Indirect Plant-based Surfactant Impregnated Activated Carbon for Adsorption

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***Abstract*—Activated carbon is widely used in removing toxic substances and contaminants in wastewater. However, removal of metals and inorganic wastes is nearly inefficient when using activated carbon-based adsorption as it removes organic compounds. Surface modification and impregnation method were used to improve surface adsorption and to produce high selectivity to carbon. In this study, surfactant is used to impregnate with the activated carbon to improve the adsorption efficiency and the reaction itself. Indirect impregnation was selected to modify the surface of activated carbon with surfactant in removing 25 ppm of RB4 dye. Various parameters such as surfactant loading, operating temperature and initial pH of the solution were studied to obtain an optimum condition for adsorption of Reactive Blue 4 dye. Optimum condition of 135 mg/L of surfactant loading at 60°C in weakly acidic condition has been achieved with maximum percentage of 71.47% removal efficiency in 4 hours of treatment. It was observed that modification of activated carbon by indirect impregnation with surfactant has effectively removed RB4 dye because of the strong interaction between the activated carbon and surfactant that increased the number of active site on the surface.**

Keywords— Activated carbon, Adsorption, Reactive dye, plant-based surfactant, and indirect impregnation.

I. INTRODUCTION

The textile industry is commonly known as one of the energy and water consuming industries that cause intense pollution. The consumptions of the uses of water is approximately ranged from 200-400 L of water per kilogram of finished product [1].The quantity of wastewater from the textile industries have been increasing as the demand growing but it contains many harmful dyes that could cause health problems including Reactive Blue 4 (RB4).The chemical structure of azo dyes includes of a group of double bond of Nitrogen, N atom conjugated with aromatic systems, and when joined to molecules they become monoazo, diazo or polyazo dyes [2]. According to [3], azo dyes make up the biggest class of dyes and mostly used in textile and food industries, and widely utilized to colour solvents, wool, leather, paints, varnishes, paper, plastic, medicine, and cosmetics.

In general, the dyes give a huge impact to the aquatic life in terms of toxicity while referring to [4], it can cause severe damage to human beings, such as dysfunction of kidneys, reproductive system, liver, brain and central nervous system. Due to these problems, wastewater requires an appropriate treatment before releasing into the river. In order to treat textile effluents, there are several technologies that have been widely used which are physical, chemical and biological method [5]. All methods have been improved by varying in effectiveness, economic cost, and environmental impact.

Even though these methods have been widely utilized, they still have several disadvantages. The biological methods needed longer time and they are usually less efficient in removal of dyes that have highly structured polymers with low biodegradability and it also cannot to apply to all textile waste water due to the toxicity of most commercial dyes to the organisms used in the process [6]. Chemical coagulation can result with more pollution that caused by unwanted reactions in treated wastewater and it also generates large amounts of sludge [7]. The chemical degradation uses oxidizing agents like chlorine and it was one of the effective methods. However, it produces the toxic products like organochlorine compounds [8].

Modified activated carbon is capable to enhance its hydrophobic internal surface by attracting various type of chemicals. The development of surface modified activated carbon has created a diversity of activated carbon with far superior adsorption capacity [9]. Surface impregnation is an important part of this modification. Impregnation is defined as the well-distributed chemicals or metal particles in the pores of activated carbon. According to [10], study proves that chemical modification of carbon surfaces is necessary to improve the selectivity of carbon for chemical compound.

In recent days, surfactant is used as a development to improve adsorption in removing the toxic substances in wastewater treatment. Surfactant is a unique group of compounds consisting both hydrophobic long-chain and hydrophilic polar head group in the structures [10,11]. Complex systems introduced that surfactants were widely used in membrane protein separation, crystallization, purification and stabilization. Since the physicochemical properties of solutions below and above critical micelle concentration (CMC) demonstrate drastic changes, such as surface tension, electrical conductivity, turbidity, osmotic pressure, density, viscosity, and light scattering [12]. Surfactant impregnation has been widely applied for modification of different adsorbents such as clay, biomass and activated carbon with outstanding outcomes [13]. Based on [14], the surfactant-impregnated activated carbon adsorbs heavy metals in wastewater more efficiently than unmodified activated carbon. Many studies prove that the surface modification by impregnation can remove toxic substances and heavy metal particles in wastewater effectively.

In this study, the physiochemical properties of plant-based surfactant were investigated by studying the critical micelle concentration (CMC). The capacity of the activated carbon was being improved by impregnating with cationic surfactant to obtain an optimum condition for the highest removal of Reactive Blue 4 dye in aqueous solution. The effects of various parameters such as surfactant loading, temperature and initial pH solution were investigated in this experiment. UV-vis spectrophotometer was used to measure concentration of RB4 dye solution and the characterization of surfactant impregnated activated carbon was conducted by using Fourier Transform Infrared (FTIR) Spectrometer.

II. METHODOLOGY

A. Materials

All reagents used in the present work were analytical grade and directly used without further treatment. Stepantex 90 (SP-90) was used as plant-based surfactant with 50% of active matters. Reactive Blue 4 as dye model. Buffer solutions of pH 4, 7 and 9 for the calibration of pH-meters, and 0.1 M of sodium hydroxide (NaOH) were used in adjusting the initial pH. All the reagents and activated carbon were purchased from Sigma-Aldrich. All solutions were prepared with deionized water.

B. Conductivity Test

40 mg of surfactant was diluted with 100 mL of deionized water in 250 mL beaker. From data simulation, certain amount of deionized water was pipetted into the beaker with interval of 120 seconds. Conductivity meter was used to record the reading of the solution.

C. Fourier Transform Infrared Spectrometer (FTIR) analysis

Fourier Transform Infrared Spectrometer, FTIR was used to study the functional group of RB4 dye, plant-based surfactant, untreated and modified AC before and after treatment. A small amount of dry AC was crushed into powder form and tested. The spectra were recorded and analyzed from 4000 to 515 cm^{-1}.

D. Treatment of RB4 dye by modification of AC with plant-based surfactant.

I. Activated Carbon

Activated carbon (AC) that was purchased from Sigma-Aldrich is in granular form. The AC used to impregnate with surfactant was weighed and transferred into conical flasks.

II. Dye

Reactive Blue 4 ($C_{23}H_{14}Cl_2N_6O_8S_2$) was used without further purification. The solution was prepared by weighing 0.0125 g of RB4 and diluted with deionized water in 500 mL of volumetric flask to produce 25 ppm concentration of stock solution.

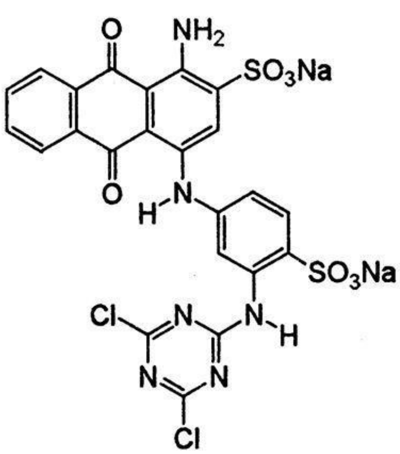

Fig. 1: Molecular structure of Reactive Blue 4 dye

III. Indirect removal of RB4 dye

In the impregnation process, 2 g of AC was impregnated with 200 mL of 100 mg/L surfactant solution. The mixture was placed into incubator shaker and left for 24 hours at temperature of 60°C and 130 rpm. The surfactant impregnated activated carbon (SIAC) solution then was filtered and dried overnight in oven at 60°C temperature. After drying, the SIAC was weighed 1.5 g to be used in 250 mL of 25 ppm of RB4 dye for treatment process in mild pH.

E. Adsorption of RB4 onto surfactant impregnated activated carbon (SIAC)

The RB4 dye was used as adsorbate that acted as pollutant model in this study. The concentration of RB4 dye was calculated using the calibration curve after obtaining the absorbance value via UV-visible spectrophotometer at the wavelength of peak maxima of RB4 at 595 nm. All samples were analyzed using a cuvette. The pH of solution was adjusted with 0.1M of NaOH solutions. The amount of dye adsorbed and percentage removal of RB4 were calculated using equations below,

III. RESULTS AND DISCUSSION

A. Conductivity Test

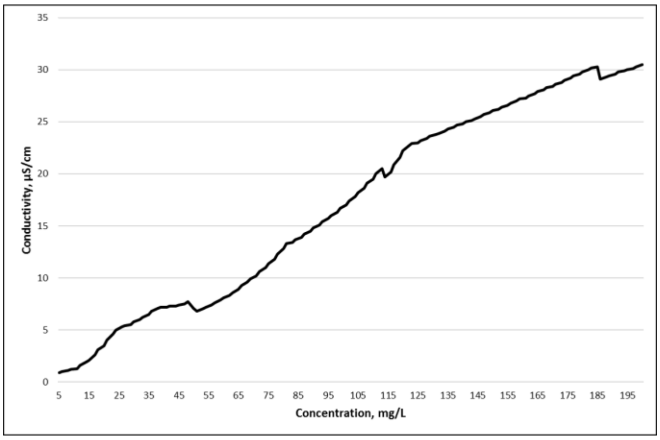

Fig. 2: Graph of conductivity against concentration

Fig. 2 shows that the conductivity increases as the concentration increases. The amount of deionized water added within time reduce the concentration. However, the graph shows the unstable reading between 5 mg/L and 115 mg/L. This is because the solution has reached its critical micelle concentration (CMC) at 125 mg/L. The trend of the graph is linear before it reaches its CMC.

B. Fourier Transform Infrared Spectroscopy (FTIR)

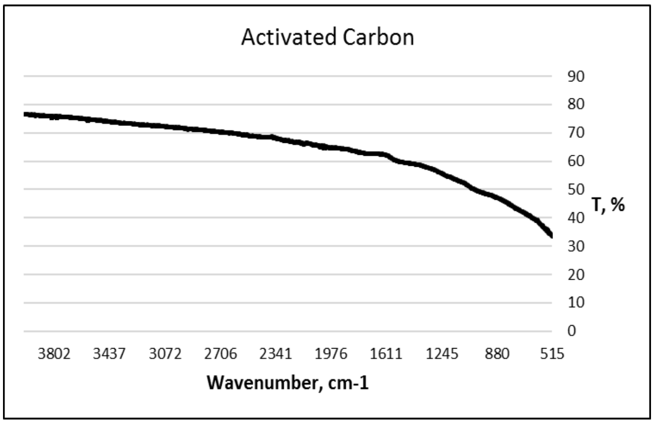

Fig. 3(a): The IR spectra of activated carbon

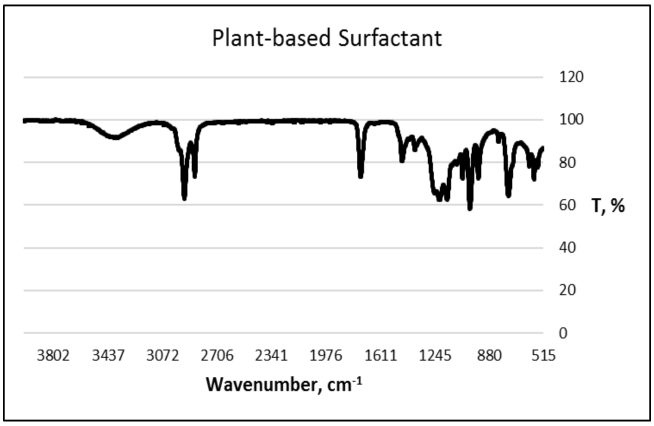

Fig. 3(b): IR spectra of plant-based surfactant

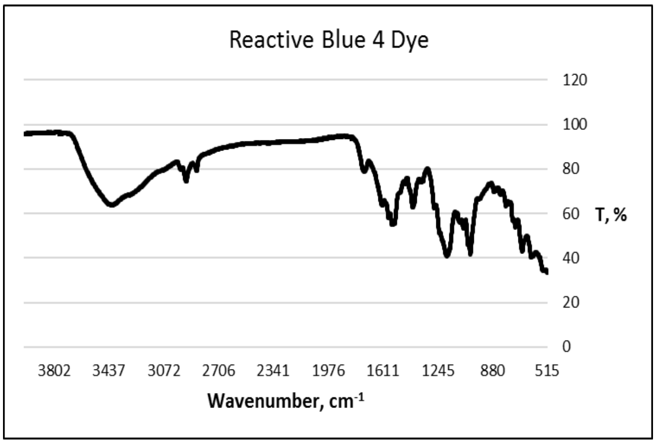

Fig. 3(c): IR spectra of RB4 dye

Fig. 3(a) shows that there is no peak in IR spectra of activated carbon analysis as pure activated carbon was used in this experiment. The graph proved that the activated carbon used before impregnated with surfactant is a pure activated carbon without any other organic compounds.

Fig. 3(b) shows that The IR spectra of plant-based surfactant are composed of vibration of -OH stretch 3418 cm^{-1}. 2956.02 cm^{-1} band was classified as aliphatic groups of asymmetrical and symmetrical stretch of CH_3 stretch at which also can be seen in 2916.13 cm^{-1}, 2849.01 cm^{-1}, and 1378.26 cm^{-1} peak. Two bands located in 1735.71 cm^{-1} and 1510 cm^{-1} are composed of an aromatic carbon or carbonyls (stretch of C=O in aromatic rings and stretch of C=C), respectively. Carboxyl group was well classified as C-O stretch at peak of 1466.90 cm^{-1}. C-N stretching of aliphatic primary amine in graph indicated at 1058.24 cm^{-1}. The –C–H band in functional group of plant-based surfactant indicated at region of 761.40 cm^{-1} to 554.95 cm^{-1}.

Fig. 3(c) shows that the broad peak around 3410.60 cm^{-1} can be classified as overlapping of -OH stretch and -NH functional groups. The peak at 2919.72 cm^{-1} and 1731.61 cm^{-1} which corresponds with C-H and C=O stretch, respectively. The band at 1183.70 cm^{-1} correspond to the S=O stretching, peaks at 790.40 cm^{-1}, 727.27 cm^{-1} for –C-H stretching. The N=N stretching may be overlapped with C-H deformation vibration. While at 681.41 and 620.25 cm^{-1} there were –C-Cl stretching.

C. Treatment of RB4 dye by adsorption

Several parameters like surfactant loading, temperature and initial pH of the solution were studied for the removal of RB4 dye.

I. Effect of surfactant loading

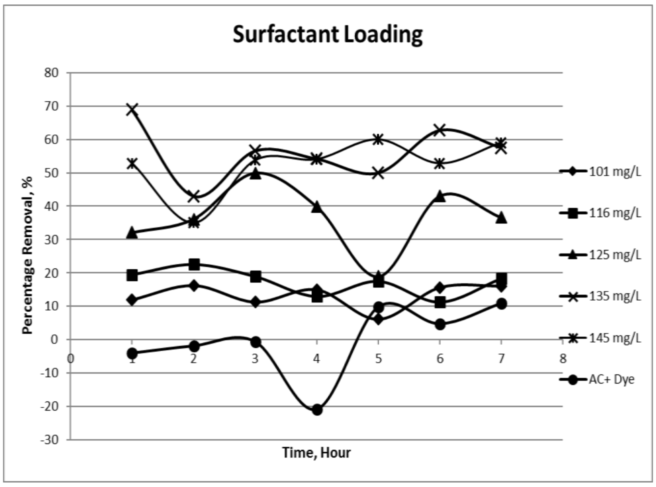

Fig. 4: Effect of surfactant loading on removal or RB4 dye

The effect of surfactant loading was studied in order to increase the efficiency of the removal of the dye. Fig. 4 shows the removal efficiency, obtained for RB4 dye at 30°C for 7 hours reaction. The surfactant loading was observed to improve the adsorptivity but the greater the adsorptivity did not always correspond to the maximum content of surfactant. The reasons the adsorptivity was increased with the increase the content of surfactant due to the active phase of surfactant reacts with RB4 dye in order to generate radicals to carry out the adsorption process. The radicals that is generated on the inner surface of the microporous material can diffuse to the external surface in order to break the large molecule into smaller segments. Thus it can then diffuse inside the microporous material due to the small number of sites exist at the external surface of the microporous material [15]. From fig. 4, the removal efficiency for RB4 dye shows less significance for 135 and 145 mg/L in the third hour. But, after sixth hours, RB4 dye with 135 mg/L surfactant concentration has been removed with the efficiency of 62.78%. Therefore, 135 mg/L of surfactant concentration is used as an optimum content for each dye to undergo adsorption process due to a good removal efficiency against time.

II. Effect of temperature

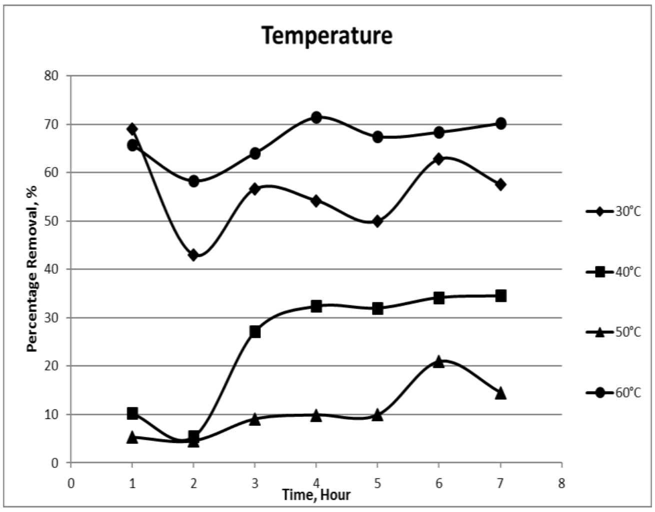

Fig 5: Effect of temperature on removal of RB4 dye

Temperature is another important parameter in the adsorption process for the removal of dye. The range of temperature being used in this study is 30, 40 and 50 and 60°C. The result shown in Fig. 5 can be observed that the dye removal is decreased as the temperature increases from 30 to 50°C. This is happening because increasing in temperature may decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface because of decreasing adsorption capacity as well detachment of cationic surfactant onto activated carbon surface [16]. But, it shows that the removal efficiency at the temperature of 60°C is at the very best which is 71.47%. The higher temperature enhanced the adsorption process. This is because as the temperature increases, it will fasten the reaction to create active sites at the surface of surfactant impregnated activated carbon (SIAC) for adsorption of RB4 dye molecule.

Based on the Arrhenius law, the rate is exponentially dependent on the reaction temperature. Thus, the high temperature is affirmative to the adsorption process due to the kinetic constant for dye radical and surfactant are exponentially elevated with system temperature. The collision of the radical is increase with the dyes molecules due to the high heat energy that resulted in degradation to smaller molecules.

III. Effect of initial pH of the solution

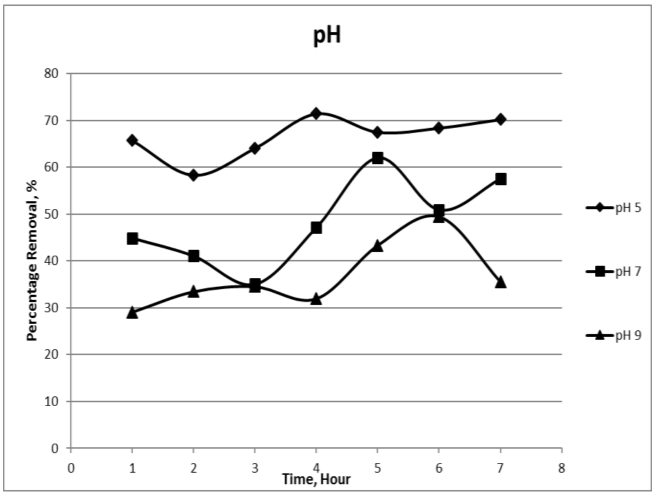

Fig 6: Effect of initial pH of the solution on removal of RB4 dye

The solution pH is one of the most important parameters in the adsorption process because it can affect the interaction of the surface functional groups of the adsorbate and the adsorbent. The effect of initial pH on adsorption of azo dyes was studied from pH of 5 to 9 at 60 °C and constant initial dyes concentration of 25 ppm. Fig. 6 shows the effect of pH on the removal of RB4 from surfactant impregnated activated carbon (SIAC) solution. The results indicate that the adsorption capacity of the nanocomposite is strongly dependent on the pH value of the solution. As can be seen from fig. 6, when the initial pH of the solution increased from 5 to 9, the removal efficiency of RB4 dye were rapidly decreased. The adsorption mechanism can be explained by the electrostatic interactions between the negatively charged dyes and the positively charged surface. Electrostatic force of attraction between the positively charged functional oxygen groups and negatively charged dyes molecules is responsible for the high adsorption capacity, which was observed at pH 5. At basic pH, the carboxylic and hydroxylic groups are deprotonated to anionic form (COO^- and O^-) and generates electrostatic repulsion force with dyes anions. Therefore, when the pH of the dye solution increases, the number of positively charged sites on SIAC decreases and the number of negatively charged sites increases which does not favor the adsorption of negatively charged dyes ions because of the electrostatic force of repulsion. Reactive dyes are applied under weakly acidic conditions. According to [17], reactive dyes have a low utilization degree compared to the other dyes since the functional group also bonds to water, creating hydrolysis. The highest removal of RB4 for pH parameters occur during the 4th hour of treatment which is 71.47%. Therefore, pH 5 was selected as an optimum condition in treating the RB4 dye with surfactant impregnated activated carbon.

IV. Conclusion

In conclusion, the study of removal of Reactive Blue 4 (RB4) dye by adsorption of surfactant impregnated activated carbon (SIAC) was successfully conducted. The value of critical micelle concentration proved that plant-based surfactant has its own capacity in removing the dye. Strong bond between the plant-based surfactant and activated carbon proved that indirect impregnation method has high efficiency on dye removal. In can be concluded that the optimum condition in removing the RB4 dye has achieved maximum percentage of 71.47% removal efficiency with 135 mg/L of surfactant loading in 1.5 g activated carbon at 60°C in weakly acidic condition. The removal efficiency has achieved its maximum within 4 hours of treatment.

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