH zero-point charge and Fourier Transform Infrared Spectroscopy (FTIR).

Moisture Content Analysis

First, the temperature of the muffle furnace was adjusted to 750°C. Then, the porcelain crucible was placed in the muffle furnace for 10 minutes. After 10 minutes, it was then taken out and cooled in the desiccator for 1 hour. The porcelain crucible was weighed together with 1 g biochar which acted as a mass of sample with crucible before drying (C). The sample was placed in the drying oven at 105°C for 2 hours. After a while, the dried sample was shifted to the desiccator for an hour to cool down. The sample was reweighed again, acting as a sample mass with a crucible after drying (D) [8].

Ash Content Analysis

Ash content analysis was performed by heating the dried samples with the porcelain crucible in the muffle furnace at 750°C for 6 hours. During the heating process, the crucible lids were removed to ensure the complete combustion occurred. After 6 hours, it was cooled in the desiccator for 1 hour and weighed. The activated carbon was burnt until the mass loss was less than 0.005 g within a 1-hour period. It was preferable when the activated carbon had low ash numbers [9].

Percentage Yield of Activated Carbon

The synthesis of rice husk activated carbon was conducted by using a slow pyrolysis process. The percentage yield of activated carbon is defined as the ratio of the weight of the rice husk activated carbon to the weight of the raw rice husk [10].

pH Zero Point Charge

A total of 0.05g of rice husk activated carbon was introduced into 45 ml of 0.1 M KNO_3 solution until it reached 50 ml and was shaken for 24 hours at 250 rpm to reach equilibrium. For the preparation of 50 ml of 0.1 M KNO_3 solution, the initial pH of each KNO_3 solution was adjusted to different pHs 3, 5, 7, 9, and 11. The initial pH of KNO_3 was adjusted by using 0.1 M of NaOH or 0.1 M of HCl solution. After 24 hours, the final pH value of the supernatant will be measured by using the pH meter. The graph of final pH against initial pH would then be plotted.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was used to determine the samples' surface functional groups and chemical properties. Infrared radiation is electromagnetic radiation (light) with a longer wavelength than visible light. Some of the samples absorbed some of the infrared radiation or passed through the samples. Thus, the generated spectrum indicates the molecular absorption and transmission, creating a molecular fingerprint of the samples. The FTIR was performed in the range of 400 to 4000 cm^{-1} wavenumbers in order to characterize the surface organic functional groups for activated carbon. The samples were prepared by mixing the rice husk activated carbon with potassium bromide (KBr) is then compressing into pellets [11].

Adsorption Process

Performance of rice husk-activated carbon was investigated through adsorption. Several parameters were used to determine the ammonium and MG dye's adsorption capacity of activated carbon, such as contact time, adsorbent dosage, initial concentration and pH of ammonium and MG dyes.

Effect of Contact Time

Different contact times had been carried out, which were 5, 30, 60, 90, 120, 180, and 200 minutes to identify the effect of ammonium and MG dye's adsorption contact time of the activated carbon. This analysis was carried out in the incubator shaker at 30°C, speed of 250 rpm, ammonium and MG dye's initial concentration of 2.5 ppm, 0.05 g of adsorbent and pH of 7.

Effect of Adsorbent Dosage

There were five different adsorbent dosages which were 0.05g, 0.1g, 0.15g, 0.2g, and 0.25g, respectively. About 50 ml with a concentration of 2.5 ppm of ammonium and MG dyes solution were used for every sample. The condition of the adsorption process was at 30°C, 250 rpm, pH of 7 for 120 minutes. The solution was agitated in the incubator shaker [12].

Effect of Initial Concentration

There were five different concentrations of ammonium and MG dyes solutions which were 0.5, 1.0, 1.5, 2.0, and 2.5 ppm. About 0.05 g of the rice husk activated carbon was mixed with the 50 ml of different ammonium and MG dyes solution concentrations. The condition of the adsorption process was at 30°C, 250 rpm, pH of 7 for 120 minutes [13].

Effect of pH of Ammonium

The pH analysis was carried out using 2.5 ppm of ammonium and MG dyes solution with pH of 3, 5, 7, 9 and 11. About 0.05 g of the rice husk activated carbon was mixed with 50 ml of different pH values of ammonium and MG dyes solution. The different initial pH of ammonium and MG dyes solution was adjusted using the 0.1 M of HCl or NaOH solution. Next, the adsorption process then conducted at 30°C, 250 rpm, 2.5 ppm for 120 minutes [14].

Kinetic Study

In the adsorption kinetics, pseudo-first-order and pseudo-second-order kinetics model was used to examine the dynamical experimental data. It was used to estimate the adsorption rate, which was very important for the characterization of the performance of adsorbents. About 0.05 g of the rice husk activated carbon was mixed with 50 ml with a concentration of 2.5 ppm of ammonium and MG dyes solution. Then, the mixture was shaken in an incubator shaker at different contact times: 5, 30, 60, 90, 120, 180, and 200 minutes. The condition of the adsorption process was at 30°C, 250 rpm, pH of 7 and 2.5 ppm.

$$\text{Pseudo-First-Order} \quad : ln[q_e - q(t)] = lnq_e - k_1 t \quad (1)$$

$$\text{Pseudo-Second-Order} \quad : \frac{t}{q(t)} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (2)$$

Isotherm Study

The adsorption isotherm is an important factor in knowing the adsorption process mechanism in this research. Two of the isotherm equations were selected in this research: the Langmuir and Freundlich isotherms. About 0.05 g of rice husk activated carbon was mixed with different concentrations (0.5 ppm, 1.0 ppm, 1.5 ppm, 2.0 ppm, and 2.5 ppm) of 50 ml of ammonium and MG dyes solution. The condition of the adsorption process was at 30°C, 250 rpm, pH of 7 for 120 minutes [15].

$$\text{Langmuir} \quad : \frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} K_L} \left(\frac{1}{C_e}\right) \quad (3)$$

$$\text{Freundlich} \quad : \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (4)$$

RESULTS AND DISCUSSIONS

Characterization of Activated Carbon

Moisture Content Analysis

Moisture content analysis was used to determine the weight loss of the water content inside the rice husk-activated carbon during the drying process. This analysis was carried out using the raw rice husk and rice husk activated carbon at different temperature ranges such as 350, 450, 550, and 650℃. The moisture content of the rice husk activated carbon decreased from 0.018999% at 350℃ to 0.004157% at 650℃. At 550℃, the percentage of moisture content was the lowest (0.0005699%). This showed that the pyrolysis temperature is inversely proportional to the moisture content; as the temperature increases, the percentage of moisture content has been reduced [16]. Theoretically, as the temperature increases, it will cause more water on the surface of rice husk-activated carbon to vaporize, making the moisture content percentage decrease. As can be seen in the analysis, all RHAC showed the percentage of moisture content lesser than 10% which is preferable in most of the pyrolysis system [17]. It can be concluded that the RHAC550 was the optimum as it has the lowest percentage of moisture content.

Ash Content Analysis

The ash is undesirable as it will affect the adsorption performance of ammonium and MG dyes and be linked directly to the pore structure of activated carbon. To clarify, the percentage of ash content would also increase when the temperature increased. The percentage of ash content increased from 0.9170% (RHAC350) to 1.2659% (RHAC650). The ash content increase indicates that lignocellulosic's destructive volatilization matters as the temperature increases [18]. A high percentage of ash content means that the activated carbons contain high levels of impurities which lead to obstruction of the pores and the surface area on the activated carbon would be reduced. Therefore, it will affect the rice husk-activated carbon's ammonium and MG dye's adsorption capacity [19]. RHAC550 was the optimum adsorbent as it has a low percentage of ash content and is completely pyrolyzed compared to the RHAC350, which is not completely pyrolyzed. Thus, RHAC550 was selected instead of RHAC350.

The percentage yield of Activated Carbon

The percentage yield was declining gradually from 54.1995% (RHAC350) to 37.5877% (RHAC650). The RHAC350 has the highest percentage yield, but brownish, depicting that the process was incomplete pyrolysis. RHAC550 and RHAC650 were fully pyrolyzed as the rice husk activated carbon was black in colour. In this analysis, RHAC350 has the highest percentage yield of activated carbon. However, it has a high percentage of moisture and ash content which are undesirable. Therefore, RHAC550 was chosen as the optimum adsorbent as it has a low percentage of moisture and ash content compared to the RHAC350.

pH Zero Point Charge

Figure 1 indicates that the pH zero charge of rice husk activated carbon. Point of zero charge is the point on the pH scale where the sum of anion and cation exchange are in equilibrium [20]. All the rice husk-activated carbon was carried out in this analysis, such as RHAC350, RHAC450, RHAC550, and RHAC650. This analysis plays an important role in determining the optimal pH value for the adsorption process and expressing the adsorbent's surface charge and its interactions with adsorbates. Furthermore, if the pH value is less than pH_{ZPC}, the surface of activated carbon is positively charged, which will generate electrostatic repulsion and thus decrease ammonium and MG dyes adsorption. When the pH value higher than pH_{ZPC}, the surface of activated carbon is negatively charged which will produce electrostatic attraction and improve the ammonium adsorption [21]. Based on Figure 1, RHAC550 showed that the final pH was 6.96 when the initial pH was 7. Thus, pH 7 was the optimum pH in this study. RHAC550 could be said to be the ideal activated carbon and has been selected for the adsorption analysis.

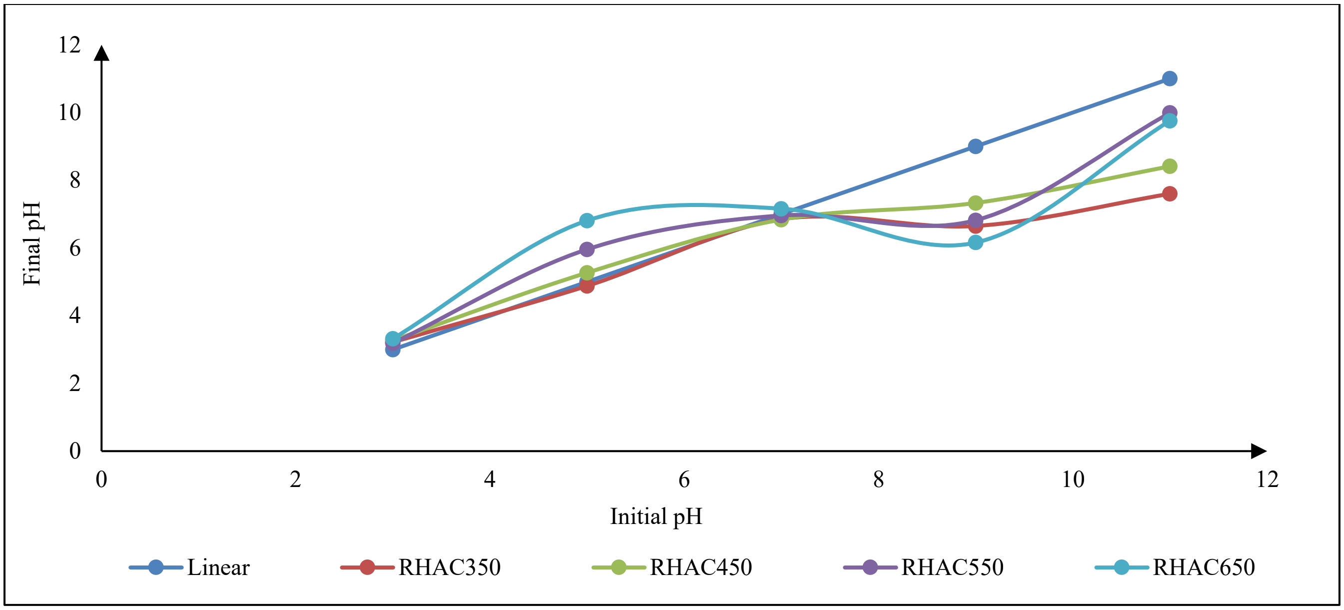


Figure 1: pH zero charge of Rice Husk Activated Carbon.

Fourier Transform Infrared Spectroscopy (FTIR)

According to Figure 2, it indicates that the FTIR spectra of raw rice husk (RAW RH), HCl treated rice husk (HCl treated RH) and Rice Husk Activated Carbon at 550°C (RHAC550). Broadband of the OH stretching vibration near 3440 cm^{-1} in the presence of alcohol, phenol, or carboxylic acid was observed. The adsorption peak for the raw rice husk is 3326.2 cm^{-1}. Then, the intensity of the peak of the HCl pre-treated rice husk has been increased to 3351.4 cm^{-1} may be due to the presence of hydrochloric acid. However, the intensity of rice husk-activated carbon (RHAC550) slowly diminished. Increasing the pyrolysis temperature will cause the loss of hydrogen and oxygen atoms due to the breaking bond from the hydroxyl group. The peaks around 1641.31 to 1737.74 cm^{-1} correspond to the C=O stretching that may be attributed to the hemicelluloses and lignin aromatic groups. The peaks located in the range between 1546.80 and 1652.88 cm-1 indicate the alkenes and aromatic functional group. However, the symmetric (~1050 cm^{-1}) stretching of C-O bonds in RHAC550 decreased due to the pyrolysis temperature increased would cause the degradation and depolymerization of the cellulose, hemicellulose, and lignin. Besides, the spectrum in the region between 1200 and 1000 cm^{-1} indicated C-O stretching vibrations of functional groups such as ethers, esters, alcohols and carboxylic acids [22]. Lastly, the peak at 807.42 represented the stretching vibration of Si-O bond for the raw rice husk, which means that it has high Si content. However, the peak of the HCl-treated rice husk and RHAC550 slowly disappeared due to the removal of inorganic materials from the surface of the rice husk by the HCl chemical activation. This observation shows the diminished silicon content of the chemically treated rice husk after HCl activation.

Adsorption Process

Effect of Contact Time

In this contact time analysis, it was conducted at different contact times (5, 30, 90, 120, 180 and 200 minutes), constant temperature (30°C), pH (7.0), initial concentration (2.5 ppm) of ammonium and MG dyes, 250 rpm and adsorbent dosage (0.05 g). Figure 3 depicts the effect of different contact times on the adsorption capacity of the RHAC550. In the adsorption process, the trend in the adsorption contact time will be divided into three stages. Initially, it can be seen clearly from Figure 3 shows that there is rapid adsorption of ammonium through mass transfer due to the ion concentration gradient between the solid and liquid phases during 5 to 30 minutes. At the same time, there is a strong, attractive force between the ammonium ions and the rice husk-activated carbon. Secondly, it is slower adsorption of ammonium which means that this stage is at the end of physical sorption and the equilibrium transfer between the solid and liquid phase with slight desorption happening during 30 to 120 minutes. At the last stage (120 to 200 minutes), it is a much slower stage and more gradual increase related to chemisorption and some extent of intraparticle diffusion occurring until saturation of the active sites [23]. For malachite green dye adsorption was fast at the initial stage and steadily slowed down before the optimum was achieved as shown in Figure 3. Therefore, 120 minutes was chosen as the optimum contact time for ammonium and MG dyes adsorption.

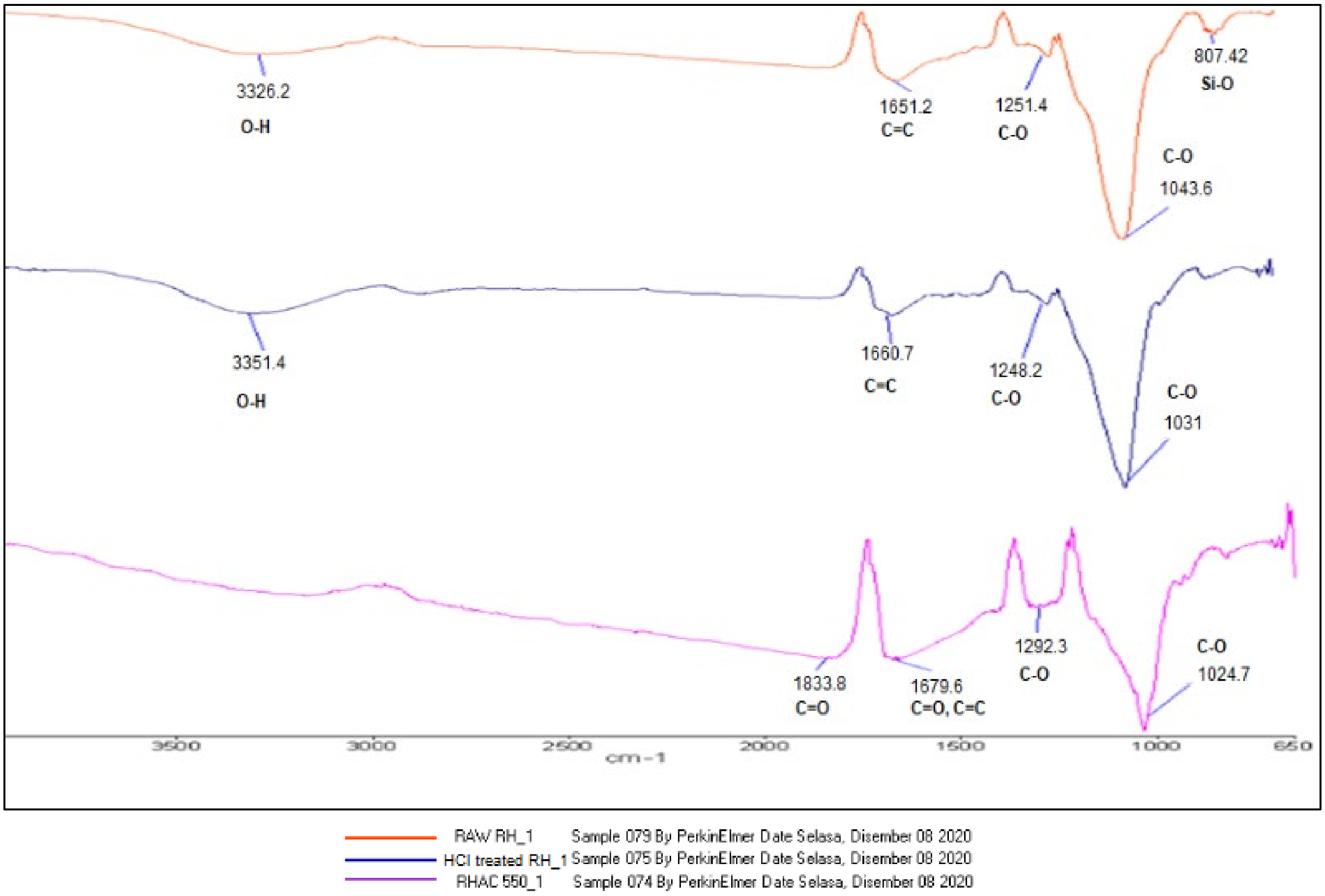


Figure 2: FTIR spectra of Raw Rice Husk (RAW RH), HCl treated Rice Husk (HCl treated RH) and Rice Husk Activated Carbon at 550°C (RHAC550).

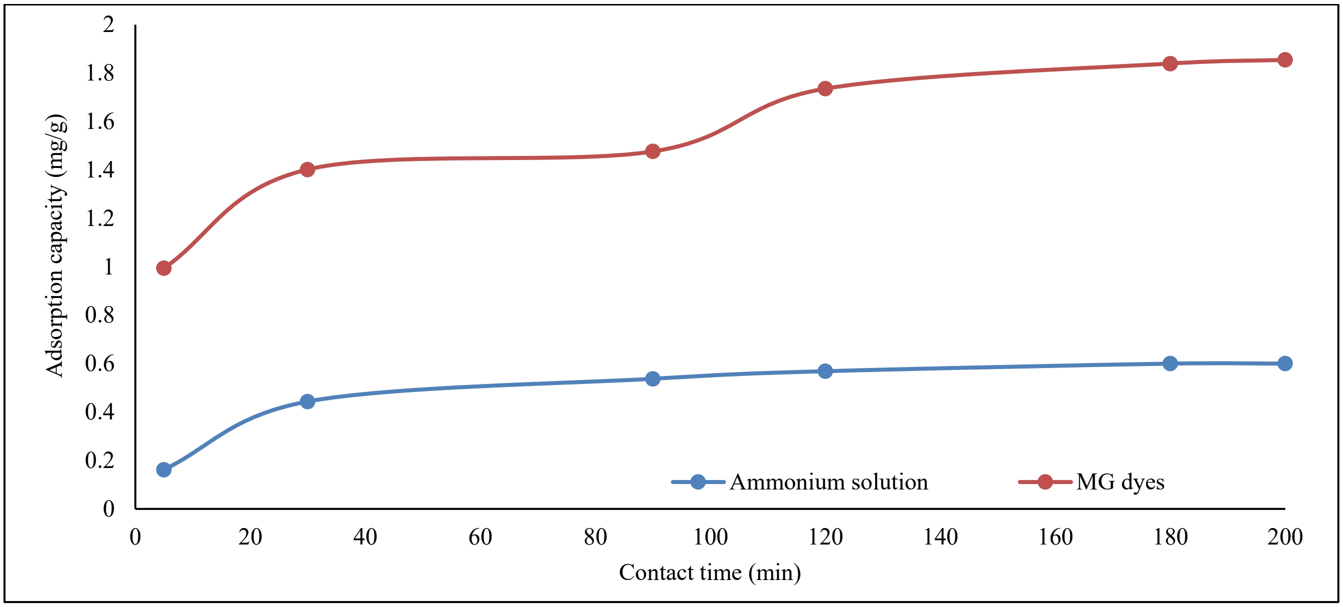


Figure 3: Graph of Ammonium and MG Dyes Adsorption Capacity of RHAC550 against Contact Time.

Effect of Adsorbent Dosage

In this research, it was carried out at different adsorbent dosages (0.05, 0.10, 0.15, 0.20 and 0.25 g of RHAC550), constant temperature (30℃), pH (7.0), initial concentration (2.5 ppm), 250 rpm and 120 minutes of contact time. Figure 4 indicates the effect of adsorbent dosage on the adsorption capacity of RHAC550. Based on Figure 4, the adsorption capacity of rice husk-activated carbon is inversely proportional to the adsorbent dosage. In other words, when the adsorbent dosage increases, the adsorption capacity of RHAC550 will be decreased. For ammonium, the adsorption capacity of RHAC550 is the highest (0.6520 mg/g) at 0.05 g and then decreases until 0.1182 mg/g, which is the lowest adsorption capacity at 0.25 g of RHAC550.

Meanwhile, the adsorption potential of MG was highest at 0.05 g. These phenomena occurred because there are lots of active sites when the adsorbent dosage is the lowest, which can be used to adsorb more ammonium and MG dyes on the rice husk-activated carbon. However, competitive adsorption of ammonium and MG dyes occurs on the surface-active sites when the rice husk-activated carbon increases. This will cause the adsorption capacity of ammonium and MG dyes to decrease slowly [24]. It may be due to the overlap of the adsorbent layers that cover the available active sites on the adsorbents when the adsorbent dosage increases. Therefore, 0.05g was the ideal adsorbent dosage for the ammonium and MG dyes adsorption.

Effect of Initial Concentration

For the initial concentration analysis, it was carried out by using a different initial concentration of ammonium and MG dyes (0.5 ppm, 1.0 ppm, 1.5 ppm, 2.0 ppm and 2.5 ppm), constant temperature (30℃), pH (7.0), adsorbent dosage (0.05 g), 250 rpm and 120 minutes of contact time. Figure 5 shows the effect of the initial concentration of ammonium and MG dyes solution on the adsorption capacity of RHAC550, respectively. Based on Figure 5, the adsorption capacity of rice husk activated carbon is increased gradually with the initial concentration of ammonium and MG dyes solution. The initial concentration of ammonium and MG dyes solution increases with the adsorption capacity. Based on both Figure 5, the adsorption capacity of the RHAC550 increased from 0.05015 mg/g (0.5 ppm) to 0.6520 mg/g (2.5 ppm). When the initial concentration of ammonium and MG dyes is lower, there are excess empty sites on the adsorbent surface.

In contrast, the initial concentration of ammonium and MG dyes increases will affect the mass flow of ammonium and MG dyes to the active sites of RHAC550. This may result from the provision of a powerful driving force from the initial concentration to overcome resistance to mass transfer of ammonium and MG dyes d between the aqueous solution and the solid phase. Ultimately, 2.5 ppm is the optimum initial concentration for ammonium adsorption.

Effect of pH of Ammonium

The ammonium adsorption of rice husk activated carbon was investigated by using different pH (3, 5, 7, 9 and 11), constant temperature (30℃), contact time (120 minutes), initial concentration (2.5 ppm), 250 rpm and adsorbent dosage (0.05g). Figure 6 shows the effect of ammonium solution's pH on the adsorption capacity of RHAC550. Based on Figure 6, it can be observed that the adsorption capacity of RHAC550 increased from 0.7432 mg/g to 2.1109 mg/g with increasing the solution pH from pH 3 to pH 7, which achieved the maximum ammonium adsorption at pH 7. After that, the adsorption capacity of RHAC550 decreased steadily from 2.1109 mg/g to 1.1079 mg/g with increasing the pH value above pH 7. There is a reduction of the hydrogen ions in the aqueous solution with increasing the pH value. Therefore, the competition between the hydrogen ions and ammonium ions to be adsorbed on the active sites of rice husk activated carbon was reduced [25]. When the pH was below 7, the concentration of H^+ ions increased and competed effectively with ammonium ions to adsorb on the surface of activated carbon. Thus, the uptake of ammonium ions by electrostatic forces decreased. When the solution's higher pH value (beyond pH 7), most ammonium ions (NH4+) changed to aqueous NH_3, which inhibited electrostatic attraction and reduced ammonium adsorption capacity. In other words, this may be due to the decrease in the number of ammonium ions reduced the degree of interaction between the contaminants and active sites on the rice husk-activated surfaces [26]. In brief, pH 7 was the optimum pH for ammonium adsorption.

Based on Figure 6, the adsorption capacity of Malachite Green dye improved as the pH of the mother solution raised from pH 3 to pH 7, reaching the optimum adsorption rate of Malachite Green dye at pH 7. After that, with the pH value above pH 7 increasing, the adsorption capacity decreased gradually. The hydrogen ions in the aqueous solution decrease as the pH value increases. The competition between the hydrogen ions and the Malachite Green ion to be adsorbed at the active sites of rice husk activated carbon was thus minimized. As the solution's pH value is higher, the H^+ concentration would be lower. Therefore, the lower H^+ ions would interfere with the adsorption of Malachite Green dye, allowing the ability of Malachite Green dye adsorption to increase [30]. Additionally, the figure shows that when the pH exceeds 7, there is a decline in the adsorption potential of the Malachite Green dye.

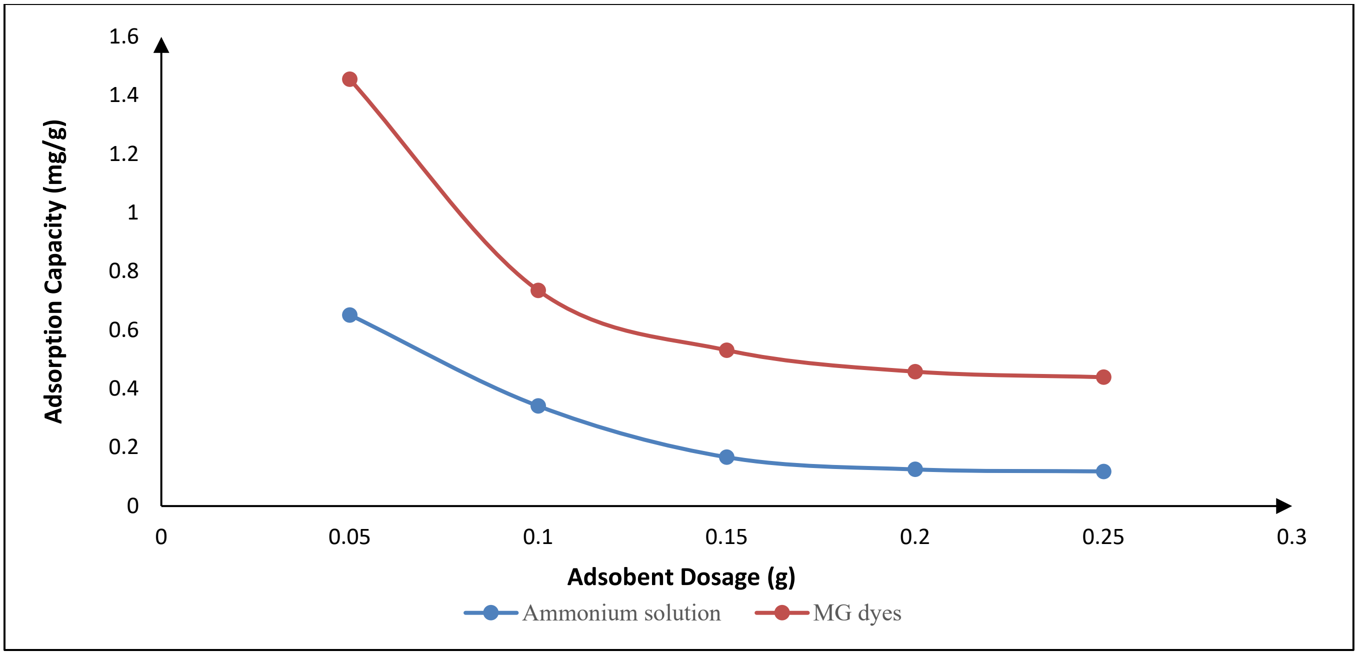


Figure 4: Graph of ammonium and MG dyes adsorption capacity of RHAC550 against adsorbent dosage.

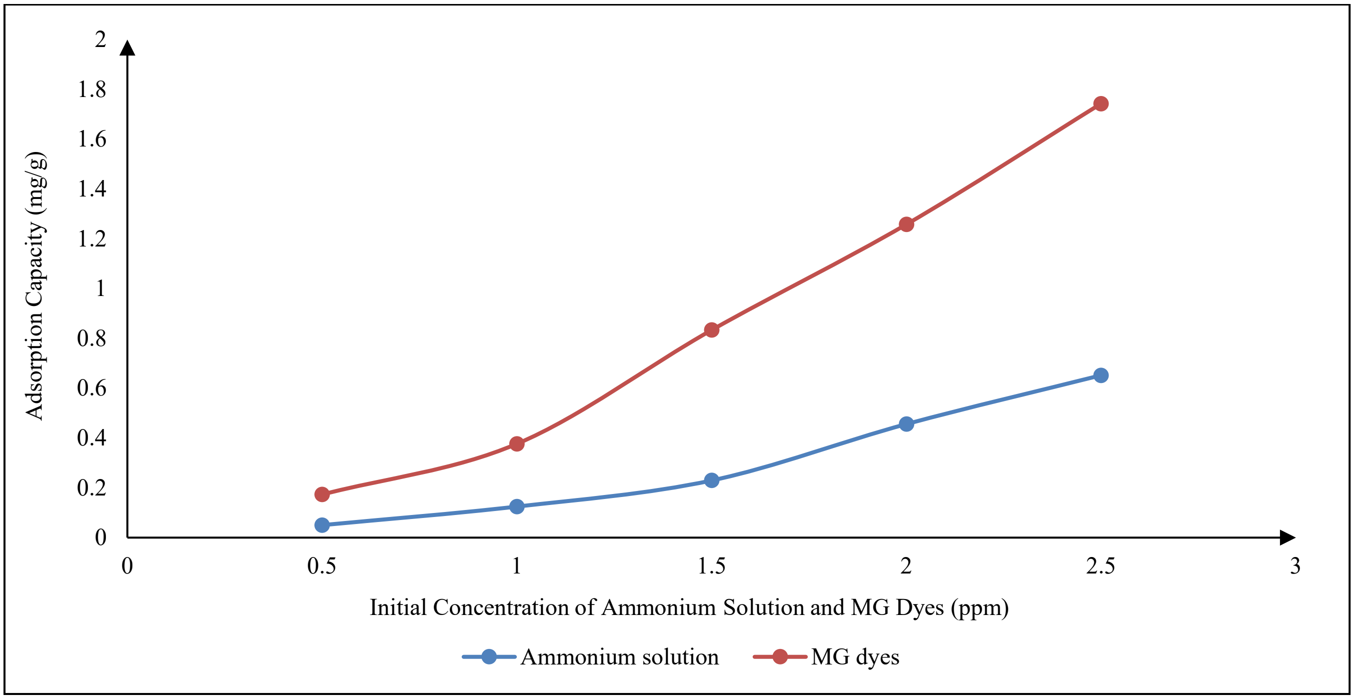


Figure 5: Graph of ammonium adsorption capacity of RHAC550 against initial concentration of ammonium solution and MG dyes.

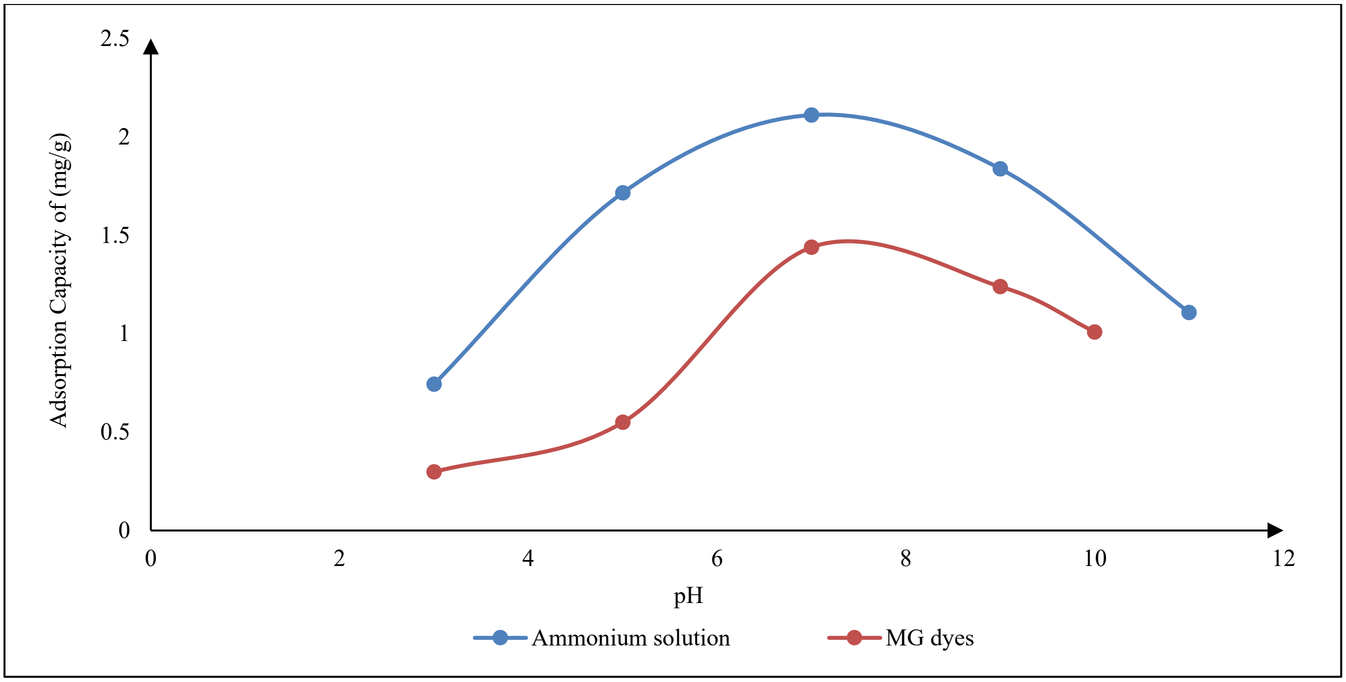


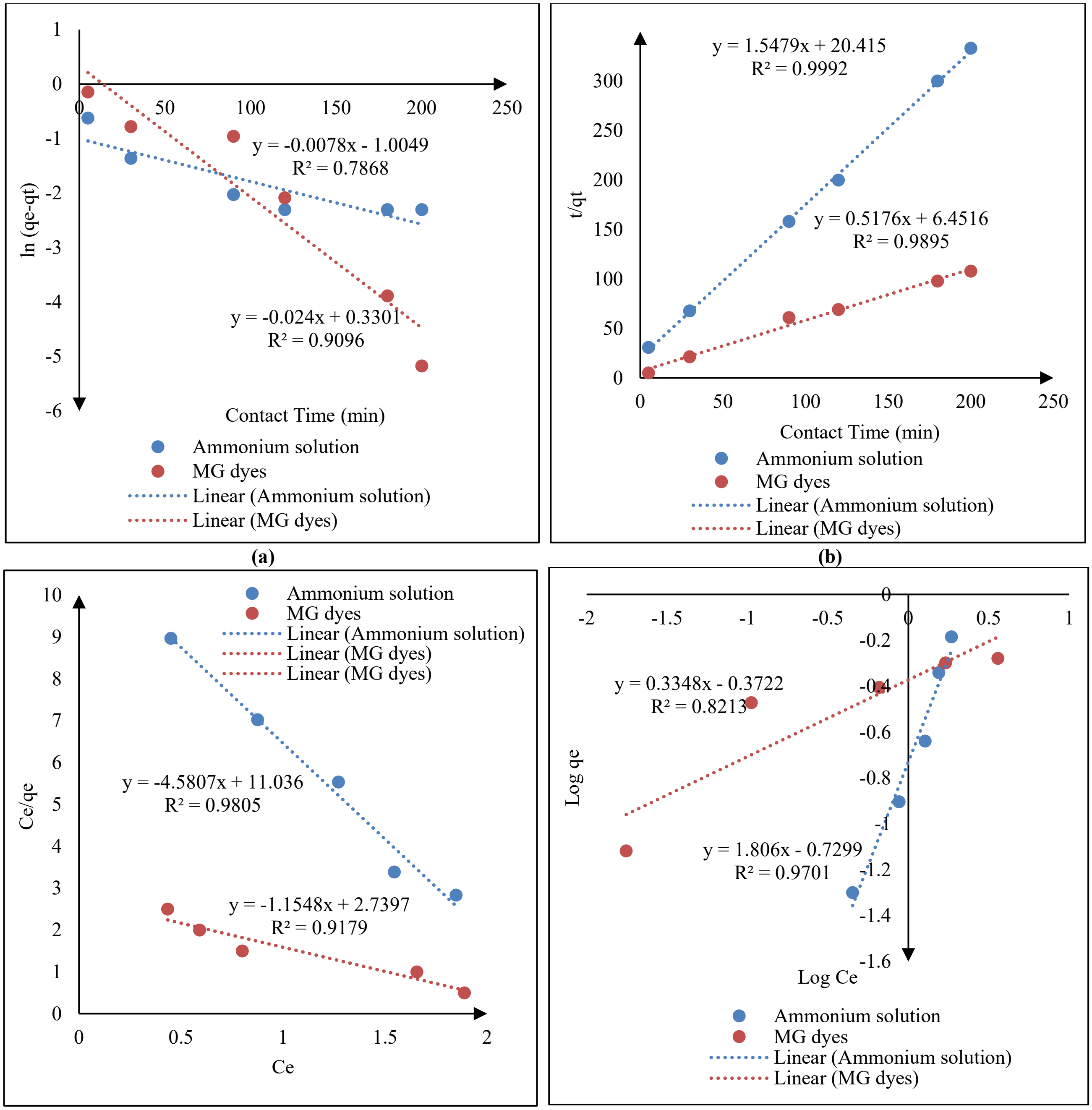
Figure 6: Graph of ammonium and MG dyes adsorption capacity of RHAC550 against pH.

Kinetic Study

Adsorption kinetic analysis can help determine the adsorption rate and understand the adsorption mechanism. Figure 7a shows the graph of pseudo-first-order and Figure 7b depicts the diagram of pseudo-second-order. For ammonium adsorption, the correlation coefficient values (R^2) of the pseudo-second order model (0.9998) are higher than R^2 of pseudo-first order model (0.9846). Based on Figure 7a and Figure 7b the R^2 value for the pseudo-second order was 0.9896, closer to 1 than the pseudo-first order, 0.8967, for MG dyes adsorption. Thus, the adsorption of ammonium and MG dyes using the rice husk-activated carbon in this experiment follows the pseudo-second order model. There is more than one step may involve in the adsorption process which are diffusion of ammonium and MG dyes from bulk solution to the external surface of adsorbent, followed by the internal diffusion of ammonium and MG dyes from a macroporous to the microporous site [27]. The pseudo-second order model is the best fit, which means that the adsorption process that occurs in this experiment is chemisorption.

Isotherm Study

Adsorption isotherm analysis was used to imply the process of the adsorbed molecules being distributed between the solid and liquid phase when the adsorption process reached equilibrium [28]. Figure 7c shows that it was the Langmuir isotherm model, which means that it was specific for monolayer adsorption and took place at specific homogenous sites within the adsorbent. Nonetheless, Figure 7d depicts that the Freundlich isotherm model showed that the multilayer adsorption occurred. There was the formation of multilayer adsorbate onto the heterogeneous surface of the adsorbent. The correlation coefficient (R^2) values for Langmuir isotherm model were 0.9805, while the Freundlich isotherm model was 0.9701 for ammonium adsorption by RHAC550. For MG dyes solution, based on Figure 7d, the frequency of R^2 Langmuir isotherm was 0.9179, which was equivalent to 1 compared to Freundlich isotherm, which was 0.82133. The R^2 for Langmuir isotherm model was near to 1 when compared with the Freundlich isotherm model for both pollutants adsorption. As a result, Langmuir isotherm model has a perfect fit for adsorbents which means that the monolayer adsorption would be the dominant process.



(a) (b)

(c) (d)

Figure 7: Graph of a) pseudo-first-order for ammonium and MG dyes adsorption b) pseudo-second-order for ammonium and MG dyes adsorption c) Langmuir Isotherm for ammonium and MG dyes adsorption d) Freundlich Isotherm for ammonium and MG dyes adsorption.

CONCLUSION

Based on the characterization analysis, RHAC550 was the ideal activated carbon for the ammonium and MG dyes adsorption process. For the contact time analysis, 120 minutes was the optimum contact time for the ammonium and MG dyes adsorption process. Before reaching 120 minutes, the adsorption capacity kept increasing. After 120 minutes, the adsorption capacity became constant as there was no empty site for the ammonium and MG dyes to adsorb on the surface of rice husk-activated carbon. For the adsorbent dosage analysis, 0.05 g was the excellent adsorbent dosage for the ammonium and MG dyes adsorption process. This is because it has higher surface area and active site when the adsorbent dosage is lower. However, when the adsorbent dosage increased, the ammonium and MG dyes adsorption capacity decreased may be due to the overlapping of adsorbent, which would block the active site of the adsorbent. For the initial concentration analysis, 2.5 ppm was the ideal initial concentration. The initial concentration of ammonium and MG dyes solution increased would make the adsorption capacity also increased. This may result from the provision of a powerful driving force from the initial concentration to overcome resistance to mass transfer of ammonium and MG dyes between the aqueous solution and the solid phase. For the pH analysis, the optimum pH of ammonium and MG dyes solution is pH 7. Based on the kinetic study of ammonium and MG dye's adsorption process, the pseudo-second-order model was the best fit due to the R^2 nearest to 1 compared to the pseudo-first-order model. This depicted that the chemisorption is the rate-limiting step in this ammonium and MG dyes adsorption process. For the adsorption isotherm analysis, R^2 for Langmuir isotherm model was near to 1 compared with the Freundlich isotherm model. Thus, Langmuir isotherm model has a perfect fit for adsorbents which means that it was the monolayer adsorption process.

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CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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