Preparation and catalytic performance of copper-containing magnetic catalysts for degradation of azo dye (direct violet)

Qiannan Duan, Jianchao Lee, Han Chen and Yunyun Zheng

ABSTRACT

A novel magnetically separable magnetic activated carbon supporting-copper (MCAC) catalyst for catalytic wet peroxide oxidation (CWPO) was prepared by chemical impregnation. The prepared samples were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) method, and scanning electron microscopy (SEM) equipped with energy dispersive spectrometry (EDS). The catalytic performance of the catalysts was evaluated by direct violet (D-BL) degradation in CWPO experiments. The influence of preparative and operational parameters (dipping conditions, calcination temperature, catalyst loading H2O2 dosage, pH, reaction temperature, additive salt ions and initial D-BL concentration) on degradation performance of CWPO process was investigated. The resulting MCAC catalyst showed higher reusability in direct violet oxidation than the magnetic activated carbon (MAC). Besides, dynamic tests also showed the maximal degradation rate reached 90.16% and its general decoloring ability of MCAC was 34 mg g\(^{-1}\) for aqueous D-BL.

Key words | catalytic, copper-load, CWPO, direct violet, magnetic activated carbon, magnetic separation

INTRODUCTION

Direct dyes are well known as one of the most refractory pollutants because of their toxicity and stability (Nguyen et al. 2011). Thus, the effective removal of direct dyes pollutants is becoming of important concern owing to their wide use and environmental hazards (Saleh & Gupta 2012). Some physicochemical technologies, such as adsorption, coagulation, and membrane separation (Singh & Arora 2011), have been used for the removal of various toxic dyes pollutants, but these processes merely transfer the pollutants from one medium to another requiring further treatment (Gupta et al. 2012), while advanced oxidation processes (AOPs), based on the generation of very active hydroxyl radicals (OH·), are becoming more and more important technologies for wastewater treatment (Saharan et al. 2014). Among the various AOPs, the catalytic wet peroxide oxidation (CWPO) technology has been proved to be able to degrade quickly the toxic or carcinogenic dye residues and their by-products (Domínguez et al. 2013).

In the heterogeneous catalytic oxidation systems, solid catalysts are porous materials with huge specific surface areas, which provide more catalytic active centers, so a high catalytic activity can be expected. More and more effective materials of modified activated carbon (AC) have been proposed as supports to prepare the CWPO catalysts in recent years. Especially, some metal-impregnated AC catalysts have been found to be very effective in pollutants removal because of their high catalytic properties. However, in a practical application, those materials were usually hindered by the difficulty of separation and the loss of AC (Lin et al. 2012). To this issue, manganese oxides have been studied as potential catalysts (Mahmoodi 2015). It was reported that MnFe\(_2\)O\(_4\) presented high activity in producing hydroxyl radicals for degradation of organic dyes and could be separated with a magnet without any loss (Nguyen et al. 2011; Yao et al. 2014). But some studies showed that the catalyst deactivation due to the leaching of manganese, and the iron from the catalyst surface, could also hinder the use of magnetic MnFe\(_2\)O\(_4\) catalysts in practical applications (Madrakian et al. 2011; Fan et al. 2012; Gupta et al. 2013).

During last decade, among various metals, Cu is a common and most-effective precursor in catalytic applications for the oxidation of organic wastewater (Hu et al.
washed with DI water several times to nearly neutral pH and dried at 105 °C. Thus, the clean AC was obtained. After that, in a typical procedure, 5 g of obtained AC was impregnated into a 150 mL solution which dissolved manganese (II) chloride (0.01 mol) and ferric chloride (0.02 mol) at RT. With constant stirring, 4 M NaOH solution was added dropwise to the above mixture until the pH value reached 11. Then, another 30 min stirring was continued. Afterwards, the suspension was heated by a water bath at 90–100 °C for 2 h. After cooling to RT, the prepared magnetic composite was repeatedly washed by DIW to remove the impurities (e.g. Cl⁻, Na⁺) associated with the procedures. Subsequently, the as-prepared composite MAC, containing 30% MnFe₂O₄, with surface area of 500 m² g⁻¹, was filtrated by magnetic separation and was fully dried at 120 °C.

**Preparation of copper-containing magnetic activated carbon (MCAC)**

The MCAC catalyst was prepared by incipient wetness impregnation of the MAC with an aqueous solution of cupric nitrate. The impregnating solid liquid (S/L) ratios of Cu(NO₃)₂/MAC were adjusted to 1:0, 1:10, 1:20, 1:30, 1:50 and 1:100, respectively. After impregnation of Cu, the sample was dried in an oven at 60 °C for 24 h to remove moisture. And then, the obtained samples were calcined in air atmosphere at 200 °C, 300 °C and 600 °C for about 1 h. To produce more active copper oxides, protection of nitrogen was not applied in the calcination process.

**CWPO reaction**

**Influencing factor tests**

The influence of preparative and operational parameters on degradation performance of CWPO process was studied. During the CWPO tests, effect of H₂O₂ dosage was studied with the addition of H₂O₂ (30wt %) from 0.1 mL to 1 mL; influence of various initial concentrations of D-BL on the degradation process was investigated between 30 mg L⁻¹ and 150 mg L⁻¹; effect of pH was examined by adjusting the initial pH of D-BL solution in the range 4–11; effect of temperature on the degradation reaction also was discussed at 25, 35, 45, and 55 °C. Besides, two anions, Cl⁻ and SO₄²⁻, were respectively added in the synthetic dye wastewater to study the influence of salt concentration (ranging from 0 to 60 g L⁻¹).
**Batch reaction**

To prove the reusability of the catalysts, some CWPO tests were also carried out in a batch reactor. Practically, in an Erlenmeyer flask, MAC and MCAC catalysts were typically reused four times under the same conditions. All catalysts were introduced into D-BL dye wastewater (100 mg L\(^{-1}\)) at S/L ratio of 1/300 (g/mL), and four reaction cycles were carried out during 4 h at 45 °C. Meanwhile, 0.8 mL H\(_2\)O\(_2\) (30wt %) was also added in reactor for each time. After each experiment, the catalysts were separated from the solution by magnetic separation, washed with DI water, and dried at 105 °C. Finally, by measuring the absorbance (A) values of the supernatant liquid, the dye degradation rate was calculated.

**Dynamic reaction**

To evaluate the performance of MCAC catalyst in the dynamic test, CWPO of D-BL was carried out in a filtration bed. As shown in Figure 1, the experimental apparatus was consisted of four main parts, a filter column, a wastewater tank, a peristaltic pump and a flow gauge. The fixed filter column was made up of a quartz glass tube (7.73 mL volume, Figure 2(g)), and 3 g MACA catalysts (Figure 2(h)) were filled in it. The D-BL dye wastewater (100 mg L\(^{-1}\)) flowed through the filter column in a flowrate of 20.4 mL h\(^{-1}\) at RT for 72 h continuously. The absorbance of water was analyzed per 1-h interval from sampling mouths (Figure 2(f)).

**Characterization and measurement**

The morphology and surface element contents of MCAC were determined by scanning electron microscopy (SEM, Holland FEM Company, Quanta 200) equipped with energy dispersive spectrometry (EDS). The phase composition and microstructure of nano-materials was observed by a D/Max-3c X-ray diffractometer (XRD) using Cu K\(_\alpha\) radiation (\(\lambda = 0.154056 \text{ nm}\)). Nitrogen adsorption and desorption isotherms were performed at \(-196\) °C in a Brunauer–Emmett–Teller (BET) method (ASAP 2020, Micromeritics, USA). All samples were degassed in a vacuum 10\(^{-5}\) torr at 150 °C for 8 h before the analysis. Surface area and micro-pore volume of samples were determined using the BET and Dubinin-Radushkevich (DR) equation, respectively. Total pore volume (\(V_t\)) was obtained at a relative pressure of 0.99. Besides, magnetization properties of materials were characterized by qualitative approach.

In addition, based on Beer-Lambert Law, between concentration and dye absorbance, there was a linear relationship in a concentration range from 0 to 100 mg L\(^{-1}\) with the following formula, \(A = 0.0206C + 0.0094\) (\(r = 0.9991\)). Therefore, A was used instead of dye concentration to calculate the dye degradation rate. Catalytic activity of catalysts was evaluated by the D-BL degradation rate (\(Q_e\)) calculating as follows:

\[
Q_e = \left(\frac{A_0 - A_t}{A_0}\right) \times 100\%
\]

where \(A_0\) was the D-BL initial absorbance, \(A_t\) was the absorbance at time \(t\). UV-VIS absorption spectrophotometer (SP-756PC, Shanghai Spectrum Instruments Co.) was used for testing the absorption spectra of D-BL solutions at 554 nm.

**RESULTS AND DISCUSSION**

**Characterization of prepared products**

A proper sintering temperature is conducive to effectively form the active-site of the catalysts in impregnation method. Here, XRD was used to investigate the crystal structure and phase composition of the samples calcinated at different sintering temperatures of 200 °C, 300 °C and 600 °C (the products were noted as MCAC2, MCAC3, MCAC6, respectively).

As shown in Figure 2(a), it was found that high annealing temperatures would be beneficial to obtain high loadings of active metal oxides, especially CuFe\(_2\)O\(_4\) around the characteristic peak intensity of 26.4°. The previous researches (Zhang et al. 2007; Zhao et al. 2004) had shown that CuFe\(_2\)O\(_4\) possessed its good properties in magnetic behavior and catalytic activity. Then, we also see that the characteristic peak intensity of CuO is higher than that of Cu\(_2\)O in the
patterns of MCAC6. This was due to the decomposition of nitrate ions (NO$_3^-$) to NO$_x$. Nitrate ions were thermally removed and the salt (Cu(NO$_3$)$_2$) was converted to metal oxide (Cu$_2$O, CuO). Therefore, among three catalytic samples, it seemed that the MCAC6 sample was more appropriate to be applied in magnetic catalytic systems. Moreover, a magnet was placed near the glass beaker to test the magnetic separability of the composite. As displayed in Figure 2(b), it is obvious that the magnetic property of MCAC6 is much higher than that of MCAC2. It means that MCAC6 can be separated easily from solutions with a magnetic separation technique, which confirms the reports that CuFe$_2$O$_4$ has a good property in magnetic behavior. It also proves that the optimum sintering temperature was 600 °C during preparation of the catalyst. The physical or porous structure is vital important to understand the oxidation process and the catalytic activity of a catalyst (Priyanka et al. 2014). Figure S2 (available with the online version of this paper) shows the nitrogen adsorption and desorption isotherms for AC, MAC and MCAC6. The isotherms exhibit a feature of type H4 hysteresis loop (Sing & Williams 2004); this type are given by many ACs and some other nanoporous adsorbents, associated with narrow slit pores in the micropore region. The textural characteristics of the AC, MAC and MCAC6 determined according to the isotherms are given in Table 1. The specific surface area, total volume and micropore of MAC are higher than those of AC. This probably has two causes. First, we found that AC obtained with ferric salt as activating agent showed high specific surface area even at lower activation temperatures (Nguyen et al. 2014). Second, the carbon gasification contributed to form microporous structures during preparation process (Leboda et al. 1998). It is also noteworthy to mention that MCAC6 exhibits a decrease of textural properties compare to AC and MAC.

![Figure 2](https://iwaponline.com/wst/article-pdf/76/11/3069/210452/wst076113069.pdf)

**Figure 2**  (a) XRD analyses of MCAC catalysts calcined under 200 °C, 300 °C and 600 °C, respectively. (b) Magnetic separation effects of MCAC2 and MCAC6.

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**Table 1**  | The element contents, textural properties of three samples: AC, MAC and MCAC6

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (wt%)$^a$</th>
<th>O (wt%)$^a$</th>
<th>Fe (wt%)$^a$</th>
<th>M (wt%)$^a$</th>
<th>Cu (wt%)$^a$</th>
<th>$S_{BET}$ (m$^2$ g$^{-1}$)$^b$</th>
<th>$V_t$ (cm$^3$ g$^{-1}$)$^c$</th>
<th>$V_{micro}$ (cm$^3$ g$^{-1}$)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>79.58</td>
<td>0.853</td>
<td>0.153</td>
<td>0.00</td>
<td>0.76</td>
<td>750.00</td>
<td>0.7962</td>
<td>0.4086</td>
</tr>
<tr>
<td>MAC</td>
<td>61.69</td>
<td>16.65</td>
<td>9.18</td>
<td>5.85</td>
<td>3.45</td>
<td>803.53</td>
<td>0.8673</td>
<td>0.4160</td>
</tr>
<tr>
<td>MCAC6</td>
<td>40.47</td>
<td>20.98</td>
<td>18.37</td>
<td>14.50</td>
<td>4.62</td>
<td>614.46</td>
<td>0.5446</td>
<td>0.3104</td>
</tr>
</tbody>
</table>

$^a$EDS analyses of loading element types and contents.

$^b$$S_{BET}$: BET surface area.

$^c$Total pore volumes were obtained at P/Po = 0.99.

$^d$Micropore volume.
This was probably due to pore blockage by copper deposited on the mouth of small pores.

Moreover, morphology and surface element contents of catalysts also were studied by SEM equipped with EDS. The SEM images of AC, MAC and MCAC6 are displayed in Figure 3(a)–3(c), respectively. Figure 3(a) demonstrates that many pores pervaded homogeneously on the surface of pure AC. As shown in Figure 3(b), the agglomeration of many MnFe₂O₄ particles (the red frames marked, particle size: 20–35 nm) led to a rough surface and a porous structure, which might generate new binding sites in interior walls of the micropores and contribute to homogeneous Cu binding (Zhu et al. 2013). After the deposition of copper, the surface of MCAC6 (Figure 3(c)) was more rough and formed some monoliths together with thin film. Although the surface of AC was covered by many small aggregates of metal particles after being incorporated, a porous structure ($V_t = 0.5446 \text{ cm}^3 \text{ g}^{-1}$) could still be observed.

The EDS analyze of the materials in Table 1 further also indicates loading element types (Fe, Mn, Cu) on AC surface. As it can be seen, the MCAC6 has a higher metals weight fraction after calcinations. It is also noteworthy that the Mn and Fe concentration markedly increased in MCAC6, compared with MAC. It reported (Vijaya et al. 2013) that the occupancy of Cu$^{2+}$ ions into the FeMn$_2$O$_4$ spinel lattice would possibly create a lattice distortion, which contributed to changing the magnetic properties and improving morphological diversity of Mn and Fe ions.

Figure 4(a) shows XRD powder diffraction patterns for three materials AC, MAC and MCAC6 samples. Compared with AC pattern, the characteristic peaks intensity of MAC and MCAC significantly increases around 21.1°, 23.6°, 26.4°, 26.7°, 35.4° and 42.6°, corresponding to the active substance of Mn$_2$O$_7$, Fe$_2$O$_3$, CuFe$_2$O$_4$, FeMn$_2$O$_4$, CuO and Cu$_2$O, respectively. According to JADE analysis software (Materials Data, Inc., Livermore, CA, USA), it was clearly conformed that ferrite and manganese oxide (FeMn$_2$O$_4$) particles was formed on the MAC surface. Meanwhile, ferrite and copper oxides as well as manganese oxides were formed with the FeMn$_2$O$_4$ peak disappeared on MCAC6.
XRD was also used to investigate the stability of catalysts. The XRD patterns of MCACs, used once and five times, respectively, are displayed in Figure 4(b). It presents that the characteristic peak intensity of Mn$_2$O$_7$ decreased obviously, relative to the intensity of CuFe$_2$O$_4$, CuO and other metal oxides. While the stability of CuFe$_2$O$_4$ phase content contributes to maintaining the magnetic and catalytic properties.

**Preparation conditions of catalysts**

Effect of initial copper concentration and S/L ratio in the impregnating reaction were investigated by experiments. As shown in Figure 5(a), curve-a presents the effect of various initial concentrations of cupric nitrate solution (between 0.05 M and 0.8 M) on dye degradation ratio (Q$_e$). At low concentration from 0.05 M to 0.5 M, the Q$_e$ almost kept unchanged, which mainly contributed to the adsorption effect of MCACs, while, with higher copper salts loadings, Q$_e$ increased. The Q$_e$ rose to the highest of 85.44% when the impregnating concentration of 0.6 M. However, as excessive metal loadings, there was an inhibition that made Q$_e$ decrease again, which might ascribe to clogging deposition of copper on the surface and pore of carrier. Additionally, curve-b shows that Q$_e$ increases at the initial stage and reaches the highest in the impregnating S/L ratio of 1/30 (g/mL), and then starts to decrease. It indicates that the quantities of copper precursor will determine the amount of copper oxide produce on the AC surface. Compared with no-loaded materials (S/L ratio of 1/0), the Q$_e$ of MAC loaded with copper was much higher, indicating catalytic oxidation of dyes played a key role in degradation process (Khorramfar et al. 2011; Mesquita et al. 2012; Subbaramaiah et al. 2014). Therefore, impregnated concentration of 0.6 M Cu(NO$_3$)$_2$ and the impregnated S/L ratio of 1/30 (g/mL) were the optimal impregnating conditions.

Xijun Hu et al. (Hu et al. 1999) found that no significant formation of metal (Cu) or metal oxide (Cu$_2$O, CuO) between 220 to 280 °C, but two main peaks of metal oxide (Cu$_2$O, CuO) were observed with maximum at 550–600 °C. As shown in Figure 5(b), curve-a shows the decoloration performance of MCACs at different calcination temperatures from 200 to 600 °C. The C/C$_0$ ascends constantly and up to the highest at 600 °C with the increase of calcination temperature. This was due to the active phase of CuFe$_2$O$_4$ which was not fully formed at the low temperature, which had been proved by XRD analyses of MCACs (Figure 2). Moreover, curve-b (shown in Figure 5(b)) represents that the desorption rate (Q$_{ad}$) of different MCACs, and the Q$_{ad}$ was calculated according to the formula in supporting materials. Compared with other MCACs, it is found that MCAC6 presents the lowest Q$_{ad}$ and highest decoloration performance. It implied that the catalytic decomposition of MCAC6 played a main role rather than an absorption effect.

**Catalytic activity**

**Effect of H$_2$O$_2$ dosage**

To find the best conditions of composite catalysts for degradation of dye, main reaction effects were investigated. Firstly, the effect of H$_2$O$_2$ dosage on the degradation of dye is shown in Figure 6(a). With the addition of H$_2$O$_2$ (30wt %, the same below) from 0.1 mL to 0.8 mL, the Q$_e$ of dye went...
up from 28.0% to 65% at 10 min and from 58.3% to 90.16% at 120 min, respectively. Based on CWPO reaction mechanism, 
$\text{H}_2\text{O}_2$ can be decomposed by catalytic materials, and 
hydroxyl radical will be generated to oxidize dye. Therefore, 
the enhancement of $Q_e$ by addition of $\text{H}_2\text{O}_2$ was due to an 
increase in $\cdot\text{OH}$ radicals. When further increasing the
addition of H₂O₂ to 1 mL, the degradation of the dye almost unchanged at 180 min comparing with the addition of 0.8 mL H₂O₂. It can be explained by the scavenging effect of excess H₂O₂, decreasing the number of hydroxyl radicals in the solution with the addition of excess H₂O₂, which results in a decrease in Qₑ. When the reaction system only added MCAC, the Qₑ increased at 10 min due to the adsorption of the material, but the Qₑ was almost unchanged from 30 to 180 min comparing with the addition of 0.8 mL H₂O₂. In the reaction system only with H₂O₂ or MCAC, it could be noticed that the Qₑ also changed little with further increasing the reaction time. It indicates that dye degradation cannot be achieved by carbon adsorption or oxidation of H₂O₂ without catalysts. As expected, good catalytic performance of the MCAC materials was provided with addition of a certain volume of oxidants in the reaction system, and 0.8 mL H₂O₂ presented a higher catalytic ability on dye degradation.

Figure 6(a) also presents the variation of dye degradation with reaction time. When the addition of H₂O₂ was 0.8 mL, the Qₑ reached 86.75% at 60 min, and then the rate increased slowly up to 90.16% at 120 min. The curve trend stayed steady as time went on and the Qₑ began to descend at 200 min. There were maybe two reasons: for one thing, the reactions tended to slow down because the hydrogen peroxide is exhausted; for another thing, the decrease of dye wastewater concentration also would lead to the decline of the reaction rate.

Effect of the initial D-BL concentration

The influence of various initial concentrations of D-BL (between 30 mg L⁻¹ and 150 mg L⁻¹) on the degradation process was investigated. The results obtained (Figure 6(b)) shows that the Qₑ decreased by increasing initial concentrations. This could be because that competition over the -OH radicals in the solution would increase, with the increase in the number of D-BL molecules. It should be noted that the Qₑ can be achieved at about 90% after 90 min at 100 mg L⁻¹ initial concentration. So, in follow-up experiments, 100 mg L⁻¹ D-BL solutions were studied.

Effect of initial pH

The effect of pH was examined by adjusting the initial pH of D-BL solution in the range 4–11. As shown in Figure 6(c), the results show that Qₑ decreased with the increase of pH. The experiment results demonstrated that hydroxyl radical concentration would directly affect the oxidation reaction rate. Organic matter can be decomposed into inorganic molecules, or be oxidized and formed macromolecule polymers by hydroxyl radical (Türgay et al. 2011; Subbaramaiah et al. 2014). So it can be explained that pH plays a more important effect in H₂O₂ oxidation process. In the absence of H⁺, H₂O₂ was decomposed to ‘OH groups, and a higher Qₑ was obtained. Because acidic conditions significantly enhance degradation efficiency of dye and the operation under near-neutral conditions can easily apply to most wastewater, further experiments were carried out at pH 4.

Effect of temperature on the degradation reaction

Effect of temperature on the degradation reaction was also investigated at 25, 35, 45, and 55 °C. The results are given in Figure 6(d). As expected, rising temperature increased the catalytic activity of degradation and the final Qₑ. But when the temperature was above 45 °C, the concentration change degrees increased slowly, which might ascribe that excess heat will result in decomposition of H₂O₂ and reduction of effective utilization (Rey et al. 2009). Therefore, optimal treating temperature was 45 °C in this experiment. It is worth noting that industrial dye wastewater is generally at a high temperature, which is beneficial to increase catalyst activity in practice.

Effect of additive salt solution

Two salts, NaCl and Na₂SO₄, were respectively added in the DB-L wastewater to study the influence of salt concentration. As shown in Figure 6(e), it presents the effect of different salt concentrations on dye removal. The Qₑ increases gradually with the increase of NaCl salinity, while opposite results appeared in the reaction system added Na₂SO₄. The existence of sulfate in aqueous solution could result in the hydrolysis of SO₂-4, which generated sulfuric acid groups and hydrogen ions (Anipsitakis & Dionysiou 2003). Therefore, the decrease of dye decolorization efficiency might be due to the accessory consumption of hydroxyl radicals, while, it is known that molecular of direct dye is a linear structure, and its hydrophilic groups of aromatic rings usually possess an ability to generate hydrogen bond. So, in the presence of NaCl solution, the DB-L might be aggregated and its solubility decreased. It was of benefit for MCAC6 to improve its adsorption and to enhance its reaction rate, and the Qₑ would increase too.

Reusability of materials

The reusability of two materials (MAC and MCAC6) was evaluated via four consecutive experiments of D-BL degradation at same time. Between each experiment, the catalysts were
separated from the solution by magnetic separation, washed with DI water, and dried at 105 °C. As shown in Figure 7, both two materials played their efficient catalytic performance at the first reaction, and the MCAC had better results. During the next few reactions, the Qₐ of MAC catalysts obviously decreased with the increase of the run time and reaction times. It could be due to the leaching of manganese and iron from the catalyst surface, which would hinder the catalytic activity of MAC catalysts (Rey et al. 2009). However, the MCAC catalysis was highly stable and maintained its high catalytic performance over four reaction cycles. It clearly demonstrated that the MCAC catalyst was quite stable and has great application potential in water treatment.

**Reaction in the filtration bed**

A dynamic CWPO simulator (as shown in Figure 1) was used to test the stability and durability of the MCAC catalysts for practical application. As running time went on, the Qₑ was dropping continuously in Figure 8. In the initial period (0–8 h), the Qₑ almost was more than 90% and up to as high as 99.50%. The Qₑ decreased to 81.65% at 25 h and gradually declined to 65.79% at the end of 50 h run time. But, obviously, we found the Qₑ that had been running at 62% after 50 h. This was probably due to catalysts’ absorption equilibrium achieved, and the decrease of mass transfer rate with the accumulation of resultants (CO₂, O₂). Finally, the Qₑ of MCAC on aqueous D-BL was 34 mg g⁻¹ by the calculation. But, in the real application, the sustainable and high-efficient catalysis of MCAC catalysts still need us to improve, especially, for long time running. It also will be the aim of future work.

**CONCLUSION**

In this study, a magnetically separable composite photocatalyst, copper-containing magnetic activated carbon (MCAC) for CWPO, was prepared by depositing copper ion onto the surface of MAC. The MAC was prepared by incorporation of manganese ferrite particles (MnFe₂O₄) onto AC surface. In follow-up research, we found that the MCAC presented an effective activity in degradation of synthetic D-BL wastewater. The SEM/EDX observation showed that metal elements were well dispersed and bound in carbon matrix. The XRD patterns of MCAC also verified that CuFe₂O₄ as the main catalytic phase played positive effects in reaction. The textural characteristics of MCAC6 showed it had a porous structure, and its total pore volume was 0.5446 cm³ g⁻¹. H₂O₂ dosage was an important factor to dominate degradation rate in CWPO process. Experimental results also showed that the materials presented good magnetism under the optimum preparation conditions. And the good reusability and stability of materials were also proved.

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REFERENCES


Domínguez, C. M., Ocón, P., Quintanilla, A., Casas, J. A. & Rodríguez, J. J. 2013 Highly efficient application of activated carbon as catalyst for wet peroxide oxidation. *Applied Catalysis B: Environmental* 140, 663–670.


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