Synthesis of Fe$^{3+}$ by sol-gel Method Doped on Ceramic Foam for Decolorization of Dying Wastewater

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Abstract – Dyeing wastewater contains large amount of dyestuff together with significant amount of suspended solids (SS), dispersing agents, salts, and trace metals. This dyeing wastewater causes serious environmental problems that require proper treatment technologies. This research study aimed to synthesis Fe$^{3+}$ by sol-gel method doped on ceramic foam for disperse and reactive red dyes removal from synthesis dyeing wastewater. The Fe$^{3+}$ catalyst was prepared by sol-gel method with the iron salt as precursors, namely FeCl$_3$, at concentration of 3.0 M. The synthesized catalyst was characterized by the EDX spectrum from X-ray Spectrometer. The surface morphology was evaluated by using a scanning electron microscope (SEM). 1 liter batch reactor with magnetic stirrer was installed and used for decolorization testing by the Fe$^{3+}$ catalyst. The disperse and reactive red dyes concentration of 10-200 mg/L, initial pH 5-8 and 1-4 pieces of catalyst was controlled for the catalytic testing. The catalyst was effectively found to remove the dyes from wastewater with optimum operating condition of using Fe$^{3+}$ catalyst 4 pieces/L solutions and initial pH 6. The result showed that the highest color removal efficiency was 96% for contaminated dye wastewater.

Keyword: Fe$^{3+}$, Sol-gel, Decolorization, Dying Wastewater
1. Introduction

The color contaminants in aquatic environments from dye industry are an issue of environmental concern. While color is used to a fabric or yarn processes, some remains in the dye bath solution was then released in the form of an effluent [1]. Dyeing wastewater contains large amount of dyestuff, suspended solids, dispersing agents, salts and trace metals. These things cause serious environmental problems. Furthermore, the composition of wastewater from dyeing and textile process are greatly from day to day and hour to hour, depending on the dyestuff, fabric and concentration of fixing compounds which are added [2]. In addition, these effluents are threatened to ecosystems because of its toxicity and resistance to destroy by biological treatment methods [3].

Reactive dyes are the most important class of dyes used for cellulosic substrate because of their high wet fastness, brilliance and range of hues. The most attractive feature of these dyes is the essential simplicity of the dyeing process. However, these dyes cause certain problems such as high electrolyte concentrations and low wet fastness properties of dye materials. The dyeing effluent of high alkalinity cannot be treated efficiently by traditional wastewater technologies so highlighted the need to explore a technically feasible, high efficiency and reducing cost method. Thus, method for the removal of dyes under alkaline conditions using magnetic chitosan-Fe(III) hydrogel was proposed[4]. Decolorization of disperse and reactive dye solutions are using ferric chloride [2].

Conventional treatments of dyestuff wastewater include biological oxidation, chemical coagulation, advanced oxidation and adsorption. However, this method is high cost due to the pH must be adjusted prior to the treatment of waste water is acidic. And chemicals will be eliminated along with the sediment.

The various methods are quite cumbersome and costly. The iron in form of Fe^{3+} or Fe^{2+} from the ferric sulfate (Fe_{2}SO_{4}), ferric nitrate (Fe(NO_{3})_{3}) or ferric chloride (FeCl_{3}) were used for color removal in wastewater. The Fenton reaction is another way to get rid of colors in the water, but this method is costly because the pH of the wastewater before treatment is acidic and chemicals will be eliminated along with the sediment. Development of iron coating on medium in the heterogeneous catalyst can practically be used without chemical lost as sediment waste after treatment process.

This research aimed to decolorize the reactive dye wastewater Fe^{3+} heterogeneous catalyst. The catalyst was synthesized applying ferric chloride as precursor by sol-gel method and dip coating. The decolorization of synthesis wastewater were performed and tested in batch reactor. The interesting parameters were pH of wastewater, concentration of dye, and amount of catalysts. The dye concentrations were measured using UV-Vis Spectrophotometer. These optimal conditions will be further developed for industry.

2. Materials and Methods

2.1 Reagents and chemicals

Analytical grade magnesium nitrate hexahydrate (Mg(NO_{3})_{2}·6H_{2}O, 99.5%) and oxalic acid ((COOH)_{2}·2H_{2}O, 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 Merk Ltd., Germany. Foam ceramic (20 ppi) purchased from Assab steels (Thailand) public company limited and the commercially available disperse and reactive red dyes.

2.2 Catalyst preparation

Fe^{3+} catalyst was obtained from sol-gel method and dip coating described by Kumar and Kumar [5] and explained as a schematic flow chart in Fig.1. The A, B, and C solution was prepared by dissolving Mg(NO_{3})_{2}·6H_{2}O, (COOH)_{2}·2H_{2}O and FeCl_{3} in ethanol, respectively. The sol–gel was prepared by premixing the B solution into the A solution and stirring at room temperature for 10 min to form catalyst solution. Then the C solution was added into the catalyst solution and stirred at room temperature to prepare catalyst sol [6]. Before dip coating, foam ceramic were degreased by cleaning thoroughly and drying in an oven at 100°C for 1 hr. The circular foam ceramic was dipped into the catalyst solution. Subsequently the films were 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 were 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. (1). The calcination was performed in air flowing for 2 h under atmospheric pressure and cooled at a rate of 10 °C/min. The reaction of the calcination step is given in Eq. (2) [7]:

\[
\text{Mg(NO}_{3}\text{)}_{2}\cdot6\text{H}_{2}\text{O} + (\text{COOH})_{2}\cdot2\text{H}_{2}\text{O} \rightarrow \text{MgC}_{2}\text{O}_{4}\cdot2\text{H}_{2}\text{O} + 2\text{HNO}_{3} + 6\text{H}_{2}\text{O} \quad (1)
\]

\[
\text{MgC}_{2}\text{O}_{4}\cdot2\text{H}_{2}\text{O} + 0.5\text{O}_{2} \rightarrow \text{MgO} + 2\text{CO}_{2} + 2\text{H}_{2}\text{O} \quad (2)
\]
Mixing and stirring 10 min

FeCl₃ in absolute ethanol

Stirring for 10 min

“C” solution

Calcined at 600 °C for 2 h

Fe³⁺-doped on foam ceramic

Dried at 100 °C for 1 h

Sol-gel dip coating on foam ceramic

Stirring for 10 min

Mixing to form sol

“B” solution

COOH

in absolute ethanol

(H₂O)₂

Mg(NO₃)₂.6H₂O

in absolute ethanol

“A” solution

Stirring for 10 min

“B” solution

(COOH)₂

in absolute ethanol

Mg(NO₃)₂.6H₂O

in absolute ethanol

“A” solution

Stirring for 10 min

Fig.1 Schematic diagram of the Fe³⁺-doped on foam ceramic synthesis by sol-gel dip coating technique.

2.3 Batch experimental set and analytical method

Fig.4 shows schematic diagram of the laboratory scale batch reactor consisting of magnetic stirrer, reactor (beaker 1000 ml), and catalyst. The synthesis wastewater at dye concentration of 0.01-0.20 g/L was prepared by dissolving the reactive red and … dye in distilled water at pH 5-8, amount of catalyst 1-4 pieces/L, and retention time of 24 hour. Samples were taken every hour and analyzed using a UV-Vis spectrophotometer at visible maximum absorbance range decreasing of the absorbance peaks was directly proportional to reduction of the dye concentration.

The color removal efficiency (%) can be determined by Eq.(3) using the concentration of initial and final color wastewater after treatment as follows:

\[
\text{Color removal} = \frac{C_I - C_F}{C_I} \times 100
\]

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

3. Results and Discussion

3.1 Characterization of the Fe³⁺ catalyst

To ensure that the Fe³⁺ catalyst was obtained on the surface of ceramic foam, Energy Dispersive X-ray Spectrometer (EDS: Oxford ISIS 300) was used as presented in Fig.2. The EDX spectra from X-ray Spectrometer showed elemental of Fe on the synthesized Fe³⁺ catalyst. The result indicated that Fe³⁺ can be present in groups of ionic on the ceramic surface. The surface morphology was evaluated by a scanning electron microscope (SEM) as shown in Fig.3.
3.2 Effect of dye concentration in wastewater on the decolorization

Fig. 5 shows the color removal efficiency from dyeing wastewater at various concentrations of 0.01, 0.05, 0.10, 0.15, and 0.20 g/L using Fe$^{3+}$ catalyst 1 piece/L at initial pH 7.5. It was found that the pH 6 in batch reactor that promoted the highest efficiency for color treatment with 95% for 24-hour run time. Moreover, the efficiency of color removal in wastewater was 96% that taked only 2-hours run time.

3.3 Effect of pH on the decolorization

The color removal efficiency of dyeing wastewater at concentration of 0.01 g/L using Fe$^{3+}$ catalyst at various pH is presented in Fig. 6. From the spectrum found that pH 6 in batch reactor promoted the highest efficiency for color treatment with 96% within 2 hour run time. The efficiency of color removal of wastewater was 96% at initial pH 6 for 2-hours.

3.4 Effect of amount of catalysts on the wastewater decolorization

Color removal efficiency of the dyeing wastewater using of Fe$^{3+}$ catalyst 1-4 pieces/L at dye concentration of 0.01 g/L and initial pH 6 is shown in Fig. 7. It was found that the 4 pieces/L in batch reactor was promoted the highest efficiency for color treatment with 94% at 2-hour. Due to the increasing amount of pieces catalyst will effect to the amount of surface area between iron and dyeing wastewater.
4. Conclusions

The Fe$^{3+}$ catalysts were synthesized by a sol–gel method and coating on ceramic foam media. The successful Fe$^{3+}$ catalyst were characterized by XRD and SEM tests that showed well dispersion of Fe$^{3+}$ on the media. Batch reactor with the catalyst was effectively performed for decolorization of synthesis dyeing wastewater. The optimum condition of the decolorization for the dye concentration of 0.01–0.20 g/L was initial pH 6 and using catalyst 4 pieces/L to achieved 96% of color removal efficiency within 2 hr operating time.

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References