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Catalytic Wet Peroxide Oxidation of Methyl Orange over Al/Fe Pillared Sepiolite

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Abstract In this work, oxidation of methyl orange azo dye with hydrogen peroxide on Al/Fe pillared sepiolite catalysts was studied. The catalytic tests were carried out in a glass reactor in batch operation mode at the atmospheric pressure. The effects of various operating parameters such as catalyst dosage, active metal ratio, calcination temperature, pH, H_2O_2 concentration, temperature and time on the elimination of methyl orange were investigated. Optimum conditions were determined as 0.1 g/100 mL for catalyst dosage, 8% for active metal ratio, 500°C for calcination temperature, 3.7 for pH, 0.15 M for H_2O_2 concentration and 25°C for temperature. Under these conditions 90.68% methyl orange elimination was achieved at 4 hours of reaction time without considerable iron leaching.

Keywords: Sepiolite, azo dye methyl orange, catalytic wet peroxide oxidation, pillared clays, catalyst.

1. Introduction

Different types of dyes are used in many industries such as textile, paint, ink, plastics and cosmetics. A certain amount of them are lost in the process of their manufacturing and utilization and often cause environmental problems (Tanaka *et al*., 2000). Since dyes are intended to be used for specific applications that require their durability under environmental conditions, dye effluents are correspondingly characterized with intense color, high chemical and optical stability and non-biodegradability (Drasinac *et al*., 2017). Therefore, considerable research efforts are focused on the development of efficient technologies to remove this type of pollutants. In the last decade great research efforts have been addressed to advanced oxidation processes (AOPs). Among these techniques, catalytic wet peroxide oxidation (CWPO) allows performing the degradation of many pollutants under mild conditions (20-80°C and atmospheric pressure), which is considered to be an effective and economical method for treating contaminants. In a typical CWPO process, the redox properties of dissolved transition metal cations (Fe^{2+}, Cu^{2+}) allow generating highly active hydroxyl radicals in the presence of hydrogen peroxide (Zhong *et al*., 2012). Alumina, silica, zeolites, activated carbon and pillared clays are some of the most commonly used support materials in CWPO process (Zazo *et al*., 2012).

Sepiolite, which has a $Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4.8H_2O$ unit cell formula, is a fibrous clay mineral comprising tetrahedral and octahedral sheets of oxides. The mineral has molecular-sized channels (0.37 x 1.06 nm), oriented along the longitudinal direction of the fiber (Brauner and Preisinger, 1956). It differs from laminar clays in that it has a fibrous morphology at microscopic and sometimes macroscopic levels. The fibrous morphology, the presence of intra-crystalline channels as well as the small particles size result in high specific surface area values (Suarez and Garcia-Romero, 2012). This mineral is commonly used as adsorbent, filler, catalyst or catalyst support (Tabak *et al*., 2009). Most of the world sepiolite reserves are in Turkey. The deposits in Eskişehir province are considered to be the most commercially important.

The aim of this study is to investigate the usability of Al/Fe pillared sepiolite as catalyst for the catalytic wet peroxide oxidation of methyl orange. The effects of catalyst dosage, active metal ratio, calcination temperature, pH, H_2O_2 concentration, temperature and time on the oxidation process of methyl orange were investigated.

2. Experimental

2.1. Materials

The sepiolite used in the experiments was meerschaum carving residue supplied from a workshop and originated from Türkmentokat-Gökçeoğlu region in Eskişehir (Turkey). The sample was ground and sieved under 75 µm (200 meshes) and dried at 100°C for 3 hours. The chemicals used in the experiments and in analyses were analytical reagent grade.

2.2. Preparation and characterization of catalyst

To prepare pillared sepiolite, 2 g of sepiolite was put in a 250 mL beaker and 100 mL of distilled water was added on it to form a clay-water suspension of 2 wt.%. The mixture was stirred at room temperature for 24 hours at 400 rpm on a Heidolph MR 3001 model magnetic stirrer.

In another 500 mL baker, a total volume of 50 mL solution was prepared by mixing 0.2 M $Al(NO_3)_3.9H_2O$ and 0.2 M $Fe(NO_3)_3.9H_2O$ in the volume ratios required to provide the desired active metal ratio (AMR). The AMR value is defined as the atomic percent ratio between the active metal (Fe) and the total content of metals (Al and Fe) in the intercalating solution. This solution was heated to 70°C and then 100 mL of 0.2 M NaOH solution pre-heated to the same temperature was slowly added on it. The mixture was stirred at 400 rpm at 70°C for 2 hours. During this time period the aluminum and iron in the solution were converted into hydroxides. Then, the mixture was cooled to the room temperature and the previously prepared clay-water suspension was added on it drop by drop. Thus, in the final mixture, the ratio of metal amounts to the sepiolite was 0.005 mole metal/g sepiolite. The mixture was stirred at 400 rpm for 24 hours; in the meantime, the metal hydroxides in the solution were sorbed by sepiolite. Then, the mixture was filtered by suction, repeatedly washed with distilled water, dried at 60°C and calcined at determined temperatures for 2 h. During calcination, the metal hydroxides impregnated on sepiolite were converted into metal oxides.

The AMR value can be calculated as follows:

$$AMR\ (\%) = \frac{mol\ Fe}{mol\ Fe + mol\ Al} \times 100 \qquad (1)$$

In the experiments, catalysts were prepared at 0, 2, 4, 6, 8 and 10% active metal ratios. These catalysts were coded as SepAl, SepAlFe2, SepAlFe4, SepAlFe6, SepAlFe8 and SepAlFe10, respectively.

The chemical compositions of sepiolite and SepAlFe8 catalyst calcined at 500°C were determined by a Rigaku ZSX Primus model X-ray fluorescence (XRF) analyzer. The BET specific surface areas and pore properties of sepiolite and SepAlFe8(500°C) catalyst were determined by N_2 adsorption isotherm with a surface area analyzer (Quantachrome, Autosorb-1 C). SEM analyses were performed using FEI Quanta-250 FEG device in order to explore the surface structures of sepiolite and SepAlFe8(500°C) catalyst.

2.3. Catalytic tests

Catalytic tests were performed in a 150 mL heater-jacketed glass reactor at atmospheric pressure. The reactor was kept at the desired temperatures by circulating water from a Lauda E200 model constant temperature bath. Chemical oxidation was carried out using 100 mL of 100 mg/L methyl orange solution with continuous stirring of the reaction mixture by a magnetic stirrer at 200 rpm. After the determined amount of catalyst had been added into solution, the mixture was stirred for 15 minutes and pH was adjusted to the desired value. The pH of the solution was continuously monitored with a Hanna HI 8314 brand pH-meter. In order to keep the pH constant at the desired value diluted HNO_3 or NaOH solutions were dropped when needed. During the experiment, air bubbles were pumped into the solution at a rate of 0.15 L/min. 8.0 mL of fresh-prepared 0.15 M hydrogen peroxide solution was fed into the system with a flow rate of 2.0 mL/h. The H_2O_2 added was 0.9 times the stoichiometric amount for the complete oxidation of methyl orange, according to the following equation:

$$C_{14}H_{14}N_3NaO_3S + 43H_2O_2 \rightarrow 14CO_2 + 3HNO_3 + NaHSO_4 + 48H_2O \qquad (2)$$

The beginning of the H_2O_2 addition was taken as zero time point of the reaction, and the periodic sampling was made throughout 4 hours of reaction in all the experiments.

Samples of 2 mL were taken and separated from the catalyst by centrifugation. Methyl orange concentration in the solution was determined by reading on a Hach DR 4000 spectrophotometer at 492 nm. Using the concentrations of methyl orange in the solution at the beginning and at any time *t* (min), methyl orange (MO) elimination was calculated according to the following equation:

$$MO\ elimination = \frac{C_0 - C_t}{C_0} \times 100 \qquad (3)$$

In the equation, C_0 (mg/L) is the initial concentration of MO and C_t (mg/L) is the concentration of MO remaining in the solution at the time *t* (min).

The iron concentrations in the final solutions at the end of the experiments were also determined by using an atomic absorption spectrometer (Thermo ICE 3300) at 248.3 nm wavelength.

Effects of active metal ratio, catalyst dosage, calcination temperature, pH, H_2O_2 concentration, temperature and time on the elimination of methyl orange were investigated.

3. Results and Discussion

3.1. Characterization of the catalyst

The chemical composition of sepiolite sample determined by the XRF analysis was 30.73% MgO, 48.91% SiO_2, 2.38% CaO, 0.24% Fe_2O_3 and 17.73% loss on ignition. The composition of SepAlFe8 catalyst calcined at 500°C was determined as 27.51% MgO, 57.50% SiO_2, 4.64% Fe_2O_3 and 9.67% Al_2O_3.

The BET surface areas (S_{BET}), micropore volumes (V_{micro}), total pore volumes (V_{total}) and average pore diameters (D_p) of sepiolite and SepAlFe8(500°C) catalyst were given in Table 1. As seen from the table, the BET surface area of the SepAlFe8(500°C) catalyst slightly increased compared to raw sepiolite. In addition, the total pore volume and especially the micropore volume considerably increased.

SEM images magnified at 10000 times for sepiolite and SepAlFe8(500°C) catalyst were given in Fig. 1. It is understood from the SEM images that the raw clay has a smoother and layered surface. SepAlFe8(500°C) become much rougher and much more porous. These results are consistent with the BET analyses.

Table 1. Surface areas and pore properties of sepiolite and SepAlFe8 catalyst calcined at 500°C.

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{total} (cm^3/g)	D_p (Å)
Sepiolite	182.19	0.0054	0.2160	47.59
SepAlFe8(500°C)	185.90	0.0973	0.3044	65.50

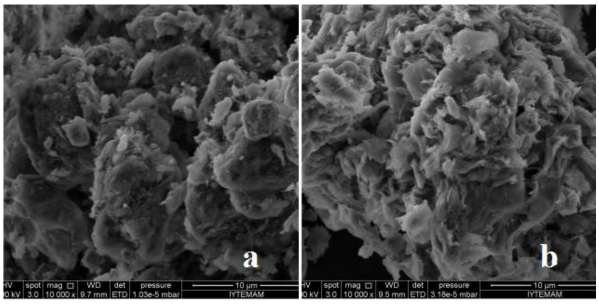

Figure 1. SEM images of (a) sepiolite, (b) SepAlFe8 catalyst calcined at 500°C.

3.2. Effect of catalyst dosage

In order to investigate the effect of catalyst dosage on the MO elimination, 0.1 g, 0.3 g and 0.5 g of SepAl catalyst calcined at 500°C were added to 100 mL, 100 mg/L MO solution at the conditions of pH 3.7, 0.15 M of H_2O_2 concentration and 25°C temperature. The results are given in Fig. 2. As seen in the figure, MO elimination was increased with increasing catalyst dosage. This increase is due to an increase in the number of active sites per unit amount of dye. The maximum MO eliminations reached at 240 min were 80.64%, 87.91% and 89.15% for 0.1 g, 0.3 g and 0.5 g catalysts in 100 mL of dye solution, respectively. The optimum catalyst dosage was chosen as 0.1 g/100mL since catalytic performance, namely MO elimination per unit amount of active metal was higher than the other doses and the subsequent experiments were carried out with this dosage.

3.3. Effect of active metal ratio

The effect of active metal ratio was studied using 0.1 g SepAl, SepAlFe2, SepAlFe4, SepAlFe6, SepAlFe8 and SepAlFe10 catalysts calcined at 500°C. In the experiments, the pH was kept constant at 3.7, the temperature was kept constant at 25°C and H_2O_2 solution at the concentration of 0.15 M was fed into the reactor. The results were given in Fig. 3. The highest elimination values of 90.68% and 90.89% were achieved at 240 min when using SepAlFe8 and SepAlFe10 catalysts, respectively. Since these values are almost the same and less amount of iron was used during the preparation of SepAlFe8, this catalyst was chosen as the best catalyst and used in subsequent experiments.

Iron concentrations of the solutions after oxidation for different catalysts were given in Table 2. The concentration values showed that the elimination of methyl orange was achieved without considerable iron leaching.

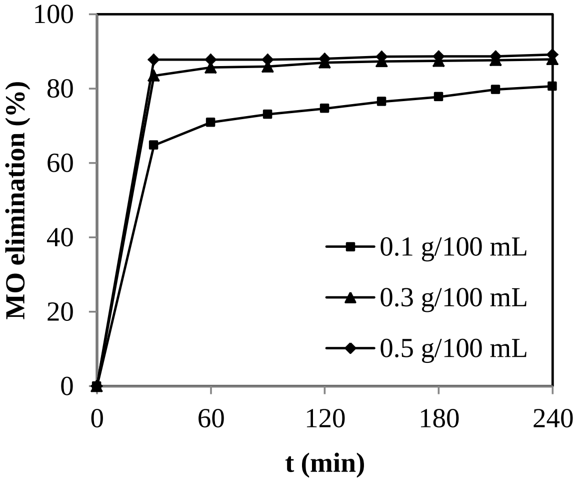

Figure 2. Effect of catalyst dosage on the elimination of methyl orange.

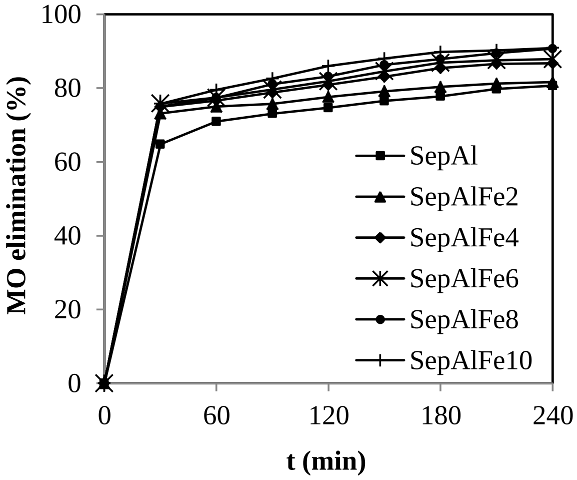

Figure 3. Effect of active metal ratio on the elimination of methyl orange.

Table 2. Iron concentrations in the final solutions for different catalysts.

Catalyst	Fe concentration (mg/L)
SepAl	0.00
SepAlFe2	0.02
SepAlFe4	0.04
SepAlFe6	0.05
SepAlFe8	0.17
SepAlFe10	0.17

3.4. Effect of calcination temperature

In order to investigate the effect of calcination temperature on the elimination of methyl orange, SepAlFe8 catalyst samples were prepared by calcination at 400, 500, 600 and 700°C. The oxidation experiments were achieved under the conditions of 0.1 g/100 mL catalyst dosage, pH 3.7 and

25°C temperature, with 0.15 M H_2O_2. As seen in Fig. 4, MO elimination increased with increasing calcination temperature. Since the elimination values were lower for 400°C, this temperature was not suitable for calcination. The elimination values were very close to each other for 500°C, 600°C and 700°C. Weight losses during the calcinations were determined as 8.83% for 400°C, 10.61% for 500°C, 14.72% for 600°C and 18.73% for 700°C. These results showed that weight losses for 600°C and 700°C were considerably higher than that of 500°C. More weight loss means more sepiolite mineral and metal consumption for the same amount of catalyst production. Despite slightly higher MO elimination at 600°C and 700°C calcination temperatures, it is considered to be more appropriate to make calcination at 500°C because of less energy consumption and less weight loss during the calcination.

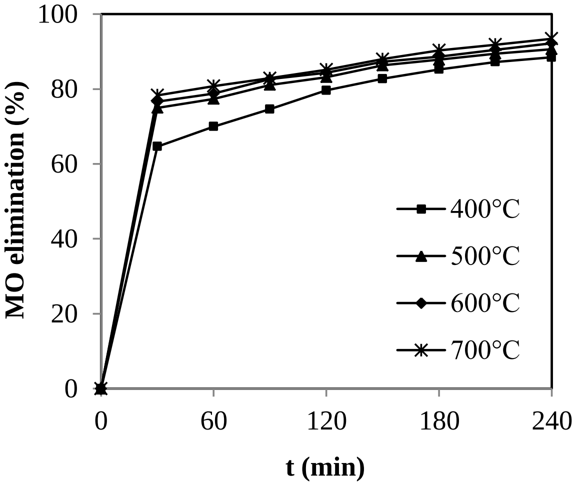

Figure 4. Effect of calcination temperature on the elimination of methyl orange.

3.5. Effect of pH

To investigate the effect of pH on MO elimination, pH values of the solution were kept constant at 3.0, 3.4, 3.7, 4.0 and 4.5. The experiments were achieved at 0.1 g/100 mL catalyst dosage, 25°C temperature, with SepAlFe8 catalyst calcined at 500°C and 0.15 M H_2O_2. As seen in Fig. 5, MO elimination was increased with decreasing pH value. Even at pH 3.0, the elimination value was reached to 100% in 120 min. However, it was observed that the iron on the catalyst was further extracted by the solutions at lower pH values (Table 3). This indicated that the catalyst would be decomposed into fewer cycles when studied at lower pH values. When studied at pH 3.0 and 3.4, the amounts of iron passed to the solution were high. At pH 4.0 and 4.5, the MO elimination was low. So the optimum pH value was determined as 3.7.

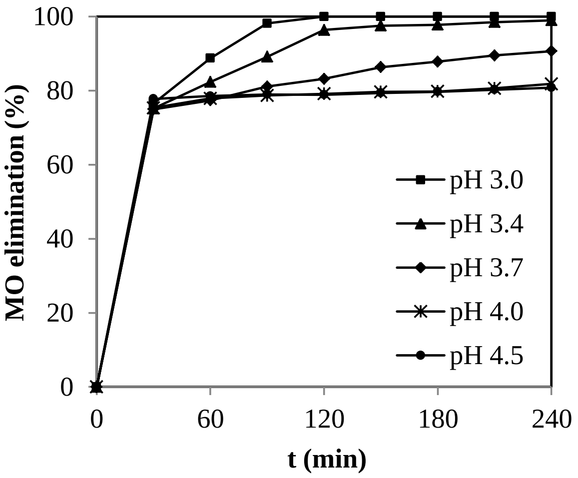

Figure 5. Effect of pH on the elimination of methyl orange.

Table 3. Iron concentrations in the final solutions for different pH values.

pH	Fe concentration (mg/L)
3.0	1.79
3.4	0.81
3.7	0.17
4.0	0.03
4.5	0.02

3.6. Effect of H_2O_2 concentration

The effect of H_2O_2 concentration on the elimination of methyl orange was studied at the concentrations of 0.05 M, 0.10 M, 0.15 M and 0.20 M. The experiments were carried out at the conditions of 0.1 g/100 mL catalyst dosage, SepAlFe8 catalyst calcined at 500°C, pH 3.7 and 25°C temperature. The results were given in Fig. 6. It was observed that the MO elimination increased with increasing H_2O_2 concentration, but the increase was not much. Especially, the elimination values were almost the same for 0.15 M and 0.20 M concentrations. For this reason, the optimum H_2O_2 concentration was determined as 0.15 M.

3.7. Effect of temperature

Investigation of the temperature effect on the elimination of methyl orange was carried out at 15°C, 25°C, 35°C and 45°C. The results were given in Fig. 7. In addition, iron concentrations in the solutions after oxidation at mentioned temperatures were given in Table 4. The low iron leaching (<0.3 mg/L) indicated that the active phase of the catalyst was strongly fixed to the support and that it was highly stable under oxidizing conditions of the reaction medium (Table 4). As seen from Fig. 7, the elimination values at the end of the first 30 min decreased with increasing temperature. However, the highest elimination values were reached at the end of 4 hours as 90.68% at 25°C and 93.54% at 45°C. Despite this slightly higher elimination value at 45°C, the iron leaching amount for this temperature was 65% higher than that of 25°C (Table 4). Considering being able to use the catalyst into more cycles and energy saving, 25°C was determined as more suitable temperature for the oxidation.

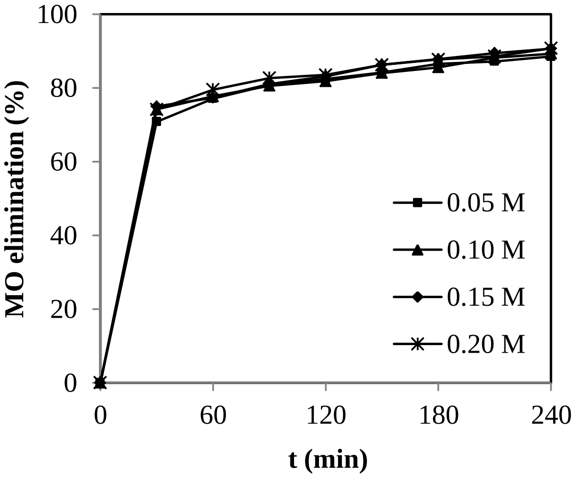

Figure 6. Effect of H_2O_2 concentration on the elimination of methyl orange.

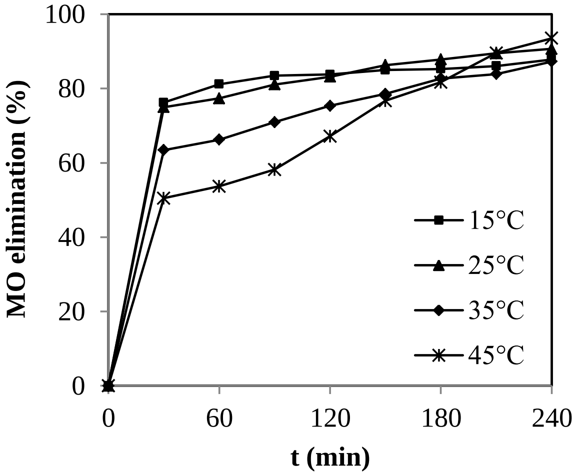

Figure 7. Effect of temperature on the elimination of methyl orange.

Table 4. Iron concentrations in the final solutions for different temperatures.

T (°C)	Fe concentration (mg/L)
15	0.17
25	0.17
35	0.22
45	0.28

4. Conclusions

The catalytic wet peroxide oxidation of methyl orange was investigated by batch oxidation experiments with the aim of determining the usability of sepiolite as a catalyst support. The effects of catalyst dosage, active metal ratio, calcination temperature, pH, H_2O_2 concentration, temperature and time parameters on the elimination of methyl orange were investigated. The optimum conditions were determined as 0.1 g/100 mL for catalyst dosage, 8% for active metal ratio, 500°C for calcination temperature, 3.7 for pH, 0.15 M for H_2O_2 concentration and 25°C for temperature. Under these conditions, 90.68% of methyl orange elimination was achieved at the end of 4 hours, and the iron concentration in the final solution was determined as 0.17 mg/L. The low iron leaching indicated that the active phase of the catalyst was strongly fixed to the support and that it was highly stable under oxidizing conditions of the reaction medium. Consequently, it was concluded that the Al/Fe pillared sepiolite could be used as an effective catalyst in azo dye removal by oxidation process.

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