Direct Plant-Surfactant Based Impregnated Activated Carbon for Adsorption of Reactive Dye

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***Abstract*— In textile industry, there is major problem concerning colour effluent in 'excess with serious consequences to human health and environment. In this work, surfactant impregnated activated carbon has been chosen as the adsorbent in the adsorption process. The aim of this study is to characterized of critical micelle concentration (CMC) of plant-based surfactant and activated carbon and to investigate the direct impregnation plant-based surfactant on activated carbon. The suspension was prepared by using direct impregnated plant based surfactant method. The best reacting condition was found to be at 125 mg/L surfactant loading with 88.56% of RB4 removal efficiency. Moreover, the ideal temperature for process was found to be at 40°C with highest percentage of removal at rate 52.84% and pH value was at pH 7 with 98.41% removal.**

Keywords- plant based surfactant, activated carbon, reactive blue 4, direct impregnated activated carbon

I. Introduction

Textile industry which consumed large volumes of water will produce large amount of wastewater from different steps in dyeing and finishing processes. Due to the large amount of textile wastewater effluent, dye pollutants represent one of the major environmental problems. About 15% of the dye is lost during dyeing and finishing processes and is released in wastewater (Ersöz, 2014).

Dyes usually have a synthetic origin and complex aromatic molecular structures which possibly come from coal-tar based hydrocarbons such as benzene, toluene and xylene. Reactive dyes are most typical type of dyes due to their favorable properties such as bright colour, water-fatness and simple application techniques. Unfortunately, reactive dyes have been detected as problematic compounds due to its solubility in water that caused the concentration to be higher than other type of dyes in the textile effluent.

Adsorption was found to be a promising technique for dye removal from the textile effluent. Furthermore, by using adsorption method, there was reported not to present environment issues due to absence of sludge and yield high quality of purified water (Mahmoud, Sharaf El-deen, & Soliman, 2014). Moreover, due to availability of adsorbents, its simplicity in operation and high efficiency making adsorption as usual method to treatment of wastewater for dye removal. In reality, this type of method is focused in the use of natural solid materials, which are able to remove pollutant such as reactive dye in the wastewater with low-cost. Clay minerals, siliceous materials or zeolites are proposed as natural adsorbent based on their physical and chemical interactions with the dyes. Based on the previous research, activated carbon is among the best as adsorbent in adsorption of pollutant such as heavy metals. This is because of activated carbon have large surface area, porous structure, high adsorption capacity and large reactive surface. Also, due to its exceptional high surface area which ranges from 500 to 5000 m^2g^{-1}), well developed micro porosity and wide spectrum of surface functional group making the activated carbon is widely used in wastewater treatment. On the other hand, the physical properties of the activated carbon are depending on the manufacturer which produced activated carbon, nature of raw materials, activating agents and conditions of activation (Mahmoud et al., 2014).

However, functional group of the activated carbon is not sufficient enough to adsorb the metal ion economically. So, several modification methods have been introduced such as surface modification and chemical or physical treatment, which modified the surface of the activated carbon to increase its adsorption capacity towards metal ions. The modification of activated carbon with cationic surfactant for adsorption of anionic contaminants has been studied by many previous researches (Lin, Chen, Cheng, & Li, 2013). This is because the ability of surfactant such as to foam, form self-assembled structures and adsorb to surfaces of support makes them widely for industrial and domestic wastewater treatment (Krivova, Grinshpan, & Hedin, 2013).

Nonetheless, there have drawback of ineffectiveness if activated carbon treated chemically in present of acidic solution. Thus, surfactant was used in surface modification because it can enhance the adsorption capacities of the activated carbon for adsorption of metal ions. Based on the current study, the surfactant impregnated activated carbon has been used for removal of Ce(IV) radionuclides from aqueous solutions (Tsang et al., 2007).

The aim of this study is to study the characterization of critical micelle concentration (CMC) of plant-based surfactant and activated carbon. Also, to investigate the direct impregnated plant based surfactant on activated carbon. Also,

II. MATERIALS AND METHODS

A. Materials

Granular activated carbon (GAC) was used as the solid support material in the adsorption process. It was obtained from the supplier which is Soon Ngai Engineering. The Reactive Blue (RB4) which is 35% purity was purchased from Sigma Aldrich. The sodium hydroxide with 97% purity was purchased from Merck Chemicals. Also, the plant-based surfactant, Stepantex SP90 was obtained from the Age D'or Industrial Sdn Bhd. The chemical structures of these materials are shown in Figure 1 and Figure 2.

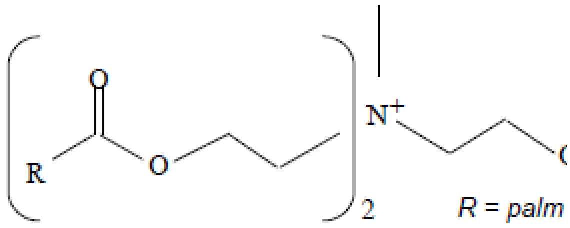

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Figure 1: Stepantex SP90

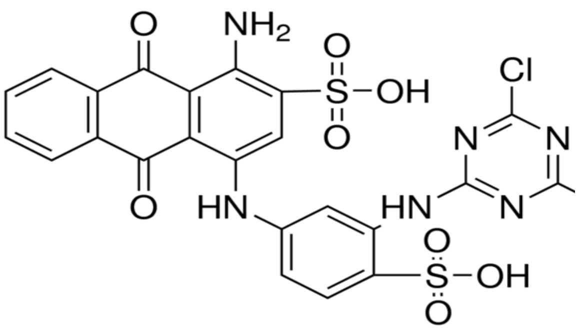

Figure 2: Reactive Blue 4 (RB4)

B. Conductivity test by using UV-Vis Spectrophotometer

The experiment is carried out at room temperature (25°C). The ten different samples with different concentration such as 20 ppm, 40 ppm, 60ppm, 80 ppm, 100 ppm, 120 ppm, 140 ppm, 160 ppm, 180 ppm and 200 ppm were prepared. 1 mL of 0.1wt% RB4 was added into 50 mL of plant based surfactant sample. The solution was mixed for 10 minutes at 300 rpm by using hotplate stirrer. The reaction between the surfactant and RB4 dye produced soluble precipitate and filtered. The filtrate solution which consist of dye-surfactant mixture was analyzed by using UV-Vis Spectrophotometer.

C. Direct Plant-Based Impregnated Activated Carbon

Batch adsorption experiment were conducted to study the adsorption of reactive dyes into surfactant-impregnated activated carbon (SIAC). In this experiment, 250 mL of conical flask was used in every experiment. The granular activated carbon (GAC) and plant-based surfactant (PBE) were applied to adsorb selected dye which is RB4 from Sigma Aldrich. A 1.5 g of GAC was mixed with the calculated amount of PBE surfactant along with 12.5 mL of dye solution in the conical flask. Then, all the conical flask contains solution were place in the batch incubator shaker at 130 rpm at room temperature 30 ºC for 7 hours to produce SIAC. During the 7 hours duration, the samples were taken in every 1 hour interval. The mixture was filtered by using filter paper. The concentration of the dye in the filtrate solution was determined by using UV-visible spectrophotometer at 595 nm wavelength of maximum absorbance (Tsang et al., 2007). Meanwhile, the filtrate AC was dried in the oven at 60°C for 12 hours and was analyzed by using Fourier Transform Infrared Spectroscopy (FTIR). The kinetic of adsorption was studied using 25 mgL^{-1} dye solution.

D. Chemical and Physical Characteristic of AC

The characterization of the AC and SIAC were performed before and after the impregnation process. The binding strength of PBE surfactant with AC were determined based on changes in funtional group of AC after impregnation process and was conducted by using Fourier Transform Infrared Spectroscopy (FTIR).

E. Preparation of dye solution

Basically, dye solution was prepared by dissolving 0.0125 g of Reactive Blue 4 (RB4) in 500 mL of deionized water. Then, the stock solutions were diluted to the required initial concentration at 25 mg/L for catalytic activity process.

F. Effect of various parameter

Surfactant loading, temperature and pH are important parameters in adsorption process. These parameters need to be optimized in order to achieve the objectives of the experiment.

The effect of PBE surfactant loading on AC was studied by varying the amount of surfactant from 100 mg/L, 115 mh/L, 125 mg/L, 135 mg/L and 145 mg/L. The pH, agitation speed and temperature were maintained at pH 5, 130 rpm and 30°C, respectively. A 1.5 g of GAC was mixed with the calculated amount of PBE surfactant along with 12.5 mL of dye solution in the conical flask. Deionized water was added into the samples to fill in the 250 ml conical flask. Then, all the conical flask contains solution were place in the batch incubator shaker at 130 rpm at room temperature 30 ºC for 7 hours to produce SIAC. During the 7 hours duration, the samples were taken in every 1 hour interval. The mixture was filtered by using filter paper. The concentration of the dye in the filtrate solution was determined by using UV-visible spectrophotometer at 595 nm wavelength of maximum absorbance. The kinetic of adsorption was studied using 25 mgL^{-1} dye solution.

The effect of temperature on solution was conducted with surfactant loading, 125 mg/L at various temperature which are at 40°C, 50°C and 60°C. The pH of the solution was maintained at surfactant natural pH which is around pH 5.5. After that, 1.5g of AC was mixed with the calculated amount of PBE surfactant along with 12.5 mL of dye solution in the conical flask. Deionized water was added into the samples to fill in the 250 ml conical flask. Then, all the conical flask contains solution were place in the batch incubator shaker at 130 rpm at room temperature 30 ºC for 7 hours to produce SIAC. During the 7 hours duration, the samples were taken in every 1 hour interval. The mixture was filtered by using filter paper. The concentration of the dye in the filtrate solution was determined by using UV-visible spectrophotometer at 595 nm wavelength of maximum absorbance. The kinetic of adsorption was studied using 25 mgL^{-1} dye solution.

Another experiment was conducted by using different initial pH of surfactant which are at pH 7 and pH 9. The pH of the suspensions was adjusted before conducted the experiment by using 0.1 M of sodium hydroxide (NaOH). The other parameters were maintained with 125 ppm surfactant loading and at temperature 40°C. Then, all the samples were agitated at 130 rpm for 7 hours. The samples were taken every 1-hour interval and were analyzed by using UV-Vis spectrophotometer at wavelength 595 nm.

III. RESULTS AND DISCUSSION

A. Conductivity test by using UV-Vis Spectrophotometer

In conductivity test, surfactant and dye was undergone different method in conducting the catalytic activity. Conductivity test was conducted to obtained the critical micelle concentration of the surfactant in the presence of dye. The conductivity test was conducted by using UV-Vis spectrophotometer at range 800 nm to 200 nm in order to observe the surfactant behavior at different concentration (Puasa, 2013).

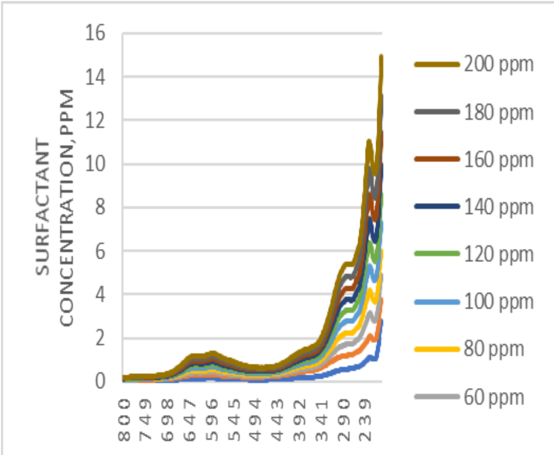

Figure 3: The UV-Vis spectrophotometer recorded data for changing the concentration of surfactant in RB4 at wavelength 800 nm to 200 nm.

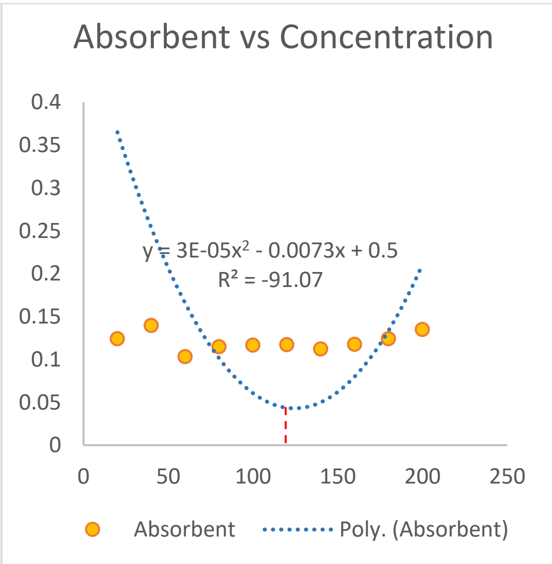

Figure 4: The recorded data of different surfactant concentration at wavelength 595 nm.

The graph in Figure 3 represented the magnification of the recorded spectra in the wavelength range of 800 nm to 200 nm. Meanwhile, the data from the Figure 3 has been extracted and simplified to become new graph as shown in Figure 4. It shows that the critical micelle concentration can be obtained by plotting the graph of absorbent versus concentration at wavelength 595 nm.

Based on Figure 4, the curve of the graph decreased at the beginning because of the precipitation occurred. At certain point, the curve started to bend upward which is increased. It is because of the agglomeration of the micelle and more dye has been absorbed by the micelle (Puasa et al., 2013). The graph in Figure 4 also shows that the point of CMC was determined by using quadratic formula which is at 125 mg/L.

B. *Effect surfactant loading*

The effect of surfactant loading on the AC was investigated by preparing the AC and RB4 with different concentration of surfactants (100 mg/L, 115 mg/L, 125 mg/L, 135 mg/L and 145 mg/L). The results are shown in Figure 4.

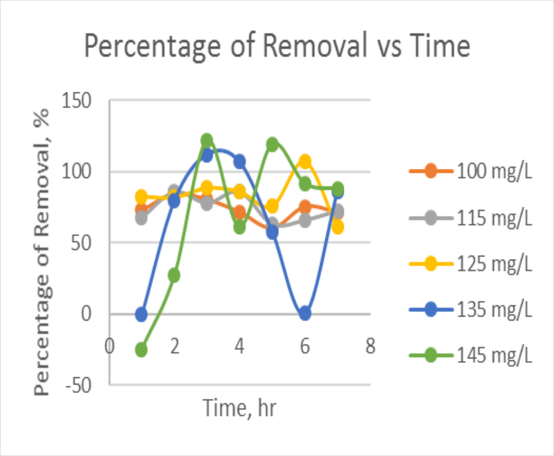

Figure 4: Effect of surfactant loading in 7 hours. Reaction condition: [RB4] = 25 mg/L, activated carbon dosage = 1.5 g, temperature = 30°C and agitation speed = 130 rpm.

The results showed that the percentage of removal of the RB4 influenced by the concentration of the surfactant loading. The best percentage of removal was obtained at 125 mg/L of surfactant loading with highest percentage 88.56% removal within 7 hours reaction time. Basically, the concentration will increase as the surfactant loading increased and it will have leveled off when it reached certain value. Based on that theory, the result in Figure 4 shows that the percentage of removal for concentration below CMC value (100 mg/L, 115 mg/L, 125 mg/L) is higher than concentration above CMC (135 mg/l and 145 mg/L). It is because of the surfactant molecules was easily adsorbed onto activated carbon due to its existence as monomer when the concentration was lower than CMC. The micelle formation also was initiated when the concentration approaching CMC. Due to micelle formation, the amount of surfactant attached to the activated carbon was limited since the micelle aggregation occurred or their hydrophobic tails already agglomerated between them. According to Lin et al. (2013), micelle diameter gave some impact to the adsorption process between surfactant and activated carbon when at the lower concentration, the micelle were formed and it may be difficult to diffuse into the activated carbon's pores. Meanwhile, the higher concentration of surfactant loading took more time to form micelle and give high chances to diffuse more into the activated carbon pores (Lin et al., 2013). Therefore, the optimum surfactant concentration is at 125 mg/L with percentage of removal 88.26%. The following parameters which are effect of temperature and effect of pH were using same surfactant concentration which is at 125 mg/L.

C. *Effect of temperature*

The effect of temperature was investigated by varying the temperature from 40°C to 60°C and using surfactant concentration at 125 mg/L. Based on the Figure 5, The temperature at 40°C showed highest percentage of removal of RB4 at rate 52.84% compared to temperature 50°C and 60°C, their highest percentage of removal of RB4 are 8.47% and 10.55% respectively. The percentage of removal of RB4 dye was slowly decreased along the reaction time at all temperature. It also stated that during the adsorption process, the dye molecules bind to the loaded surfactant molecules via van der Waals force. Also, as the temperature increased, the van der Waals force might decreased which means the interaction between the surfactant molecules and the dye molecules are weak (Zhang, Dong, Sun, Wu, & Li, 2017).

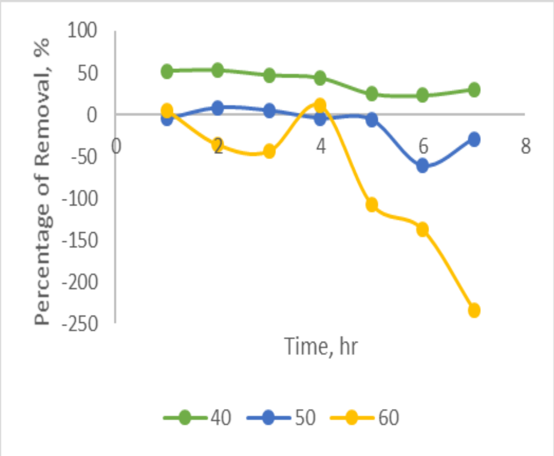

Figure 5: Effect of temperature within 7 hours. Reaction condition: [RB4] = 25 mg/L, activated carbon = 1.5 g, surfactant loading = 125 mg/L and agitation speed = 130 rpm.

D. *Effect of pH*

The initial pH of the surfactant solution is important factor that controls the removals of dye.

The effect of pH on the adsorption efficiency of activated carbon was varied at pH 7 and pH 9 by using surfactant concentration at 125 mg/L and temperature at 40°C.

Based on the graph constructed in Figure 6, the percentage of removal of RB4 dye was higher at pH 7 which is 98.41% compared to pH 9 which at rate 95.87%. In contrary, as the pH values increased, the percentage of removal of RB4 also increased. It is because if the pH values are lower or acidic, there are attributed to the competition between the hydrogen and surfactant ions for the binding sites of the activated carbon. Thus, the higher pH values contributed to the decreased in hydrogen ions concentrations and activated carbon surfaces provided more negatively active sites to the cationic surfactant to bind with (Mahmoud et al., 2014).

However, it was found that RB4 removal was effectively higher at lower pH values which is at pH 2 (Vakili et al., 2017). On the other hand, the amount of surfactant loading also might affected the percentage of RB4 removal at certain pH values.

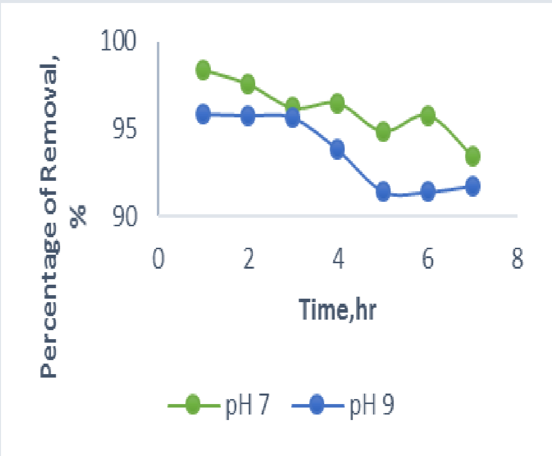

Figure 6: Effect of pH within 7 hours. Reaction condition: [RB4] = 25 mg/L, activated carbon = 1.5 g, surfactant loading = 125 mg/L temperature = 40°C and agitation speed = 130 rpm.

IV. CONCLUSION

The result and analysis showed that the best amount of surfactant loading was 125 mg/L with 88.56% of RB4 removal efficiency. Moreover, the ideal temperature for process was found to be at 40°C with highest percentage of removal at rate 52.84% and pH value was at pH 7 with 98.41% removal.

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