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Synthesis and Scaling up of Fe^{3+} by Sol-gel Method Doped on Ceramic Foam for Decolorization of Reactive Red Dyeing Wastewater

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Abstract

Wastewater from the *Batik* textile industry contains large amounts of dyestuff together with significant amounts of suspended solids (SS), dispersing agents, salts and trace amounts of metals. Since this can lead to severe environmental problems, proper wastewater treatment processes are essential. The synthesis of Fe^{3+} by sol-gel method doped on a ceramic foam for reactive red and disperse dyes removal from synthetic dye wastewater. In this research, the effect of color concentration, amount of catalyst and volumetric flow rates for industrial scale were studied. The Fe^{3+} catalyst was prepared by sol-gel method in which 3M of $FeCl_3$ was used as a precursor. The synthesized catalyst was characterized by the EDX spectrum from an X-ray spectrometer. The surface morphology of the catalyst was investigated using a scanning electron microscope (SEM). To determine optimum operating conditions for catalytic testing, variations of disperse and reactive red concentrations (10 to 200 mg/L) were used. The results indicated that the highest color removal efficiency (up to 96%) was observed when using Fe^{3+} catalyst; 4 pieces per litre of solution, and initial pH of 6.0. These conditions were then scaled up for a continuous packed bed column study. It was found that the optimal operating conditions obtained from the mathematical model for reactive red wastewater were: concentration of reactive red in the synthetic wastewater 20 to 80 mg/L; amounts of catalyst 432.5 to 1,730 mg and volumetric flow rates of wastewater 20 to 200 mL/min. Up to 84.85% of color removal efficiency was achieved.

Keywords: Fe^{3+}; Sol-gel; Decolorization; Dyeing Wastewater; Mathematical model; Ceramic foam

Introduction

In Thailand, the textile-dyeing industry is a medium sized business. The dye industry is one of the key chains in the garment and textile manufacturing industry, which accounts for USD 3.677 billion/year at national level [1]. Dyeing is a value-adding process, a transformation of fabric and calico, a plain-woven textile made from unbleached and often not fully processed cotton, into prefabricated products used in diverse downstream industries. Today, the dye industry has expanded significantly, leading to growing environmental concerns due to their heavy dependence on toxic water-soluble chemicals and dyes [2]. Moreover, the industry is a heavy user of water, with each cleaning step consuming large amounts. Hence, colors and chemicals contaminated in the effluent become an environment problem [3]. However, treatment of this wastewater is expensive, which can be a problem for small-to-medium size manufacturers, especially for community-based production under the 'OTOP' (One Tumbol One Product) scheme.

Dyes, commonly used in the bleaching and dyeing industries include large, complex organic compounds, many of which are potentially toxic and carcinogenic. The industrial classification of dye method identifies 11 categories: color acid, direct dye colors, basic dye, disperse dye, reactive dye, azoic dye, vat dye, mordant dye and sulfur dye. The group of atoms or electrons forming part of an organic molecule that confers its characteristic color is called the chromophore. Reactive dyes are widely used for cellulosic substrates and offer a wide range of hues. The most attractive feature of these dyes is the simplicity of the dyeing process. However, reactive dye-contaminated wastewater is highly alkaline, and cannot be treated efficiently by traditional wastewater technologies.

Conventional processes for wastewater treatments in the dyeing industry include biological oxidation, chemical coagulation, advanced oxidation and adsorption. These methods are costly and unwieldy. Iron in the form of Fe^{2+} or Fe^{3+} from ferrous sulfate ($FeSO_4 \cdot 4H_2O$), ferrous nitrate ($Fe(NO_3)_2$) or ferric chloride ($FeCl_3$) are used for color removal in wastewater treatment processes. The Fenton reaction is an alternative method of color removal from waste water, but this method is also costly due to the need to adjust the pH of wastewater before treatment, and elimination of chemicals along with the sediment. Development of an iron-coated medium as a heterogeneous catalyst can practically be used without loss of chemicals lost as sediment waste after the treatment process.

It is therefore necessary to explore a technically feasible, efficient and economical method to remove reactive dyes from highly alkaline wastewater. Examples of research in this area include the removal of dyes under alkaline conditions using magnetic chitosan-Fe (III) hydrogel [4] and decolorization of disperse and reactive dye solutions using ferric chloride [5]. Heterogeneous ferric-type catalysts have been developed by incorporating iron ions or iron oxides into porous support structure, so that Iron (III) species are present on the porous support. The main reaction mechanism of the heterogeneous process is described as follows:

$$X\text{-}Fe^{3+} + \text{dye} \rightarrow X\text{-}Fe^{2+} + {}^{\cdot}\text{dye}^{+} \quad \text{(Eq.1)}$$

$$\text{Oxidative radicals} + {}^{\cdot}\text{dye}^{+} \rightarrow \text{Intermediate products} \rightarrow CO_2 + H_2O \quad \text{(Eq.2)}$$

$$X\text{-}Fe^{2+} + 2O_2 + 4H^{+} \rightarrow 4Fe^{3+} + 2H_2O \quad \text{(Eq.3)}$$

where X represents the surface of the catalyst. Iron (III) can then react through Eq. 1-2 and regeneration of iron (II) is continuously performed by oxygen in Eq. 3 during the decolorization process.

This study aimed to decolorize reactive red wastewater using a Fe^{3+} heterogeneous catalyst. The catalyst was synthesized by applying ferric (Fe^{3+}) and chloride (Cl^{2+}) as precursor by the sol-gel method combined with dip coating. The decolorization of synthesis wastewater were performed and tested in a batch reactor. The variable parameters were initial pH of wastewater, concentrations of dye, and the amount of catalyst. The dye concentrations were measured using a UV-vis Spectrophotometer. In addition, the mathematical model to determine optimal conditions was studied and developed for the continuous packed-bed column, for further application at industrial scale.

Materials and Methods

1) Reagents and chemicals

Analytical grade magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, 99.5%) and oxalic acid ($(COOH)_2 \cdot 2H_2O$, 99.5%) were obtained from Ajax Finechem Co., USA. Ferric chloride ($FeCl_3$), commercial grade was obtained from Qualitech Ltd., Thailand. Analytical grade ethanol 99.9% was obtained from Merck Ltd., Germany. Ceramic foam (20 ppi) was purchased from Assab Steels (Thailand) Public Co. Ltd. In this study, 3 types of support were used for treatment of wastewater from the dyeing industry, as shown in Figure 1.

2) Catalyst preparation

Iron (III) ion catalyst was obtained using the sol-gel method and dip-coated as described by Kumar and Kumar [6]. The process is explained in the schematic flow chart as shown in Figure 2. The solutions were prepared by dissolving $Mg(NO_3)_2 \cdot 6H_2O$, $(COOH)_2.2H_2O$ and $FeCl_3$ in absolute ethanol, referred to as A, B and C, respectively. The sol-gel was prepared by premixing the B solution into the A solution and stirring at room temperature for 10 minutes to form the catalyst solution. Then the C solution was added into the catalyst solution and stirred at room temperature to prepare the catalyst sol [7]. Before dip coating, the ceramic foam pieces were degreased by cleaning thoroughly and drying in an oven at 100 °C for 1 hr. The circular ceramic foam pieces were dipped into the catalyst solution, and the films were then dried at 100 °C for 1 h, calcined at 600 °C for 2 h, and cooled at 10 °C/min. Finally, the Fe^{3+} doped on ceramic foam was obtained. The synthesized catalysts were characterized by Energy Dispersive X-ray Spectrometer (EDX) [7].

The sol was subsequently dried at 100°C for 24 h. The reaction equation of the precursor mixture can be expressed in Eq. 4. Calcination of the dried sol was performed in flowing air for 2 h at 600°C under atmospheric pressure and cooled down at a rate of 10°C/min. The reaction of the calcination step is given in Eq. 5 [7]:

$$Mg(NO_3)_2 \cdot 6H_2O + (COOH)_2 \cdot 2H_2O \rightarrow MgC_2O_4 \cdot 2H_2O + 2HNO_3 + 6H_2O \quad (4)$$

$$MgC_2O_4 \cdot 2H_2O + 0.5O_2 \rightarrow MgO + 2CO_2 + 2H_2O \quad (5)$$

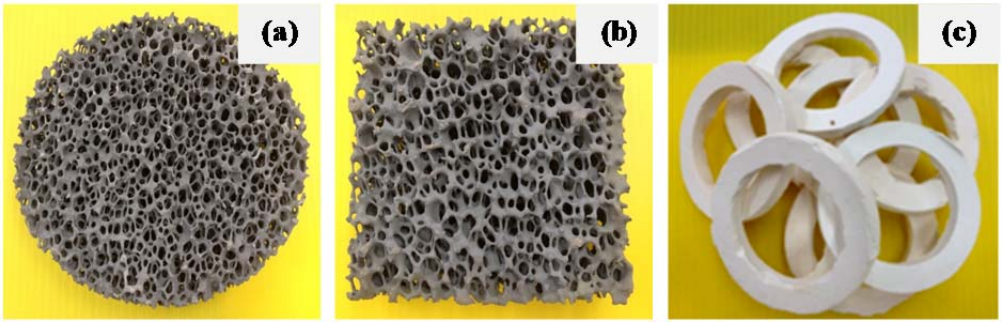

Figure 1 Demonstration of (a) circular ceramic foam used as support material; (b) square type ceramic foam; and (c) fresh circular ceramic foam before dip-coating with iron catalyst.

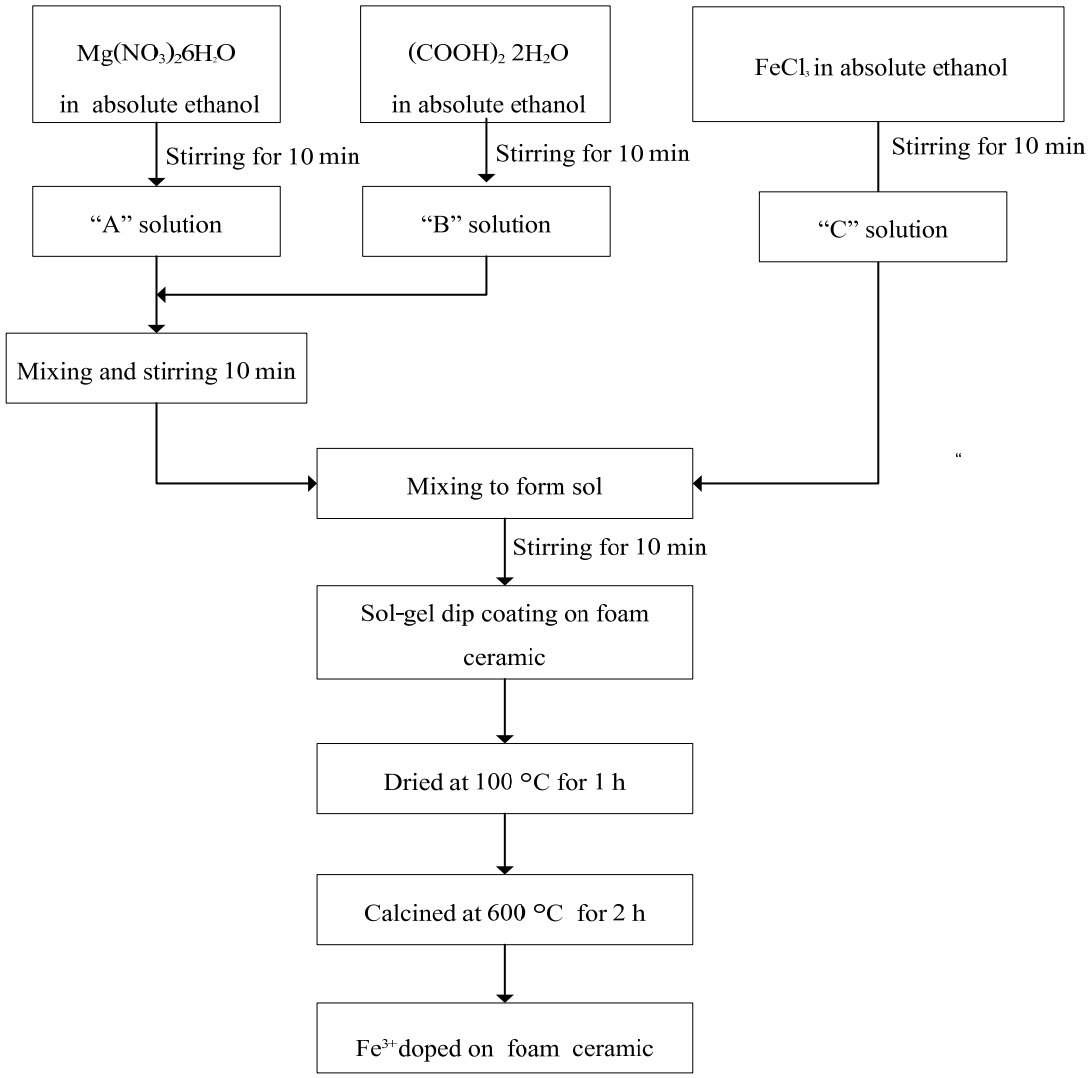

Figure 2 Schematic diagram of the Fe^{3+}-doped on ceramic foam synthesis by sol-gel dip coating technique.

3) Synthetic wastewater preparation.

The required chemicals for preparation of the synthesis wastewater are reactive red. Therefore, NaOH, HCl and distilled water were used to adjust the pH. In this study, the selected candidate for synthetic wastewater is reactive red at various concentrations (0.01, 0.05, 0.10, 0.15, and 0.20 g/L).

4) Scaling up to continuous scale for dyeing wastewater treatment

In this study, a packed-column continuous reactor was constructed for dye removal from wastewater, as shown in Figure 3(a); the treated wastewater is shown in Figure 3(b). The column was constructed from transparent acrylic pipe with 11cm internal diameter, 2 mm column thickness and 90 cm in height. Holes were cut along the column in order to sample treated wastewater samples at 30, 42, 60, 78 and 90 cm. The column was packed with circular and square types of ceramic foam to increase the surface area. The wastewater was stored in Storage tank 1 and pumped into the base of the column for complete mixing. The r effluent stream flowed out from the top of column. This experiment studied the effect of amount of catalyst (432.5-1,730 pieces), concentration of reactive red in waste water (0.01-0.08 g/L) and volumetric flow rate (0.01-0.1 L/min).

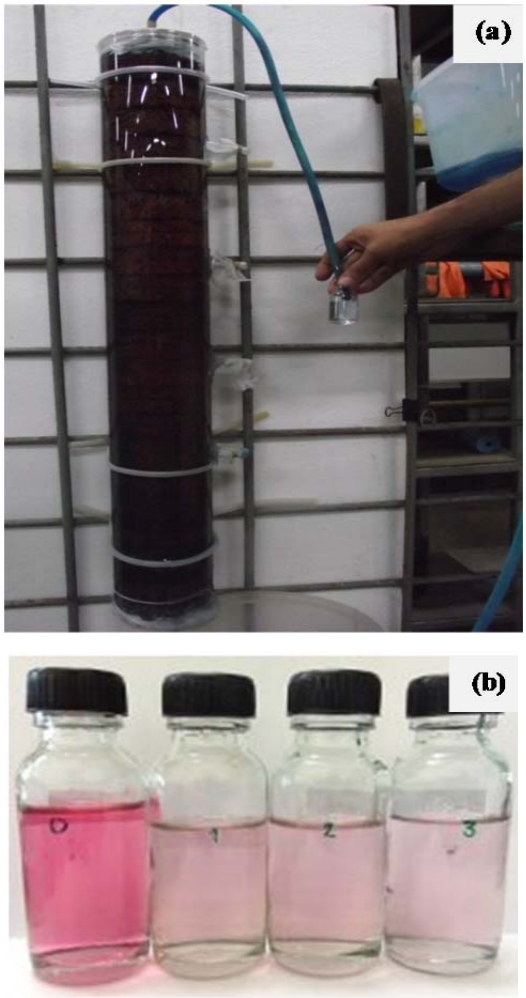

Figure 3 Pictures showing (a) the packed column and sampling port, (b) reactive red in wastewater at 0, 1, 2 and 3 minutes.

The Response Surface Methodology (RSM) technique is a statistical collection and mathematical technique to improve experimental designs aiming to determine optimal operating conditions. RSM comprises mathematical parameters combined with statistical methods to elucidate the relationships between responses and independent variables. In this study, the RSM technique, central composite design (CCD) type was used to design and fit a quadratic model, and analysis of variance (ANOVA) was used to determine which parameters significantly affect the desired response (dependent variables). Data analysis was performed for the process of wastewater treatment for reactive red using the continuous packed column.

The results indicate the response- in this case the color removal efficiency- is shown in Eq. 6:

$$\%\text{Color Removal Eff.} = [(C_0-C_1)/ C_0]*100 \quad (6)$$

C_o is the concentration of reactive red before treatment, C_1 is the concentration after treatment. The independent variables of interest included concentration of reactive red (mg/L), amount of catalyst (mg) and volumetric flow rate (mL/min). The contributions of these variables to the response were determined using multiple regression analysis.

5) Experimental setup and characterization methods

5.1) Batch experimental set up and analytical method

The magnetic stirrer, reactor (beaker 1000 ml) and catalyst was prepared for the batch experiment. The synthesis wastewater at dye concentrations of 0.01-0.20 g/L was prepared by dissolving reactive red and dye in distilled water at pH 5-8, with 1-4 pieces of catalyst per liter, and retention time of 24 hour. HCl and NaOH were used for pH adjustment. 1-4 pieces of circular ceramic foam pieces with Fe^{3+} ion coating catalyst were added into the reactor. The amount of catalyst was found to be 40.5 mg Fe^{3+}/piece as measured by weighing the coated catalyst comparing with the original and then using a magnetic stirrer to increase the surface contact on the ceramic surface. Samples were collected at 1, 5, 10, 20, 40, 80 and 120 minutes, and then analyzed using a UV-vis spectrophotometer at visible maximum absorbance range. The decreases in the absorbance peaks were directly proportional to reductions in dye concentration.

Color removal efficiency (%) can be determined by Eq. 7 using the initial and final color concentrations in the wastewater, as follows:

$$\%\text{Color Removal} = [(C_1-C_F)/ C_1]*100 \quad (7)$$

where % color removal is the percentage color removal efficiency, C_I and C_F is initial and final color concentration in the wastewater (g/L), respectively.

After preparation of the iron catalyst by sol-gel method on ceramic foam, the Fe^{3+} concentration on the ceramic foam was determined by sampling from leaching with 100 μL concentrated acid using a micropipette. A sample was taken in a 50 mL flask containing 10mL ammonium acetate buffer and 20 mL phenantharoline solution, and diluted with deionized water to obtain 50mL of solution. The solution was then shaken and left to stand. When the color of the solution changed to orange, a sample was taken to measuring absorbance at a wavelength of 510 nm using a UV-vis spectrophotometer [8]. For Total Fe measurement using an atomic absorption spectrometer (AAS), absorbance was determined using a 50 μL sample, to which 2% nitric acid was added, before adjusting the volume to 50 mL with distilled water. The concentration of Fe^{3+} was then calculated at various time intervals from Total Fe and concentration of Fe^{2+} as represented in Eq. 8:

$$Fe^{3+} = \text{Total Fe} - Fe^{2+} \quad (8)$$

5.2) Characterization and Analytical Method

The presence of the Fe^{3+} catalyst on the surface of ceramic foam was confirmed using an Energy Dispersive X-ray Spectrometer (EDS: Oxford ISIS 300). The EDX spectra from X-ray Spectrometer confirmed the presence of elemental Fe on the synthesized Fe^{3+} catalyst, indicating that Fe^{3+} was indeed present on the ceramic surface. The analysis result of each element on dip coating catalyst on circle type ceramic foam were analysed before and after use as a catalyst for a 6 month period. The result indicated that it contained C, O, Mg, Al, Si, Fe and Cl. However, it could also be observed that elemental Fe decreased slightly due to loss of the iron dip coating on the ceramic foam during usage.

Surface morphology was evaluated by a scanning electron microscope (SEM) as shown in Figure 4. From the SEM characterization, magnification of 3,500 times indicated a rough surface of fresh ceramic foam as shown in Figure 4(a) and ceramic foam after dip coating with Fe^{3+} catalyst, indicating that the Fe catalyst was well-dispersed on the ceramic foam surface. The iron catalyst adhered well to the rough surface of the foam, as shown in Figure 4(b).

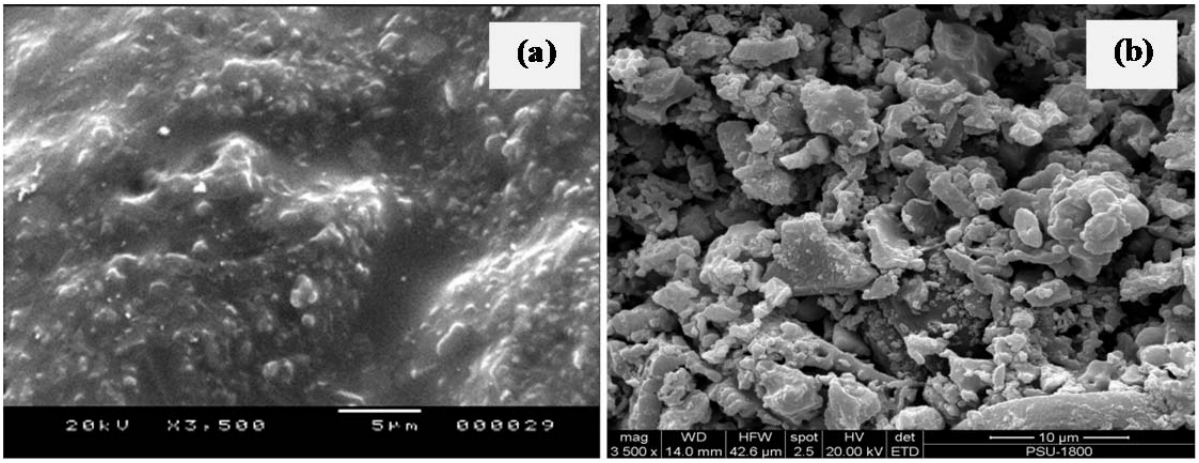

Figure 4 Surface morphology of Fe^{3+} on ceramic foam carried out by scanning electron microscope (SEM); (a) fresh ceramic foam; and (b) dip coating iron catalyst ceramic foam.

Results and Discussion

1) Characterization of the Fe^{3+}catalyst

The concentration of Fe^{3+} dip coating on ceramic surface was analyzed as described above, for three types of catalyst on ceramic foam, before and after the treatment process. Levels of total Fe, Fe^{2+} and Fe^{3+} are reported in Table 1. It should be noted that after the treatment process, Fe^{3+} can be transformed back into Fe^{2+} in a reversible reaction using O_2. Fe^{3+} and Fe^{2+} dip coating catalyst could therefore be used effectively for dye removal from wastewater.

2) Effect of dye concentration in wastewater on decolorization

Figure 5 shows the color removal efficiency from dyeing wastewater at various concentrations (0.01, 0.05, 0.10, 0.15, and 0.20 g/L) using Fe^{3+}catalyst at 1 piece/L at an initial pH of 7.5. The highest efficiency of color removal treatment was found at a wastewater dye concentration of 0.05 g/L, with 95% removal over the 24-hour run time. This concentration was optimal due to the proper retention time on the catalyst. At higher dye concentrations, the catalyst seems to have fewer active sites for treatment; as was the case at very low dye concentration (0.01 g/L).

3) Effect of pH on decolorization

The color removal efficiency of Fe^{3+} catalyst 81 mg/L for dyeing wastewater at a concentration of 0.01 g/L was determined at various pH points. The results, presented in Figure 6, show that the highest efficiency for color treatment was found at Ph6 in the batch reactor, with 96% removal within a 2-hour run time. It should be noted that decolorization of reactive red was found to be not much different at pH 5-8. At pH 6, decolorization efficiency was slightly improved. The medium pH range influenced removal properties by its effect in increasing the number of Fe^{3+} active catalyst sites to enhance degradation.

4) Effect of amount of catalyst on wastewater decolorization

The color removal efficiency of the dyeing wastewater using 1-4 pieces /L of Fe^{3+}catalyst (40.5 mg/piece) at dye concentration of 0.01 g/L and initial pH 6 is shown in Figure 7. It was found that 4 pieces/L (162 mg/L) placed in the batch reactor resulted in the highest efficiency for color treatment, with 94% removal at 2-hour run-time, confirming the work of Phlaharn [9]. A higher number of active Fe^{3+} sites would result in a higher contact surface area between catalyst and dyeing wastewater. However, the amount of catalyst needed (162 mg) was highest, which could lead to increased overall operating costs. With this in mind, the optimal amount of catalyst was determined at 2 pieces/L (81 mg/L) which could maintain the % color removal over 24 h.

Table 1 Amount of Fe, Fe^{2+} and Fe^{3+} on iron catalyst dip coating on each type of support material before and after used

Support material	Ferrous (Fe^{2+}) (mg Fe^{2+}/piece)		Ferric (Fe^{3+}) (mg Fe^{3+}/piece)		Total Fe (mg Fe/piece)	
	Fresh	Spent	Fresh	Spent	Fresh	Spent
Circle type ceramic foam Ø10×2 cm (10ppi)	13	11	46	39.1	59	50.1
Square type ceramic foam 8×8×2 cm (10ppi)	11	9.3	40.5	36.1	51.5	45.4
Circular type ceramic foam Surface area 28.3 cm^2	5.1	5	16.3	16	21.4	21

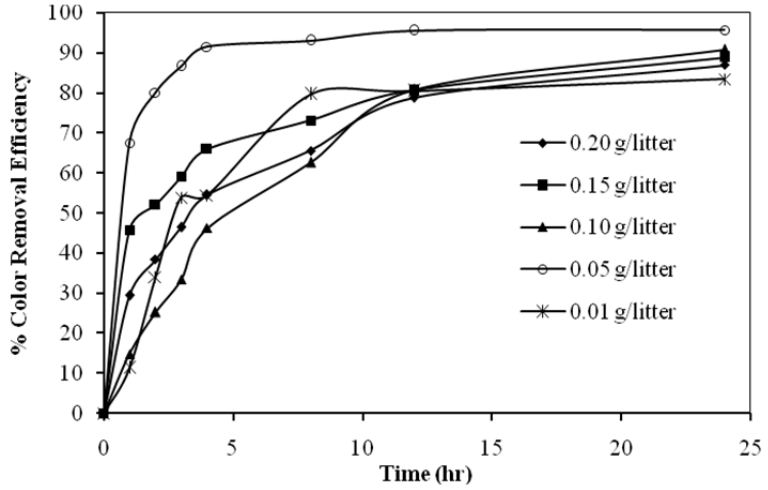

Figure 5 Effect of dye concentration in wastewater on decolorization by Fe^{3+} catalyst in the batch system.

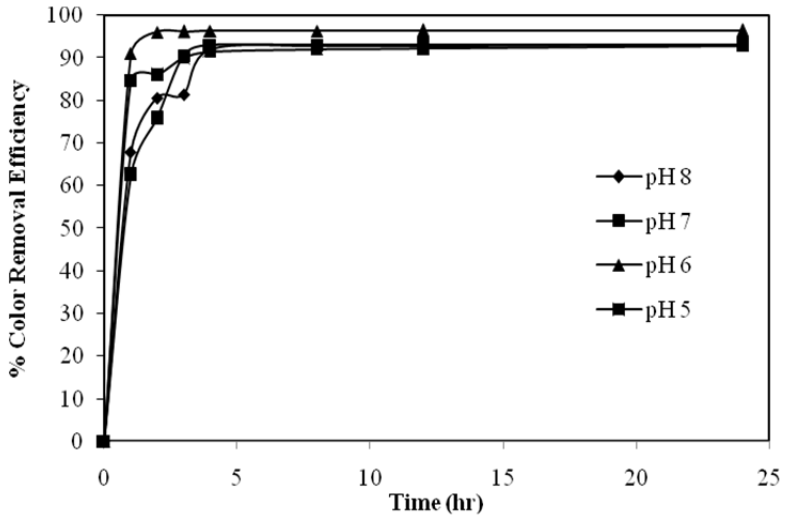

Figure 6 Effect of pH on color removal in reactive red 0.01 g/L in wastewater treatment in the batch system.

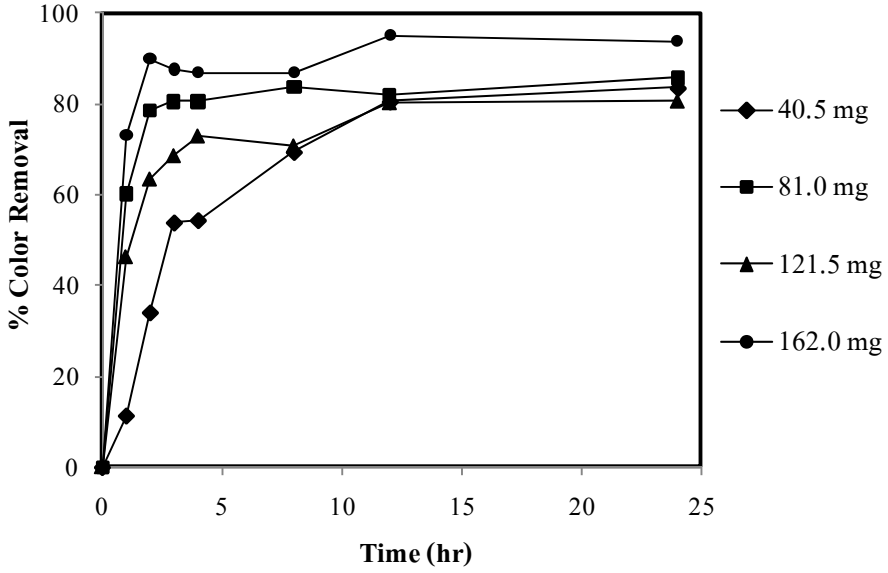

Figure 7 Effect of amount of catalyst (pieces) on decolorization of dyeing wastewater in a batch system.

5) Effect of added air (O_2 and N_2) to regenerate the catalyst

The effect of adding O_2 to wastewater efficiency treatment in this batch system was determined at pH 6, dye concentration of 0.01 g/L, using 81mg/L of catalyst. It was found that addition of air had only a slight effect on color removal efficiency, since the amount of O_2 in wastewater was already sufficient for regeneration, allowing continuous transformation of the Fe catalyst coating on ceramic from Fe^{3+} to Fe^{2+}. Thus, the catalyst could be used continuously. The effect of added air to treatment process was shown in Figure 8.

The result of wastewater treatment with Fe dip coating catalyst on chemical oxygen demand (COD) was also determined. The chemical oxygen demand of synthetic wastewater was reduced from 52 to 37 mg/L which was 28.84% COD removal. The wastewater of reactive red was analyzed at pH 6, dye concentration of 0.01 g/L, and 81mg catalyst/L. The results indicated that the quality of wastewater was improved and meet the requirements of the Pollution Control Department (PCD). It should be noted that synthesis wastewater does not contain any other contaminants apart from reactive dye.

6) Scaling up to continuous scale treatment of for dyeing wastewater

In order to determine optimal conditions for scaling up the continuous process using the packed column packed with circle and square type catalyst). Key operating conditions were selected as a range of independent variables that affect the color removal efficiency; these are dye concentration (x_1) (mg/L), amount of catalyst (x_2) (g) and wastewater flow rate (x_3) (ml/min). The data were analyzed and a mathematical model developed to relate the efficiency of color removal to the independent variables (x1, x2 and x3). The resulting quadratic model isrepresented in Eq. 9.

$$y = 24.71 - 0.07X_1 + 0.02X_2 - 0.04X_3 - 0.000008X_2^2 + 0.0004X_3^2 \quad (9)$$

where y = efficiency color removal (percent)
X_1 = dye concentration in the inlet stream (mg/L)
X_2 = amount of catalyst (mg)
X_3 = volumetric flowrate of the wastewater inlet stream (mL/min)
R^2 = 0.9862

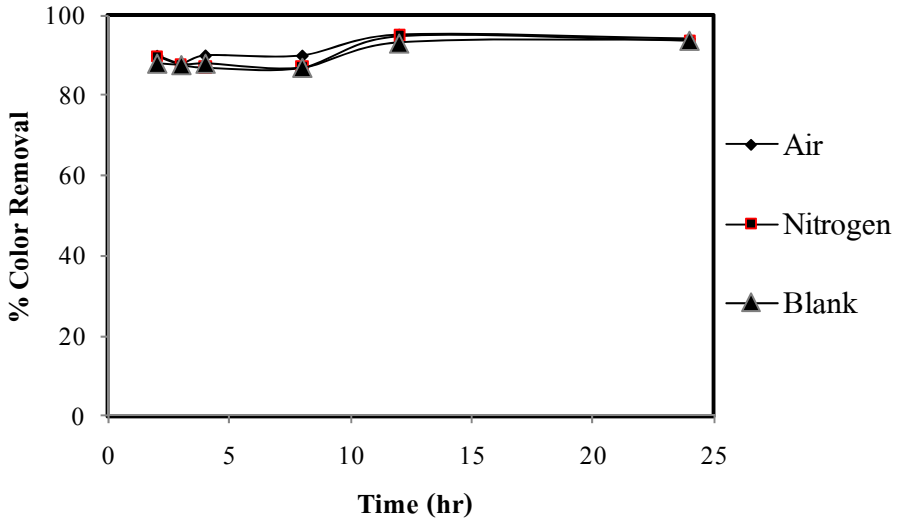

Figure 8 Effect of added air to removal efficiency of reactive red in synthesis wastewater which have dye concentration 0.01 g/L, pH 6, catalyst 81 mg/L in batch system.

Eq. 9 was used to determine the significance of the independent variables on color removal efficiency. The significance of each parameter was analyzed using ANOVA, and the mathematical model for reactive red wastewater treatment by continuous packed column was used to establish correlation of variables with efficiency of color removal on the response surface. The RSM model was able to indicate the effect on efficiency of color removal (y) of 3 independent variables simultaneously: these are concentration of reactive red (X_1), amount of catalyst (X_2) and volumetric flowrate (X_3). The proposed mathematical model and RSM described the effect as shown in Figure 9 below.

1) Effect of independent variables on color removal in wastewater

Regression analysis was conducted to establish the relationship between the 3 independent variables (concentration of reactive red (X_1), amount of catalyst (X_2) and volumetric flowrate (X_3)) on efficiency of color removal. Figure 9(a) represents the effect of X_1 and X_2 on efficiency of color removal (y) at a volumetric flowrate of 56.49 mL/min. It was found that efficiency (y) decreased as the dye concentration X_1 increased, as related to the correlation in Eq. 9. This was due to the limited availability of catalyst reaction sites at higher concentrations.

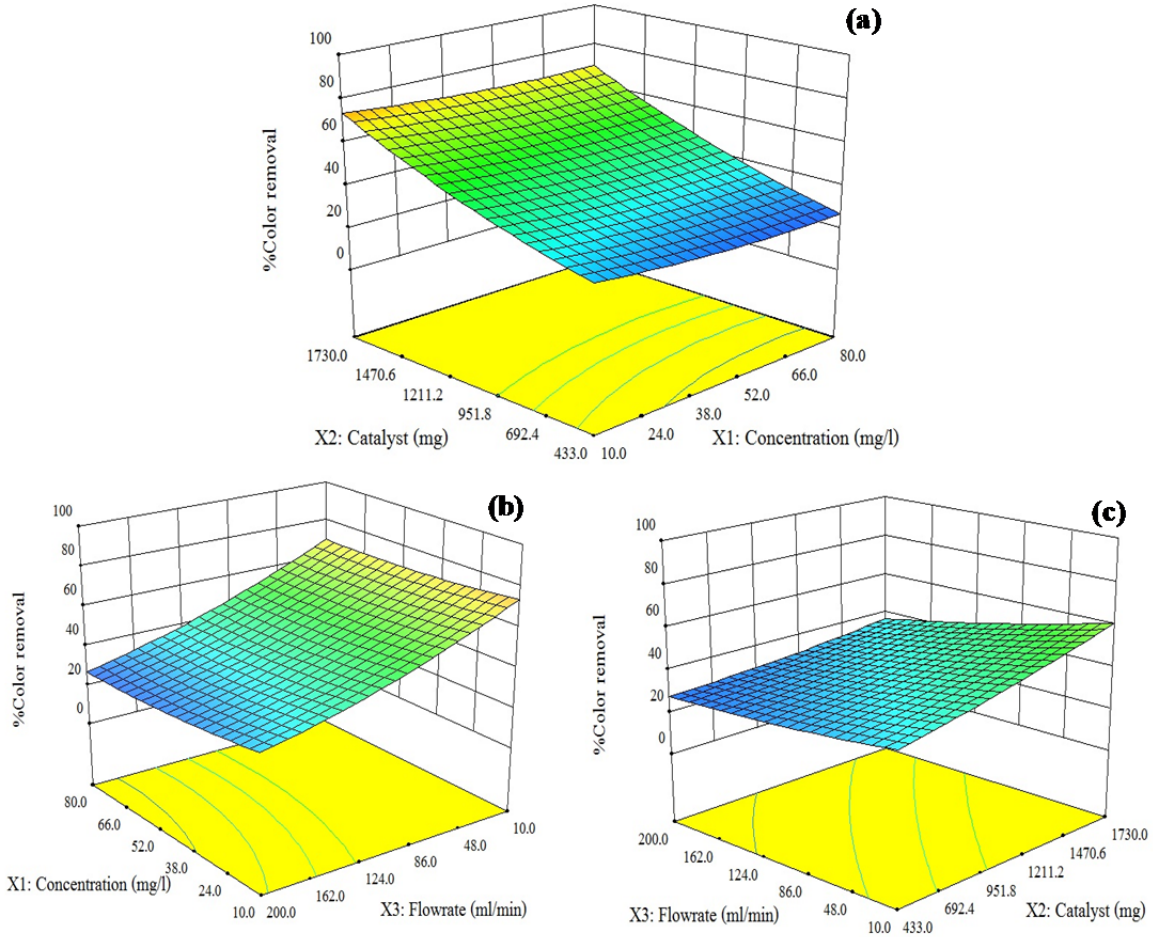

Figure 9 Response surface of (a) X_1 and X_2, (b) X_2 and X_3 and (c) X_2X_3 on efficiency color removal (y)

This conclusion was confirmed by the observation as shown in Figure 9(b) that at a dye concentration of 32 mg/L, increasing the amount of catalyst increased the number of active sites, leading to increased efficiency of color removal. The effects of X_2 and X_3 were also found to be significant. The coefficient of X_2 and X_3 in Eq. 9 are negative, indicating that efficiency of color removal decreases with increasing volumetric flowrate (X_3) and amount of catalyst increase (X_2); this is consistent with the findings of Phalharn [9].

2) The optimal operating condition for color removal of reactive red in wastewater

From Eq. 9, the simulated operating condition using *Design Expert Software* indicated the following optimal conditions: concentration of 20-80 mg/L of reactive red in the wastewater stream, 432.5-1,730 mg of catalyst, and a volumetric wastewater flow rate of 20-200 mL/min. Under these conditions, an efficiency of 84.85% was achieved. Experimental results achieved 4.6% higher efficiency than predicted by the mathematical model, representing a deviation of less than 5%. Therefore this mathematical model could be useful in providing guidance for scale-up of the process to industrial scale.

Conclusions

The Fe^{3+} catalysts were synthesized by a sol–gel method and coated onto the surface of a ceramic foam medium. The Fe^{3+} catalyst were characterized by EDX and SEM tests that showed excellent dispersion of Fe^{3+} over the media surface. A batch reaction using this catalyst resulted in successful decolorization of synthesis dyeing wastewater. Optimal conditions for the process were determined. At dye concentrations of 0.01-0.20 g/L, initial pH of 6, 0 and using 4 pieces of catalyst/L, color removal efficiency within of 96% was achieved within a 2 hr operating time. Moreover, a mathematical model was developed to determine optimal conditions for a pilot continuous scale process. Under concentrations of 20-80 mg/L of reactive red in the inlet wastewater stream, 432.5-1,730 mg of catalyst and a wastewater volumetric flowrate of 20-200 mL/min, a color removal efficiency of 84.85% was achieved. The mathematical model was in acceptable agreement with experimental result, which means this approach and mathematical model could be further developed for application to industrial-scale processes.

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