Cationic Surfactant Impregnated Activated Carbon for Adsorption of Reactive Dye

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***Abstract*— Textile industry is one of the biggest users of water that produce waste consists of complex chemicals structure including dye during various processing stages. Reactive Blue 4 is one of the reactive dye that released by this industry. An effective method in treating RB4 is by a chemical treatment that is adsorption. The RB4 pollutant was treated by adsorption process with activated carbon impregnated with cationic surfactant. The adsorption performance of AC-Cationic Surfactant was investigated by studying parameters that effecting the efficiency of removal of reactive dye, RB4 from aqueous solution that were surfactant loading impregnated with AC, temperature and pH of initial solutions. Cationic surfactant greatly increased AC adsorption capacity for RB4 with 67.25% of removal in 5 hours in acidic pH range 5.0-5.9 at 50°C temperature by direct method while by indirect method, the removal achieved 71.25% of RB4 removal in 7 hours in acidic pH of initial solution at 30°C. It was observed that adsorption of RB4 dye was greatly enhanced by modification of AC with cationic surfactant impregnated by indirect method compared to direct method.**

Keywords-component; Activated Carbon, Adsorption process, Cationic surfactant, plant-based surfactant and Reactive dye.

I. INTRODUCTION

Textile industry used up a vast expanse of water and caused large amount of waste water discharged from dyeing processes. Synthetic waste water that produced by textile industry comprise by several groups of dye such as reactive, basic, acid dyes and many more. Basically, the wastewater from this industry under uncontrollable condition contains a lot of components in various hazardous chemical such as dissolved oxygen, dissolved carbon dioxide, and contained heavy metal ions [1]. Due to presence of these dissolved particles, water becomes inadequate for practical uses which need to be treated in a way to minimize waste water that can give a huge impact to the environment, aquatic ecosystem as well as human's life.

Treatment of dyes from textile waste water is difficult to treat and required specific methods in achieving the best result of removing dye [2]. Dyes have synthetic origin and complex aromatic molecular structures that make dyes are hard to degrade. In treatment of dye process, there are various types of methods that commonly used such as physiochemical treatment, coagulation flocculation sedimentation, biological treatment, membrane separation process, chemical oxidation treatment and conventional adsorption process [3]. Each method has some benefits and drawbacks. Recently, many research and studies stated that absorption process is a reliable alternative with inexpensive materials and numerous adsorbents have been proposed for treating complex structure of dye [4]. The most common adsorbents used is an activated carbon that capable in removing very large amount of material adsorbed due to the physical characteristic of having large internal surface and high degree of porosity [5].

However, adsorption capacity of activated carbon in treating reactive dye is quite low compared to its capability in treating other pollutants [6]. Hence, to enhance the ability of activated carbon in adsorption of reactive dye, a modification should be conducted onto surface of activated carbon according to application of using the activated carbon [7]. There are several studied that have been made in modification of activated carbon such that application in heavy metals, using anionic surfactant functionalization can significantly enhance the capacities of activated carbon to adsorb heavy metals such as cadmium [8]. While in other study proved that cationic surfactant give a significant role in enhancing color removal of reactive dye [9].

Therefore in this study the best condition for the removal of Reactive Blue 4 dye in aqueous solutions was conducted by characterized the functional group changes on the surface of AC impregnated with cationic surfactant by using Fourier Transform Infrared (FTIR) Spectroscopy. The performance of adsorption AC-CS for RB4 removal were studied by effects of surfactant loading impregnated with AC, adsorption operating temperature and the pH of initial solution that effecting the efficiency of RB4 removal by direct method impregnation. Indirect method of AC-CS impregnated was also investigated by parameter of surfactant loading. The removal performance was analyzed by using UV–vis spectrophotometer that used to measure concentration of RB4 dye solutions.

II. METHODOLOGY

A. Materials

1) Adsorbent

The adsorbent used in this study is in granular form of activated carbon (AC) that was purchased from Soon Ngai Engineering.

2) Cationic Surfactant

The cationic surfactant employed was plant-based surfactant at 53% of active matters. The critical micelle concentration (CMC) of cationic surfactant was reported as 98 mg/L [10]. The molecular structure of cationic surfactant is shown in figure 1.

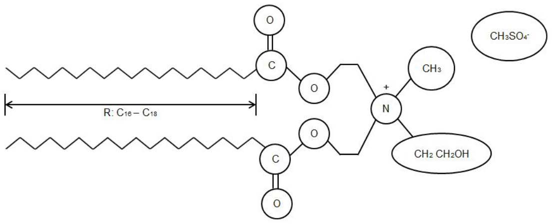

Figure 1: Molecular Structure of Cationic Surfactant

3) *Adsorbate*

Reactive Blue 4 ($C_{23}H_{14}Cl_2N_6O_8S_2$) was obtained from Sigma-Aldrich and was used without further purification. The structure of RB4 dye is shown in figure 2.

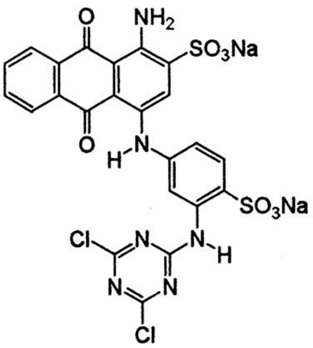

Figure 2: Molecular structure of Reactive Blue 4 dye

B. Methods

1) Dye Preparation

The solution was prepared by dissolving 0.0125 g amount of dye in 500 mL deionized water as 25 ppm concentration of stock dye solution.

2) Treatment of RB4 dye by modification of AC with Cationic Surfactant

I.Direct removal of RB4

Direct removal treatment is performed whereby RB4 dye, cationic surfactant and AC were mixed together in one solution. 1.5 g of AC and 38 mg/L of cationic surfactant were mixed directly into conical flask of 250 mL of dye solution. The conical flask was enclosed with aluminum foil. The solutions was placed in incubator shaker to maintain the condition with constant heat supply of 30°C at 130 rpm for 7 hours with different 7 conical flasks for each hour. The suspensions were allowed to settle down and the AC were separated by filtration through filter papers without rinsing, and finally dried in an oven overnight at 60°C. The pH of solution was adjusted with 0.1M of NaOH solutions.

II.Indirect removal of RB4

In the impregnation process, 2 g of AC was impregnated with 200 mL of 38 mg/L, cationic surfactant solution. The conical flask was enclosed with aluminum foil. The mixture was placed into incubator shaker for 24 hours at temperature 60°C and 130 rpm to achieve homogenous solution of surfactant. The solution and AC was filtered without rinsing and dried overnight in oven at 60°C temperature. After drying, the product was transferred to 50 mL of glass bottle. The AC-Cationic Surfactant was weighted 1.5 g to be used in 25 ppm of 250 mL of RB4 dye for the adsorption treatment process.

3) Ultraviolet–Visible Spectroscopy,(UV-Vis)

The concentration of RB4 dye was calculated using the calibration curve after obtaining the absorbance value via running a UV-visible spectrophotometer at the wavelength of peak maxima of RB4 at 595 nm. All samples were analysed using a quartz cuvette. The amount of dye adsorbed and percentage removal of RB4 were calculated using equations below,

$$\text{Percentage Removal RB4, \%} = \frac{C_o - C_f}{C_o}$$

$$C_o = \text{Concentration of RB4 dye at initial}$$

$$C_f = \text{Concentration of RB4 dye at final}$$

4) Fourier Transform Infrared Spectroscopy, (FTIR) analysis.

Fourier Transform Infrared Spectroscopy, FTIR analysis was utilized to confirm the functional group of RB4 dye, cationic 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}.

III. RESULTS AND DISCUSSION

A. Characterization of FTIR

I. FTIR analysis before treatment

FTIR Spectra in figure 3 shows the IR spectra for virgin activated carbon as to analyze the difference on the surface of activated carbon before and after treatment adsorption process. There is no stretch or bending in IR spectra of activated carbon analysis as the virgin activated carbon is used in this adsorption study. The FTIR analysis of activated carbon showed and proved that the activated carbon used before impregnated and mixed with cationic surfactant is a pure activated carbon without any impurities.

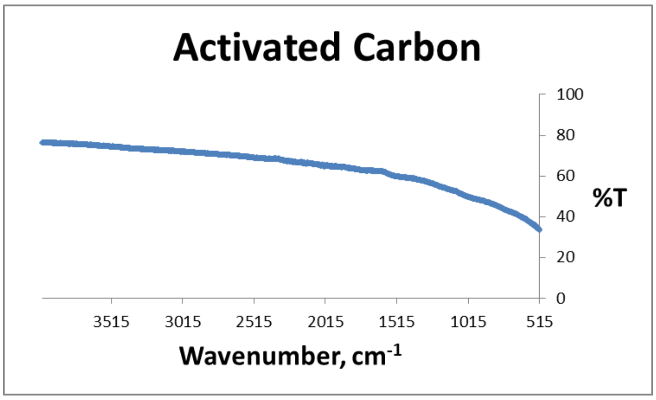

Figure 3: The FTIR Spectra for Activated Carbon

The IR spectra of cationic surfactant presented in figure 4 are mainly composed of vibration of -OH stretch 3418 cm^{-1}. 2956.02

cm^{-1} was usually ascribed to the aliphatic groups of asymmetrical and symmetrical stretch of CH$_3$ that also can be seen in 2916.13 cm^{-1}, 2849.01 cm^{-1}, and 1378.26 cm^{-1} peak. Two sharp bands located in 1735.71 cm^{-1} and 1510 cm−1 corresponded to an aromatic carbon or carbonyls (stretch of C=O in aromatic rings and stretch of C=C), respectively. Carboxyl group was well indicated as C-O stretch at peak of 1466.90 cm^{-1}. C-N stretching of aliphatic primary amine in cationic surfactant indicated at 1058.24 cm^{-1}. The –C–H bend in functional group of cationic surfactant indicated at region of 761.40 cm^{-1} to 554.95 cm^{-1}.

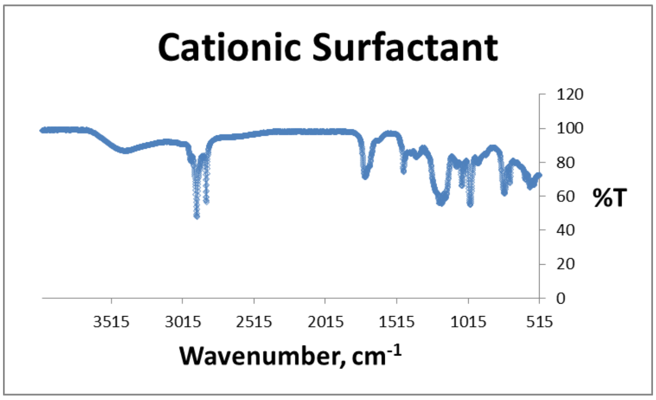

Figure 4: FTIR Spectra for Cationic Surfactant

The FTIR spectrum in figure 5 shows the IR spectrum of RB4 that have broad region around 3410.60 cm^{-1} which can be assigned to 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.

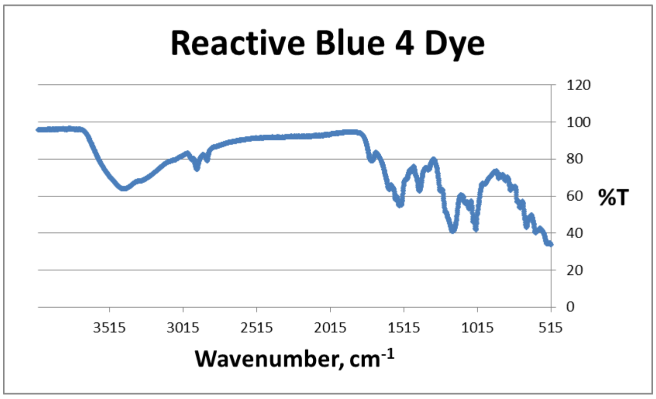

Figure 5: FTIR Spectra for Reactive Blue 4 dye

IR spectra of AC-CS after treatment of RB4 dye is shown in figure 6 that observed there are stretch bands compared to the virgin IR spectra of activated carbon. These stretch developed indicates that surface modification of activated carbon is due to the attachment of the cationic surfactant or RB4 dye molecules that represent functional groups on the activated carbon. The changes can be seen on band of 1700 cm^{-1} to 1400 cm^{-1} that indicates in changes of corresponded to an aromatic carbon or carbonyls of stretch of C=O an aromatic rings and stretch of C=C after treatment of RB4 dye. This formation of C=O stretch which mainly in range of 1735 cm^{-1} to 1744 cm^{-1} is due to the hydrophobic tail attachment of cationic surfactant on the surface of activated carbon that contain C=O functional group as in figure 4 at band of 1731.61 cm^{-1} [11].

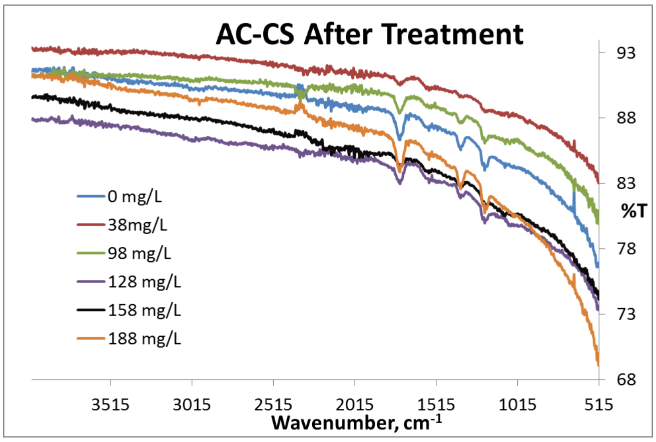

Figure 6: FTIR Spectra after treatment with AC-CS

B. Removal of RB4

Removal efficiency of RB4 was studied based on surfactant loading in solution, operating temperature and pH of initial dye solution.

I. Effect of Surfactant Loading

a) Direct removal of RB4

The surfactant loading that used along with 1.5 g of AC as to treat RB4 were varied at 38 mg/L, 98 mg/L, 128 mg/L, 158 mg/L and 188 mg/L. RB4 also was treated by virgin AC without surfactant impregnation as to study the effect on how surfactant loading significantly influence the removal percentage of RB4 dye. It is evident in figure 7 that the highest removal of RB4 dye for most of surfactant loading was at 5th hour. Fluctuation of percent removal for each surfactant loading is due to the diffusion of dye molecules into the surface pores of the AC and also probably due to the migration of dye molecules from the solution exchange site with the cationic surfactant to the surface of AC that showed the reaction is a reversible reaction [12]. In figure 7 shows that, the higher the concentration of surfactant in the solution, the higher the percentage of removal of RB4 dye. The enhancement of the adsorption capacity of AC-Cationic Surfactant into RB4 dye increases in the concentration of cationic surfactant from 38 mg/L to 128 mg/L in the solution might be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents to adsorb dye [12]. This shared the same trend with virgin AC. Even though 188 mg/L of surfactant concentration percentage removal shows the highest of about 70% however, through observation the solution was cloudy as there is leached of cationic surfactant in the solution. At high concentrations of cationic surfactants introduced, there can be aggregation or dye solubilization with cationic surfactant thus decreases the dye adsorption [13]. As there was increasing of cationic surfactant, the AC's porosity was gradually occupied by cationic surfactant instead of dye [14]. It is significantly obvious that the adsorption of AC-CS was much higher compared to the virgin AC that was only 9.87% at the 5th hour as presented in figure 8. Therefore, the optimum surfactant loading is at 128 mg/L at 41.25% of removal and the following experiments of temperature and pH effect were carried out with the surfactant loading of 128 mg/L.

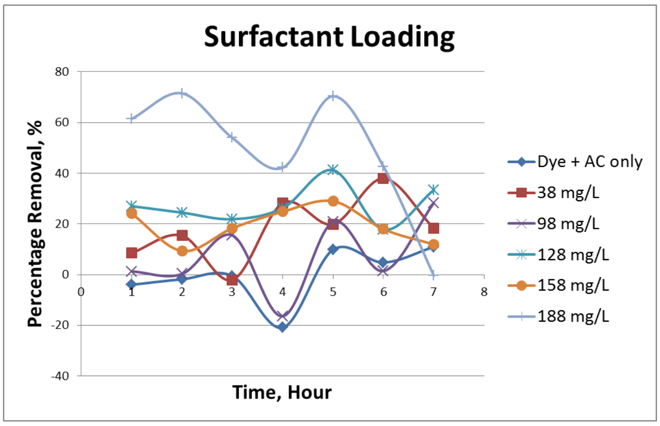

Figure 7: Effect of Surfactant Loading within 7 hours

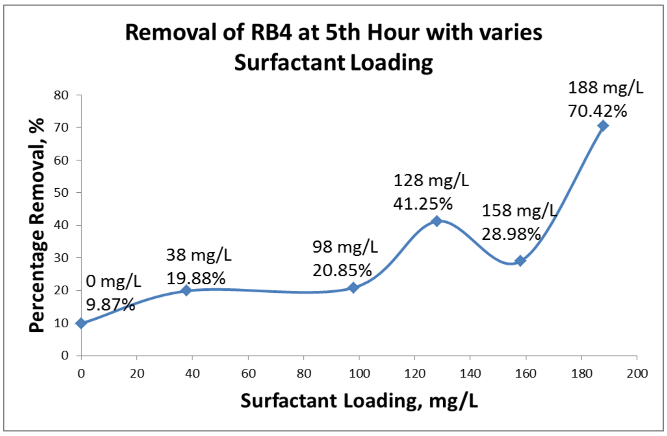

Figure 8: Removal percentage of RB4 at 5th hour

b) *Indirect removal of RB4*

In indirect method of removing RB4 dye, the activated carbon was directly impregnated first in cationic surfactant solution. The AC-CS then was used to remove RB4 dye. The activated carbon is known to be amphoteric, that is, its variable charge surface can develop positive or negative charge depending on solution of the pollutant [22]. AC-CS impregnated hence provides well-structured of cationic surface as the AC was modified with cationic surfactant. The modified AC can causes the change in the surface chemistry and porosity of the adsorbents, which affects the sorption capacity of AC-CS to remove RB4 dye [15]. In figure 9 shows that, the percentage removals of RB4 of 38 mg/L, 98 mg/L, 128 mg/L and 158 mg/L surfactant loading at 7th hours are, 71.25%, 44.3%, 50.78%, and 0.388 % respectively. The removal percentages of RB4 dye by indirect method evidently highest at surfactant loading of 38 mg/L at 71.25% in 7 hours as referred in figure 9. This is due to most of amount cationic surfactant were attached to the surface of AC. The hydrophobic tail of cationic surfactant was the main interactions between surfactants and AC that enhance the removal of RB4 dye as the cationic surfactant have completely attached onto AC's surface [16]. Thus, the head of cationic surfactant composed by hydrophilic nature can easily attract molecules of RB4 dye resulted in high rate removal of RB4 dye. Introduced higher concentration of cationic surfactant tends to conglomeration of surfactant particles within itself, hence there is no increase in effective surface area of modified AC as the solution considered to have reached their saturation limit [17]. This is most likely because the number of hydrophobic interactions between AC and cationic surfactant molecules was not further increased by the formation of self-aggregation of cationic surfactant that can be evidenced in figure 9 as surfactant loading increased to 98 mg/L, 128 mg/L and 158 mg/L resulting in decreasing removal of RB4 dye [18]. The higher the contact time, the higher the percentage removal of RB4 dye of indirect method compared to direct method. This is due to the slow intraparticular diffusion of cationic surfactant in granular activated carbon [13]. In direct method, contact time for cationic surfactant to attach onto AC is limited as the cationic surfactant was competing with dye molecule to be adsorbed onto AC surface which results in reversible adsorption process [12]. In contrast, indirect method provides sufficient time for cationic surfactant to be attached onto AC's surface hence results in better performance in treating RB4 dye than direct method.

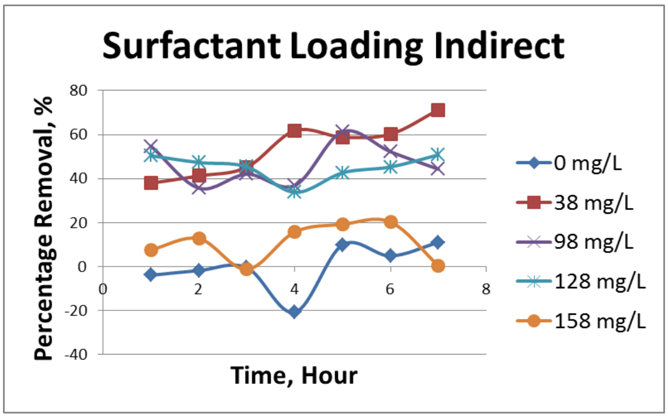

Figure 9: Effect of Surfactant Loading of Indirect Method

II. *Effect of Temperature*

Temperature was varied from 30°C to 70°C in order to determine the best operating temperature of removal of the RB4 dye. Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process [13][19]. At constant concentration dye, the increasing of temperature decreases the concentration of dye hence increase the percentage removal of RB4 dye from 30°C, 40°C and 50°C which were 41.25%, 38% and 67.25% respectively as presented in figure 10. As the temperature is raised from 30°C to 50°C, the adsorption RB4 dye by adsorption onto AC-CS increased from 41.25% to 67.25% indicating that the process is endothermic as the operating temperature increases, the adsorption capacity also increases [20][13]. The increasing in percentage removal of RB4 is may be due to attributed in increased penetration of RB4 dye inside micro pores of AC-CS at higher temperatures or the creation of new active sites for adsorption of RB4 dye molecules [19][15]. The number of the adsorption sites would increase because of breaking of some internal bonds near the edge of active surface sites of AC-CS and at high temperature, the pore sizes of AC-CS particles would enlarge hence increase capacity of AC-CS to adsorb RB4 molecule dye [21][22]. The reaction rate between the modified carbon and pollutant increase when the precursor is subjected to high activation temperature, thus leading to the formation of well-developed pores [21]. Further in increase of the operating temperature at 60°C and 70°C however, shows the decreasing in percentage removal of RB4 dye as increasing in temperature may decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing adsorption capacity as well detachment of cationic surfactant onto activated carbon surface [13]. The solubility of the large RB4 dye ions increases with increasing temperature which leads to increase in the adsorption capacity of AC with further increasing temperature that indicates the temperature to be a controlling factor in the process of adsorption [20].

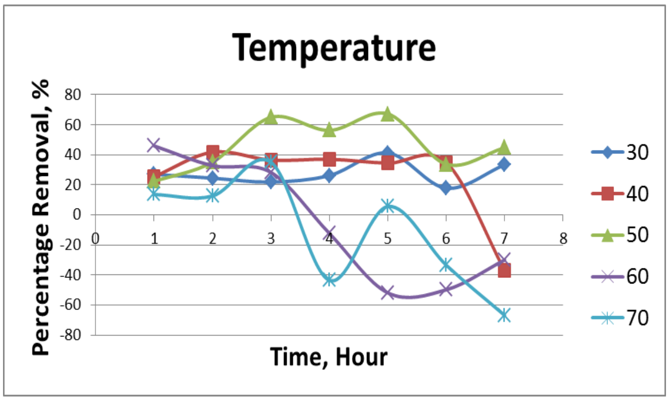

Figure 10: Effect of Temperature within 7 hours

III. Effect of pH

Among the parameters that will affect the treatment of degradation of dye efficiency is pH of initial solution. pH is a measure of the acidity or alkalinity of an aqueous solution. The acidity or alkalinity of an aqueous solution is determined by the relative number of hydrogen ions, H$^+$ or hydroxyl ions, OH$^-$ present [23]. In most of previous study stated that the optimum pH value of initial dye is less than 3 without considering the types of dyes used. pH at 3 was believed to achieve highest degradation of dye by chemical process [24]. Adsorption capacity decreased with the increase of initial solution pH which indicated that RB4 dye adsorption was favoured at low pH [14]. Adsorption capacities of AC-CS were found to decrease at 5th hour from 67.25%, 37% and 1% of percent removal of RB4, as for initial pH of 5, 7, and 9.9 pH respectively as shows in figure 11. Cationic surfactant modified activated carbon is preferable used in the initial dye solution of pH 4 in removing anionic Cr(VI) [25]. AC-CS modified removed RB4 dye molecule both in ion exchange and electrostatic interaction [25]. Decreasing in the pH of the RB4 solution, there are increasing of RB4 dye molecules that protonated and get adsorbed on the surface of the activated carbon. This is due to the fact that the RB4 molecules become less nucleophilic at lower pH which results in more adsorption on the nucleophilic sites of the AC-CS [26]. At low pH there is an increase in the H$^+$ ions in solution which result in electrostatic interaction between the RB4 dye molecules and the AC-CS resulting in higher percentage RB4 dye removal due to negatively charged of sulfonic (–SO3–) functional group of RB4 dye molecule [21]. This functional group are attracted to the positively charged of cationic surfactant that have been modified on the site of AC at lower pH. In contrast, at high pH solution the percentage removal of RB4 decreased due to the presence of the negative charge on the AC-CS site thus resulting in electrostatic repulsion between AC-CS and the negatively charged RB4 dye molecules [23]. Reactive dye molecules become nucleophilic at higher pH hence results in less adsorption on the nucleophilic sites of AC-CS [26]. This finding, correlated with study of adsorption characteristic of basic dye, methylene blue (MB) that consists of positive charge (cationic) molecule, with the negatively charged surface enhanced adsorption of cationic contaminants at a higher pH [27]. The AC impregnated with cationic surfactant then provides high positively charged surface that improved the removal of anionic reactive dye of RB4.

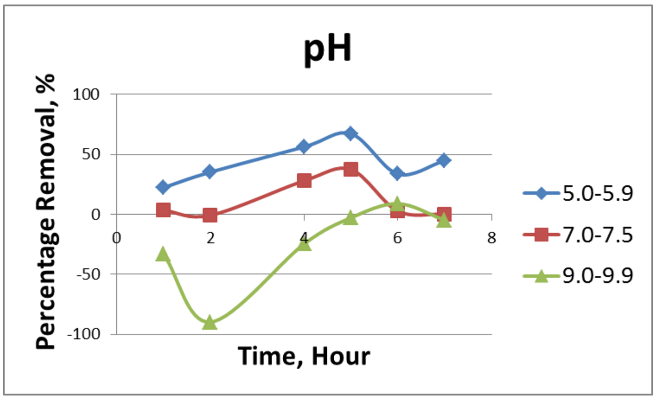

Figure 11: Effect of pH within 7 hours

IV. CONCLUSION

In conclusion the study of removal of Reactive Blue 4 dye by adsorption of activated carbon impregnated with cationic surfactant was successfully been carried out. Strong interaction between the cationic surfactant and activated carbon proved that impregnation method of indirect method is more effective than direct method in achieving higher removal efficiency of dye from textile wastewater. It can be conclude that at the optimum condition, RB4 dye has achieved maximum percentage of 67.25% removal efficiency by direct method of 25 ppm initial concentration, with presence of 128 mg/L of surfactant loading in 1.5 g of activated carbon at 50°C within 5 hours. While indirect method that only focusing on controlling surfactant loading parameter achieved the optimum removal of RB4 dye of 71.25% in 7th hours.

ACKNOWLEDGMENT

Thank you to my supervisor and Universiti Teknologi Mara through Training Scheme to the first author is greatly acknowledged.

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