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HETEROGENEOUS FENTON-LIKE OXIDATION OF METHYLENE BLUE USING ALTERNATIVE CATALYSTS

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Abstract

The usage of the low-cost catalysts for methylene blue removal from wastewater was investigated. Heterogeneous Fenton-like process consists of the use of a hydrogen peroxide solution, and an iron-rich catalyst, red mud and black nickel mud were used for that purpose. The factors such as the catalyst dose and the hydrogen peroxide solution volume were monitored. The results of experiments showed that the degradation of methylene blue dye in Fenton-like oxidation process using selected catalysts can be described by a pseudo-second-order kinetic model. The highest dye removal efficiency (87.15 %) was achieved using the black nickel mud catalyst after 30 minutes of reaction.

Keywords

Fenton-like process, red mud, black nickel mud, methylene blue

INTRODUCTION

In recent years, the rapid development of textiles, food, cosmetics, and printing industries has led to an increase in the highly toxic and carcinogenic pollutants from organic dyes in wastewaters [1, 2]. It was reported that the effluents from textile industries typically contain 0.6−0.8 g L^{-1} of dye [3]. Dyes are chemicals which consist of aromatic structures; without proper wastewater treatment, they can be harmful to the aquatic environment and human health [4]. The molecules of dyes may shield light penetration in watercourses and affect the photosynthesis of aquatic plants [2]. Methylene blue (MB) can stimulate and injure the eyes of humans and animals. Eating food contaminated with MB results in nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [5−7].

There are several decolorization methods applicable for the regeneration of dyed wastewaters. Common treatment methods consist of various processes involving the biological, physical, and chemical methods, but biological treatment is not preferred owing to biological resistance of some dyes [8, 9]. Traditional treatment techniques include ion-exchange, coagulation/flocculation, microelectrolysis, advanced oxidation processes, adsorption, membrane filtration, photocatalysis and various combinations of these methods. The advantages and disadvantages of every removal technique have been reviewed [10].

Homogeneous Fenton process is an effective treatment technique to degrade organic pollutants by generation of strong, relatively non-selective hydroxyl radical ($^{\bullet}OH$) [11, 12]. However, secondary contamination and difficulty in recycling the catalyst is the main problem in application of Fenton in the industrial scale in wastewater treatment [13, 14]. This problem can be solved by using a heterogeneous catalyst in Fenton process, because it is usually environmentally more acceptable and easily separable from treated wastewater [15,16]. Heterogeneous catalysts are divided into the catalysts from natural minerals and the ones from composites by artificial synthesis [17]. Iron-rich waste can be served as a raw material for the preparation of heterogeneous catalysts, but it is very important to develop a low-cost, green, and efficient method for its preparation [18].

Red mud (RM) is alkaline solid waste from alumina production. Normally, it consists of Fe_2O_3, SiO_2, Al_2O_3, TiO_2, Na_2O, CaO, α-FeOOH, γ-AlOOH, etc. [19]. Yearly production of red mud in Slovakia was about 7×10^4 kg, and supplies are estimated at 8 million tons [20].

Black nickel mud (BNM) is a waste generated during the leaching of nickel and cobalt from lateritic iron-ore. Chemical composition of black nickel mud is Fe, Cr_2O_3, SiO_2, Al_2O_3, CaO, Ni, and P_2O_3 [21]. In Slovakia, nickel was produced in the southern edge of Dolnovažská niva. Annual production of BNM was about 3×10^5 kg, and supplies in Slovakia are estimated at 5.6 million tons [21, 22].

In the experiment described in this article, the red mud and black nickel mud were used as catalysts for removal of the methylene blue water solution using Fenton-like process. The study focuses on usage of low-cost industrial waste for wastewater treatment. The factors such as catalyst dosage and volume of the hydrogen peroxide solution were studied. The efficiency of removal process was calculated, and degradation kinetics (C/C_0 versus time plots) are shown. Kinetic study of the reactions was also performed.

MATERIALS AND METHODS

Chemicals and catalysts

Methylene blue was dissolved in distilled water to reach a 10 mg L^{-1} concentration of solution. The hydrogen peroxide (HP) solution was prepared at a concentration of 30 % w/v. RM – industry waste from metal production was supplied from Žiar nad Hronom, which was produced in an aluminium mill from bauxite between the years 1957-1997. BNM – industry waste from metal production, supplied from the area between Sereď and Dolná Streda, which was produced by leaching of nickel and cobalt from lateritic iron-ore in Niklová huta š.p (1963-1993). Soldán and Kobetičová (2015) investigated the chemical composition and surface morphology of those catalysts using the SEM and EDX analyses [20].

Experimental procedure

A sample of 25 mL of methylene blue solution (10 mg L^{-1}) was pipetted into the beaker. Then 0.1 and 0.2 g of red mud and black nickel mud were added separately. Finally, 0.5 and 1 ml of H_2O_2 (30% w/v) were added. The suspension was then stirred by a glass rod for a few seconds at the beginning. The reaction was run for 5, 10, 15 and 30 minutes. After time, the suspension was transferred to a test tube and centrifuged in Nahita centrifuge (model 2640/12) for 3 minutes at 4000 rpm. The MB removal efficiency was determined by the UV/Vis spectroscopy. All experiments were performed at the room temperature.

UV/Vis spectroscopy

The degradation of MB was determined by the GENESYS 8 spectrophotometer in UV/Vis area (500-800 nm). Plastic cuvettes 1 cm thick were used. The highest achieved value of absorbance (at 665 nm) was used to calculate the efficiency of removal process.

RESULTS AND DISCUSSION

Removal of MB using RM as a catalyst

Figure 1 shows the monitored degradation kinetics of MB using Fenton-like process with red mud. For comparison, the degradation kinetics of individual experiments with hydrogen peroxide solution and RM are also given.

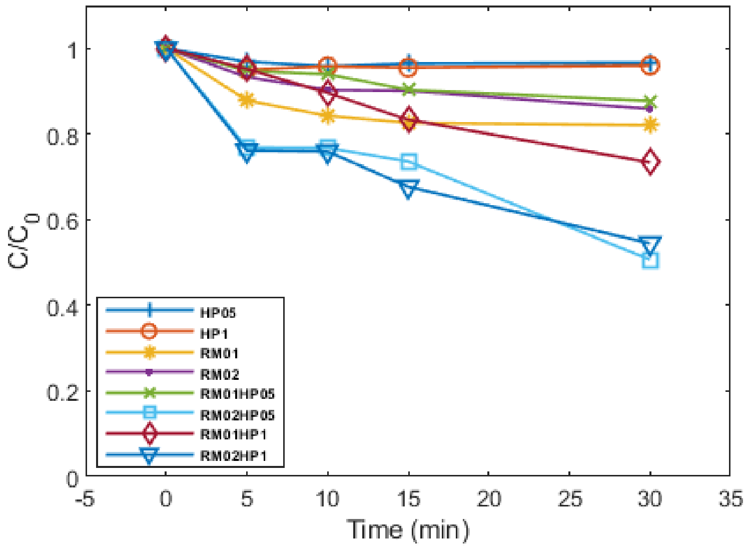

Figure 1 *Comparison of degradation kinetics of MB removal using RM as catalyst*

Figure 1 also shows that a higher volume of hydrogen peroxide solution used in this case does not have a significant effect on the resulting removal efficiency. Although the reactions were initially copied using 0.2 g of RM, 0.5 and 1 ml, the RM02HP05 reaction ultimately reached its highest efficiency (49.34 %) after 30 minutes.

Removal of MB using BNM as a catalyst

Degradation kinetics of MB using BNM as a catalyst for Fenton-like process are shown in Figure 2. For comparison, the degradation kinetics of individual experiments with HP solution and BNM are also given.

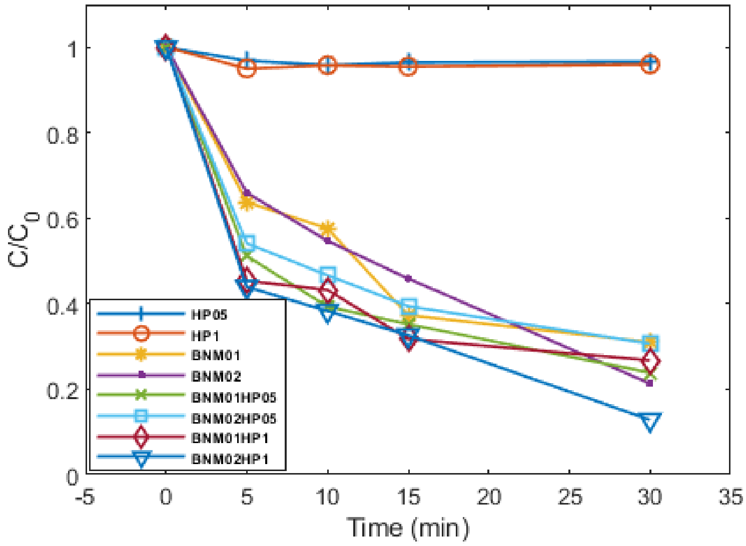

Figure 2 *Comparison of degradation kinetics of MB removal using BNM as catalyst*

The highest removal efficiency of MB from all experiments performed can be seen in Figure 2. using 0.2 g of BNM and 1 mL of hydrogen peroxide solution; 87.15 % of dye solution was removed after 30 minutes.

Kinetics of MB removal

The kinetic study of Fenton-like process can be performed by assuming that the reaction between hydroxyl radicals and the pollutant is the rate-determining step. Thus, by assuming that hydroxyl radical concentration was a constant, the law of pseudo-first-order reaction can be written as follows:

$$-\frac{dC}{dt} = k \times C_{\bullet \mathrm{OH}} \times C = k_{\mathrm{app}} \times C \Rightarrow \ln\frac{C_0}{C} = k_{\mathrm{app}} \times \mathrm{t}, \quad (1)$$

where C and C_0 are concentrations of MB at any time and initial MB concentration in mg L^{-1}, k is the rate constant of reaction, and k_{app} is the apparent pseudo-first-order constant.

Table 1 shows the kinetic parameters (rate constant k and coefficient of linear regression R^2) of selected reactions. Rate law of the pseudo-second-order reaction can be written as follows:

$$\frac{1}{C_{\mathrm{MB}}} = k \times t + \frac{1}{C_0}. \quad (2)$$

Table 1 Parameters of kinetic models for different catalysts in Fenton-like process			
Kinetic type	**Reaction**	***k***	$\boldsymbol{R^2}$
Pseudo-first-order	RM02HP1	0.0182	0.91
	BNM02HP1	0.0615	0.93
Pseudo-second-order	RM02HP1	0.0026	0.95
	BNM02HP1	0.0219	0.94

From Table 1, it can be read that the coefficient of linear regression (R^2) acquires the highest values for the pseudo-second-order kinetic type. Figure 3 shows the pseudo-second-order models of MB degradation with different catalysts.

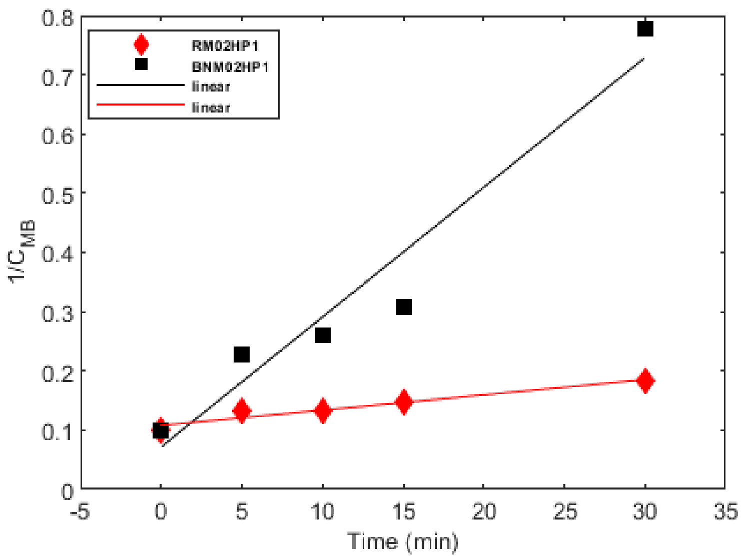

Figure 3 *Pseudo-second-order models for Fenton-like oxidation of MB with different catalysts*

CONCLUSION

The results stated above show the efficiency of MB removal using red mud and black nickel mud as catalysts. Time of the reaction, catalysts dosage and volume of hydrogen peroxide solution are important factors, because they affect the cost and simplicity of the process.

Removal of methylene blue using the Fenton-like process with RM catalyst achieved the highest efficiency of 49.34 % using 0.2 g of catalyst and 0.5 ml of HP solution. Given that the reaction using a 1 ml volume of HP solution ultimately had less than 6 % lower efficiency, we can conclude that these reactions were identical, and the volume of HP solution did not affect the resulting MB removal efficiency. This could also be because the slurry was stirred for only a few seconds at the beginning of the reaction, which resulted in an inefficient use of the entire catalyst surface with hydrogen peroxide.

The highest MB removal efficiency was achieved using black nickel mud as a catalyst. Using 0.2 g of BNM and 1 ml of HP solution, 87.15 % dye removal was achieved after 30 minutes.

It can be concluded that BNM was proven to be a more effective catalyst for the removal of MB in the Fenton-like oxidation process than RM. Based on these facts, it should be noted that in future research, it would be appropriate to monitor possible secondary pollution and other factors, such as the effect of pH, the effect of temperature, the effect of catalyst pre-treatment, etc.

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