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## DEGRADATION OF PULP MILL WASTEWATER BY A HETEROGENEOUS FENTON-LIKE CATALYST Fe/Mn SUPPORTED ON ZEOLITE

A novel heterogeneous catalyst, Fe/Mn supported on NaY zeolite, was effectively applied for treating pulp mill effluents. The results of the wastewater quality analysis showed that aromatic structures were present in raw pulp mill effluents, which indicated the difficulty for biodegradation treatments. Two different catalysts were prepared by impregnation (Fe-Mn/NaY<sub>im</sub>) and sol-gel (Fe-Mn/NaY<sub>sg</sub>) methods, respectively. The Fe-Mn/NaY<sub>sg</sub> catalyst demonstrated higher COD removal efficiency and was more stable than the Fe-Mn/NaY<sub>im</sub> catalyst. The synergistic effects were found between Fe and Mn for COD removal. The highest COD removal efficiency (75.2%) was yielded with the Fe-Mn/NaY<sub>sg</sub> catalyst (Fe/Mn molar ratio of 2) with 4 mmol/dm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> and 1.2 g/dm<sup>3</sup> of catalyst addition. A constant COD removal over time was obtained; the COD removal efficiency amounted to 45% after the Fe-Mn/NaY<sub>sg</sub> catalyst repeatedly degrading pulp mill effluents for five times. The distribution and transformation of the polarity and molecular weight (MW) of dissolved organic carbon (DOC) in the heterogeneous Fenton process were also studied. Experiments showed that the hydrophobic fraction comprised the largest fraction of DOC (60%) in raw wastewater and high MW molecules were transformed into low MW molecules after the heterogeneous Fenton process. This study broadened the application of the Fenton technology.

### 1. INTRODUCTION

Industrial processes generate a wide variety of wastewater requiring the application of expensive advanced treatments. Advanced oxidation processes (AOPs) for the abatement of contaminants such as the Fenton process, H<sub>2</sub>O<sub>2</sub>/UV ozonation and TiO<sub>2</sub>-photocatalysis [1–3] have attracted a great deal of attention. To date, many studies have been carried out with Fenton oxidation to treat reverse osmosis concentrate, dye effluent, landfill leachate, pulp and paper mill effluents [4–6], due to its simple equipment, mild operating conditions (room temperature and atmospheric pressure), and high oxidation

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efficiency. In general, Fenton processes have produced better overall results for treating pulp and paper mill effluents than other AOP-based treatment technologies [7]. However, the homogeneous Fenton process has some drawbacks. Non-recyclable soluble iron salts yield large amounts of sludges of ferric hydroxide which require further removal from the treated wastewater [1]. The homogeneous Fenton reaction must be carried out in an acidic solution (pH 2–4), and thus large amounts of acid must be added to the reaction medium. To some extent, such drawbacks limit the application of the homogeneous Fenton process.

To solve these problems, the use of heterogeneous Fenton process is a promising alternative. Heterogeneous catalysts use various matrices such as activated carbon, clays, resin and zeolites [5] to immobilize metal ion to separate and recycle the catalyst. Among these supporters, zeolites may be an ideal candidate since the open porous structures present the capability of accommodating a wide variety of exchangeable cations, including iron [8]. In various types of zeolites, NaY zeolite is not only favourable for ion exchange and immobility but also highly stable when exposed to an acid environment [9].

Various transition metals such as copper, aluminium, and manganese [10] have also been used as the active phase in heterogeneous Fenton oxidation process to increase the pH range of the reaction. As a common transition metal, manganese receives attention in the Fenton system because of its benign environmental effects. Some authors reported that  $\text{Mn}^{2+}$  could react with  $\text{H}_2\text{O}_2$  to produce  $\text{HO}_2^\bullet/\text{O}_2^\bullet$ , then accelerated the formation of  $\text{Fe}^{2+}$ , and consequently accelerated the production of  $\text{HO}^\bullet$  and the oxidation of pollutants [11]. However, few bimetallic oxide heterogeneous Fenton catalysts also were reported.

In this work, a heterogeneous Fenton catalyst, Fe/Mn bimetallic oxide supported NaY zeolite was developed by two methods. The catalytic effect of the heterogeneous catalyst was evaluated by degradation of pulp mill effluents. The distribution and transformation of the polarity and molecular weight of dissolved organic carbon in wastewater were investigated in the heterogeneous Fenton process.

## 2. MATERIALS AND METHODS

*Materials and wastewater samples.* Ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), manganese sulfate monohydrate ( $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and high purity nitrogen (all analytic grade) were purchased from the First Chemical Reagent Manufactory (Tianjin, China). NaY zeolite ( $\text{Na}_2\text{O} < 13\%$ , surface area  $620 \text{ m}^2/\text{g}$ , Si/Al 2.8) was obtained from the Catalyst Factory of NanKai University (Tianjin, China). The pulp mill effluents were obtained from the secondary sedimentation tank of the Tranlin Company located in Shandong province, China. A pulp mill middle section effluent treated by physicochemical process coupled anaerobic-aerobic biological treatments. The characteristics of raw pulp mill effluents are given in Table 1.

Table 1

Characteristics of raw pulp mill effluents

Parameter	COD [mg O <sub>2</sub> /dm <sup>3</sup> ]	BOD [mg O <sub>2</sub> /dm <sup>3</sup> ]	Color [PCU]	Total nitrogen [mg N/dm <sup>3</sup> ]	Conductivity [μS/cm]	Turbidity [NTU]	TSS [mg/dm <sup>3</sup> ]	pH
Value	130–250	4–12	20–50	10–15	5000–7000	20–40	150–200	7–8

*Analytical methods.* Three-dimensional excitation emission matrix spectrometry (EEM, F-4500 FL spectrophotometer, Hitachi, Japan) was applied to analyze the fluorescence characteristics of dissolved organic matters (DOM) in pulp mill effluents. The spectra were collected with scanning emission wavelengths from 300 to 600 nm at 5 nm increments by varying the excitation wavelength from 220 to 400 nm at 2 nm increment. Excitation and emission were scanned with a 5 nm slit width at a scan rate of 2000 nm min<sup>-1</sup>. The components of organic matters in pulp mill effluents were identified by the GC-MS. Samples were filtered through 0.45 μm membrane and dichloromethane was used as solvent to extract the organic compounds retaining in the filtrate at room temperature. Prior to analysis, the extracts were evaporated and reconstituted with dichloromethane to a volume of 1 cm<sup>3</sup>. The analytical GC column was a HP-5MS 30 m×0.25 mm internal diameter. The oven was programmed as follows: 40 °C maintained for 4 min, then raised at 50 °C/min up to 250 °C, raised at 10 °C/min up to 300 °C, and maintained for 10 min. 1 μL of extract containing the dichloromethane was injected by the autosampler in the injector by the splitless mode. The injector temperature was set at 250 °C. Helium was used as a carrier gas at a constant flow of 1 cm<sup>3</sup>/min. These criteria are in accordance with the NIST05 Decision.

*Catalysts preparation.* The catalyst samples were prepared by two different methods: the impregnation method [11] and sol-gel synthesis [1]. Considering possible effects of Fe(II) oxidation/hydroxide precipitation, the initial pH of the solution was adjusted to 4.0 by addition of nitric acid in both catalyst preparation procedures. In impregnation, 2.0 g of NaY zeolite was slowly added into a 100 cm<sup>3</sup> FeSO<sub>4</sub>·7H<sub>2</sub>O and MnSO<sub>4</sub>·H<sub>2</sub>O mixed solution with the total concentration of metal ions of 0.06 mol/dm<sup>3</sup> and the molar ratio Fe<sup>2+</sup>: Mn<sup>2+</sup> fixed as 1:0, 1:1, 0:1, 2:1 and 1:2. The mixture was stirred for 6 h at room temperature until a viscous fluid was obtained which was dried at 110 °C for 12 h and calcined at fixed temperature in a muffle furnace for 2 h to obtain Fe-Mn/NaY<sub>im</sub>. In the sol-gel synthesis procedure, citric acid was used as the chelating agent. The molar ratio of metal ions (Fe<sup>2+</sup> and Mn<sup>2+</sup>) to citric acid was kept 1. Other procedures were similar as in the impregnation method. Then obtained Fe-Mn/NaY<sub>sg</sub> catalyst was subject to further analysis.

*Degradation experiments and chemical analyses.* The catalytic activity of the catalysts was tested by the degradation of pulp mill effluents. The catalyst dosage and H<sub>2</sub>O<sub>2</sub>

dosage were fixed at  $1.2 \text{ g/dm}^3$  and  $4 \text{ mmol/dm}^3$ , respectively. The initial pH was adjusted by using HCl or NaOH solutions. Then prepared Fe-Mn/NaY catalyst and  $\text{H}_2\text{O}_2$  (30 wt. %) were added to the wastewater samples under vigorous magnetic stirring. After reaction times of 10 min, 20 min, 30 min and 60 min, the Fenton reaction was terminated by addition of NaOH. The treated wastewater was kept standstill for 30 min and the COD analysis for the supernatant was performed by the spectrophotometry method (DR900, Hach, USA). pH was measured with a portable pH analyzer (pHB-2, China).

The polarity (hydrophobic (HPO)/hydrophilic (HPI)) distribution of wastewater was analyzed based on the method of Quanrud [12]. The organics were extracted and fractionated using XAD-8/XAD-4 resin chromatography. Three-way distributions of dissolved organic carbon (DOC) were obtained based on fractions retained on the XAD-8 and XAD-4 resins. The retained fractions on XAD-8 were HPO, whereas the retained fractions on XAD-4 were transphilic (TPI), and the non-retained fractions on either resin were HPI [12].

The MW distributions were determined by the ultrafiltration method [13] using a  $300 \text{ cm}^3$  stirred ultrafiltration cell (SINAP, SCM-300, China). The samples were filtered through  $0.45 \text{ }\mu\text{m}$  pass-through ultrafiltration membranes with the nominal molecular weight cut-off of 30, 10, 3 and 1 kDa successively. The MW distribution was categorized as follows: 0–1, 1–3, 3–10, 10–30 kDa, and 30 kDa– $0.45 \text{ }\mu\text{m}$ . The driving force for filtration was 0.015 MPa with nitrogen (99.5%) flow.

### 3. RESULTS AND DISCUSSION

#### 3.1. ORGANIC COMPOUNDS ANALYSIS OF RAW PULP MILL EFFLUENTS

EEM fluorescence analysis was used to reveal distribution of organic compounds in raw pulp mill effluents sample. According to the research of Chen et al. [14], the EEM spectrum was divided into five regions based on the operationally defined excitation – emission boundaries of DOM, which represents different fluorescence features caused by various kinds of DOM.

In Figure 1, showed the EEM fluorescence spectrum of raw pulp mill effluents sample is shown. Only one fluorescence characteristic peak was observed at the excitation and emission wavelengths of 325 nm and 425 nm approximately. This characteristic peak was turned out to be in accordance with the humic-acid-like (ex. 320–330 nm/em. 410–450 nm) component in wastewater sample. This result confirmed that some soluble biodegradable compounds might be removed in anaerobic and aerobic biological treatments prior to the Fenton process. Similar peak pattern comprising a major peak at ex. 343 nm/em. 433 nm associated with a subpeak at ex. 300 nm/em. 425 nm was obtained for tissue mill polluted river water [15]. Several fluorophores were the contributors for this specific fluorescence characteristic peak (em.  $>380 \text{ nm}$ ) reported in our

research, including lignins, humic acids, quinones, aromatic ketones, fluorescent whitening agents [16]. Some studies also indicated that the complex compounds derived from lignin and other degraded plant materials might be related to this fluorescence feature [17]. Therefore, relatively complicated chemical bonding structures such as aromatic structures were probably present in organic compounds. Since the raw pulp mill effluents was first treated by anaerobic and aerobic biological processes before the Fenton process, the remained pollutants showed biorefractory characteristic in the Fenton process.

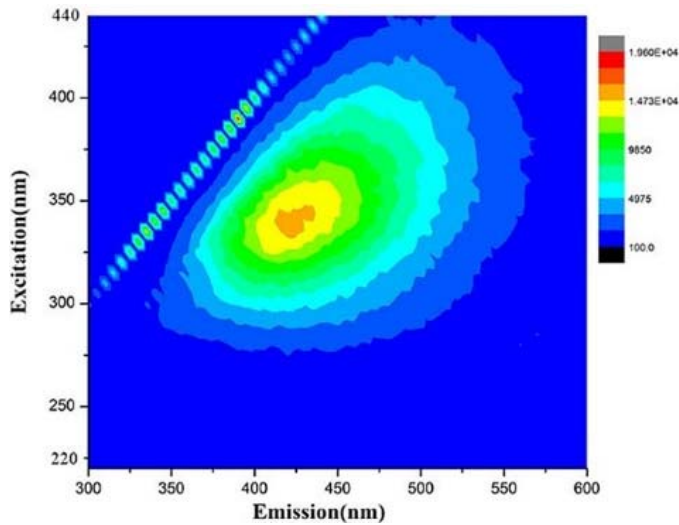


Fig. 1. EEM fluorescence spectra of raw pulp mill effluents

To clarify the specific composition in a raw sample, a GC-MS analysis has been conducted. Six main organic compounds identified and their relative amounts constituting more than fifty percent of total organic compounds in raw pulp mill effluents are presented in Fig. 2 and in Table 2. Most of the compounds were synthetic chemicals. Wood raw material such as hemicelluloses, pectin, lignin, were not found. Due to some whiteners, defoamers and dispersion agents added in the papermaking process [18] wood raw materials were broken down in primary and secondary treatments for pulp mill effluents. The organic compounds detected by GC-MS showed the presence of benzene rings related to preliminary degradation of lignin. Besides, chlorinated organic compounds were found in the effluent. The chemical structure characteristics performed consistency with the humic-acid-like component detected in EEM analysis. Thus, considering the difficulty for treating pulp mill effluents with the specific complex components and complicated chemical structures in our research, a novel catalyst was proposed to improve the treatment.

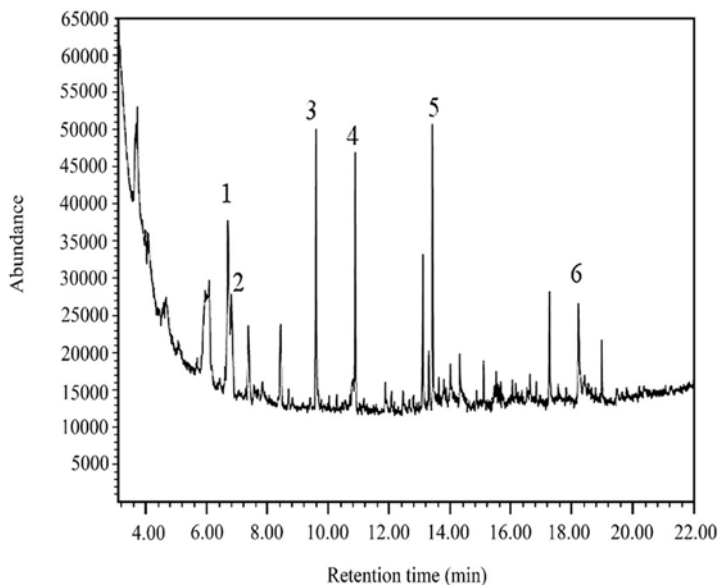


Fig. 2. GC-MS chromatogram of the raw pulp mill effluent; the peak numbers correspond to those given in Table 2

Table 2

Main organic components of raw pulp mill effluents identified by GC-MS

Peak number	Retention time	Organic component	Relative content [%]
1	6.702	monobutyl trithiocarbonic acid	13.4
2	6.818	2,3-dichloro-2-methylpropanal	6.3
3	9.594	pyrocatechol	9.3
4	10.887	dodecamethylcyclohexasiloxane	7.4
5	13.424	N-phenyl-butanamide	8.9
6	18.215	diisobutyl phthalate	6.3

### 3.2. EFFECT OF CATALYST PREPARATION METHODS ON THE DEGRADATION OF PULP MILL EFFLUENTS

Differences between preparation methods of catalysts may affect the dispersion of the active phase on the matrix surface, and finally affect the degradation properties of wastewater. The current publishing trends indicated that the characterization of the active sites was the eye-catching topic, while synthesis methods received less attention in the last year (Fig. 3). The impregnation method was widely applied in preparing heterogeneous catalysts because of easy handling and simple operating conditions.

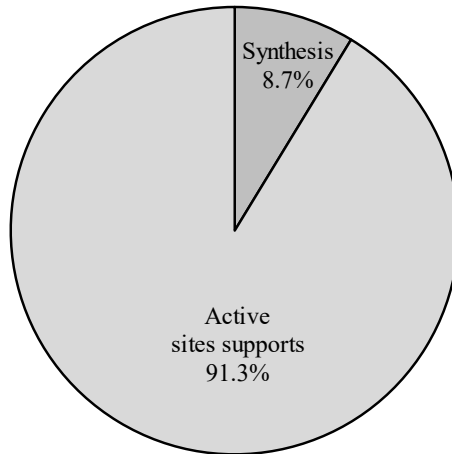


Fig. 3. Publishing trends on heterogeneous catalysts during the 2001–2016 period. Source: SCI, Web of Knowledge

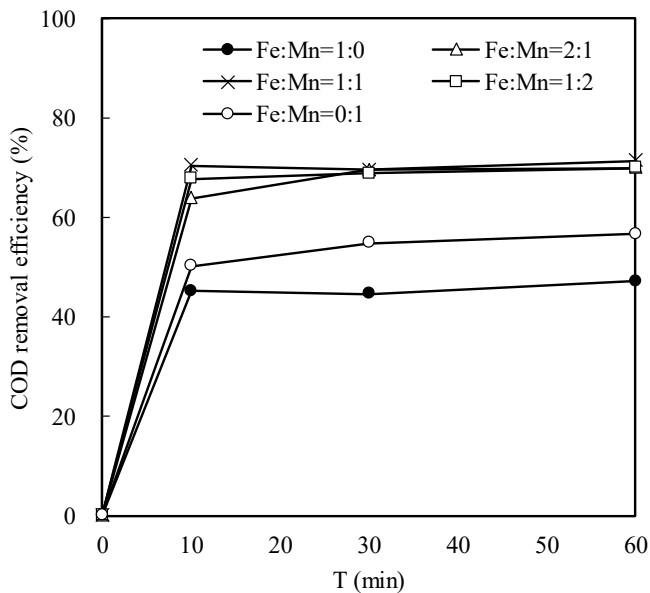
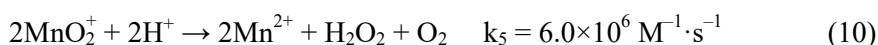
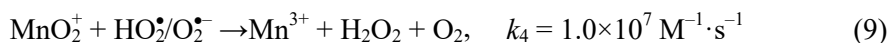
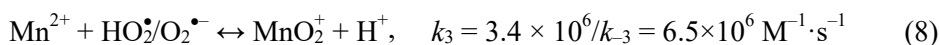
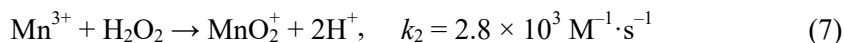
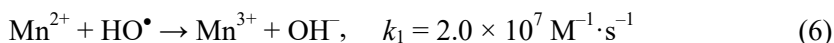
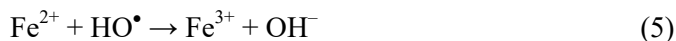
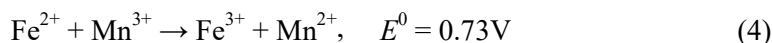
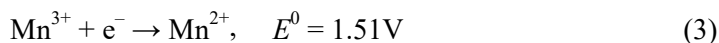
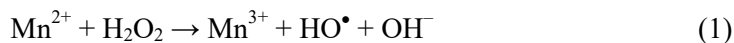


Fig. 4. Effect of Fe-Mn/NaY<sub>im</sub> catalyst on COD removal of pulp mill effluents in the Fenton system (initial concentrations: [H<sub>2</sub>O<sub>2</sub>] = 4.0 mmol/dm<sup>3</sup>, [Fe-Mn/NaY<sub>im</sub>] = 1.2 g/dm<sup>3</sup>, COD of raw wastewater = 220 mg O<sub>2</sub>/dm<sup>3</sup>, pH 3.0)

Effects of Fe-Mn/NaY<sub>im</sub> catalyst on COD removal are shown in Fig. 4. The COD removal efficiencies with two-component metal-ion catalysts were evidently higher than that with single metal-ion catalysts.

In the case of two metal ion impregnation, the molar ratio of  $\text{Fe}^{2+}$  to  $\text{Mn}^{2+}$  in the Fe-Mn/NaY<sub>im</sub> catalyst showed slight effects on COD removal. The COD removal efficiency amounted to 71.4% under the optimal condition with  $\text{Fe}^{2+}$  to  $\text{Mn}^{2+}$  ratio of 1, which was 23.8% and 14.7% higher than that catalyzed by single  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$  catalysts, respectively. Zhao et al. [19] reported similar phenomenon that Mn(II) enhances the oxidation of benzoic acid by Fe(III)/H<sub>2</sub>O<sub>2</sub> system. The results of increasing COD removal efficiencies were concerned with the introduction of Mn. As a transition metal ion with variable valence, manganese ion may participate in the chain reaction of radicals in Fenton system by reacting with HO• or HO<sub>2</sub>•/O<sub>2</sub>• and thus enhance the efficiency of COD removal [19]. Costa et al. [20] studied the reaction of Mn with Fe in Fenton reaction (Eqs. (1)–(5)), and Jacobsen et al. [21] provided the reactions of Mn<sup>2+</sup> with HO• and HO<sub>2</sub>•/O<sub>2</sub>• in detail (Eqs. (6)–(10)). However, by increasing the proportion of  $\text{Fe}^{2+}$  or  $\text{Mn}^{2+}$  in Fe-Mn/NaY<sub>im</sub> catalyst, the COD removal efficiencies maintained a constant value after 30 min, showing that the enhancement was not significant with various Fe/Mn ratios in Fe-Mn/NaY<sub>im</sub> catalyst. This result could be possibly concerned with metal-ion loss from catalyst, which leads to the inconspicuous difference among different Fe/Mn ratio. Similar explanations were provided by Aniruddha et al. [22] that total dissolved iron attained the value of 8.1 mg/dm<sup>3</sup> from Fe<sub>3</sub>O<sub>4</sub>-CeO<sub>2</sub> catalyst after 120 min.





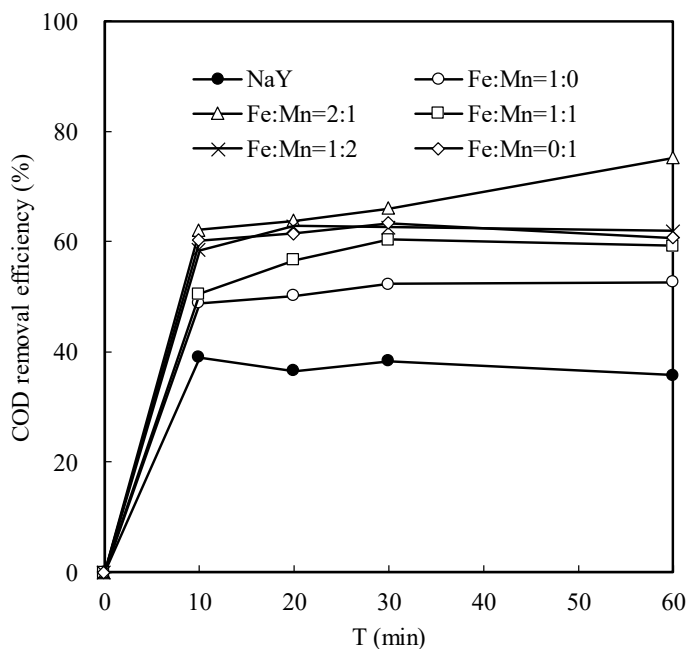


Fig. 5. Effect of Fe-Mn/NaY<sub>sg</sub> catalyst on COD removal of pulp mill effluents in the Fenton system (initial concentrations: [H<sub>2</sub>O<sub>2</sub>] = 4.0 mmol/dm<sup>3</sup>, [Fe-Mn/NaY<sub>sg</sub>] = 1.2 g/dm<sup>3</sup>, COD of raw wastewater = 220 mg O<sub>2</sub>/dm<sup>3</sup>, pH = 3.0)

The Fe-Mn/NaY<sub>sg</sub> catalyst with Fe/Mn ratio of 2 yielded the highest COD removal efficiency (75.2%, Fig. 5)). When two metal ions were applied, different COD removal efficiencies with various Fe/Mn ratios were obtained compared with Fe-Mn/NaY<sub>im</sub>. Besides, comparing with the COD removal efficiency of Fe/NaY catalyst, some authors reported that the introduction of Mn improved the HO<sup>•</sup> generation rate and accordingly enhanced the catalytic activity [11]. Mn<sup>2+</sup> could trigger Fenton-like reactions with H<sub>2</sub>O<sub>2</sub> to generate HO<sup>•</sup> and a higher valence manganese ion species of Mn<sup>3+</sup> (Eq. (1)). In this condition, Fe<sup>2+</sup> tended to be oxidized to Fe<sup>3+</sup> under the impetus of electrode potential between Fe<sup>2+</sup>/Fe<sup>3+</sup> (0.77V) and Mn<sup>2+</sup>/Mn<sup>3+</sup> (1.51V), resulting in the decreased consumption of HO<sup>•</sup> by Fe<sup>2+</sup>, and thus enhance the catalyst activity for oxidation (Eqs. (2)–(5)). Thus, the higher COD removal efficiencies achieved by two metal ions catalysts indicated that synergistic effects should be present between Fe<sup>2+</sup> and Mn<sup>2+</sup> for enhancing the oxidation process by a series of chain reactions in the heterogeneous Fenton reaction. Similarly, Li et al. [23] also found that Mn<sup>2+</sup> and Fe<sup>2+</sup> ions have an interaction effect on improving bisphenol A degradation. Besides, unlike the rapid COD removal by Fe-Mn/NaY<sub>im</sub> catalyst with the highest value at around 10 min, a gradual degradation occurred and a slight increase of COD removal efficiency was observed with the Fe/Mn ratio of 2 in Fe-Mn/NaY<sub>sg</sub> catalyst after 10 min. The reason is that Fe<sup>2+</sup> is much more

sufficient and effective to generate  $\text{HO}^\bullet$  upon sufficient  $\text{Mn}^{2+}$  addition, thus a gradual oxidation of organic matters may occur. As  $\text{Mn}^{2+}$  could also induce Fenton-like reaction forming  $\text{HO}^\bullet$  species (Eq. (1)), this degradation also implied that  $\text{Mn}^{2+}$  was less effective for generating  $\text{HO}^\bullet$  to hold oxidation process than  $\text{Fe}^{2+}$ . Anipsitakis et al. [24] found that iron is the most efficient transition metal to catalyze  $\text{H}_2\text{O}_2$  to generate  $\text{HO}^\bullet$ , while manganese ion is very inert. This finding strongly supported the results showed in this study.

Although both two-component metal-ion catalysts showed high COD removal efficiencies, the catalysts prepared by the sol-gel method ( $\text{Fe-Mn/NaY}_{\text{sg}}$ ) were opted as heterogeneous catalysts in subsequent experiments because of less metal ion loss and better performance for catalysts reuse. The better catalytic performance and stability of  $\text{Fe-Mn/NaY}_{\text{sg}}$  may be attributed to the chelating effect of citric acid. This effect resulted in better dispersion, stronger anchorage of Fe/Mn on NaY zeolite surface and larger mesoporous volume, which also explained different COD removal efficiencies and performances over time with various ratio in  $\text{Fe-Mn/NaY}_{\text{sg}}$  catalyst compared with  $\text{Fe-Mn/NaY}_{\text{im}}$  catalyst. The  $\text{Fe-Mn/NaY}_{\text{sg}}$  (Fe/Mn molar ratio of 2) catalyst was evaluated in the subsequent experiments.

### 3.3. CONTINUING CATALYTIC ABILITY OF HETEROGENEOUS CATALYST

The stability of catalysts is an important factor in practical application. The principal problem is possible leaching of iron under the operating conditions. Therefore, the catalytic activity of  $\text{Fe-Mn/NaY}_{\text{sg}}$  catalyst after being repeatedly used was studied by conducting five successive experiments with the same operating conditions. The catalyst was washed out with DI water after each experiment to regenerate its catalytic activity. The results in Figure 6 showed the reusability of  $\text{Fe-Mn/NaY}_{\text{sg}}$  catalyst on COD removal with five consecutive experiments. As presented in Fig. 6, the COD removal efficiency of pulp mill effluents after 60 min duration reaction was about 57.9% by the end of the first cycle. The removal rates were 55.3%, 54.3% and 50.3% in the next 3 cycles, respectively. After repeating this experiment five times, the COD removal efficiencies remained above 45%, and the effectiveness run as 77.8% of the beginning of catalytic processes. The  $\text{Fe-Mn/NaY}_{\text{sg}}$  catalyst presented continuous catalytic ability in the treatment of degrading pulp mill effluents and the COD removal efficiencies slightly decreased after the usage of five successive cycles. That result indicated that little catalytic sites were inactivated during this process. In addition, the result was also consistent with the analysis of chelating effect of citric acid for holding more available iron ion on NaY zeolite. Therefore, from the perspective of reuse, the  $\text{Fe-Mn/NaY}_{\text{sg}}$  heterogeneous catalyst exhibited better performances compared with the homogeneous catalyst. But further research is needed to investigate the reasons of catalyst deactivation and to develop some effective regeneration procedures.

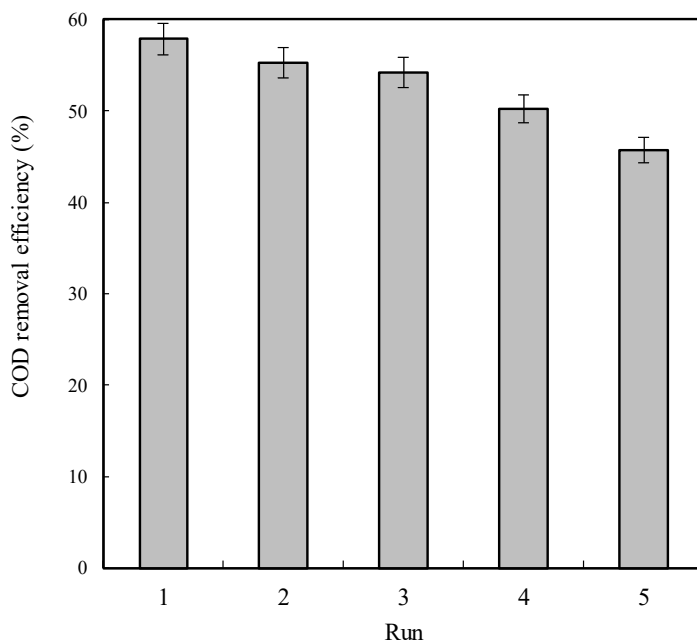


Fig. 6. COD removal by Fe-Mn/NaY<sub>sg</sub> catalyst of pulp mill effluents in the heterogeneous Fenton five consecutive runs (initial concentrations: [H<sub>2</sub>O<sub>2</sub>] = 4.0 mmol/dm<sup>3</sup>, [Fe-Mn/NaY<sub>sg</sub>] = 1.2 g/dm<sup>3</sup>, COD of raw wastewater = 220 mg O<sub>2</sub>/dm<sup>3</sup>, pH = 3.0)

#### 3.4. WATER QUALITY ANALYSIS

The polarity (HPO/HPI) distribution analysis is beneficial to make an evaluation for treatment methods. HPO compounds are typically resistant to microbial degradation and biological treatment processes, whereas HPI fractions are generally, readily biodegradable [25]. Figure 7 shows the polarity distribution of DOC in raw pulp mill effluents and heterogeneous Fenton-treated effluents. The HPO compounds represented the largest (ca. 60%) proportion of DOC in raw pulp mill effluents, whilst HPI constituted a remarkable proportion at around of 38.2% (Fig. 7a). This result indicated that the prior processes, i.e., chemical physical treatments coupled anaerobic-aerobic biological treatments showed limited degradation ability for HPO compounds. In addition, based on the absence of wood raw materials such as lignin and hemicellulose, in GC-MS analysis (Fig. 2, Table 2), we may confirm that HPO components were not fully degraded and considerable amounts remained in the raw pulp mill effluents prior to the treatments of Fenton process. Lacorte et al. [18] reported that HPO compounds are rich in aromatic carbon (phenolic structures with conjugated double bonds), including lignin derivatives and are of high molecular weight, however, HPI compounds are of low molecular weight derivatives from lignin and others. This finding was also consistent with our

GC-MS results that aromatic structures were detected. After heterogeneous Fenton treatment, the change of the polarity distribution was not significant (Fig. 7b). The HPO fraction of DOC reduced from 59.2% to 55.6% indicating that that the Fenton process was a non-selective reaction degrading organic compounds with generating of  $\text{HO}^\bullet$  radicals. Further oxidation of HPO and HPI was conducted to achieve higher COD removal (75.2%), This mechanism could overcome the limitation of insufficient degradation by biological processes and the difficulties in degrading HPO compounds.

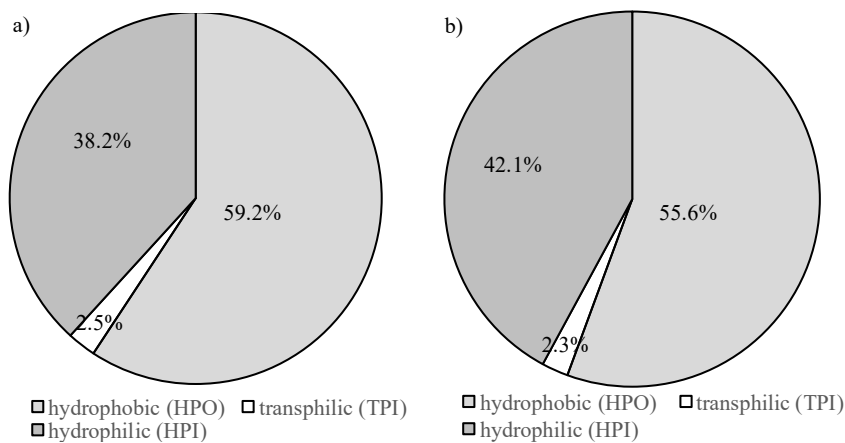


Fig. 7. Polarity distribution of DOC: a) in the raw wastewater, b) in the effluent treated by heterogeneous Fenton process

The MW distribution and transformation of DOC was further studied to evaluate the heterogeneous Fenton process in pulp mill effluents treatment. As shown in Fig. 8, most of the organic matter (70%) in raw wastewater were high molecular weight organic compounds (MW > 10 kDa). They could not be degraded in the biological treatment process. Shon et al. [26] reported that most MW distribution in biologically treated wastewater effluent was in the range of 300–5000 Da. However, this part of organic compounds just accounted to limited proportion in raw pulp mill effluents, which implied that high MW fraction was resistant to biodegradation. The heterogeneous Fenton process remarkably reduced the amount of high MW organic matters which contributed for wastewater COD. The molecules with MWs of 10–30 kDa, and over 30 kDa were mainly transformed into 0–1 kDa molecules (comprising 88.0% of the total molecules) in the heterogeneous Fenton process effluent. This result was similar as that of He et al. [27] who reported that the ratio of organic matter with MW < 3000 Da was increased from 7% to 78% after the Fenton process in the landfill leachate. Thus, it seems that the heterogeneous Fenton process could increase the biodegradability of wastewater. As shown by the differences in the organic matter MW transformation between the two processes,

the retention and degradation performance of the heterogeneous Fenton process improved the quality of the treated pulp mill effluents.

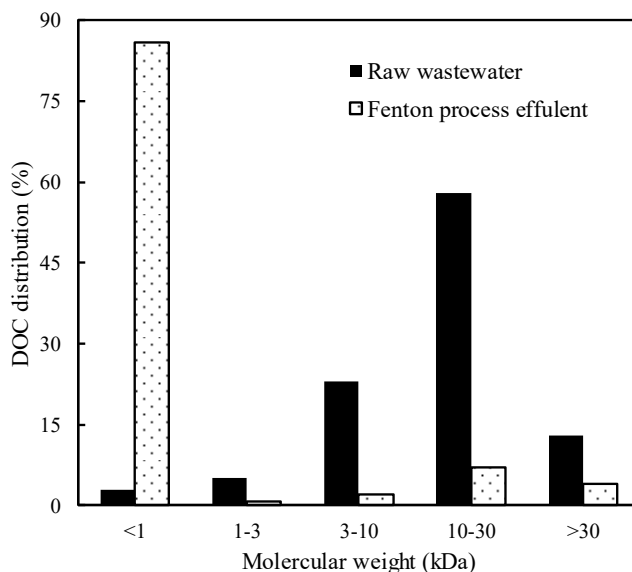


Fig. 8. Molecular weight distribution of DOC in raw wastewater and the heterogeneous Fenton process effluent

#### 4. CONCLUSIONS

A heterogeneous catalyst, Fe-Mn supported on NaY zeolite, was prepared by impregnation and sol-gel methods for treating pulp mill effluents. Aromatic structures were present in raw pulp mill effluents, which indicated the difficulty in biodegradation treatments. Synergistic effects were found between Fe and Mn on COD removal. The highest COD removal efficiency (75.2%) was obtained with the Fe-Mn/NaY<sub>sg</sub> catalyst (Fe/Mn molar ratio of 2) with 4 mmol/dm<sup>3</sup> of H<sub>2</sub>O<sub>2</sub> and 1.2 g/dm<sup>3</sup> of catalyst addition. The constant COD removal was obtained under this condition over time. Its efficiency amounted to above 45% after application of the Fe-Mn/NaY<sub>sg</sub> catalyst for five times. The results of the polarity distribution analysis indicated that the HPO fraction comprised the largest fraction of DOC (ca. 60%) in raw wastewater. MW distribution analysis showed that the high MW molecules in DOC were transformed into low MW molecules via the heterogeneous Fenton process.

#### ACKNOWLEDGEMENT

This research was supported by the National Science and Technology Major Project Water Pollution Control and Treatment (No. 2012ZX07203-004-44).

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