The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)
ISSN: 2602-3199

The Eurasia Proceedings of Science, Technology, Engineering & Mathematics (EPSTEM)

Volume 1, Pages 131-138

ICONTES2017: International Conference on Technology, Engineering and Science

SYNTHESIS AND CHARACTERIZATION OF Al/Fe PILLARED SEPIOLITE FOR CWPO OF METHYL ORANGE

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Abstract: In this study, Al/Fe pillared sepiolite catalysts with different Fe/(Al+Fe) molar ratios were synthesized for catalytic wet peroxide oxidation (CWPO) of methyl orange azo dye. Furthermore, the catalysts were characterized by BET, XRD, XRF and SEM-EDX techniques. The catalysts were very efficient in the methyl orange oxidation reaction in diluted aqueous medium under mild experimental conditions (25°C and atmospheric pressure). 90.68% methyl orange elimination was achieved at 4 hours of reaction time under the conditions of 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. Meanwhile, low loss of Fe species was observed on all of the catalysts.

Keywords: Azo dye methyl orange, catalytic wet peroxide oxidation, pillared clays, sepiolite

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. Due to their complex structures, it is very difficult to successfully treat using traditional biological processes. Therefore, the treatment of the effluent containing these compounds is important for the protection of natural waters (Han et al., 2016). Reutilization of wastewater-contaminated dyes in industrial water is a critical concern for the suitable development of human activities. The need for effective water recycling has reinforced the research on tailored low cost pollution abatement since the existing solutions are not longer universal (Fathy et al., 2017). In recent years, several researchers have explored various advanced oxidation processes (AOPs) for the degradation of recalcitrant organic pollutants. In AOPs, hydroxyl radicals are generated which have very high oxidation potential (2.8 V) next only to fluorine. This hydroxyl radical reacts and oxidizes wide range of organic compounds present in water (Priyanka et al., 2014). Catalytic wet peroxide oxidation (CWPO) has been reported to be one of the most promising technologies for the removal of toxic organic compounds in wastewaters, because it could deplete nearly completely a wide range of non-biodegradable pollutants under very mild conditions of atmospheric pressure and room temperature (Zhou et al., 2014).

Sepiolite is a fibrous hydrated magnesium silicate and a natural clay mineral with a unit cell formula $[Si_{12}Mg_8O_{30}(OH)_4(H_2O)_4 \cdot 8H_2O]$ and a general structure formed by the alternation of blocks and tunnels which grow up in the fiber direction. Each block consists of two tetrahedral silica sheets enclosing a central magnesia sheet (Özcan and Gök, 2012). A diversity of solids has been used as catalysts for the oxidation of various organic pollutants from wastewaters. Among these catalysts, pillared interlayered clays (PILCs) containing mixed aluminum oxide/iron oxide pillars (AlFePILCs) seem to be promising catalysts, combining a good (reasonable) catalytic activity with a high stability against leaching (Catrinescu et al., 2011).

This study focuses on the synthesis of Al/Fe pillared sepiolite catalysts at different active metal ratios (AMR) and the use of them in catalytic wet peroxide oxidation of methyl orange. The physico-chemical properties of the catalysts were characterized by BET, XRD, XRF and SEM-EDX techniques.

- Selection and peer-review under responsibility of the Organizing Committee of the conference

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Methods

Synthesis of Al/Fe Pillared Sepiolite

The sepiolite sample used in the experiments was obtained from Türkmentokat-Gökçeoğlu region in Eskişehir (Turkey). It was ground and sieved under 75 µm (200 meshes) and dried at 100°C for 3 hours before used. During the preparation of catalysts, the molar ratio of the amount of active metal (Fe) to the total amount of the metals (Al and Fe) in the intercalating solution is defined as the active metal ratio (AMR).

$$Active\ metal\ ratio(\%) = \left(\frac{molFe}{molAl + mol\ Fe}\right)x100 \tag{1}$$

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 (Table 1). To prepare the catalysts, 2 g of sepiolite were 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 for 24 hours at 400 rpm on a Heidolph MR 3001 model magnetic stirrer at room temperature. 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. This solution was heated to 70°C and then 100 mL of 0.2 M NaOH solution pre-heated to 70°Cwas slowly added on it on a magnetic stirrer. During this time period the aluminum and iron in the solution were converted into hydroxides. The mixture was stirred at 400 rpm at 70°C for 2 hours. Then, the mixture was cooled to the room temperature. Previously prepared clay suspension was added onto this mixture drop by drop. Thus, the ratio of metal amounts to the sepiolite was 0.005 mole metal/g sepiolite in the final mixture. The mixture was stirred at 400 rpm for 24 hours, at the meantime, the sepiolite was provided to adsorb the metal species in the solution. Then, the mixture was filtered from a black ribbon filter paper under vacuum. The sample on the filter paper was dried at 60°C for 24 hours and then washed 10 times with 40 mL distilled water. The sample was dried again at 60°C and then calcined at 500°C for 2 hours. During calcination, the metal hydroxides impregnated on the sepiolite were converted to metal oxides.

Table 1. The Fe/Al ratios and the active metal ratios in the intercalating solutions

Sample	Fe/Al Ratio (mol/mol)	AMR (Fe/Al+Fe) (mol/mol, %)
SepAl	0/100	0
SepAlFe2	2/98	2
SepAlFe4	4/96	4
SepAlFe6	6/94	6
SepAlFe8	8/92	8
SepAlFe10	10/90	10

Characterization Studies

X-Ray Fluorescence (XRF) analysis was performed to determine the chemical compositions of sepiolite and SepAlFe8 by using Rigaku brand ZSX Primus model and Spectro IQ II devices.

X-ray diffractogram (XRD) analyses of sepiolite and SepAlFe8were performed with Rigaku brand Rint 2000 model XRD device and the Philips X'Pert Pro device to illuminate the mineralogical structures.

The BET specific surface areas, pore volumes and average pore diameters of sepiolite and SepAlFe8 were determined by nitrogen gas adsorption at -196°C. Analyses were performed with Quantachrome Autosorb 1C surface characterization device.

SEM-EDX analyses were performed using FEI Quanto-250 FEG device to illuminate the surface structures and compositions of sepiolite, SepAl, SepAlFe8 and SepAlFe8 after experiment.

In addition, in order to determine the iron contents of SepAl, SepAlFe2, SepAlFe4, SepAlFe6, SepAlFe8 and SepAlFe10 samples, 0.1 g sample was weighed into a baker and 10 mL of pure water, 10 mL of concentrated HCl and 2 mL of concentrated HNO_3 were added onto it. Then the mixture was boiled for about 2 hours and filtered through a blue ribbon filter paper. The amount of iron in the filtrate was determined with a Thermo ICE 3300 model Atomic Absorption Spectrophotometer (AAS) at a wavelength of 248.3 nm. Then, the iron contents of the samples were calculated.

Catalytic Wet Peroxide Oxidation Studies

Catalytic wet peroxide oxidation experiments were performed in a 150 mL glass reactor. Oxidation experiments were carried out at pH 3.7 and 25°C temperature, at atmospheric pressure. The reactor temperature was kept constant using a Lauda E200 model circulating water bath. Chemical oxidation of the methyl orange was carried out using 100 mL of 100 mg/L dye solution, with continuous stirring of the reaction mixture by a magnetic stirrer at 200 rpm. After 0.1 g 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 it constant diluted HNO_3 or NaOH solutions were dropped when needed. During the experiment, air bubbles were pumped into the solution at 0.15 L/min. 8.0 mL of freshly-prepared 0.15 M H_2O_2 started to be fed into the system under 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. In every 30 minutes, 2 mL of the sample was taken and the solution part of it was separated from the catalyst by centrifugation. The concentration 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:

$$\text{MOelimination (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \qquad (3)$$

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

In order to investigate the effect of active metal ratio on the methyl orange elimination, experiments were carried out using SepAl, SepAlFe2, SepAlFe4, SepAlFe6, SepAlFe8 and SepAlFe10 catalysts. The reusability of the catalyst was tested for three cycles.

In addition, the iron concentrations in the solutions at the end of the experiments were determined by AAS and the iron leaching rates were calculated according to the following equation:

$$\text{Fe leaching rate (\%)} = \frac{C_{Fe} \times V}{m \times Fe\ rate\ in\ sample\ (\%\ wt)} \times 100 \qquad (4)$$

In the equation, C_{Fe}(mg/L) is the iron concentration in the solution after the experiment, *V*(L) solution volume and *m* (mg) is the used catalyst amount.

Results and Findings

Characterization Studies

The compositions determined by XRF analysis of the sepiolite sample and SepAlFe8 catalyst were given in Table 2. XRD diffractograms of them were also given in Figs. 1 and 2. It can be seen in Table 2 that the Ca component in the sepiolite sample was completely removed and the amount of Mg component was also decreased during the preparation of the catalyst. In addition, the magnesite ($MgCO_3$) and dolomite ($MgCO_3CaCO_3$) peaks in the XRD of sepiolite sample were not seen in the XRD of SepAlFe8 (Fig. 1 and 2). It can be concluded from these results that magnesite and dolomite components were removed from sepiolite sample during the preparation of catalyst. The Fe_2O_3 and Al_2O_3 ratios in the SepAlFe8 catalyst were higher than that of sepiolite because of the iron and aluminum species coming from the pillaring solution (Table 2). In addition, SepAlFe8 catalyst has monoclinic crystal structure (Fig. 2).

Table 2. Chemical compositions of the sepiolite sample and the SepAlFe8 catalyst

Sample (w/w, %)	**MgO**	**SiO_2**	**CaO**	**Fe_2O_3**	**Al_2O_3**	**L.O.I.**
Sepiolite	30.73	48.91	2.38	0.24	-	17.73
SepAlFe8	27.51	57.50	-	4.64	9.67	0

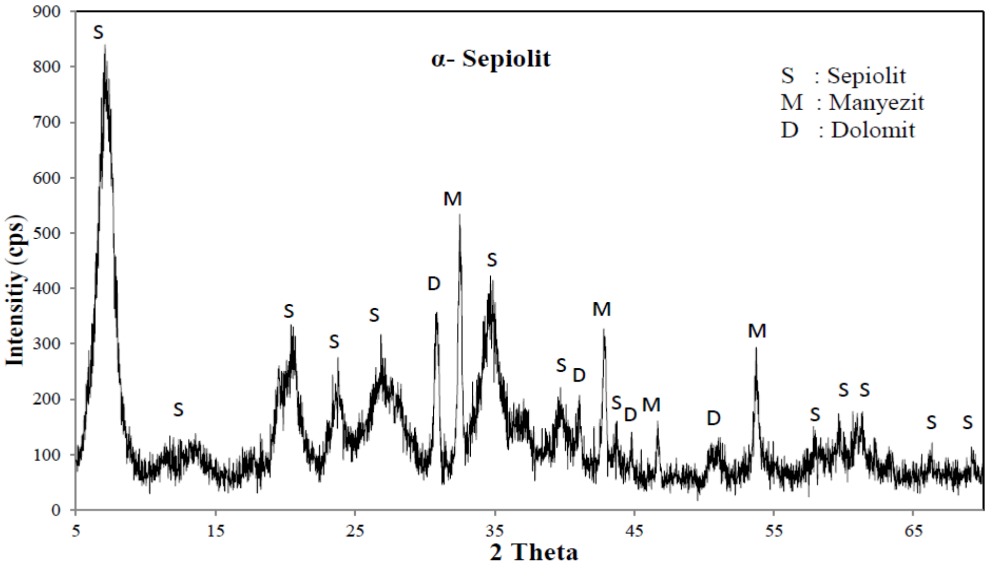

Figure1. X-Ray diffractogram of the sepiolite sample

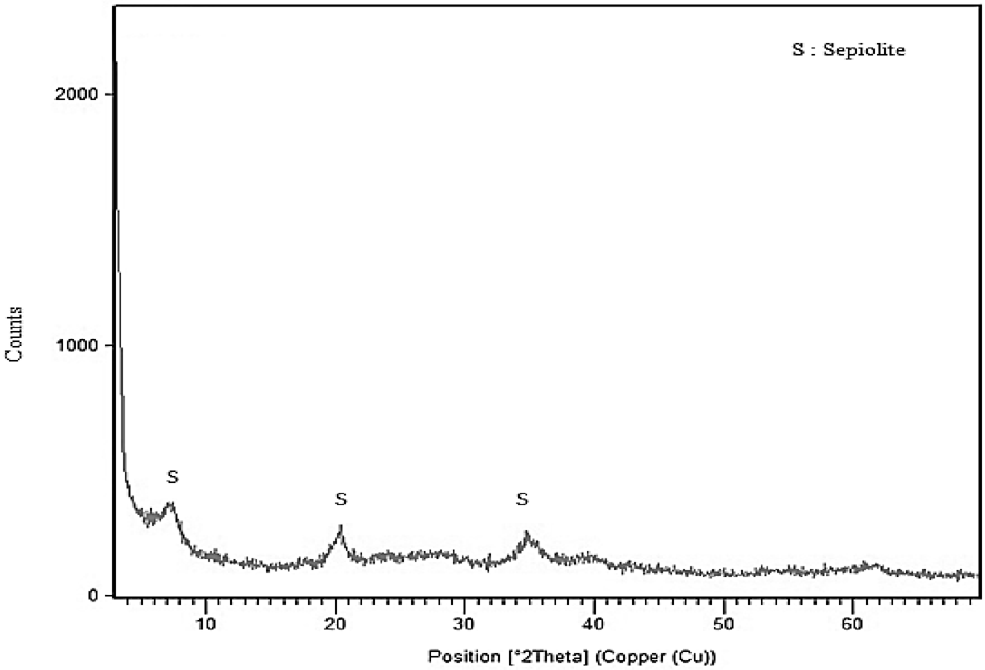

Figure 2. X-ray diffractogram of the SepAlFe8 catalyst

The BET surface area (S_{BET}), micropore volume (V_{micro}), total pore volume (V_{total}) and average pore diameter (D_p) of sepiolite sample and SepAlFe8 catalyst were given in Table 3. It can be seen from the table that the surface area and the average pore diameter of the SepAlFe8 catalyst were slightly increased, and total pore volume and especially the micropore volume were considerably increased compared to sepiolite sample.

Table 3. Surface and pore properties of the sepiolite sample and the SepAlFe8 catalyst

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	185.90	0.0973	0.3044	65.50

SEM images magnified at 10000 times for sepiolite sample, SepAl, SepAlFe8 and SepAlFe8 after experiment were given in Fig. 3. It is understood from the SEM images that sepiolite has a smooth, typical layered surface, SepAl has a rougher structure and SepAlFe8 become much rougher and much more porous. These results are consistent with the BET results given in Table 3. In addition, EDX analyses of sepiolite, SepAl, SepAlFe8 and

SepAlFe8 after experiment were given in Table 4. It can be seen that Ca and Mg ratios were decreased during the preparation of the catalyst. This result is consistent with XRF and XRD results given in Table 2 and Figs. 1 and 2. It can be seen from the EDX results of SepAlFe8 catalyst that Fe/Al molar ratio on the catalyst (calculated as 29%) is higher than AMR (8%). It can be also seen that iron content of the catalyst after experiment is less than that of SepAlFe8 which showed that small amount of iron was dissolved during the reaction. Furthermore, the appearance of sulfur(S) on the catalyst after experiment at the ratio of 0.43% indicated that methyl orange and/or reaction products like $NaHSO_4$ were held on the catalyst.

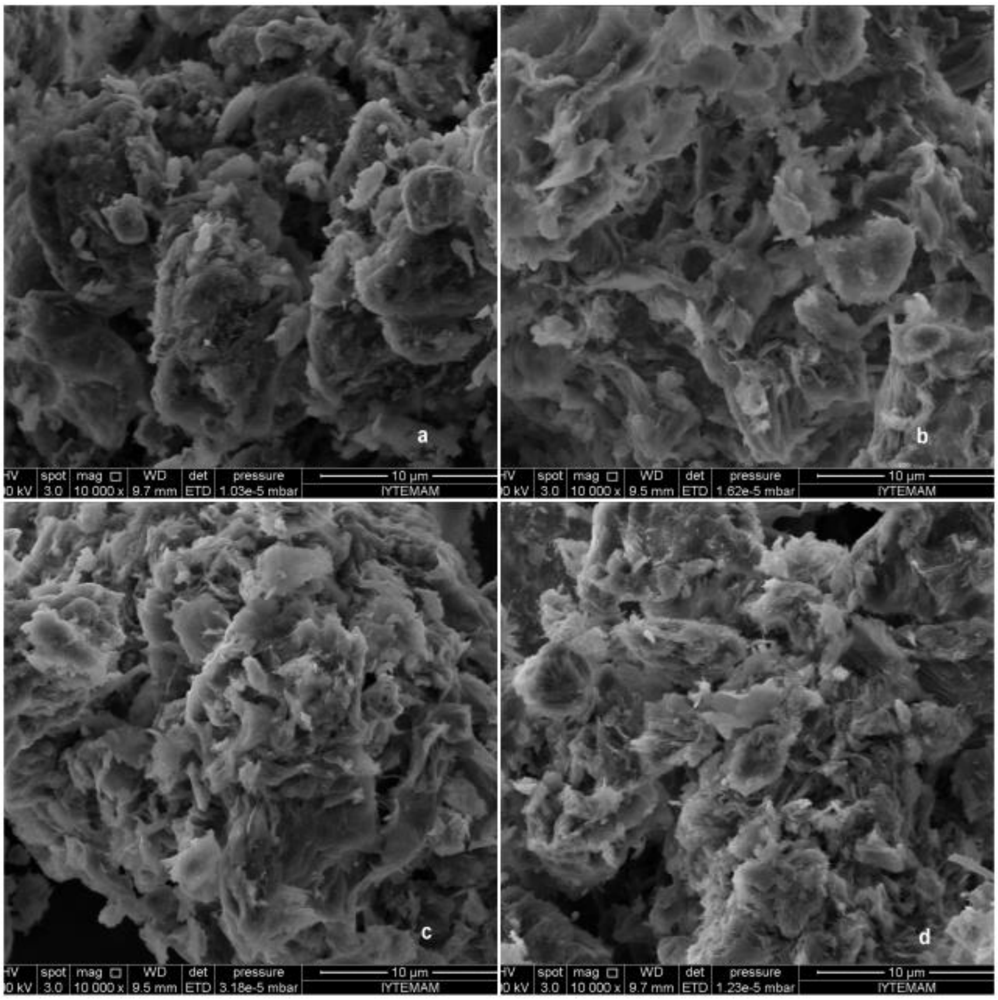

Figure 3. SEM images of (a) sepiolite, (b) SepAl, (c) SepAlFe8, (d) SepAlFe8 after experiment

Table 4. The EDX analyses of sepiolite, SepAl, SepAlFe8 and SepAlFe8 after experiment

Element (w/w, %)	Sepiolite	SepAl	SepAlFe8	SepAlFe8 (after experiment)
O	56.44	54.66	54.43	56.36
Mg	17.18	15.60	15.24	13.71
Si	25.32	25.66	24.19	24.01
Ca	1.06	-	-	-
Al	-	4.09	3.31	3.13
Fe	-	-	2.83	2.36
S	-	-	-	0.43

Effect of AMR on the MO Elimination

The effect of active metal ratio on the elimination of methyl orange was investigated by using SepAl, SepAlFe2, SepAlFe4, SepAlFe6, SepAlFe8 and SepAlFe10 catalysts. The results were given in Fig. 4. The iron contents of the catalysts, the iron concentrations in solutions after the experiments and the iron extraction rates for different catalysts were given in Table 5. As seen in Fig. 4, methyl orange elimination increased with increasing AMR, namely increasing iron content of the catalyst (Table5). The highest methyl orange elimination values of 90.68% and 90.89% were determined at the end of 4 hours for the SepAlFe8 and SepAlFe10 catalysts, respectively. These values were very close to one another. In addition, the iron concentration in the solution after experiment was 0.17 mg/L for both catalysts, and the iron leaching rates were also calculated as 0.67 and 0.66%, respectively (Table 5). These values showed that the elimination of methyl orange was achieved without considerable iron leaching.

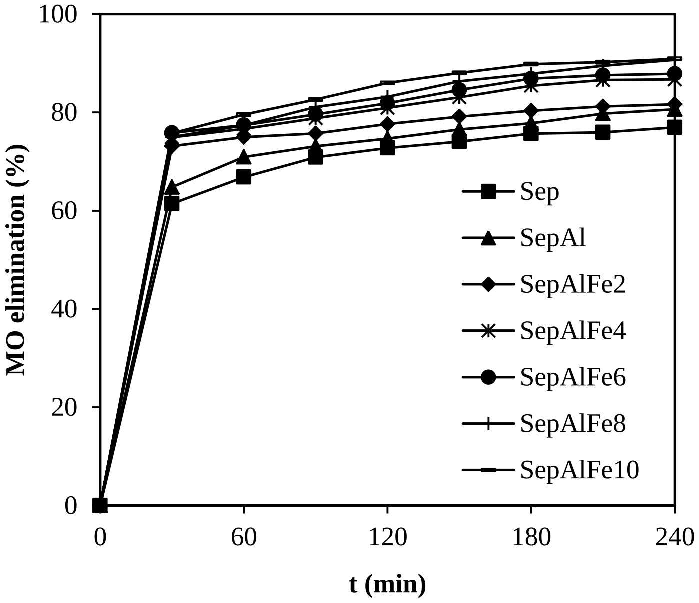

Figure 4. Effect of the active metal ratio on the elimination of methyl orange
(m: 0.1g, Tcalc: 500°C, pH: 3.7, T: 25°C, H_2O_2: 0.15 M)

Table 5. Iron contents of the catalysts, iron concentrations in the solutions and iron leaching rates

Parameter	**Sepiolite**	**SepAl**	**SepAlFe2**	**SepAlFe4**	**SepAlFe6**	**SepAlFe8**	**SepAlFe10**
Fe content of the catalyst (w/w, %)	-	0.07	0.67	1.12	1.54	2.52	2.56
Fe concentration in the solution (mg/L)	0.00	0.00	0.02	0.04	0.05	0.17	0.17
Fe leaching rate (%)	0.00	0.00	0.30	0.36	0.32	0.67	0.66

If the catalytic activity is considered to depend on the amount of active metal in the binary Fe+Al mixture, while the active metal ratio increases the catalytic performance per active center decreases significantly (Fig. 5). High active metal ratio causes to deteriorate excessively the critical physicochemical properties, such as textural properties and to form external aggregates (Galeano et al., 2010). For this reason, the best results per active center were obtained for the 2% active metal ratio in which the absorbed iron on the sepiolite formed more active phase.

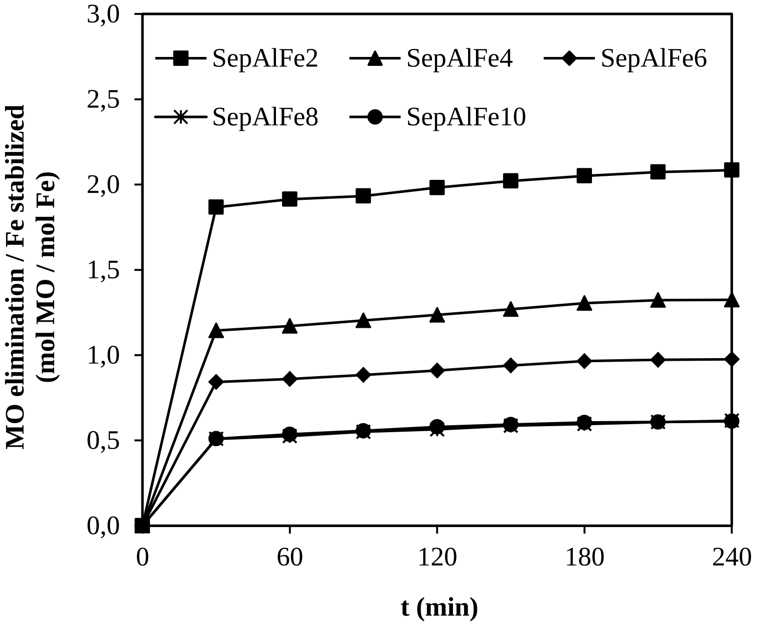

Figure 5. Catalytic performance of catalysts referred to the net amount of active metal stabilized

Reusability of the Catalyst

In order to investigate the reusability of the catalyst on the elimination of methyl orange, the catalyst (SepAlFe8) separated from solution by filtration at the end of the experiment and used again after calcining at 500°C for 2 hours. This process was carried out for 3 cycles and the results were given in Fig. 6. Furthermore, the iron concentrations in solutions at the end of the experimentswere determined and the iron leaching rates were calculated and given in Table 6. As seen in Fig. 6, methyl orange elimination value was decreased slightly from 90.68% for the first cycle to 88.42% for the second cycle and to 86.18% for the third cycle. The iron content of the catalyst decreased a bit in every cycle because of the dissolution of it in the acidic medium (Table 6). This may be responsible from the decrease in MO elimination; but, it should also be kept in mind that after each cycle some contaminants may remain on the catalyst.

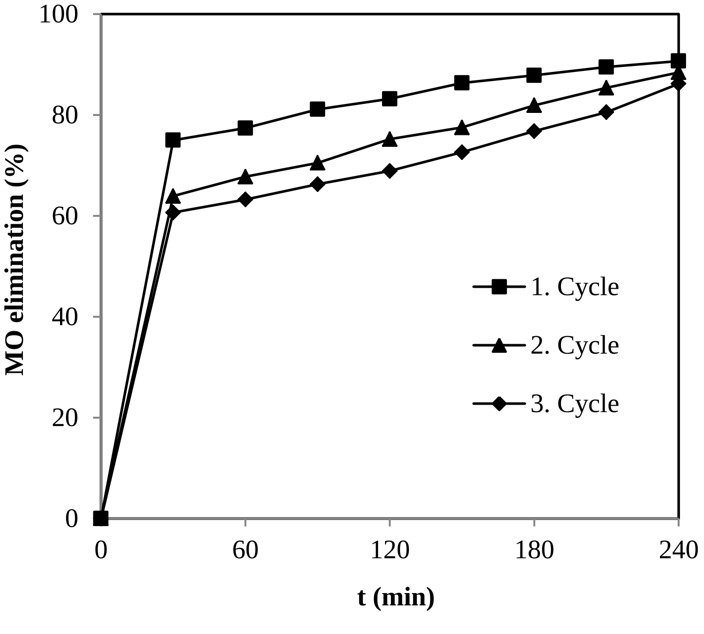

Figure 6. Effect of the reuse of catalyst on the elimination of methyl orange

Table 6. For reusability, the iron concentrations in solution and the iron leaching rates of iron in sample after the experiment

Parameter	1. Cycle	2. Cycle	3. Cycle

Fe concentration in the solution (mg/L)	0.17	0.18	0.23
Fe leaching rate (%)	0.67	0.71	0.91

Conclusion

Usability of Al/Fe pillared sepiolite catalysts with different active metal ratio in the catalytic wet peroxide oxidation of methyl orange was investigated. By this aim, SepAl, SepAlFe2, SepAlFe4, SepAlFe6 SepAlFe8 and SepAlFe10 catalysts in the active metal ratios of 0, 2, 4, 6, 8 and 10% were prepared. XRD results showed that dolomite and magnesite minerals in the sepiolite sample didn’t appear in the SepAlFe8 catalyst. From BET results, it was determined that the surface area of the catalyst increased slightly and the micropore volume increased significantly compared to the sepiolite sample. SEM analysis showed that sepiolite has smoother, typical layered surface and the catalyst had a rather rough and porous structure. In addition, EDX analysis showed that 2.83% Fe and 3.31% Al by weight were found on SepAlFe8 catalyst. The highest methyl orange elimination was observed when using SepAlFe8 and SepAlFe10 catalysts. The elimination values for these catalysts were almost the same. For SepAlFe8 catalyst, 90.68% of methyl orange removal was achieved by the end of 4 hours. It was found that the iron concentration in the solution after the oxidation experiment was 0.17 mg/L and 0.67% of the iron on catalyst was leached. In order to investigate the reusability of the catalyst, the experiments were carried out for 3 cycles under the same conditions and it was found that the elimination efficiencies were 88.42% and 86.18% for the second and third cycles, respectively. 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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