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Advanced treatment of coking wastewater by heterogeneous photo-Fenton technology with Cu/Fe oxide catalysts

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ABSTRACT

This study presents an evaluation of catalytic performances of Cu/Fe oxides containing TiO_2/Al_2O_3 for the coking wastewater advanced treatment through heterogeneous photo-Fenton. Fe and Cu were loaded by the impregnation method, and the tests were carried out in a three-phase fluidized bed photo reactor. The prepared catalysts were characterized by SEM, XPS, and BET. The results showed that the catalytically active materials in the fabricated catalyst are iron and copper oxidates FeOOH, Fe_2O_3, CuO, and Cu_2O. The catalyst showed high activity in a neutral environment without any pH adjustment in the coking wastewater advanced treatment. The focus of this method was on COD and TOC removal efficiencies. The results showed that higher COD and TOC removal rates were achieved with a longer reaction time and an increased dosage of H_2O_2 and catalyst. In a neutral environment, with 14.68 mmol/L H_2O_2 and 1.0 g/L catalyst, approximately 65% COD and TOC removal was obtained in 2.0 h. In this current work, the conditions were changed during the continuous reaction process, and the reaction system reached equilibrium in a shorter amount of time. These results imply the great potential of the heterogeneous photo-Fenton system in engineering applications, such as an advanced treatment of coking wastewater.

Keywords: Coking wastewater; Heterogeneous photo-Fenton; Fe/Cu oxide catalysts; Advanced treatment

1. Introduction

Coking wastewater, generated from coal conversion processes, contains a high amount of organics, suspended solids, ammonia, and other toxic compounds. It also includes phenol, cyanide, thiocyanate, and other aromatic hydrocarbons in the form of mono- and polycyclic aromatic hydrocarbons and heterocyclic aromatic hydrocarbons, which contain nitrogen, oxygen, and sulfur [1–3]. Most of these compounds are chemically resistant and pose a threat to both the environment and human health if not properly treated.

Biological treatment is widely employed for treating coking wastewater, such as conventional activated sludge [3,4], the anoxic/oxic process (A/O) [5,6], anaerobic/anoxic/oxic (A^2/O) process [7], fixed biofilm system [8], and sequencing batch reactor [9]. These processes exhibited a high efficiency in removing some

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of the organics in coking wastewater. However, refractory compounds in the coking wastewater are not biodegradable and therefore cause COD concentrations in the final effluent to be higher than 200–250 mg/L. These levels cannot achieve the stringent discharge standard and reusing requirement in China [1]. Consequently, environmentally friendly and economically advanced treatment techniques are required.

The homogeneous Fenton, producing highly oxidative and non-selective hydroxyl radicals, has been proven to be a promising and efficient wastewater technology for the degradation and mineralization of refractory and toxic pollutants. However, its application has been hindered by strict pH control (around 2–3) and the presence of iron in the sludge. Both of these problems require additional manpower and reagents in the whole reaction process [10,11]. To overcome these disadvantages, researchers have been preparing heterogeneous iron catalysts by coating iron ions or iron oxides onto solid but porous supporting materials [10,12]. In this way, catalysts containing iron could be used for the degradation of various organic pollutions, such as phenols [13,14], synthetic dyes [15], and chlorophenols [16]. However, catalysts that only contain iron oxides still need proper pH adjustments for efficient treatment.

It has been reported that doping copper ions into goethite led to a strong increase in catalytic activity [17]. The incorporation of Cu into FeZSM-5 increased catalytic activity in the oxidative degradation of rhodamine 6G in aqueous solutions [18]. The outstanding catalytic activity of bimetallic catalysts may be generally ascribed to its synergistic effects in relation to the creation of defects, novel active sites, and the facile redox interplay between copper and iron redox couples. Moreover, the addition of copper to the catalyst may stabilize the activity for the oxidation of organic pollutants in comparison with monometallic catalysts [19].

This paper presents the feasibility of heterogeneous photo-Fenton as an advanced treatment of coking wastewater. Catalysts consisting of Cu/Fe oxides were prepared by the impregnation method. The aim is to optimize the advanced treatment of coking wastewater in a neutral environment and to investigate the effects of reaction conditions such as the dosage of catalysts, H_2O_2 concentration, and reaction time on the removal of COD and TOC.

2. Materials and methods

2.1. Materials and regents

The commercial Al_2O_3/TiO_2 support, with diameters of 0.30–0.45 mm, was purchased from Yixing YiPu Catalyst Co., Ltd. Analytical-grade sodium hydroxide, ferrous sulfate, copper sulfate, and hydrogen peroxide (30%, w/w) were purchased. Deionized water was used throughout the study. The wastewater was the effluent of the A–A–O process from a coking plant. Table 1 shows the characteristics of wastewater used in the experiments.

2.2. Preparation of bimetal catalysts

Catalysts were prepared by impregnating 20 g of prepared TiO_2/Al_2O_3 into 500 mL of 0.1 mol/L $FeSO_4$ and 0.02 mol/L $CuSO_4$ aqueous solution. The mixture was vigorously stirred for 2 h. Then, 600 mL of 0.2 mol/L NaOH aqueous solution was added drop by drop. After aging for 40 h at 105°C, the solid product was separated and washed several times with deionized water until the sulfate was washed out. It was then dried at 80°C, followed by calcination at 200°C for 5 h. The final product was the Cu/Fe oxide catalysts.

2.3. Experimental procedure

The advanced treatment of coking wastewater was carried out in a three-phase fluidized bed photoreactor (Fig. 1). The light source was a UV lamp (Philips, 8 W, 254 nm) fixed inside a cylindrical quartz tube. The total volume of wastewater used was 4,000 mL. To ensure a good dispersion of catalysts in the solution, compressed air was bubbled from the bottom at a flow rate of 3.3 L/min. For each experiment, the wastewater and H_2O_2 were pumped into the photoreactor by peristaltic pumps. The measurement of reaction time was started when the UV light was turned on. Samples were tested at regular time intervals, and 0.1 mol/L sodium sulfite was added as a terminator.

2.4. Analytical methods

The catalysts were characterized by an SEM S-4700 (Hitachi Ltd, Japan), gas phase adsorption of specific

Table 1
Characteristics of wastewater used in the experiments

Parameter	Unit	Value
COD	mg/L	147
TOC	mg/L	45
BOD	mg/L	9
TDS	μs/cm	1,295
pH		7.1
Salinity	‰	0.66

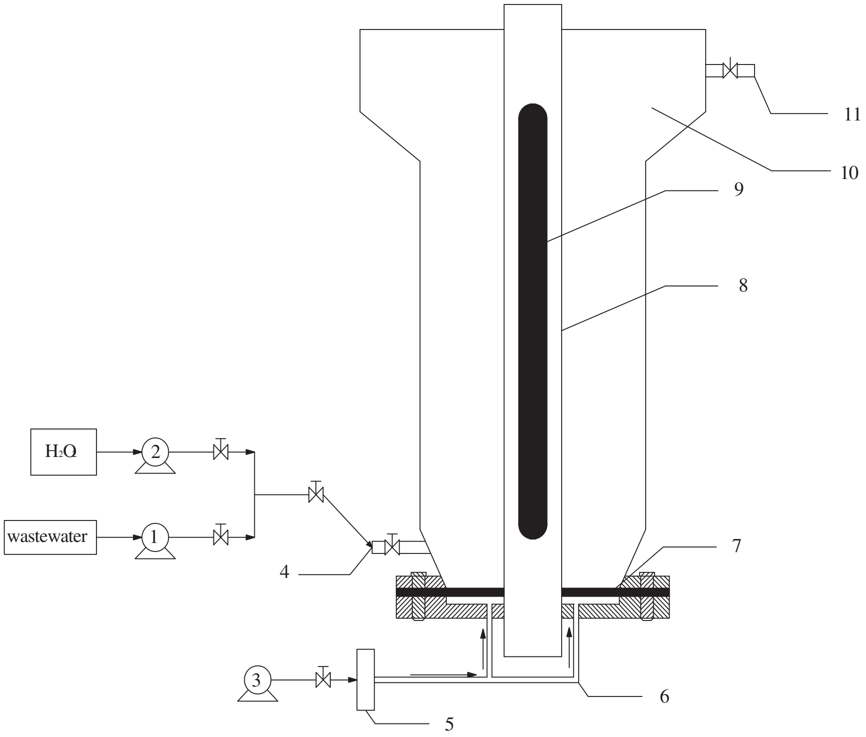

Fig. 1. Schematic diagram of the three-phase fluidized bed photo reactor: (1,2) peristaltic pump; (3) air compressor pump; (4) water inlet; (5) flow meter; (6) air inlet; (7) aeration titanium plate; (8) quartz tube; (9) UV lamp; (10) sedimentation zone; (11) water outlet.

surface area analyzer (Autosorb-1-C, Quantachrome Instruments, USA), and X-ray photoelectron spectrometer (PHI5700, Physical electronics companies, USA).

The GC–MS (6890GC/5973MSD, Agilent, USA) was employed for the chemical analysis of the initial effluents with a 30 m × 0.25 mm × 0.25 μm (HP5MS) capillary column. The carrier gas (helium) flow rate in the GC was 1.0 mL/min. The sample was injected at 280˚C. The temperature ramp rates used in the GC–MS analysis were as follows: hold at 45˚C for 5 min, increase to 320˚C at 10˚C/min, hold at 320˚C for 15 min. Compound identification was assessed using the National Institute of Standards and Technology database.

COD was measured by titration using dichromate as the oxidant in acidic solution at 150˚C for 2 h (Hach Corporation, USA). TOC removal was determined using TOC–V_{CPN} (Shimadzu, Japan) for the evaluation of the mineral content of the wastewater.

3. Results and discussion

3.1. Physicochemical characterizations

3.1.1. BET analysis

Nitrogen adsorption isotherms and BJH pore size distributions of the carrier and prepared catalysts are shown in Figs. 2 and 3. Both display type IV N_2 adsorption isotherms, and a wide hysteresis area of N_2 adsorption isotherms can be seen. This corresponds to their mesoporous structure with a narrower pore size distribution. The catalysts displayed a similar adsorption quantity as the carrier, which indicated that the catalysts retain the high adsorbability of the carrier. The BET surface area, total pore volume, and average pore size of the studied catalysts are listed in Table 2. The BET surface areas of bimetal catalysts were less than the carriers, which confirm the presence of an additional phase. This could be due to the blockage of the TiO_2/Al_2O_3 pores being partially filled by an iron and/or copper species.

3.1.2. Morphology observation and X-ray energy spectrum analysis

The typical surface morphologies of the carrier and prepared bimetal catalysts are shown in Fig. 4. Fig. 4(A) reveals that the surface of the carrier Al_2O_3/TiO_2 is porous with irregular agglomerate particles, while the catalyst prepared (Fig. 4(B)) is uniform and clogged, with no cracking detected on the surface. According to the chemical EDX analysis, Al and O are

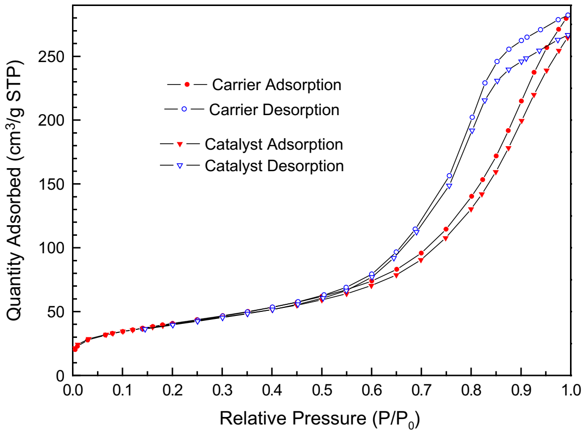

Fig. 2. Nitrogen adsorption/desorption isotherms for carrier and catalyst.

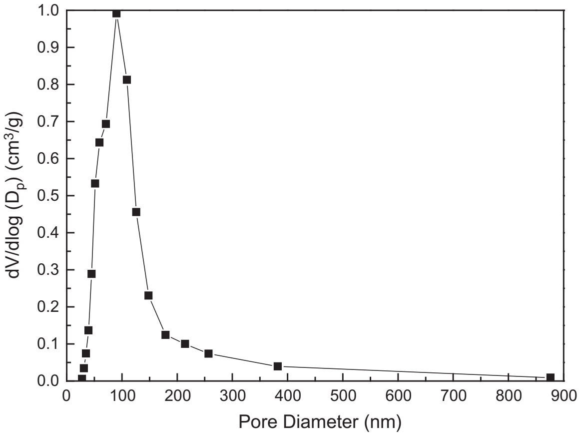

Fig. 3. BJH pore size distributions of the prepared catalysts.

the major elements in the carrier Al$_2$O$_3$/TiO$_2$ surface, with some minor amounts of Ti. The mole ratio of Fe and Cu is 2.8:1. There is no S in the EDS spectra, indicating that the sulfates were completely converted to oxides. Meanwhile, Cu, Fe, Al, O, and Ti elements coexisting in the catalysts indicate that the catalysts are not contaminated with other elements during the preparation processes.

3.1.3. XPS analysis

To illuminate the surface composition of the prepared bimetal catalysts and to obtain detailed information on the chemical states of the ions, XPS was performed. Fig. 5 shows the general survey spectrum of the catalyst, which shows that the catalyst surface contains Al, C, O, Fe, and Cu elements. The photoelectron peak for C 1s indicates the existence of a small amount of elemental carbon, which may be the result of contamination caused by specimen handling or by the pumping oil used in the XPS instrument itself [20].

The normative peak position of C 1s at 284.6 eV from the XPS handbook was used for calibration. A C 1 s peak of carbon impurity was scanned at 290.25 eV, which revealed that all of the peaks measured have a positive offset of 5.65 eV (Table 3). It is shown that all of the peaks measured were calibrated. In addition, the Fe 2p and Cu 2p$_{3/2}$ spectra shown in Fig. 6 were roughly fitted to evaluate how much Fe and Cu was loaded onto the carriers. It can be observed in Fig. 6(A) that the Fe 2p peaks can be fitted with two peaks: one peak attributed to Fe$_2$O$_3$ and the other assigned to FeOOH. The percentage of cover area of Fe$_2$O$_3$ and FeOOH is 42.3 and 57.7%, respectively. Meanwhile, Fig. 6(B) shows the Cu 2p$_{3/2}$ core level peaks. Note that in this work, Cu 2p$_{3/2}$ is discussed because Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ play similar roles in determining the Cu valence [21]. The Cu 2p$_{3/2}$ peaks can be fitted with two peaks: one peak attributed to CuO and the other assigned to Cu$_2$O. The percentage of cover area of CuO and Cu$_2$O is 67.5 and 32.5%, respectively.

3.2. The component analysis of coking wastewater secondary effluent

The detailed chemical analyses were carried out by GC–MS to identify representative species. Two extracting agents, namely methylene dichloride and methyl tert-butyl ether, were used. The major organic pollutants were identified by classifying them into hydrocarbons, phenols, nitrogen-containing heterocyclic compounds, and others. Table 4 shows the percentage

Table 2
Summary of surface characteristics of carriers and catalysts

Samples	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore width (Å)
Carrier	147.6441	0.419242	113.5818
Bimetal catalyst	144.2326	0.393709	109.1865

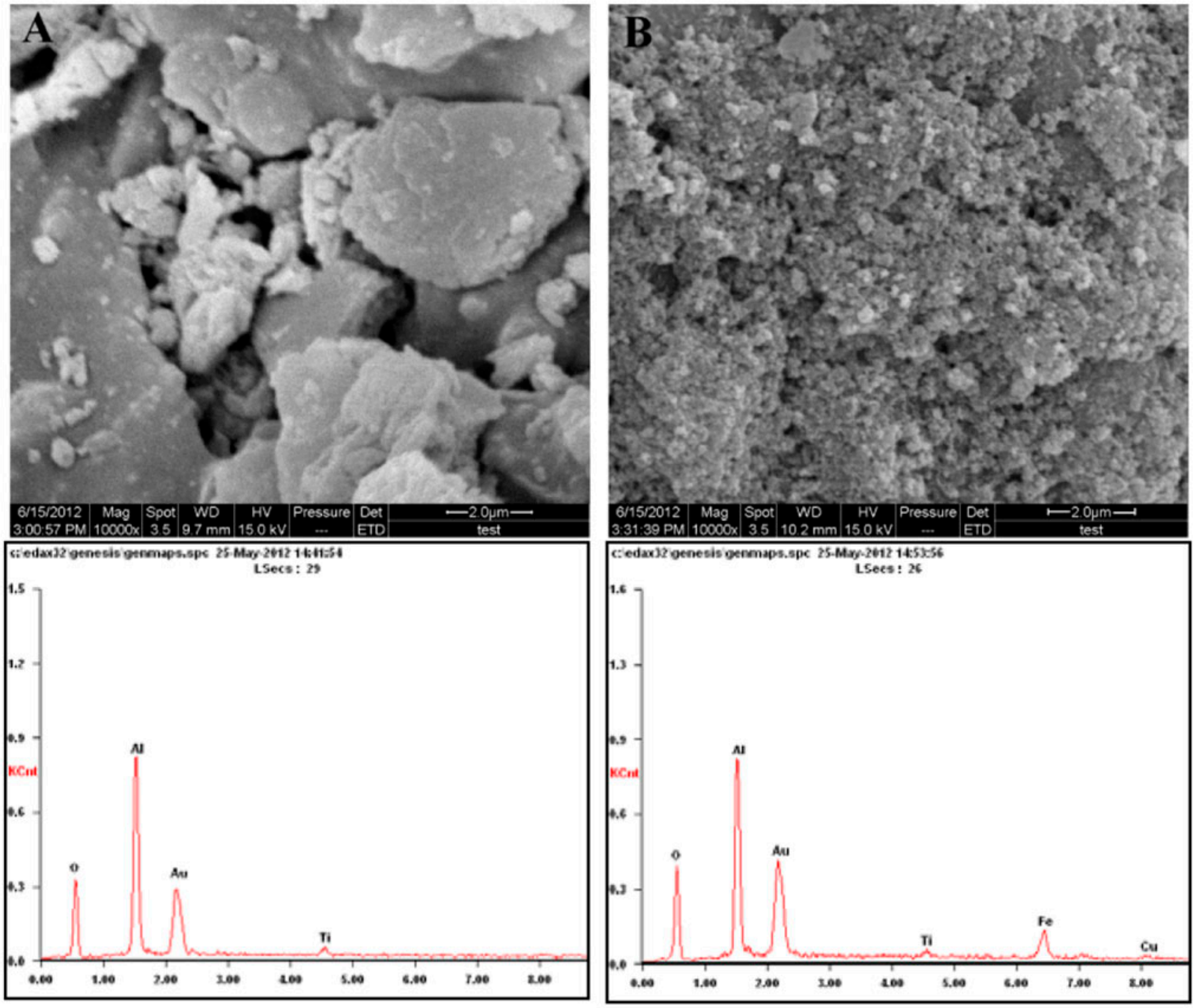

Fig. 4. SEM photographs and EDS spectra of (A) carrier, (B) prepared bimetal catalysts.

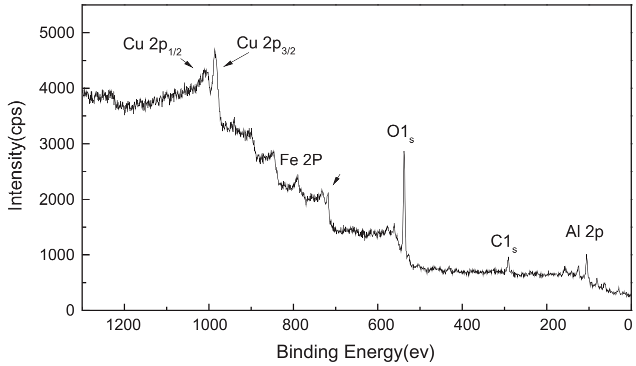

Fig. 5. XPS spectrum of the prepared bimetal catalysts.

for each of the main compound species. The results indicate that heterocyclic compounds containing nitrogen occupy the largest fraction at 30.66%. It is because most of these compounds are difficult to biodegrade; less than 1% can be degraded through biological processes. Hydrocarbon and phenols are readily biodegradable substances. The main organics are long-chain alkane, halogenated phenols, and polyphenol. Others include multi-ring organics and some sulfur- and phosphorus- containing organics.

3.3. Performance of prepared Cu/Fe oxide catalysts in photo-Fenton treatment of coking wastewater

To evaluate the performance of prepared Cu/Fe oxide catalysts, comparative experiments were carried

Table 3
The normative, measured, and corrected binding energies (E_b in eV) of the catalyst

	C 1s	Cu $2p_{3/2}$ (CuO)	Cu $2p_{3/2}$ (Cu_2O)	Fe $2p_{3/2}$ (Fe_2O_3)	Fe $2p_{3/2}$ (FeOOH)
E_b from handbook	284.6	933.6	932.3	710.7	710.8
Measured E_b	290.25	939.35	937.85	718.05	716.25
E_b after calibration	284.6	933.7	932.2	712.4	710.6

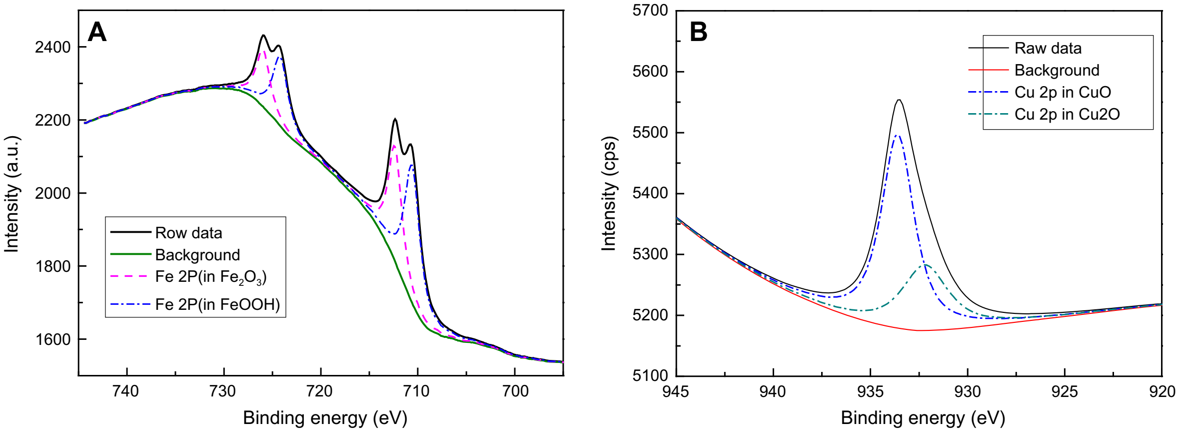

Fig. 6. The best fit curves of Fe and Cu line after offset.

out and the results are shown in Fig. 7. No significant TOC removal was noted using aeration alone, suggesting that the volatile organic compounds content in the wastewater was small. The tests with UV and aeration only caused approximately 21% TOC removal within 180 min, which was similar to the results obtained in the process with aeration, H_2O_2, and catalysts. In contrast, the test with aeration, UV, and H_2O_2 induced approximately 44% TOC removal after 180 min. The presence of carriers enhanced the wastewater mineralization only slightly. However, the combined photo-Fenton (aeration + UV + H_2O_2 + catalysts) tests yield synergistic mineralization of coking wastewater; approximately 68% TOC removal was detected after 180 min of treatment.

During oxidation tests (shown in Fig. 7), the leached metal ion concentrations in solution were also determined to evaluate the stability of Cu/Fe oxide catalysts in the photo-Fenton system. As shown in Fig. 8, only 0.47 mg/L iron ion and 0.07 mg/L copper ion leached from the catalysts during the whole reaction. Based on the maximum amount of metal

Table 4
The percentage of the main species of compounds from GC–MS

Organics species	Percentage (%)
Hydrocarbon	7.92
Phenols	6.75
Heterocyclic containing nitrogen	30.66
Benzene series	12.41
Polycyclic aromatic hydrocarbon	10.03
Others	32.23

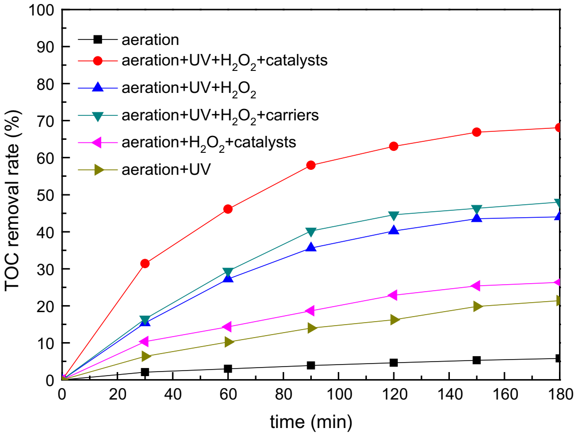

Fig. 7. Different systems for wastewater treatment.

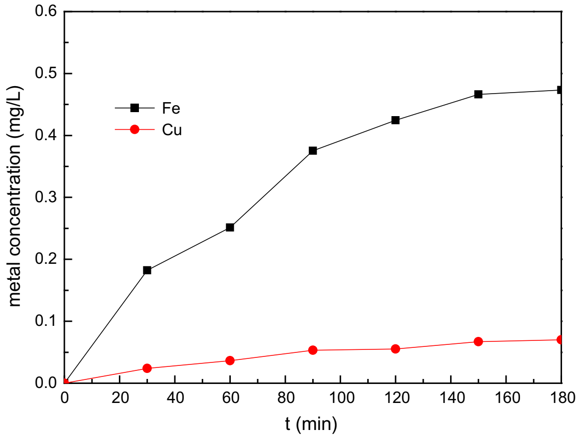

Fig. 8. Time-dependent leached metal ion concentrations in the photo-Fenton process (catalyst = 1.0 g/L; H_2O_2 = 14.68 mmol/L).

leaching from catalysts, simulated experiments using iron and copper salts in similar concentrations (0.5 mg/L Fe^{2+} and 0.1 mg/L Cu^{2+}) were performed to further evaluate the effects of homogeneous photo-Fenton oxidation. Only 45% TOC removal was detected after 180 min of treatment, which was similar to the results obtained in the system without catalysts (aeration + UV + H_2O_2). This result suggests that the effect of the homogeneous reaction could be ignored. Therefore, the conclusion in this study is that the wastewater mineralization was mainly due to the heterogeneous photo-Fenton oxidation.

3.4. Parameters for coking wastewater advanced treatment

3.4.1. Effect of catalyst dosage

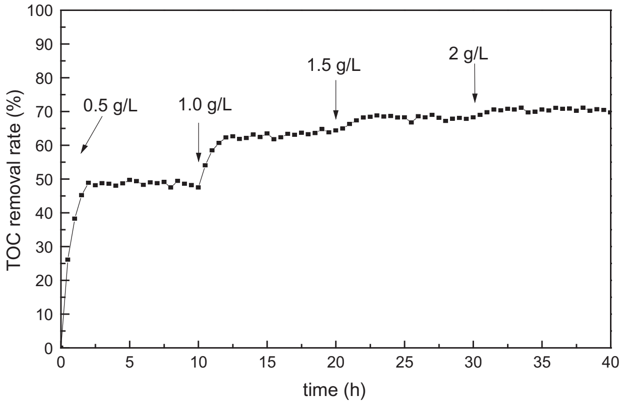

Fig. 9. TOC removal rate during operation with respect to catalyst dosage change.

The influence of catalyst dosage on the coking wastewater advanced treatment by heterogeneous photo-Fenton was investigated at different levels (0.5, 1.0, 1.5, and 2.0 g/L) when the H_2O_2 concentration was 14.68 mmol/L in 2.0 h. At the beginning, the reactor consisted of 0.5 g/L of catalyst, and 0.5 g of catalyst was added every 10 h during the reaction process. Figs. 9 and 10 show that the catalyst dosage has a great effect on the degradation of COD and TOC at a certain dosage range. As the catalyst dosage increases from 0.5 to 2.0 mg/L, the TOC and COD removal rates increase from 48 to 70% and 47 to 67%, respectively. This may be because the catalysts could significantly accelerate the decomposition of H_2O_2 producing ·OH radicals. However, the main improvement was in the range from 0.5 to 1.0 g/L. That may be because a larger quantity of ·OH radicals might have reacted with each other, and the practical generation of ·OH radicals was therefore not improved. Consequently, the most economical catalyst dosage was 1.0 g/L, and both the TOC and COD removal rates reached 65%.

3.4.2. Effect of H_2O_2 concentration

H_2O_2 concentration is also an important operating parameter in the photo-Fenton reaction. The effect of H_2O_2 concentration was investigated at different levels of H_2O_2 concentration (7.34, 9.79, 14.68, and 19.58 mmol/L) with catalyst dosage remaining at 1.0 g/L for 2.0 h. The H_2O_2 concentration was changed by adjusting the peristaltic pump speed. Figs. 11 and 12 show that the increase in the concentration of H_2O_2 led to an enhancement of the photocatalytic performance of the heterogeneous Fenton reaction. The TOC and COD removal rate increased from approximately

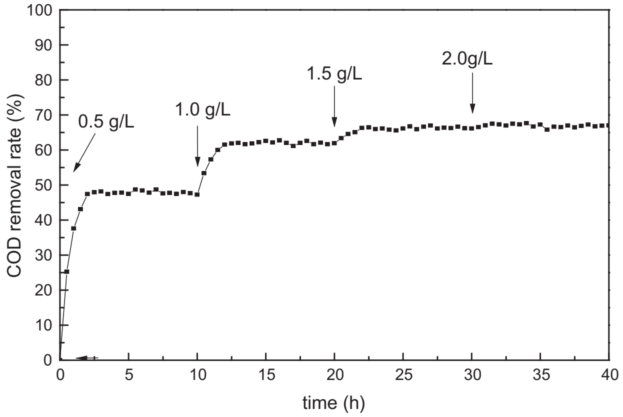

Fig. 10. COD removal rate during operation with respect to catalyst dosage change.

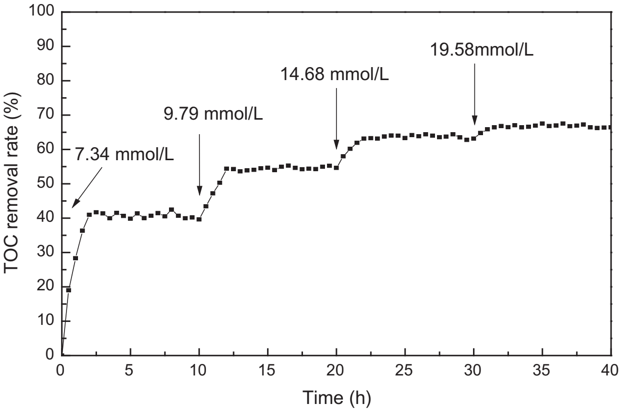

Fig. 11. TOC removal rate during operation with respect to H_2O_2 concentration change.

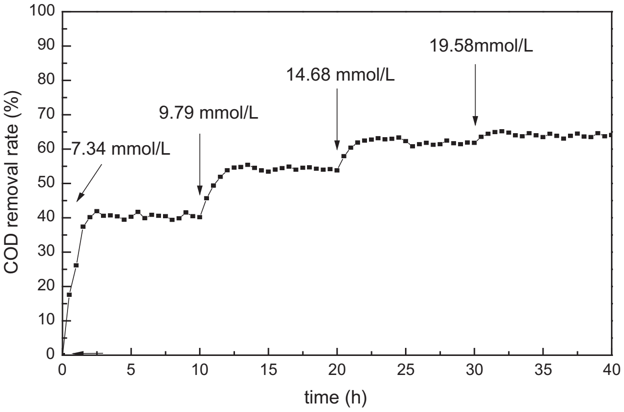

Fig. 12. COD removal rate during operation with respect to H_2O_2 concentration change.

40 to 65% as the H_2O_2 concentration increased from 7.34 to 14.68 mmol/L. Further addition of H_2O_2 (to 19.58 mmol/L) as the reaction progressed did not improve removal efficiency. A higher concentration of H_2O_2 might have acted as a scavenger of ·OH radicals and transformed the ·OH radical to the ·OOH radical, which has much lower oxidation capabilities than the ·OH radical [22].

3.4.3. Effect of reaction time

Reaction time is an important operating parameter that links the running cost of the coking wastewater advanced treatment. The effect of reaction time was investigated with different levels (0.5, 1.0, 2.0, and 3.0 h) at a constant catalyst dosage of 1.0 g/L and a H_2O_2 concentration of 14.68 mmol/L. The reaction time was changed by changing the wastewater flow rate. Fig. 13 shows the profile of TOC removal during the experimental periods with respect to the reaction time. As the reaction time increased from 0.5 to 2.0 h, the average TOC removal efficiency improved from 32 to 65%. However, it was also observed that the TOC removal increased slightly when the reaction time was further increased from 2.0 to 4.0 h.

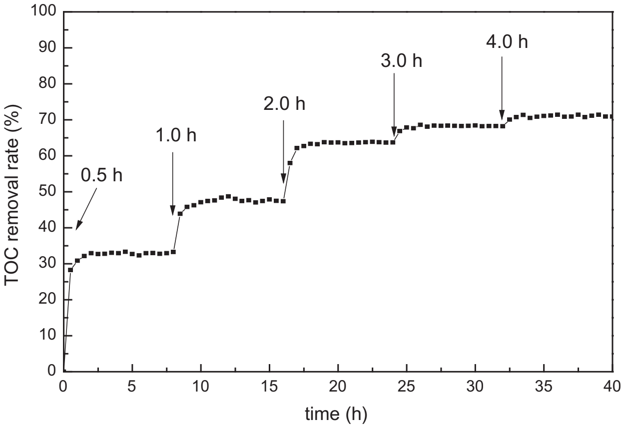

Fig. 13. TOC removal rate during operation with respect to reaction time change.

4. Conclusions

In this study, a novel heterogeneous photo-Fenton catalyst has been successfully prepared by means of the impregnation method. The Cu/Fe oxide catalysts were characterized by SEM, XPS, and BET. The result showed that FeOOH, Fe_2O_3, CuO, and Cu_2O are the main catalytically active materials. These catalysts were then used as the new heterogeneous photo-Fenton catalysts for coking wastewater advanced treatment. Due to its high efficiency, any changes in reaction conditions reached equilibrium in a very short period of time. Both the TOC and COD removal rates reached 65% in 2 h, when the catalyst dosage and H_2O_2 concentration were 1.0 g/L and 14.68 mmol/L, respectively. The treated effluent may be used at the inlet of the reuse process such as the UF-RO technology. Meanwhile, heterogeneous photo-Fenton technology used as an advanced treatment mechanism can retain the existing wastewater treatment system and reduce potential improvement costs.

Acknowledgments

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