Removal of Reactive Dyes using Micellar Solubilization followed by Coagulation and Flocculation Process

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Abstract **— Wastewater produced from dyeing process become an environmental threat to conserve biodiversity. Performance of conventional method for removing dyes like coagulation and flocculation is either high in cost operation or insufficient to meet effluent limits. Previous study discovered that a combination of membrane filtration with micellar solubilization such as micellar-enhanced ultrafiltration (MEUF) was quite efficient, however, the use of membrane was prone to cause fouling. Because of that, the aim of this research is to study the effectiveness of biodegradable plant-based surfactant, known as palm based esterquat (PBE) in removing Reactive Blue 4 (RB4) from synthetic wastewater via micellar solubilization followed by coagulation and flocculation process. The effect of PBE surfactant concentration and pH on RB4 removal efficiency were observed. In order to create an environmental-friendly and economical process, comparison between micellar solubilization and coagulation-flocculation process were discussed. Results from the studies revealed that RB4 was completely removed from synthetic wastewater at pH 4 via micellar solubilization followed by coagulation and flocculation with PBE surfactant concentration of 150 mg/L. Statistical analysis via multi linear regression shows that R^2 and adjusted R^2 for micellar solubilization were 0.968 and 0.886 whereas for coagulation and flocculation process were 0.902 and 0.412, respectively. Regression statistics and ANOVA verified that regression expression accounts for variability in the response variable.**

Keywords—Reactive Blue 4; Surfactant; Coagulation and flocculation; Micellar solubilization

1. INTRODUCTION

In the era of modernization and globalization, development of textile industry increases tremendously due to high demands on clothing and fabrics. This is because clothes are certainly a need for comfort, identification and protection for human. A diversity in clothing colour is vital for the textile industry as it is key for customer preferences. Therefore, multiple colour of dyes are used in processing and production of textile industry. Apart from the textile industry, dyes are also used in other industries like coatings, paper and pulp, paints, polymers and cosmetics.

Even though dyes consist of bright and attractive colour but in fact, they can be toxic and carcinogenic to human due to its chemical structure. Furthermore, the presence of dyes in water might prevent light penetration. This condition could threaten aquatic life. According to Huang *et al.* (2012), wastewater produced from dyeing process can be a primary pollutant since remaining dyes in industrial effluents can cause critical problems, which can affect humans health and environment [1]. Because of that, a major consideration of the environmental preservation and protection must be considered by industries which involved with the usage of dyes.

Dyes can be categorized into various classes and types, but the most preferable in the textile industry is reactive dyes due to its usability, low energy utilization and variety in colour [2]. This type of dyes is crucial in process of colorization of cellulosic and wool fibers [3]. During dyeing stage, reactive groups of dyes form covalent bonds with fiber polymer and then act as an integral part of the material [4]. When the dyeing process is completed, the material is washed off to remove any extra dyes that failed to absorb to its surface during the reaction process. At the end of the process, unfixed dyes which are soluble in water are discharged through wastewater streams and caused pollution to the environment [5].

Generally, there are various dyes treatment technologies such as carbon activated adsorption. Unfortunately, this conventional method is becoming insufficient to meet current stringent regulatory effluent limits, also is increasing in cost [6]. Another process like membrane filtration also faced the same problem as adsorption where process involving membrane is high in cost and the process is more complicated since the membranes are prone to fouling. In addition, coagulation and flocculation process are commonly used in water treatment plant, however, the process is still ineffective in protecting the environment since high amount of hazardous chemicals are used to complete the treatment processes. Also, this processes can lead to the production of high volume of sludge [7].

In recent decades, the use of surfactant in removing dyes from aqueous solution has been widely developed. The term surfactant is a blend of surface active agent which act as cleansing agents that are widely used in many applications especially in the industry for the formation of products like detergents, soaps and lubricants [8]. Specifically, process that involved the usage of surfactant is known as micellar solubilization. The micelle surface resulted from the aggregation of surfactants monomer will strongly attract the contaminants or solute, then, they will solubilize and entrapped in the interior of the micelles before being removed from the solutions [9]. There were previous studies discovered that a combination of membrane filtration with micellar solubilization such as micellar-enhanced ultrafiltration (MEUF) and micellar-enhanced microfiltration (MEMF) were quite efficient, but, both processes were not environmental-friendly processes since hazardous chemical surfactants were used in the processes and further treatments to recover the surfactants were needed at the end of the processes [10-14] .

Because of that, an environmental-friendly technology in dyes removal treatment was investigated in this study since protection and preservation of the environment are one of the most critical problems to deal with in this developing country. Therefore, the use of a biodegradable plant-based surfactant, known as palm based esterquats (PBE) is introduced in removing Reactive Blue 4 (RB4) from aqueous solution using micellar solubilization followed by coagulation and flocculation process.

In general, RB4 contains two amino groups (electron-donating groups) in the 1, 4-α-positions, and a sulfonate group in the 2-position [15]. RB4 dye is known as the second largest class of textile dyes after azo dyes which is usually used in the textile industry for colouring process [16]. Apart from that, anthraquinone reactive dyes like RB4 are highly resistant towards biodegradation and also highly toxic (LD_{50} = 8.98 mg/kg) [16]. Thus, there is an urge to create an effective treatment in removing RB4 from solutions. Hence, the effectiveness of PBE surfactant, a cationic surfactant which contained an excellent biodegradability in removing RB4 was analyzed since an environmental-friendly and economical treatment process were crucial nowadays.

In short, the aim of this research is to study the effect of pH and surfactant concentration on the removal of RB4 dye with and without the presence of surfactant. Afterwards, the data of the treatment process will be verified using statistical analysis via multi linear regression.

2. METHODOLOGY

2.1 Materials

Reactive Blue 4 (RB4) (MW 637.43 g/mol, CAS 13324-20-4) was purchased from Sigma Aldrich (M) Sdn. Bhd [17]. The surfactant used was palm based esterquat (PBE). Critical micelle concentration (CMC) of PBE surfactant is 125 mg/L. Structure of RB4 dye and PBE surfactant are displayed in Fig. 1 and Fig. 2. For coagulation and flocculation process, 4% polyaluminium chloride (PAC) which act as coagulant and flocculant, 4% polyacrylamide (PAM) (CAS 9003-0508), also 7.5% sodium hydroxide (NaOH) (MW 40.00 g/mol, CAS 1310-73-2) that used for adjustment of pH were purchased from Sigma Aldrich (M) Sdn. Bhd.

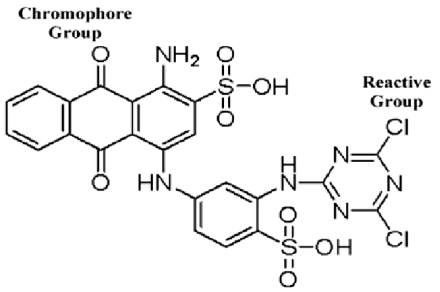

Fig. 1: Structure of Reactive Blue 4 dye [18]

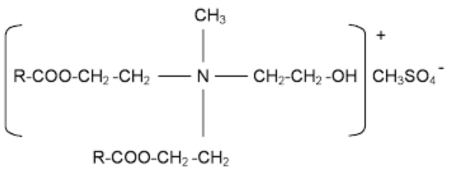

Fig. 2: Structure of palm-based esterquat (PBE) [19]

2.2 Methods

2.2.1. Coagulation

Synthetic wastewater samples were prepared with basis concentration of 50 mg/L of RB4 dyes which was closed to that found in textile effluent [20]. The dyes solution was prepared into six beakers which were then placed in jar tester. Flocculator speed was set up to 100 rpm for samples to mix homogeneously. Then, initial pH of each beaker was recorded using pH meter. Coagulation process begun with addition of PAC (4%) that act as coagulant until desired pH of the each beaker was achieved. The volume of PAC added for each beaker was recorded. The samples were mixed through rapid stirring at 100 rpm in approximately 3 minutes for the destabilization of the colloid particles in the sample to form micro flocs.

2.2.2. pH adjustment and flocculation

Coagulation process in 2.2.1 was continued with the addition of NaOH (7.5%) into each sample in order to adjust the pH of each beaker to pH range of 7.5 to 8.0. Next, the volume of NaOH solution use for each beaker was recorded. For flocculation process, 0.4 mL of flocculant, polyacrylamide (4%) was added in each beaker. The stirring speed was slowed down to 50 rpm for 15 minutes for the occurrence process of flocs bridging. Here, the formed flocs were aggregated into large particles. Flocculator was stopped and the samples were rested for 5 minutes after stirring process. Supernatant solution in each beaker was taken in order to analyze any residual dye concentration by using UV-Vis Spectrophotometer.

2.2.3. Micellar solubilization at constant pH

12.5 mL of prepared synthetic wastewater was added into four beakers, followed by addition of different volume of surfactant and distilled water into the same beakers in order to produce different surfactant concentration, with total volume of 250 mL sample in each beaker. Then, the beakers were placed in jar tester. The flocculator speed was set up to 300 rpm for 15 minutes. The samples were stirred under vigorous stirring until surfactants were completely dissolved in each beaker. At this stage, micellar solubilization process was occurred. Initial pH of each beaker was recorded. Afterward, the process was continued with coagulation and flocculation process where coagulant, PAC (4%) was added until desired constant pH in each beaker was achieved. The volume of PAC added for each beaker was recorded. Specifically, the samples were mixed through rapid stirring at 100 rpm in approximately 3 minutes for the destabilization of the colloid particles in the sample to form micro flocs. Next, the procedure was continued with pH adjustment and flocculation method as stated in *2.2.2.*

2.2.4. Micellar solubilization at constant PBE concentration

12.5 mL of prepared synthetic wastewater was added into six beakers, followed by addition of 75 mL of surfactant and 162.5 mL of distilled water into the same beakers in order to produce an equal amount of surfactant concentration which is 150 mg/L, with total volume of 250 mL sample in each beaker. Then, the beakers were placed in jar tester. The flocculator speed was set up to 300 rpm for 15 minutes. The samples were stirred under vigorous stirring until surfactants were completely dissolved in each beaker in order to initiate micellar solubilization process to occur. Then, initial pH of each beaker was recorded. This process was continued with coagulation and flocculation process where coagulant, PAC (4%) was added until desired pH in each beaker was achieved. The volume of PAC added for each beaker was recorded. Generally, the samples were mixed through rapid stirring at 100 rpm in approximately 3 minutes for the destabilization of the colloid particles in the sample to form micro flocs. Afterwards, the procedure was proceed with pH adjustment and flocculation method as stated in *2.2.2*.

2.2.5. Analysis

Supernatant solutions resulted from the experiments which contained residual of RB4 dye and PBE surfactant were measured using UV-Vis spectrophotometer whereas pH of each samples were determined using pH meter. The dye removal efficiency, R_d (%) was calculated using equation (1).

$$R_d\ (\%) = \frac{c_{initial} - c_{final}}{c_{initial}}\ x\ 100\ \% \qquad (1)$$

Where $C_{initial}$ is feed RB4 dye concentration and C_{final} is RB4 dye concentration left in the supernatant solution.

3. RESULTS AND DISCUSSION

3.1 Characterization study on PBE surfactant via FTIR analysis

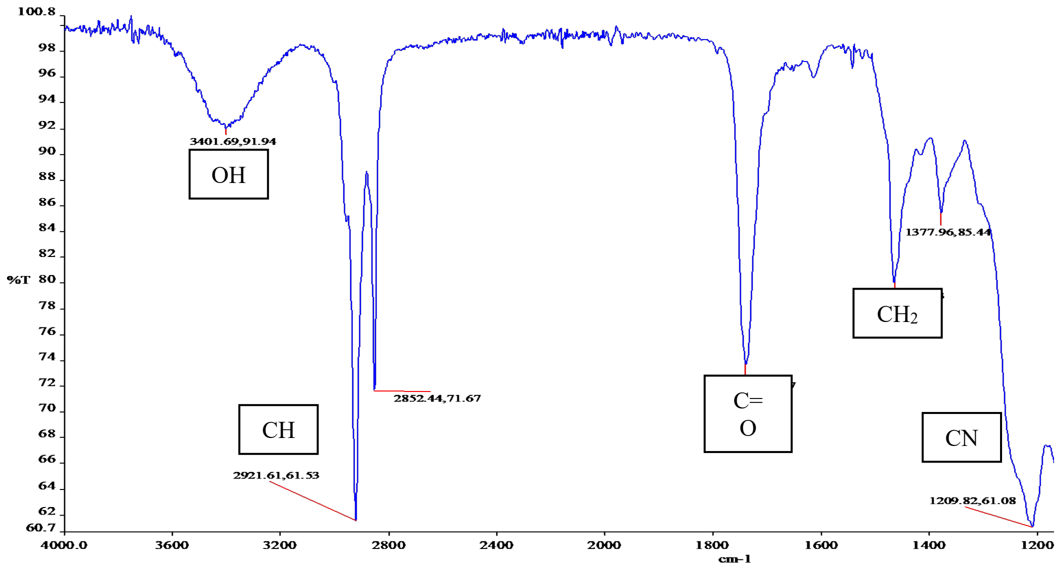

Fig. 3: FTIR spectra of PBE surfactant

Fig. 3 displays characterization of PBE surfactant which analyzed via FTIR spectra. Strong absorption peaks was observed at 2921.61 cm^{-1} and 1209.82 cm^{-1}, represented by alkanes C-H and amine C-N stretch, respectively. Amine C-N stretch contributed to positive charge of PBE surfactant which categorized as cationic surfactant. Next, the figure shows moderate absorption peaks at 1739.73 cm^{-1} and 1465.41 cm^{-1}, which belonged to C=O stretch and alkanes CH_2 bending mode. Last but not least, the visible peak 3401.69 cm^{-1} indicates hydroxyl O-H stretch.

3.2 Effect of PBE surfactant concentration on RB4 removal efficiency

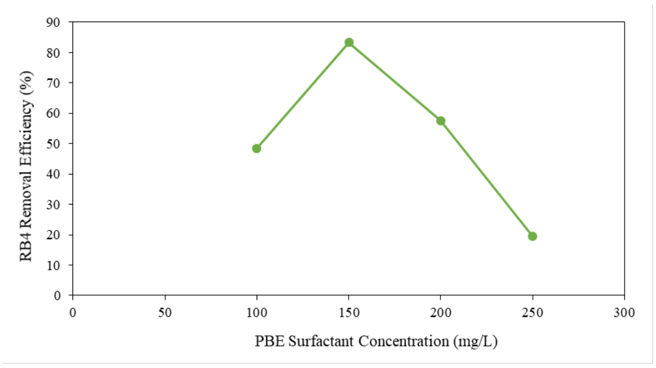

Fig. 4: Graph of RB4 removal efficiency versus PBE concentration. ([PBE] = 100, 150, 200 and 250 mg/L)

Fig. 4 reveals the effect of PBE surfactant concentration in removing RB4 dye from synthetic wastewater solutions. The PBE surfactant concentrations were varied from 100 mg/L to 250 mg/L. The previous study stated that large amphiphilic transparent micelles formed when the concentration of surfactant exceeded the CMC value and caused the surfactant monomer to assemble and aggregate together [12, 21]. Therefore, this experiment was performed to investigate the significance of surfactant concentration and CMC on RB4 removal efficiency. Based on figure above, it is observed that the highest percentage of RB4 removal efficiency was 83.32 % which occurred at PBE surfactant concentration of 150 mg/L. Specifically, PBE surfactant was added into the solutions in order to enhance the removal of RB4 dye through coagulation and flocculation. Therefore, when the PBE surfactant concentration exceeded the CMC value, surfactant monomer started to form aggregates and caused RB4 dye to solubilize in the micelles due to strong interaction between positively-charged amines C-N in PBE surfactant with negatively-charged sulfonic group of RB4 [22]. Consequently, some of dyes trapped in micelles while excess of dyes which were not trap in micelle react with coagulant, PAC via coagulation process, producing precipitate.

Apart from that, the removal of RB4 dye at PBE surfactant concentration of 100 mg/L was only 48.43%. It can be interpreted that removal of RB4 dye was completely relied on coagulation and flocculation process instead of micellar solubilization since the micelle failed to form in the solution. This is because of PBE concentration was lower than the CMC value. Furthermore, percentage of RB4 removal declines gradually as PBE surfactant concentration increases steadily from 200 mg/L to 250 mg/L. Surface tension of solution became constant when PBE concentration exceed the CMC [23]. Thus, the continuous addition of surfactant concentration only increases the number of micelles. This condition caused the solutions became saturated by the micelles. When the surfactant concentration increase, the shape of micelle tend to change into packed multilamellar vesicles which caused the solution to turn cloudy [24]. The changes in micelle shape contributed to the difference in solubilization efficiency [25]. Hydroxyl groups of surfactant could increase polarity of micelle which caused the outer region of the micelle became less favorable environment for the dyes [25]. This findings describe that CMC value is vital for micellar solubilization as this factor initiated the formation of micelle that contributed to the solubilization of dyes. Thus, PBE surfactant concentration of 150 mg/L is ideal to be used to analyze the effect of pH on micellar solubilization followed by coagulation and flocculation process as it exceeded the CMC value which were the best condition for the formation of micelle.

Table 1: Comparison between coagulation and flocculation with micellar solubilization method

Methods	**Coagulation and Flocculation**			**Micellar Solubilization**		
pH	3.50	3.70	4.00	3.23	3.50	4.00
PAC						

Dosing (mL)	101.00	80.00	25.00	106.00	7.60	4.40
NaOH Dosing (mL)	126.00	100.55	25.10	106.00	9.60	7.30
RB4 Concentr-ation (mg/L)	1.01	0.15	4.91	23.38	4.24	-0.92
RB4 Removal Efficiency (%)	97.97	99.69	90.19	53.24	91.53	100.00

3.3 Effect of pH on RB4 removal efficiency

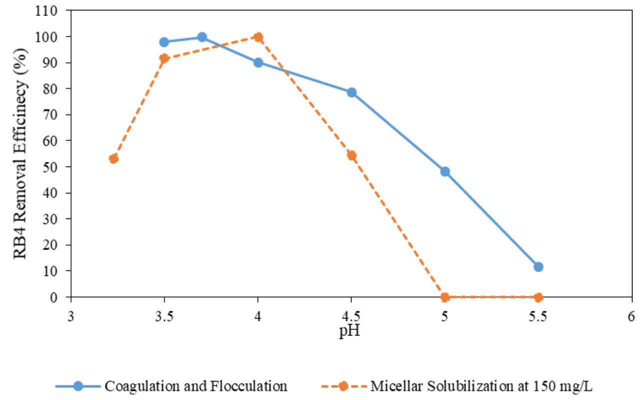

Fig. 5: Graph of RB4 removal efficiency versus pH

Fig. 5 interprets the effect of pH on the removal of RB4 for coagulation and flocculation process without the usage of PBE surfactant, also micellar solubilization followed by coagulation and flocculation process at constant PBE concentration which was 150 mg/L. Both processes were compared in order to determine the effectiveness of PBE surfactant in removing RB4 dye from solutions. Previous research indicated that acidic and neutral pH values were found to be more effective for the degradation of RB4 dye compared to basic pH [16]. Hence, pH range of 3.0 to 5.5 were selected for this experiment. The figure shows that the removal of RB4 for coagulation and flocculation at pH 3.5 and 3.7 were 97.97% and 99.69%, respectively whereas for micellar solubilization followed by coagulation and flocculation process, the percentage of RB4 removal rises steeply from 53.24% to 91.53% at pH 3.23 and 3.5. Even though coagulation and flocculation process shows higher percentage of RB4 removal in pH range of 3 to 4 compared to micellar solubilization, however, coagulation and flocculation process requires high amount of polyaluminium chloride (PAC) and sodium hydroxide (NaOH) dosing compared to micellar solubilization which resulted in the production of high volume of sludge. The amount of chemical dosing for both processes are listed in Table 1. The usage of high amount of chemicals in dyes treatment could increase costs, also the sludge produced at the end of the process could pollute the environment. Because of that, PBE surfactant was introduced before coagulation and flocculation process since the surfactant reduced the usage of chemicals dosing which lead to the generation of small amount of sludge. At low pH, micellar solubilization portrays lower percentage of RB4 removal compared to coagulation and flocculation process due to presence of surfactant which became hindrance towards coagulation and flocculation process. At pH range of 3 to 4, micelles formed in the solutions start to attract and trap RB4 in the core of the micelle. Therefore, instead of precipitate, most of the RB4 dye trapped and remained in the micelle.

The removal of RB4 using PBE surfactant shows that the dye was completely removed at pH 4 meanwhile for coagulation and flocculation process, the percentage slightly decreases to 90.19%. This could occur because of electrostatic interactions between anionic groups in RB4 with cationic groups in PBE surfactant [26]. Solubilization became very high as polar head group interact strongly with the dyes [25]. Besides, stable RB4 dye solubilized and trapped in micelles, reducing dependent of the dye on chemicals. The presence of micelles in the solutions with the addition of excellent precipitation at pH 4 resulting in high efficiency of RB4 removal. Apart from that, the figure displays that both processes declines tremendously as the pH value increases up to 5.50. The efficiency of dye removal for coagulation and flocculation decreases as pH increases caused by of the reduction of chemical dosing. Specifically, small volume of coagulant, PAC could reduce the formation of flocs and hence, decrease the efficiency of RB4 removal. In contrast to micellar solubilization, the increment of pH towards alkaline condition reduced the PBE concentration, therefore, decreased the amount of RB4 solubilized in micelles.

Besides, the removal of RB4 in micellar solubilization was not occur at pH 5 to 5.5. At higher pH, PBE surfactant tend to break which prevent the formation of micelle. This condition inhibited precipitation of RB4 from occur. Therefore, pH 4 with concentration PBE surfactant of 150 mg/L were found to be the best condition for removal of RB4 dye through micellar solubilization followed by coagulation and flocculation process since less volume of sludge, also produced high removal of RB4 from synthetic wastewater compared to coagulation and flocculation without the usage of surfactant.

3.4 Regression analysis via excel software

3.4.1Micellar Solubilization followed by Coagulation and Flocculation Process

A multiple regression analysis was conducted using Excel Software in order to determine a statistically significant relationship between RB4 removal efficiency as response, y and parameters selected in this research which were polyaluminium chloride (PAC) dosing, x_1 and sodium hydroxide (NaOH) dosing, x_2. A mathematical expression is expressed in equation below:

$$y = -(2.158 \times 10^{-2})\, x_2^2 x_1 + (2.156 \times 10^{-2})\, x_1^2 x_2 + (3.692)\, x_2^2 + (2.189)\, x_1^2 - (5.879)\, x_1 x_2 + 53.478 \quad (2)$$

Based on regression statistics of mathematical expression above, the value of R^2 and adjusted R^2 were 0.968 and 0.886, respectively. Predicted R^2 value indicates that approximately 89% of RB4 removal efficiency in regression model can be predicted by predictors, x_1 and x_2. Analysis of variance (ANOVA) reported significance F value was 0.079 which indicates relationship between x_1 and x_2 are significant.

Fig. 6 portrays plot of predicted versus experimental value in a regression model for micellar solubilization followed by coagulation and flocculation process. From the figure, the data are scattered around 45 degree line. This result express that the variables were statistically significant since predicted value from the mathematical expression were close with experimental data.

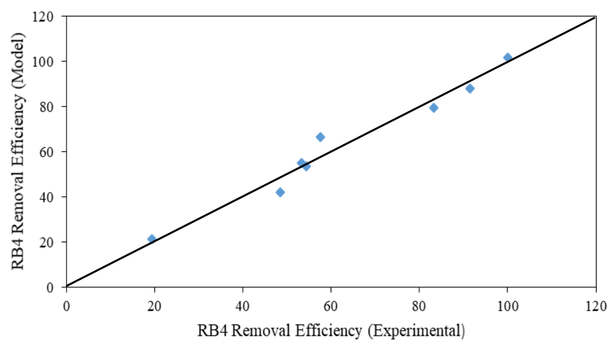

Fig. 6: Plot of predicted data versus experimental data of RB4 removal efficiency for micellar solubilization

3.4.2 Coagulation and Flocculation Process

For coagulation and flocculation process, a remarkable relationship between RB4 removal efficiency as response, y with selected parameters which were polyaluminium chloride (PAC) dosing as x_1 and sodium hydroxide (NaOH) dosing as x_2. A mathematical expression is expressed as:

$$y = -(24.833)\, x_2^2 x_1 + (30.313)\, x_1^2 x_2 - (859.917)\, x_2^2 - (2115)\, x_1^2 + (2835.498)\, x_1 x_2 + 42.719 \quad (3)$$

Based on regression statistics of mathematical expression above, the value of R^2 and adjusted R^2 were 0.902 and 0.412, respectively. Predicted R^2 value indicates that the data for coagulation and flocculation process were not well fitted. Analysis of variance (ANOVA) reported significance F value was 0.506 which was much higher than 0.05, indicates that the results were not significant.

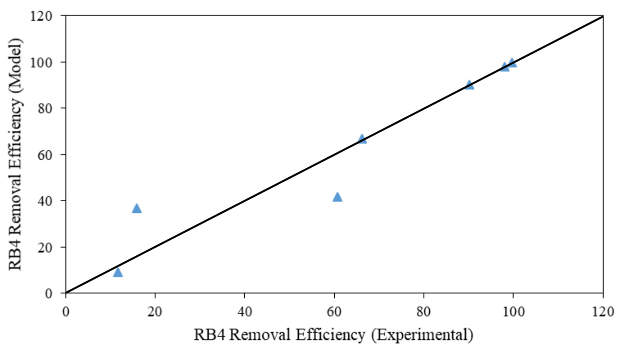

Fig. 7: Plot of predicted data versus experimental data of RB4 removal efficiency for coagulation and flocculation

Fig. 7 shows plot of predicted versus experimental value in a regression model for coagulation and flocculation process. From the figure, the most of the data are scattered around 45 degree line. This result express that predicted value from the mathematical expression were quite close with experimental data.

4. Conclusion

Removal of RB4 from synthetic wastewater using micellar solubilization followed by coagulation and flocculation process has been studied. It can be observed that PBE concentration and pH have significant effect on RB4 removal efficiency and both parameters were correlated. For the effect of PBE surfactant concentration, the maximum percentage of RB4 removal was 83.32% which occurred using PBE concentration of 150 mg/L at constant pH of 3.7. Apart from that, study on the effect of pH on RB4 removal efficiency found that the dye was completely removed at pH 4 with low usage of chemicals dosing compared to coagulation and flocculation process in which high amount of chemicals were dosed, resulting the removal of RB4 at pH 3.7 was 99.69%. Last but not least, statistical analysis via multi linear regression indicates that R^2 and adjusted R^2 for micellar solubilization were 0.968 and 0.886 whereas for coagulation and flocculation process were 0.902 and 0.412, respectively. Overall, it can be concluded that results obtained from this study proved that performance of PBE surfactant is efficient in removing RB4 dye from synthetic wastewater. Surfactant acted excellently as special ingredient in enhancing coagulation and flocculation process. Furthermore, the usage of surfactant in removing the dyes shows high potential to create an environmental-friendly condition and also generate a cost-effective process.

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