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Research paper

Direct Surfactant-Impregnated Activated Carbon for Adsorption of Reactive Blue 4

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Abstract

The present investigation deals with the enhanced of adsorptive removal of Reactive Blue 4 (RB4) from an aqueous solution using Surfactant-impregnated Activated Carbon (SIAC). The study on direct impregnation method was investigated using palm-based esterquat (PBE) surfactant. The effects of surfactant concentration, temperature and pH on dye removal were discussed to determine the efficiency of adsorption process. Results obtained from this study shows that the best RB4 dye removal obtained was 67.25% at PBE concentration of 128 mg/L in 5 hours contact time and operating temperature of 50^{0}C. It was observed that adsorption of RB4 dye was enhanced by modification of AC with cleavable cationic surfactant via direct impregnation method. The selected data obtained was fitted using multilinear regression via Excel Software. The regression analysis shows that the R^2 and adjusted R^2 obtained were 0.973 and 0.905, respectively. The ANOVA analysis proved that the mathematical expression can be used to predict the adsorptive removal of RB4 dye from an aqueous solution.

Keywords: *Activated carbon; adsorption process; esterquat; impregnated; cationic surfactant; plant-based surfactant; reactive dye.*

1. Introduction

The textile industry utilizes excessive amounts of water in dyeing process. Therefore, large amounts of colored wastewater are discharged from dyeing process. Wastewater from the textile industry consists of several types of dye such as reactive and acid dyes. Generally, the textile wastewater contains various chemicals inclusive inorganic materials and organic complexes such as dyes and surfactants [1]. The presence of these materials in dye effluents lead to environmental issue due to its toxicity and resistance to conventional treatment [2]. Therefore, it is required to treat the textile wastewater before it is discharged to the environment.

Treatment of textile wastewater is very selective depending on the nature of dyes used in dyeing process [3]. Reactive dye consists of complex aromatic molecular structures that resist degradation. There are various types of treatment methods that are commonly used to treat textile wastewater such as coagulation/flocculation process, biological treatment, membrane separation process, chemical oxidation treatment and conventional adsorption process [4]. Several studies were performed on adsorption of dyes using numerous adsorbents for treating dyes with complex structures [5]. The most common adsorbents used for wastewater treatment is activated carbon (AC).

AC is proven capable in removing various types of materials due to its advantage of having large surface area and a high degree of porosity [6]. The ionic pollutant was removed by complexation or by electrostatic attraction of ionic pollutant to various surface functional group of AC while hydrophobic organic pollutants will be adsorbed onto AC due to its hydrophobic properties [7]. However, the removal of ionic pollutant via adsorption using AC is less efficient because the functional groups of commercial AC which cover only a small portion of carbon surface [8]. Several researchers studied on adsorption of reactive dyes and found that AC was unable to decolorize the anionic reactive dyes due to less sufficient functional group to adsorb ionic dyes efficiently [9]. Therefore, surface modification of activated carbon is possible to increase the surface charge and enhance AC's adsorption capacity for anionic dyes [10].

The surface modification of AC can be performed via impregnation of AC using chemical and/or surfactant. The studies on impregnation of AC have been explored in literature [7, 8, 11-16]. However, most of the studies focused on the use of chemicals/chemical surfactant in impregnation of AC process which is not environmental friendly since the chemical may have the possibility to desorb into the aqueous solution during adsorption process. In addition, less research has been conducted on the impregnation of AC using cationic surfactant on adsorption of reactive dyes. Therefore, it is necessary to investigate the performance of plant-based cleavable surfactant impregnated-activated carbon on adsorption of reactive dyes to ensure the technology is safe and environmental friendly.

The objective of this research is to study the removal of Reactive Blue 4 (RB4) from aqueous solution via adsorption process using direct surfactant-impregnated activated carbon (SIAC). A cationic biodegradable cleavable surfactant, palm-based esterquat (PBE) was used in this study and its effectiveness was investigated. Theoretically, the hydrophobic tail of PBE surfactant will create binding with AC through impregnation process while the head of PBE surfactant composed by hydrophilic nature with cationic charge can easily attract molecules of anionic RB4 dye. The effects of surfactant concentration, temperature and pH on dye removal were discussed to determine the efficiency of adsorption process. The experimental data will be analyzed using multilinear regression via Excel Software to verify the relationship between operating parameters and dye removal through mathematical expression obtained from the regression analysis.

2. Materials and Methods

2.1. Materials

Reactive Blue 4 (RB4) (MW 637.43) was purchased from Sigma Aldrich (M) Sdn. Bhd. The plant-based surfactant (PBE) was obtained from Malaysian Palm Oil Board (MPOB) at 53% of active matters. Commercial activated carbon (AC), obtained from Soon Ngai Engineering was used as adsorbent for the experiments.

2.1. Methods

2.2.1. Surfactant-impregnated Activated Carbon (SIAC)

The RB4 dye concentration and mass of AC were kept constant at 25 mg/L and 1.5 g, respectively. The PBE surfactant concentration was varied from 38 mg/L to 188 mg/L. The critical micelle concentration (CMC) of PBE surfactant in aqueous medium is 93.5 mg/L [17]. For direct impregnation method, PBE surfactant and AC were mixed directly into conical flask containing 250 mL of RB4 dye. The conical flask was enclosed with aluminum foil. The solution was placed in incubator shaker with constant heat supply of 30°C at 130 rpm for 1 to 5 hours. Then, the SIAC was separated from the treated solution using Whatman filter papers and was dried in an oven overnight at 60°C. The schematic representation of experimental works is shown in Fig. 1. The best surfactant concentration was selected for study on effect of operating temperature and pH.

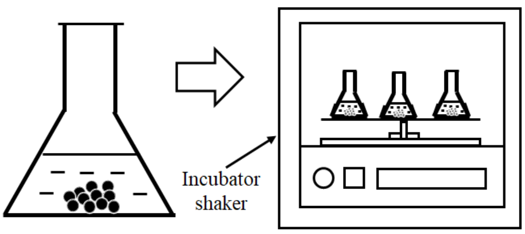

Fig. 1: Schematic representation of experimental works

2.2.2. Analysis

The RB4 dye concentration in treated solution was analyzed and measured spectrophotometrically using UV-Vis Spectrophotometer (Perkin Elmer Lambda 750) at wavelength of 595 nm. The treated RB4 dye in aqueous solution were analyzed at PBE surfactant concentration varies from 38 mg/L to 188 mg/L, operating temperature between 30^0C to 70^0C and operating pH ranges from 5 to 9. Dye removal (R_{dye}) was calculated using equation (1).

$$R_{dye} = \left(\frac{C_o - C_f}{C_o} \right) \times 100\% \quad (1)$$

where C_o is feed dye concentration and C_f is final dye concentration [18].

3. Results and Discussion

3.1. Effect of Surfactant Concentration

Fig. 2 shows the effect of surfactant concentration on RB4 dye removal. The adsorption of RB4 using virgin AC (at PBE concentration of 0 mg/L) was performed to investigate the effect on how surfactant loading significantly influences the removal percentage of RB4 dye. It is observed that the highest removal of RB4 dye using virgin AC obtained was only 9.87% at 5^{th} hour contact time whereas higher RB4 removal can be achieved by using SIAC as adsorbent. Therefore, it is proven that SIAC has potential to enhance the removal of RB4 dye from an aqueous solution.

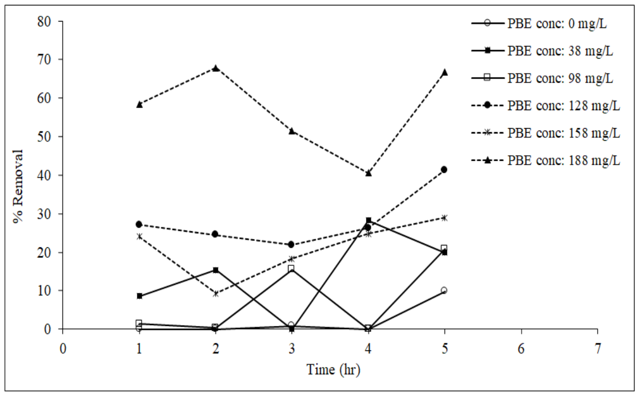

Fig. 2: Percentage of RB4 removal within 5^{th} hour of contact time at different PBE concentration at operating temperature of 5^{th} contact time and pH of 5

The removal of RB4 dye was fluctuated from 1^{st} hour to 5^{th} hours of contact time at every PBE concentration. The fluctuation phenomenon is probably due to three factors; the formation of sparingly soluble precipitate between PBE surfactant and RB4 dye [19], the diffusion of dye molecules into the surface pores of the SIAC and/or reversible reaction which involved migration of dye molecules from the solution exchange site with the PBE surfactant to the surface of AC [20]. For every PBE concentration, the highest RB4 removal was obtained mostly at 5^{th} hour of contact time. The highest RB4 removal obtained was 66.81% at PBE concentration of 188 mg/L.

It can be observed from Fig. 2 that the RB4 removal increased with increase in PBE concentration. The enhancement of the adsorption capacity of RB4 dye onto SIAC increases from 19.88% to 41.25% as the concentration of PBE surfactant increased from 38 mg/L to 128 mg/L, respectively. At higher PBE concentration, the tendency of PBE surfactant monomer to impregnate onto AC is greater, hence enhanced the potential of RB4 dye to get adsorb onto the SIAC. Even though the RB4 removal was highest at 188 mg/L of PBE concentration, through observation the solution was cloudy which indicated that the presence of high PBE surfactant in the treated solution. At high PBE concentrations exceeds its critical micelle concentration (CMC), the PBE surfactant has the tendency to form an aggregation. This anionic RB4 dye tends to solubilize into the cationic PBE aggregation, hence decreasing the dye adsorption [21]. In addition, at high PBE concentration, there is a possibility that the AC's porosity was gradually occupied by PBE surfactant instead of dye [22]. Therefore, it is concluded that the best PBE surfactant concentration selected for the next parametric study is at 128 mg/L.

3.2. Effect of Operating Temperature

Fig. 3 presents the effect of adsorption operating temperature on RB4 dye removal. It is observed that highest removal of RB4 mostly achieved at 5^{th} hours of contact time. As the temperature is raised from 30°C to 50°C, the adsorption RB4 dye by adsorption onto SIAC increased from 41.25% to 67.25% indicating that the process is endothermic [23]. The increase in RB4 removal be attributed to an increase in penetration of RB4 dye inside micro pores of SIAC at higher temperatures or the creation of new active sites for adsorption of RB4 dye molecules [24, 25]. The number of the adsorption sites would increase because of breaking of some internal bonds near the edge of active surface sites of SIAC. In addition, the pore sizes of SIAC particles would enlarge hence increase capacity of SIAC to adsorb RB4 dye at high temperature [26].

Further increase in adsorption operating temperature from 50°C to 70°C however, shows the decrease in percentage removal of RB4 dye from 67.25% to 5.64%. As the temperature is further increased, the adsorptive forces between the dye species and the active sites on the adsorbent surface may decrease the as a result of decreasing adsorption capacity as well detachment of cationic surfactant onto activated carbon surface [21]. Therefore, the best operating temperature chosen for the next parametric study is at 50^0C.

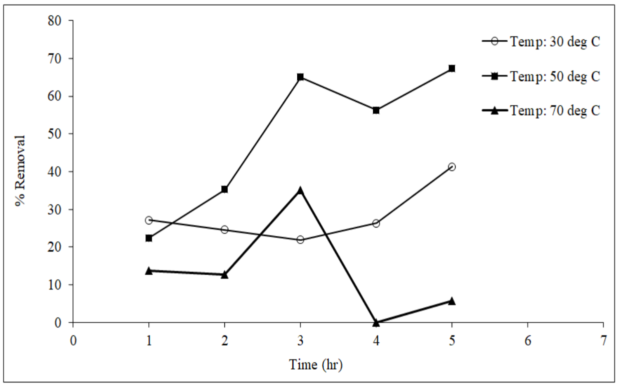

Fig. 3: Percentage of RB4 removal within 5th hour of contact time at operating temperature at PBE concentration of 128 mg/L and pH of 5

3.3. Effect of Initial pH

The effect of initial pH on adsorption of RB4 onto SIAC is presented in Fig. 4. From this figure, it is shown that the percentage of RB4 removal reduced as pH value increased which indicated that RB4 dye adsorption was favored at low pH [22]. Most of the maximum RB4 removal obtained at 5^{th} hours contact time. The RB4 removal deceased from 67.25%, 37% and 1% of as the initial pH increased from 5, 7, and 9 respectively. At lower pH, there is an increase in the H^+ ions in solution which causes the surface area of SIAC to be more protonated. There is an increase in electrostatic force between negatively charged of sulfonic ($–SO_3–$) functional group of RB4 dye molecules and the SIAC resulting in higher percentage RB4 dye removal [27]. In contrast, the percentage removal of RB4 decreased at high initial pH due to the presence of the negative charge on the SIAC site thus resulting in electrostatic repulsion between SIAC and the negatively charged RB4 dye molecules [28]. Reactive dye molecules become nucleophilic at higher pH hence results in less adsorption on the nucleophilic sites of SIAC [29].

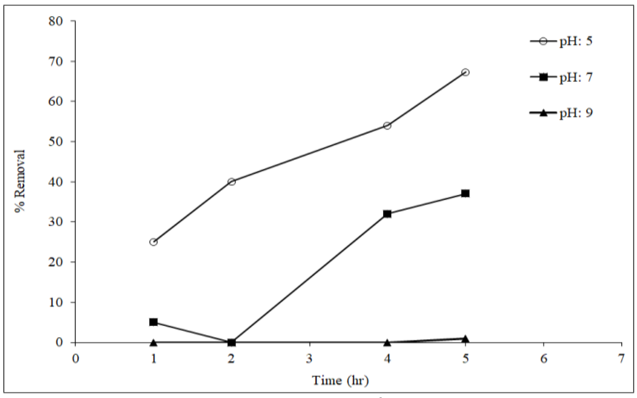

Fig. 4: Percentage of RB4 removal within 5^{th} hour of contact time at operating temperature at PBE concentration of 128 mg/L and operating temperature of 50^0C

3.4. Multilinear Regression

A multilinear regression model via Excel Software was used to analyze and verify the relationship between RB4 removal as response (y) and parameters involved in this research. The parameters selected were surfactant concentration (x_1) varying from 0 mg/L to 128 mg/L, operating temperature (x_2) at 30°C to 70°C and initial pH (x_3) in the range of 5 to 9. The selected data were obtained at 5^{th} hours of contact time. The mathematical expression can be expressed as in equation 2:

$$y = \left(3.388\times10^{-6}\right)x_1^2x_2^2 + \left(1.595\times10^{-3}\right)x_1^2x_3 - \left(2.093\times10^{-6}\right)x_1^2x_2^2x_3 - \left(5.066\times10^{-1}\right)x_1x_3 + \left(1.686\times10^{-2}\right)x_1x_2x_3 + 12.2326 \quad (2)$$

Based on the regression statistic of the mathematical model above, the value of R^2 and adjusted R^2 obtained were 0.973 and 0.905, respectively. The value of adjusted R^2 indicated that about 90% of RB4 removal variations in the model can be predicted by the predictor parameters (surfactant concentration, temperature, and initial pH). From ANOVA analysis, the significance F obtained was 0.066 and proved that the correlation is acceptable [30].

Fig. 5 shows the comparison between experimental and predicted value of RB4 removal. It is clearly shown that the scatter plots are more dense around 45 degree line which indicates that the experimental data were close to predicted value calculated from mathematical expression.

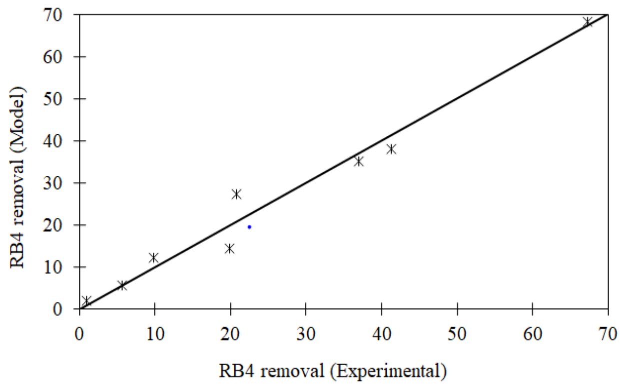

Fig. 5: Comparison between experimental and predicted value of RB4 removal

4. Conclusion

Direct surfactant-impregnated activated carbon for adsorption of Reactive Blue 4 was investigated. The study on effect of surfactant concentration shows that the maximum RB4 dye removal achieved at 188 mg/L of PBE concentration is possibly due to the solubilization of RB4 dye into surfactant aggregates rather than adsorption of RB4 onto surface site of AC. The temperature and initial pH shows significant effects to the adsorption of RB4 dye. The best RB4 removal obtained from this study was 67.25% at PBE concentration of 128 mg/L, operating temperature of 50^0C and initial pH of 5, respectively. These findings confirm that SIAC obtained from isolate impregnation method is possible to remove reactive dyes from an aqueous solution. The mathematical expression was developed from data fitting using multilinear regression via Excel software. The ANOVA analysis of the mathematical expression proved that the developed expression can be used to predict the RB4 removal at PBE concentration varies from 0 mg/L to 128 mg/L, operating temperature at 30°C to 70°C and initial pH in range of 5 to 9, respectively.

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