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FENTON-LIKE OXIDATION OF REACTIVE BLACK 5 IN THE PRESENCE OF $LABO_3$ (B: Fe, Co, Mn, Ni) PEROVSKITE CATALYSTS

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Abstract: The catalytic performances of $LaBO_3$ (B: Fe, Co, Mn, Ni) perovskite catalysts in Fenton-like oxidation of the textile dye, Reactive Black 5 were compared, and, the optimum reaction conditions were investigated in the presence of the most efficient catalyst. Reactive Black 5 was selected as the model dye due to its complex chemical structure, high water solubility and common usage in the textile industry. The performances of the catalysts in Reactive Black 5 degradation and decolorization were compared by testing different catalyst loadings. According to the catalyst screening experiments, $LaFeO_3$ showed the highest catalytic performance whereas $LaCoO_3$, $LaMnO_3$, and, $LaNiO_3$ were not effective in the degradation and decolorization of Reactive Black 5. A parametric study was carried out in the presence of $LaFeO_3$ catalyst in order to determine the most suitable reaction conditions. In the parametric study, the effect of catalyst loading, pH and the initial H_2O_2 concentration were investigated. The initial dye concentration and the reaction temperature were kept constant at 100 ppm and 50℃, respectively. The most suitable reaction conditions were determined as 0.1 g/L of catalyst loading, 3 and 1 mM of H_2O_2, and, 96.9% degradation, and complete decolorization were achieved under these conditions.

Keywords: Reactive Black 5, Fenton-like oxidation, Perovskite catalysts.

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INTRODUCTION

Textile dyes are one of the most commonly used organic compounds constituting a threat to the environmental health. A remarkable fraction of the dyes is nonfixed during the dyeing process and released into the textile effluents [Akpan and Hameed, 2009]. Most of the conventional wastewater treatment methods generate great amounts of sludge and solid waste which need further treatment before disposal. Advanced oxidation process including the Fenton-like oxidation is one of the most environmentally friendly and effective method for the degradation of the dyes. The following Fenton like reactions are proposed for the formation of hydroxyl radicals and the removal of industrial pollutants [Sun *et al.*, 2007]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\bullet + OH^-$$

$$\text{Polutant} + OH\bullet \rightarrow \text{End Products}$$

In the literature, there are many studies on decolorization of textile dyes by Fenton like oxidation. However, neither of these studies focused on the comparison of the catalytic performances of the Lanthanum based perovskite type of catalysts in Fenton like oxidation of textile dyes. Therefore, this study has an innovative approach due to the investigation of the Fenton like oxidation performances of perovskites in both of the degradation and decolorization of textile dyes. In this regard, the main objective of this study is the removal of the reactive azo dye, Reactive Black 5 (RB5) by Fenton-like oxidation in the presence of perovskite type of catalysts. The perovskite catalysts have been attracted interest due to their thermal stability, high oxidation activity, and inexpensive prices [Labhasetwar *et al.*, 2015]. In the context of this study, four types of Lanthanum based perovskites ($LaFeO_3$, $LaCoO_3$, $LaNiO_3$, $LaMnO_3$) were prepared by sol-gel citrate method and their catalytic performances were compared. The most suitable reaction conditions were also determined in the presence of the selected perovskite catalyst.

EXPERIMENTAL

Catalyst Preparation

Four types of Lanthanum based perovskite catalysts including $LaFeO_3$, $LaNiO_3$, $LaCoO_3$, and $LaMnO_3$ were prepared by sol-gel citrate method. Equimolar amounts of $La(NO_3)_3.6H_2O$ and the transition metal nitrate were dissolved in distilled water. Excess amount of citric acid was added into the mixture of lanthanum nitrate and metal nitrate in order to form a cross linked structure. The mole of citric acid was equal to 3/2 times of the summations of moles of metal nitrates. The mixture is heated at 80-90°C under vigorous stirring until the gel form was obtained. The gel was dried at 150°C for 6 h and calcined at 750°C for 5 h to remove the nitrates.

Experimental Set-up and Procedure

The experiments were carried out in 250 mL three necked volumetric flasks for 2 hours using a temperature controlled hot-plate. dye solutions of 100 ppm were prepared and the pH was adjusted to the desired value using diluted H_2SO_4 or NaOH solutions. When the temperature reached the set value, certain amounts of catalyst and hydrogen peroxide were added into the reaction medium. Samples were taken periodically to analyze the degradation and the decolorization efficiencies.

Experiments

In order to determine which perovskite catalyst showed the highest catalytic performance on Fenton like oxidation of RB5, catalyst screening experiments were performed. In these experiments, the initial dye concentration, the initial H_2O_2 concentration and the initial pH were fixed at 100 ppm, 4 mM and 3, respectively, while the catalyst loading and the reaction temperature were between 0.25-0.5 g/L and 50-70 °C, respectively. A parametric study was carried out in the presence of the selected catalyst to investigate the effect of the catalyst loading, initial pH and the initial H_2O_2 concentration on Reactive Black 5 removal.

Analysis

The decolorization and degradation efficiencies of Reactive Black 5 were analyzed by using a UV–VIS spectrophotometer. The absorbance values of the samples were measured at 390 and 597 nm which were associated with the degradation of the aromatic part and color removal, respectively. The spectrum of the Reactive Black 5 was presented in Figure 1.

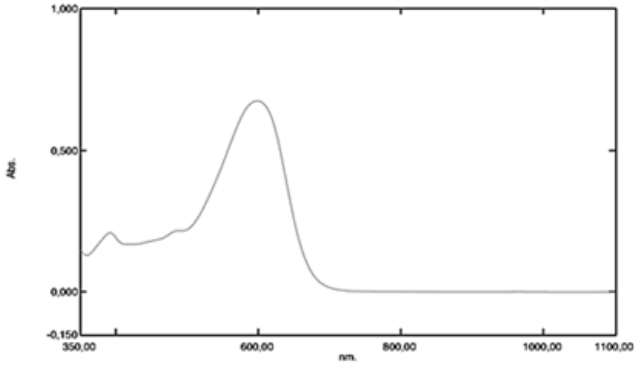

Figure 1: UV-Vis spectrum of the Reactive Black 5.

The decolorization and degradation efficiencies were calculated using the following equation:

$$\%Degradation = \left[\frac{A_O|_{@390\ nm} - A_t|_{@390\ nm}}{A_O|_{@390\ nm}}\right] \times 100$$

$$\%Decolorization = \left[\frac{A_O|_{@597\ nm} - A_t|_{@597\ nm}}{A_O|_{@597\ nm}}\right] \times 100$$

where A_0 is the initial absorbance, A_t is the absorbance at time t.

RESULTS AND DISCUSSION

Catalyst Screening

The Fenton like oxidation performances of $LaBO_3$ (B: Fe, Mn, Ni, Co) catalysts were assessed under various reaction conditions and the results are shown in Figure 2.

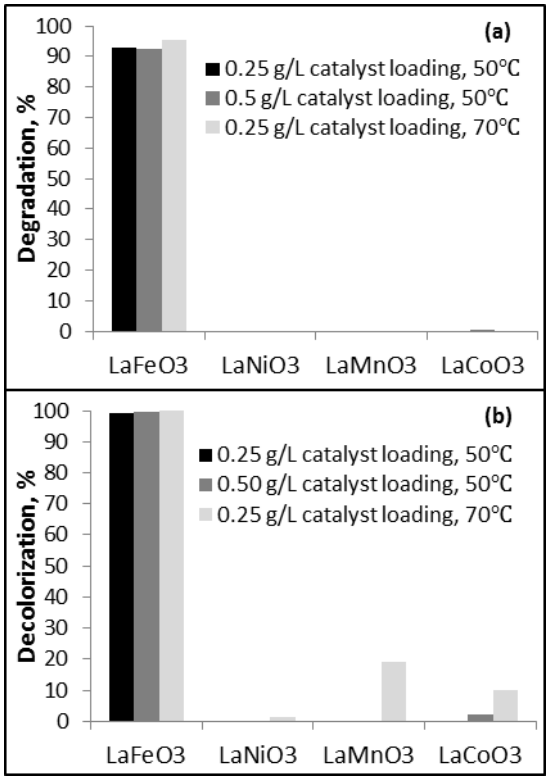

Figure 2: Comparison of the catalytic performances of the perovskites at various catalyst loading and temperature values. Reaction conditions: $[RB5]_o$=100 ppm, pH=3, $[H_2O_2]_o$= 4 mM.

According to the catalyst screening results, degradation could not be achieved in the presence of $LaMnO_3$, $LaNiO_3$ and $LaCoO_3$ whereas the decolorization efficiencies were below 20% even at high reaction temperatures. Nevertheless, $LaFeO_3$ was very effective in both degradation and decolorization of Reactive Black 5 under all the reaction conditions tested. Almost complete decolorization was accomplished and the degradation efficiencies were above 92% in the presence of $LaFeO_3$. Similarly, Taran *et al*. concluded that $LaMnO_3$, $LaNiO_3$ and $LaCoO_3$ catalysts were ineffective in Fenton-like oxidation of an organic pollutant whereas high degradation rates were accomplished in the presence of $LaFeO_3$ and $LaCuO_3$ [Taran *et al.*, 2016]. The most suitable reaction conditions were determined in the parametric study by using $LaFeO_3$ catalyst since it was remarkably more effective than the other perovskites.

Parametric Study

Effect of the catalyst loading

The influence of the catalyst loading on RB5 removal was investigated in the presence of $LaFeO_3$ by varying the catalyst loading between 0.1 and 0.5 g/L. Additionally a set of experiments were performed in the absence of catalyst. The results are presented in Figure 3.

The results showed that the presence of catalyst was crucial for dye degradation. Only 21.9% decolorization was achieved and no degradation was accomplished in the absence of catalyst. As the catalyst loading increased the dye removal rates were enhanced due to the availability of more catalyst active sites resulting in acceleration of the hydroxyl radical production on the catalyst surface [Gan and Li, 2013]. Additionally, the decolorization rates are faster than the degradation rates since nitrogen double bonds are degraded more easily when compared to the aromatic rings [Wu *et al.*, 2008]. Though the highest degradation and decolorization rates were achieved by using 0.5 g/L of catalyst loading, 0.1 g/L could be proposed as the most suitable loading since nearly the same dye removal efficiencies were obtained at the end of the oxidation reaction.

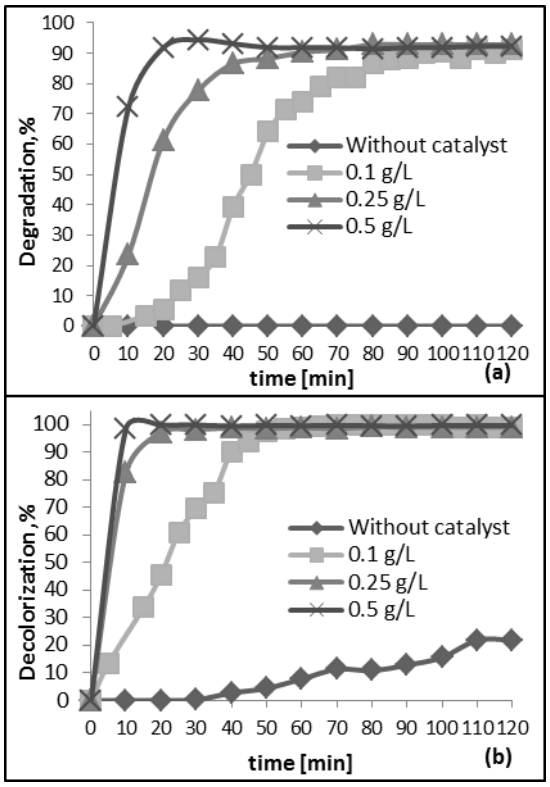

Figure 3: Influence of the catalyst loading on RB5 degradation (a) and decolorization (b). Reaction conditions: $[RB5]_o$=100 ppm, pH=3, $[H_2O_2]_o$= 4 mM, T=50°C.

Effect of the initial pH

The impact of the initial pH on the degradation and decolorization of RB5 was studied under pH 3, 4, 5 and 7, and the results are shown in Figure 4.

Figure 4 depicts that both of the degradation and decolorization efficiencies diminished with the increasing pH. When the initial pH was set 4, only 6.6% degradation and 31% decolorization was achieved. Above pH 4, the dye removal efficiencies were approximately zero. The hydroxyl radicals are generated efficiently under acidic conditions since at lower pH the catalyst surface is positively charged [Panda *et al.*, 2011] which enhances the adsorption of the negatively charged RB5 molecules. pH 3 was selected as the most suitable initial pH value since the highest RB5 removal occurred at this pH.

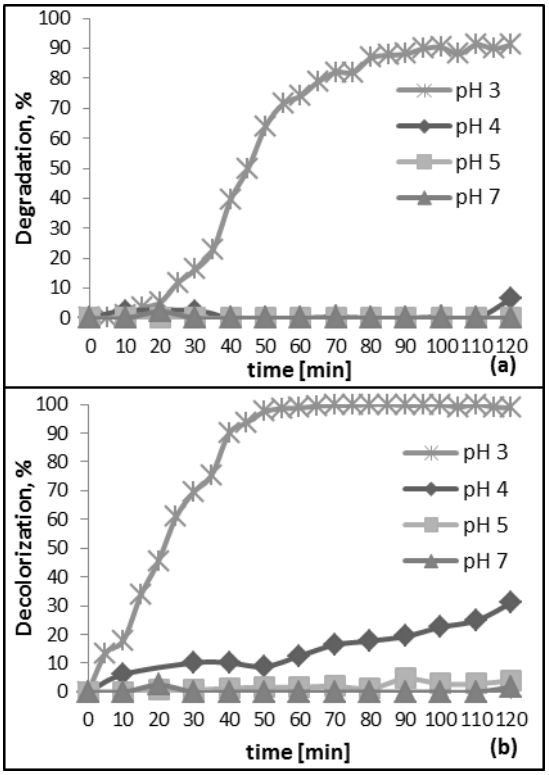

Figure 4: Influence of the initial pH on RB5 degradation (a) and decolorization (b). Reaction conditions: $[RB5]_o$=100 ppm, 0.1 g/L of catalyst loading, $[H_2O_2]_o$= 4 mM, T=50°C.

Effect of the initial hydrogen peroxide concentration

The role of the initial H_2O_2 concentration on dye removal was investigated by changing the oxidant concentration between 0.5 and 4 mM. In addition, a set of experiments was performed without using H_2O_2. The dye degradation and decolorization profiles obtained at different H_2O_2 concentrations are presented in Figure 5.

According to Figure 5, the presence of the H_2O_2 was essential for an efficient Fenton-like oxidation because neither degradation nor decolorization was observed in the absence of the oxidant. As the oxidant concentration was increased from 0.5 to 1 mM the dye removal was improved significantly. However, a further increase in H_2O_2 concentration (up to 4 mM) decreased the dye removal efficiencies remarkably due to the scavenging effect resulting from the reaction between the excess H_2O_2 molecules and the hydroxyl radicals [Kasiri *et al.*, 2008]. Therefore, 1 mM oxidant concentration was determined as the optimum condition.

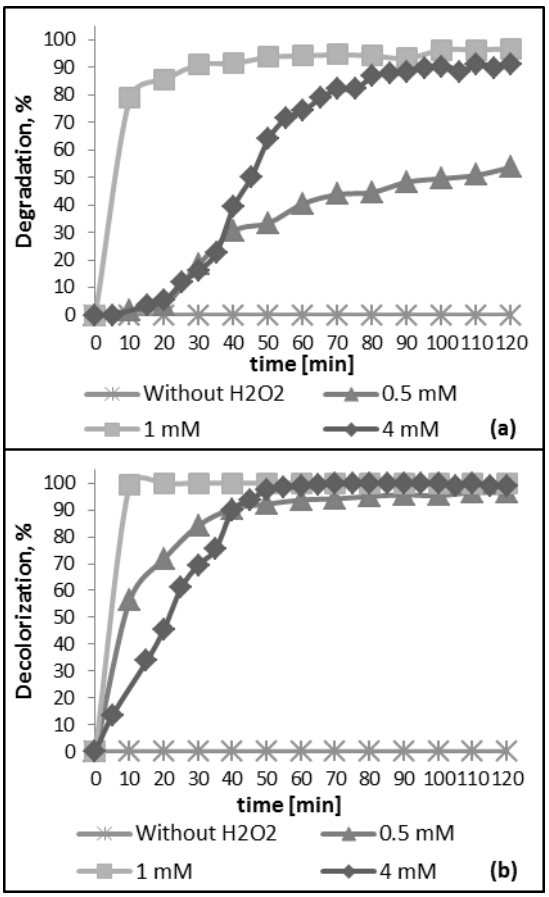

Figure 5: Influence of the initial hydrogen peroxide concentration on RB5 degradation (a) and decolorization (b). Reaction conditions: $[RB5]_o$=100 ppm, 0.1 g/L of catalyst loading, pH=3, T=50°C.

CONCLUSIONS

The textile dye, Reactive Black 5, was effectively degraded and decolorized by the Fenton-like oxidation in the presence of $LaFeO_3$ perovskite catalyst which showed the highest catalytic performance among the $LaBO_3$ (B: Fe, Co, Mn, Ni) perovskites.

The most suitable reaction conditions were determined as 0.1 g/L of catalyst loading, 3 and 1 mM of H_2O_2 when the initial dye concentration and the reaction temperature were 100 ppm and 50 °C, respectively. Under the most suitable reaction conditions, 96.9% degradation and complete decolorization were achieved in 2 hours of reaction time.

ACKNOWLEDGMENT

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