Development of mesh-type Fenton-like Cu/Feₓ/\gamma\text{-}Al₂O₃/Al catalysts and application for catalytic degradation of dyes

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ABSTRACT

The application of nanoparticle heterogeneous Fenton-like catalysts is limited due to the requirement of filtration after reaction and possible secondary pollution. In this work, a novel mesh-type monolithic Fenton-like Cu/Feₓ/\gamma\text{-}Al₂O₃/Al catalyst was developed for the degradation of dyes. The Cu and Fe species are uniformly dispersed on the mesh-type anodic monolithic γ-Al₂O₃ supports, and the results of scanning electron microscopy and X-ray diffractometry analysis show that Fe can reduce the particle size of Cu over γ-Al₂O₃. The activity results show that the degradation rate of rhodamine B (RhB) reached 99.5% within 1 h using 4 × 6 cm Cu₁₂.0/Fe₂.0/γ-Al₂O₃/Al catalyst with 1,200 ppm H₂O₂ at 50 °C. The important role of •OH as a reactive oxidant was confirmed through electron spin-resonance spectroscopy and radical scavenging experiment. The hydrogen temperature programmed reduction suggests the high redox ability of Cu/Fe bimetallic catalyst is beneficial to the production of •OH. The Cu/Fe bimetallic catalyst shows excellent recyclability in a 10-cycle experiment, the degradation rate of RhB was maintained at 98% and the leaching amount of metals was lower than 0.7 mg/L. The mesh-type catalyst will be easily applied for the continuous wastewater treatment because it does not need filtration for recovery.

Key words | bimetallic catalyst, Fenton-like reaction, RhB degradation, water treatment

HIGHLIGHTS

- A novel mesh-type monolithic Fenton-like Cu/Feₓ/\gamma\text{-}Al₂O₃/Al catalyst was developed.
- The as-prepared Cu/Fe bimetallic catalyst shows excellent capability to produce •OH and degrade dyes.
- Excellent recyclability in a 10-cycle experiment with low leaching amount of metals.
- The mesh-type catalysts will be easily applied for the continuous wastewater treatment.

GRAPHICAL ABSTRACT

INTRODUCTION

It is known that the dye-containing wastewater is difficult to be degraded through normal water treatment approaches. Fenton oxidation, one of the advanced oxidation technologies (AOPs), has been widely applied in the treatment of refractory organics wastewater (Cheng et al. 2017), but it has disadvantages such as a large amount of iron (Fe) ions remaining in the solution after reaction, which brings secondary pollution (Peng & Jin 2018).

In order to overcome the shortcomings of the homogeneous Fenton reaction, many researchers fixed Fe ions on supports to prepare the heterogeneous catalysts. The supports included γ-Al2O3 (Munoz et al. 2013), SiO2 (Yang et al. 2016), and SBA-15 (Ghuge & Saroha 2018) and some developed FeOOH (Shahwan et al. 2011), Fe (Soler et al. 2013), and nano Fe3O4 (Chen et al. 2013) as catalysts. In heterogeneous systems, these catalysts are more easily separated by nanofiltration membranes or external magnetic fields. It avoids the disadvantage of producing Fe-containing sludge, which is difficult to treat. The heterogeneous Fenton system has therefore become a research hotspot in recent years.

In the past few years, people have paid great attention to Fe-free catalysts. Among them, Cu-based Fenton-like catalysts show excellent redox properties (Lai et al. 2015; Zhang et al. 2016), which have higher catalytic reaction efficiency than Fe-based catalysts. The capacity of Cu-based catalysts to generate -OH is described in Equations (1) and (2) (Li et al. 2016).

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2\text{O}_2 &\rightarrow \text{Cu}^+ + \cdot\text{OOH} + \text{H}^+ \\
\text{Cu}^+ + \text{H}_2\text{O}_2 &\rightarrow \text{Cu}^{2+} + \cdot\text{OH} + \text{OH}^- 
\end{align*}
\]

Furthermore, it has been found that bimetallic catalysts exhibit excellent activity, especially in the study of Cu/Fe bimetallic catalysts. Guimaraes et al. (2009) prepared Cu-doped goethite that had Cu²⁺ incorporated into the goethite structure, following a significant decrease in the chemical reduction temperature due to the synergistic enhancement (Guimaraes et al. 2009). Fontecha-Cámara et al. (2016) also reported a synergic effect between Cu and Fe ions, which were located in octahedral sites. The Cu ions appear to provide the main active sites for ·OH generation (Fontecha-Cámara et al. 2016). However, they found a large amount of Cu and Fe ions leaching from copper ferrite. At present, most of the Fenton-like catalysts cannot be used in industrial wastewater treatment because of the large leaching of metals and complicated operation. It is therefore important to develop a structurally stable and easily operated Fenton-like catalyst.

In this study, a novel mesh-type monolithic Cu/Feₓ/γ-Al₂O₃/Al catalyst was prepared and employed in the rhodamine B (RhB) Fenton-like degradation system. The catalytic degradation activities of the 4 × 6 cm Cu/Feₓ/γ-Al₂O₃/Al catalysts were evaluated in a batch stirred reactor. First, the effects of Fe-doping on the particle size of Cu were investigated by scanning electron microscopy (SEM) and X-ray diffractometry (XRD) analysis. Then, the oxidation states of Cu on the catalyst surface were analyzed using X-ray photoelectron spectroscopy (XPS) to further discuss the mechanism of RhB degradation. The important role of ·OH as a reactive oxidant was investigated using electron spin-resonance spectroscopy (ESR) and radical scavenging experiment, and the redox ability of the catalysts, which contributes to ·OH production, were analyzed by hydrogen temperature programmed reduction (H₂-TPR). Finally, a 10-cycle experiment was carried out to evaluate the recyclability of the selected catalyst and the leaching amount of metals was also investigated.

EXPERIMENTAL

Catalyst preparation

Mesh-type catalysts are developed by anodization. First, the commercial mesh-type Al (purity ≥99.6%, mesh size 1 × 2 mm, thickness 0.6 mm, Nantong Xinzyuyuan Trading Co. Ltd) was pretreated in a 10 wt% NaOH solution for 4 min and then in a 10 wt% HNO₃ solution for 2 min, washed with deionized water and air-dried. Then, the acid–base pre-treated aluminum mesh was anodized in a 0.4 M oxalic acid solution under a current density of 25 A/m² for 10 h at 20 °C. The anodic alumina mesh was calcined at 350 °C in a muffle furnace to decompose residual oxalic acid on the surface. The support was hydrated with deionized water at 80 °C and calcined at 500 °C to prepare the γ-Al₂O₃/Al.

The active components Cu and Fe are loaded by impregnation. The as-prepared γ-Al₂O₃/Al was impregnated in 0.05M Fe(NO₃)₃ solution for 4–10 h, air-dried, and calcined at 500 °C. It was then impregnated in 1.5M Cu(NO₃)₂ solution for 10 h and treated in the same method. Finally, the structured Cu/Feₓ/γ-Al₂O₃/Al catalyst was obtained.
Catalyst characterization

The catalyst surface structure was characterized by SEM (JEM-6360LV, JEOL). The phase and morphology of the sample were performed by D/max 2250 VB/PC (Rigaku, Japan) type target XRD. The specific surface area of the catalyst was analyzed by nitrogen suction–desorption isothermal experiments on ASAP 2020-M (Micromeritics, USA) instruments (BET). The weight loss characteristics of the catalysts were performed by the WRT-3P (Shanghai Jingke, China) type thermal gravimetric (TG) analyzer. The surface chemical valence of the catalyst was analyzed by XSAM-800 (Kratos, UK) type XPS. The Cu and Fe content of the catalyst was measured by a Varian 710ES (Agilent, USA) type inductively coupled plasma (ICP) atomic emission spectrometer. The reduction performance of the catalyst was determined by H2-TPR on a ChemSorb 2720 (Micromeritics, USA) instrument. ESR was performed on the Bruker BioSpin GmbH using 5,5-dimethyl pyrroline-1-oxide (DMPO) as the spin trap agent. In the radical scavenging experiment, 1 ml tert-butanol (TBA, chemically pure) was added before H2O2. After 10 min, 1 ml solution sample was immediately added to 1 ml of 20 mM DMPO to analyze the production of ·OH.

Catalyst activity evaluation

The catalyst prepared was applied in a batch stirred reactor. In the RhB degradation system, 0.4 g (6 × 4 cm) of catalyst was immersed in 100 ml of 10 ppm RhB solution and mixed at a stirring rate of 600 rpm. The reactor was placed in a water bath at a constant temperature (30–60°C), and then H2O2 (600–1,500 ppm) was added to start the reaction without additional pH adjustment. The samples were directly taken from the reactor and analyzed at intervals. The concentration of RhB was measured by the ultraviolet-visible spectrophotometer (UV752, Shanghai YoKe Instrument Co. Ltd) at the maximum absorption wavelength of 554 nm. The degradation rate was calculated according to the following equation:

\[
\text{Degradation rate} = \frac{C_0 - C_t}{C_0} \times 100\%
\]  

where \(C_0\) and \(C_t\) represent the concentrations of RhB in solution at time 0 and time \(t\), respectively.

RESULTS AND DISCUSSION

Characterization of catalysts

Figure 1 XRD patterns show that significant CuO diffraction peaks (JCPDS, No. 48-1548) appear on Cu-based catalysts. However, no obvious diffraction peak of Fe2O3 (JCPDS, No. 33-0664) was observed on the Fe12.0/γ-Al2O3/Al catalyst, and the diffraction peaks centered at 37.6°, 45.9°, and 67.0° corresponding to the diffraction peak of γ-Al2O3 (JCPDS, No. 10-0425), indicating that Fe2O3 is highly dispersed on the surface of γ-Al2O3. For Cu/Fe bimetallic catalysts, it can be seen that Fe-doping significantly reduces the diffraction peak intensity of CuO. It means that the particle size of the Cu species has decreased. Furthermore, when the content of Fe has increased to 10 wt%, the CuO diffraction peaks are very weak. Obvious Fe2O3 diffraction peaks (JCPDS, No. 33-0664) appeared in the XRD pattern of the Cu12.0/Fe10.0/γ-Al2O3/Al catalyst. This may be due to the fact that the Fe species can be well dispersed on γ-Al2O3 when Fe loading is low. When the Fe loading increases to 10 wt%, it causes the accumulation and aggregation of Fe species, causing the increase of Fe particle size. The obvious diffraction peaks of Fe2O3 appear because of the increased Fe particle size.

Figure S1(a) in the Supplementary Material shows the XRD patterns of Fe2.0/γ-Al2O3/Al catalysts that were calcined at different temperature. It can be seen that the offsets of diffraction peaks appear with the increased
calcination temperature and the crystal structure tends to stabilize at 500 °C. The diffraction peak of (311) plane of γ-Al₂O₃ was observed, and it shifted to smaller 2θ values after loading Fe. Compared with the γ-Al₂O₃ support, the 2θ values of (311) plane have shifted from 37.60° to 36.06° on the Fe₂O₃/γ-Al₂O₃/Al-500 °C catalyst in Figure S1(b), which is close to the diffraction peak position of (110) plane of Fe₂O₃ (2θ = 35.61°) (JCPDS, No. 33-0664). The transition metal oxide deposited on the support causes a shift of peak position and a slight decrease in peak intensity (Lin et al. 2018). It represents the introduction of Fe, and the modified structure of the support contributes to further Cu loading.

Figure S2(a)–(d) SEM images show the unique dense and ordered porous structure of the prepared catalysts surface. For Cu/Fe bimetallic catalyst, no obvious small solid particles were observed on the surface in contrast to the Cu-based catalyst, indicating that Fe-doping reduces the particle size of Cu and promotes the dispersion. Figure S2(e) shows the mesh-type appearance of the Cu₁₂.₀/Fe₂.₀/γ-Al₂O₃/Al catalyst. Figure S2(f) shows the cross-sectional view of the structured catalyst in which the Al layer, γ-Al₂O₃ layer, and Cu and Fe species can be clearly seen.

Furthermore, it can be seen from Table S1 BET analysis (Supplementary Material) that the specific surface area and pore volume of the catalyst were decreased after loading metals, which blocked part of the pores. A small amount of oxide film was dissolved by acidic immersion liquid, causing the pore diameter of the catalyst to slightly increase after loading metals.

**Rhb degradation activity evaluations**

As shown in Figure 2, the activities of degrading RhB over Fe-based, Cu-based, and Cu/Fe bimetallic catalysts were investigated. The effects of Cu/Fe content on catalysts, reaction temperature and initial H₂O₂ concentration are also shown in Figure S3. The results show that the RhB degradation rates over Fe₁₂.₀/γ-Al₂O₃/Al, Cu₁₂.₀/γ-Al₂O₃/Al, and Cu₁₂.₀/Fe₂.₀/γ-Al₂O₃/Al catalysts are 27.4%, 87.4%, and 99.5% within 1 h, respectively. That is, the Cu/Fe bimetallic catalyst performs the best activity in RhB degradation. The reason for the poor activity of the Fe-based catalyst may be due to the difference in the standard electrode potential between Fe³⁺/Fe²⁺ and Cu²⁺/Cu⁺. The -OH-generating reaction rate constants of Cu-based system are higher than those of the Fe-based system (Sheng et al. 2017). Figure S3(b) shows that the reactions belong to pseudo-first-order chemical reactions, and the calculated pseudo-first-order kinetic constants are 0.0054, 0.0367, and 0.0866 min⁻¹, respectively. To further demonstrate the important role of -OH on RhB degradation, TBA was used as a strong free radical scavenger. It can be seen from Figure 2 that the degradation rate of RhB with the addition of TBA is only 11.2% after 1 h. In the absence of -OH radicals, the removal of contaminants is significantly reduced. Therefore, the -OH produced by the efficient decomposition of H₂O₂ play a crucial role in this reaction and are the reactive oxidants that destroy the structure of organic matter.

The blank control experiments were carried out to study the adsorption performance of Cu₁₂.₀/Fe₂.₀/γ-Al₂O₃/Al catalyst. Figure S3(c) shows that less than 5% RhB was removed within 1 h when only the catalyst was present. It means that the removal of RhB is not due to the adsorption of catalyst and natural decomposition of H₂O₂. When the Fenton reagent (Cu₁₂.₀/Fe₂.₀/γ-Al₂O₃/Al catalyst together with H₂O₂) is formed, the RhB removal performance is significantly improved. The degradation of RhB therefore depends on the occurrence of the Fenton reaction. It can be seen from Figure S3(d) that as the Fe contents of Cu/Fe bimetallic catalysts increases from 2 wt% to 10 wt%, the activities of the catalysts decrease slightly. Fe therefore only performs as a structural auxiliary, and the excessive content of Fe will reduce the catalytic performance of the main active species Cu.

The influence of reaction temperature is shown in Figure S3(e), and it can be seen that when the temperature increased from 30 °C to 60 °C, the degradation rate of RhB went up gradually. We notice that only 20.3% of RhB degraded at 30 °C after 1 h, and the degradation rate reached 73.7% after 1 h when the temperature rose to 40 °C. A 96.4% degradation of RhB was achieved at 50 °C after 40 min, and therefore we usually performed the reaction at 50 °C. A lag phase at low temperature is observed.

![Figure 2](http://www.iwaponline.com/wst/article-pdf/81/10/2057/716082/wst081102057.pdf)
in Figure S3(e). Sufficient energy cannot be provided to overcome the reaction activation energy and so the reaction rate is really slow. As the temperature increases, more energy is provided to overcome the reaction activation energy, and the reaction rate constants are increased leading to acceleration of the reaction. When the reaction temperature increased from 30°C to 50°C, the corresponding pseudo-first-order apparent rate constants increased from 0.0037 to 0.0836 min⁻¹, leading to a higher degradation rate. It was also found that the reaction temperature had a significant effect on RhB degradation activity.

As shown in Figure S3(f), it is known that the initial H₂O₂ concentration plays an important role in the generation of ·OH, which directly influences the degradation of RhB. When the initial H₂O₂ concentration increased from 600 ppm to 1,200 ppm, the degradation rate of RhB in 1 h increased from 84.6% to 99.5%. As the initial H₂O₂ concentration increased, more ·OH were formed to participate in the degradation reaction, thereby showing an increase in activity. It should be noted that when the H₂O₂ was further increased to 1,500 ppm, the degradation of RhB was no longer significantly improved, suggesting there was an optimum initial H₂O₂ concentration for the reaction. The effects of high concentration of H₂O₂ can be explained according to the following reactions (Tunc et al. 2012):

\[
\begin{align}
H₂O₂ + \cdot OH & \rightarrow \cdot OOH + H₂O \quad (4) \\
H₂O₂ + \cdot OOH & \rightarrow \cdot OH + O₂ + H₂O \quad (5) \\
\cdot OOH + \cdot OH & \rightarrow O₂ + H₂O \quad (6)
\end{align}
\]

The oxidation potential of ·OOH is much lower than ·OH, which does not contribute to the degradation of RhB.

XPS measurements were carried out to investigate the Cu oxidation states. As shown in Figure S3(a), the peak at the binding energy (BE) of about 934 eV is assigned to Cu²⁺ species, which was shown by the appearance of a shake-up satellite peak at about 941–945 eV (Xia et al. 2011; Ye et al. 2011). It is difficult to distinguish Cu²⁺ and Cu⁰ species because their BE are very close in the Cu 2p½ XPS spectra, and so the Cu LMM Auger spectra was obtained for further discussion. The kinetic energy (KE) centered at about 914 and 918 eV in Cu LMM Auger spectra were assigned to Cu⁺ and Cu²⁺ species in Figure S3(b), respectively (Qi et al. 2012). The peak at BE of 932 eV in Cu 2p½ XPS spectra could be ascribed to Cu⁺ species. That is, the as-prepared catalysts contain two Cu species (Cu²⁺ and Cu⁺) on the surface. Figure 3 shows the change of Cu oxidation states before and after reaction on Cu₁₂.₀/Fe₂.₀/γ-Al₂O₃/Al catalyst. The Cu²⁺ to Cu⁺ ratio was 1.69 on the fresh catalyst and decreased to 0.78 after reaction, so the Cu²⁺ species is consumed during the reaction as the active species (Wang et al. 2014). It can be concluded that Cu ions are the active species in catalytically decomposing H₂O₂, and the generation of ·OH radicals depends on the redox process of Cu²⁺/Cu⁺. Table S2 shows that both of BE and KE values for Cu species on the Cu₁₂.₀/Fe₂.₀/γ-Al₂O₃/Al catalyst are lower than those on the Cu₁₂.₀/γ-Al₂O₃/Al catalyst, which could be attributed to the interaction between Cu and Fe.

Figure 4 ESR spectra shows the capability of the catalysts to generate ·OH radicals. The signals with intensity of
1:2:2:1 corresponding to the characteristic peaks of DMPO–OH adducts, and the signal peak intensity can represent the amount of -OH produced. It proves that the Cu/Fe bimetallic catalyst has the strongest ability to produce -OH. Meanwhile, it shows that the signal of -OH is almost impossible to observe after adding TBA, indicating that the generated -OH is eliminated. The degradation efficiency of RhB was minimized in the radical scavenging experiment, which proves that -OH are indeed the important active species in RhB decomposition.

Furthermore, the redox properties of the catalysts were analyzed by H$_2$-TPR as shown in Figure 5. One reduction peak corresponds to the reduction from Fe$^{3+}$ to Fe$^{2+}$ (Lin et al. 2018) observed at 395 ℃ for the Fe-based catalyst. For the Cu-based catalyst, the redox process had a peak centered at 252 ℃, which is ascribed to the reduction of Cu$^{2+}$ to Cu$^0$. For Cu/Fe bimetallic catalyst, it can be seen that the initial reduction temperature is only 216 ℃ and the H$_2$ consumption peak is divided into two small peaks with similar temperature. It is worth noting that no H$_2$ consumption peak of Fe species was observed at about 400 ℃, indicating that the reduction temperature of Fe$^{3+}$ to Fe$^{2+}$ migrates to a lower temperature. Meanwhile, the reduction temperature of the Cu species also slightly decreased. The coexistence of Cu and Fe on the Cu/Fe bimetallic catalyst reduces the original reduction temperature of the Cu and Fe phase, which is consistent with the findings of other researchers (Kiatphuengporn et al. 2014) and proves the existence of Cu/Fe interaction. In addition, the initial reduction temperature of the Cu/Fe bimetallic catalyst is the lowest, suggesting that the Cu/Fe bimetallic catalyst has the highest redox ability. The high redox ability is probably due to the bimetallic synergistic enhancement with redox cycle of Cu$^{2+}$/Cu$^+$ and Fe$^{3+}$/Fe$^{2+}$. According to the standard reduction potentials Fe$^{3+}$/Fe$^{2+}$ ($E^0 = 0.77$ V) and Cu$^{2+}$/Cu$^+$ ($E^0 = 0.17$ V), the process of reducing Fe$^{3+}$ by Cu$^+$ is thermodynamically feasible (Li et al. 2016), as the following reactions:

$$Fe^{3+} + Cu^+ \rightarrow Fe^{2+} + Cu^{2+} \Delta E^0 = 0.6V$$  (7)

This synergy enhances interface electron transfer and facilitates the redox cycle of Cu$^{2+}$/Cu$^+$ and Fe$^{3+}$/Fe$^{2+}$, thus the Cu/Fe bimetallic catalyst shows strong redox ability. It is beneficial to the activation of H$_2$O$_2$ (Wang et al. 2018). More -OH is produced to attack RhB molecules during the reaction, and so the Cu/Fe bimetallic catalyst exhibits the best -OH producing ability and catalytic activity.

The system is also applicable to other simulated dye wastewaters due to the non-selectivity of -OH. In this study, the experiments of degrading three other organic dyes were carried out in the same way. As shown in Fig. S5, the catalyst also has excellent catalytic degradation properties for MO (methyl orange), MB (methylene blue), and MG (malachite green). The -OH radicals can attack the chromophore of dye molecules during the reactions, such as azo bond (−N=N−) and carbon–nitrogen double bond (C≡N−), resulting in the destruction of the dye molecular structure. MO is a typical dye with an azo bond. RhB, MB, and MG have the carbon–nitrogen double bond.

**Stability and recyclability of Cu$_{12.0}$/Fe$_{2.0}$/γ-Al$_2$O$_3$/Al catalysts**

A 10-cycle experiment was carried out as shown in Figure 6. After each reaction, the catalyst was directly taken out from the solution without any treatment. The results show the degradation rate of RhB remains at 98% even if the catalyst was utilized for 10 cycles. As shown in Tables S3 and S4, it can be found that the leaching amount of Cu ions of Cu/Fe bimetallic catalyst is less than that of Cu-based catalyst, and is much less than similar Cu-based catalysts reported (Han et al. 2011; Singh et al. 2016), which obtained leaching amounts of 4.9 mg/l and 3.0 mg/l. The mass loss of Cu species on the surface of the Cu/Fe bimetallic catalyst is 7.5%, less than 28% of the Cu-based catalyst. This is mainly due to the stronger interaction between Cu ions and support on the Cu/Fe bimetallic catalyst.

As shown in Figure 7 thermal gravity (TG) and differential thermal gravity (DTG) patterns, when the temperature
increased to 100 °C, obvious weight loss occurred on Fe2.0/γ-Al2O3/Al, Cu12.0/Fe2.0/γ-Al2O3/Al, and γ-Al2O3/Al samples, which corresponds to the evaporation of physically adsorbed water with weak binding force. When the temperature ranged from 220 °C to 450 °C, the DTG curve of Fe2.0/γ-Al2O3/Al shows a long-width peak, which is not found for Cu12.0/Fe2.0/γ-Al2O3/Al. The peak attributed to the loss of chemically adsorbed structural –OH groups from FeOOH (Qi et al.). More –OH groups are therefore exposed on the surface of the Fe2.0/γ-Al2O3/Al sample. The –OH groups could be coordinated with Cu2+ ions, thus facilitating Cu dispersion (Han et al. 2021). As for the total weight loss curves (TG), it can be seen that the total weight loss of Fe2.0/γ-Al2O3/Al is higher than that of Cu12.0/Fe2.0/γ-Al2O3/Al and γ-Al2O3 support (the weight loss is 25%, 15%, 15%, respectively). The weight loss at about 100 °C is almost the same, indicating that the amount of physically adsorbed water is also almost the same, and thus the difference of total weight loss is due to the loss of surface –OH groups. The abundant –OH groups on the surface of Fe2.0/γ-Al2O3/Al were coordinated with Cu2+, so that the weight loss peak of –OH groups was not found in the TG/DTG patterns of the Cu12.0/Fe2.0/γ-Al2O3/Al catalyst. In consequence, the Cu ions could be chemically adsorbed on to the Cu/Fe bimetallic catalyst more easily by complexing with the surface –OH groups. For the Cu-based catalyst, there are only a few –OH groups derived from γ-Al2O3. When Cu is loaded, Cu(OH)2 will physically deposite on the catalyst surface easily, resulting in large Cu particle sizes and more Cu ions leaching after reaction. But for the Cu/Fe bimetallic catalyst, Cu species are better dispersed on the surface without Cu(OH)2 physical deposition, leading to less Cu leaching. Therefore, the Cu/Fe bimetallic catalyst has excellent activity and stability in long-term application.

CONCLUSIONS

In this study, a mesh-type monolithic Fenton-like catalyst was prepared by anodization method. Cu and Fe were uniformly dispersed on the surface of γ-Al2O3 and Fe can reduce the particle size of Cu. In the degradation reaction of RhB, the 4 × 6 cm Cu12.0/Fe2.0/γ-Al2O3/Al catalyst performed the best at 1,200 ppm H2O2 at 50 °C, and the degradation rate reached 99.5% within 1 h. Cu species were demonstrated to be the active species in catalytically decomposing H2O2, and •OH are the main reactive oxidants in RhB decomposition. Cu/Fe bimetallic catalyst has the highest redox ability, which is more conducive to the H2O2 activation and •OH generation. It also has excellent
recyclability in the 10-cycle experiment, with the leaching amount of metals lower than 0.7 mg/l after each reaction. Cu ions could be chemically adsorbed on to the Cu/Fe bimetallic catalyst easily because Fe-doping increases the surface –OH groups, leading to less Cu leaching. The excellent activity and stability of the Cu/Fe bimetallic catalyst indicate that it can be easily used for long-term and continuous wastewater treatment.

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SUPPLEMENTARY MATERIAL

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