Removal of organic phosphorus and formaldehyde in glyphosate wastewater by CWO and the lime-catalyzed formose reaction

Bo Xing, Honglin Chen and Xiaoming Zhang

ABSTRACT

Glyphosate (PMG) wastewater with 40–600 mg/L organic phosphorus (OP) and 1–4% CH$_2$O was treated by catalytic wet oxidation (CWO) and the lime-catalyzed formose reaction to remove total phosphorus (TP) and improve biodegradability. Activated carbons (ACs) modified by H$_2$O$_2$ oxidation and thermal treatment with melamine were used as CWO catalysts and characterized by N$_2$ adsorption/desorption and XPS. The CWO experiments were performed in an autoclave reactor at 110–130 $^\circ$C and 1.0 MPa. The modified AC showed higher catalytic activity than the parent AC due to the introduction of nitrogen-containing functional groups, exhibited over 90% OP removal for various real PMG wastewaters, and had good stability for 20 consecutive CWO runs. The CWO effluents were further treated by lime at 80 $^\circ$C to remove TP and CH$_2$O. The treated effluents, containing 0.5–12 mg/L TP and 20–60 mg/L CH$_2$O, showed good biodegradability with a BOD$_5$/COD ratio of 0.31–0.41. The combination of CWO and lime is an effective treatment method prior to biological treatment for solving the problems of OP and CH$_2$O encountered by the glyphosate industry.

Key words | catalytic wet oxidation, formaldehyde, formose reaction, glyphosate, nitrogen-doped activated carbon, organic phosphorus

INTRODUCTION

Glyphosate (N-phosphonomethyl glycine, PMG), is an effective, broad-spectrum, non-selective organophosphate herbicide and is widely used in agriculture for killing weeds. Currently, the iminodiacetic acid (IDA) route is one of the main industrial production processes for producing PMG. However, in this process, to obtain 1 ton of PMG, about 5–6 tons of crystalized mother liquid is produced, and this contains about 10 g/L PMG, 1–4% formaldehyde (CH$_2$O), and other byproducts. Most of the PMG in the mother liquor is recovered by nanofiltration (NF), but the effluent of NF permeate wastewater (PMG wastewater) still contains 200–3,000 mg/L PMG, 40–600 mg/L organic phosphorus (OP), and 1–4% CH$_2$O as well as other byproducts, based on our analytical results from the glyphosate companies in China.

Because of the high concentration of CH$_2$O, industrial PMG wastewater cannot be treated directly using biological treatment (Liu & Hegemann 1998), and a pretreatment step is required to reduce the CH$_2$O concentration. Lime has commonly been used for the condensation of CH$_2$O around 80 $^\circ$C to formose sugars, which have better biodegradability (Castells et al. 1983; Moussavi et al. 2002). Using the lime-catalyzed formose reaction has been an effective and economical operation, and this method has been used to pretreat industrial PMG wastewater. However, the effluent from this method still contains high concentrations of OP and PMG with low bioavailability and toxicity (Lajmanovich et al. 2011; Mei et al. 2012; Junes et al. 2013), thus it is difficult to reach the Chinese standard GB 8978-1996 (less than 0.5 mg/L total phosphorus (TP)) using biological treatment. Apart from the cultivation of efficient bacteria for PMG and OP degradation, other studies have investigated effective pretreatment methods for the degradation of OP to orthophosphate (PO$_4^{3-}$) (Chen & Liu 2007; Chen et al. 2007; Mangat-Echavia et al. 2009; Manassero et al. 2010), which can be removed easily by chemical precipitation or used by microorganisms.
We proposed a new method for the degradation of OP in PMG wastewater to \( \text{PO}_4^{3-} \) involving catalytic wet oxidation (CWO) with a nitrogen-doped activated carbon (AC) catalyst. AC is inexpensive compared to other carbon materials (like carbon nanotubes, carbon nanofiber, graphene, and carbon black), other heterogeneous catalysts (like the metal oxides of Co, Mo, Mn, Cu, Zn, and Fe), and noble metals (Pt, Pd, and Ru). In addition, because of the high surface area, well-developed pore structure, and easily-tailored surface chemistry (Stavropoulos et al. 2008), ACs, especially nitrogen-doped ACs, show higher catalytic activities for the oxidation of PMIDA (Pinel et al. 1999), \( \text{H}_2\text{S} \) (Bashkova et al. 2007), CO (Hu et al. 2012), and phenol (Messele et al. 2014). Thus, nitrogen-containing ACs produced by \( \text{H}_2\text{O}_2 \) oxidation and thermal treatment with melamine were used as CWO catalysts. The effect of operating conditions on the removal of OP was investigated. The effluent from the CWO process was further treated by lime to remove TP and \( \text{CH}_2\text{O} \), and the biodegradability of the effluent combining CWO and lime was evaluated by the BOD$_3$/COD ratio.

**EXPERIMENTAL**

**Preparation and characterization of modified ACs**

The preparation process of the modified ACs is illustrated in Figure 1. Coal-based AC (Lingxia Bote Activated Carbon Co. Ltd, 63 mm) was used in this study. The parent ACs (40–80 mesh, denoted as LXBT) were oxidized with 30% \( \text{H}_2\text{O}_2 \) and then washed with deionized water. 150.0 g of LXBT or oxidized LXBT (denoted LXBT-O) were then added to the melamine solution at room temperature (r.t.) for 4 h and then washed with deionized water. 150.0 g of LXBT or oxidized LXBT (denoted LXBT-O) were then added to the melamine solution (22.5 g melamine dissolved in 1.2 kg deionized water at 70 C) and stirred for 4 h. The mixture was then filtered, and the AC samples were dried at 120 C for 12 h. Finally, the samples impregnated with melamine were calcined at 850 C for 2 h in a tube furnace under a nitrogen atmosphere. The nitrogen-doped ACs are denoted as LXBT-M and LXBT-OM.

The textural properties of the ACs were determined by \( \text{N}_2 \) adsorption/desorption at 77 K using a Builder SSA-4200 instrument. The AC sample was separately degassed at 300 C for 2.5 h in a vacuum environment before measurements. The total specific surface areas were measured by the BET calculation method (Brunauer et al. 1938) applied to the desorption branch of the isotherms. The t-plot method was used to calculate the micropore volumes. The pore areas and volumes of the mesopores (2–50 nm) were calculated by the Barrett-Joyner-Halenda (BJH) method (Barrett et al. 1951).

The surface elemental compositions of the AC catalysts were obtained from X-ray photoelectron spectroscopy (XPS) performed on a Kratos XSAM800 equipped with an Al K\( \alpha \) X-ray source (1486.6 eV, anode operating at 12 kV and 15 mA). The binding energies were calibrated based on the graphite C 1 s peak at 284.5 eV. Quantitative analysis was performed using the CasaXPS software after a Shirley background subtraction.

**CWO experiments**

The characteristics of the real PMG wastewaters treated in this study are listed in Table 1. Real wastewaters 1# and 2# were obtained from Jiangsu Good Harvest-Weien agro-chemical Ind. Co. Ltd, real wastewaters 3# and 4# were obtained from Jiema Chemical Ind. Co. Ltd, China, and real wastewaters 5# and 6# were obtained from Guangan Ind. Co. Ltd, China.

CWO experiments were performed in a 500 mL thermostatted stainless reactor equipped with mechanical stirring, a condenser, and a thermometer (WDF-0.5, Weihai Automatic Control Reaction Kettle Co., Ltd). 300 g PMG wastewater and AC catalysts (0.5–5.0%) were introduced into the reactor. When the suspension was heated to 90 C at 700 rpm, the reactor was filled quickly with air at 0.6–1.2 MPa, and the flow rate of the exiting gas was 40 mL/min. The reactor was then heated to the set temperature (110–135 C) within 5 min, and this was designated as

<table>
<thead>
<tr>
<th>PMG wastewater</th>
<th>pH</th>
<th>( \text{CH}_2\text{O} ) mg/L</th>
<th>COD g/L</th>
<th>PMG mg/L</th>
<th>TP mg/L</th>
<th>( \text{PO}_4^{3-} ) mg/L</th>
<th>OP mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real wastewater 1#</td>
<td>2.90</td>
<td>5,114</td>
<td>-</td>
<td>579</td>
<td>625</td>
<td>36</td>
<td>589</td>
</tr>
<tr>
<td>CWO effluent 1#</td>
<td>7.30</td>
<td>3,607</td>
<td>-</td>
<td>-</td>
<td>618</td>
<td>603</td>
<td>15</td>
</tr>
<tr>
<td>Real wastewater 2#</td>
<td>2.49</td>
<td>4,557</td>
<td>10.2</td>
<td>385</td>
<td>226</td>
<td>26</td>
<td>200</td>
</tr>
<tr>
<td>CWO effluent 2#</td>
<td>6.60</td>
<td>3,283</td>
<td>3.6</td>
<td>-</td>
<td>216</td>
<td>198</td>
<td>18</td>
</tr>
<tr>
<td>Real wastewater 3#</td>
<td>2.51</td>
<td>8,497</td>
<td>10.2</td>
<td>213</td>
<td>55</td>
<td>4</td>
<td>51</td>
</tr>
<tr>
<td>CWO effluent 3#</td>
<td>4.25</td>
<td>7,895</td>
<td>9.8</td>
<td>-</td>
<td>40</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>Real wastewater 4#</td>
<td>2.56</td>
<td>15,000</td>
<td>17.8</td>
<td>850</td>
<td>355</td>
<td>25</td>
<td>330</td>
</tr>
<tr>
<td>CWO effluent 4#</td>
<td>4.86</td>
<td>13,320</td>
<td>15.5</td>
<td>-</td>
<td>338</td>
<td>325</td>
<td>13</td>
</tr>
<tr>
<td>Real wastewater 5#</td>
<td>2.47</td>
<td>18,600</td>
<td>23.8</td>
<td>102</td>
<td>42</td>
<td>2</td>
<td>40</td>
</tr>
<tr>
<td>CWO effluent 5#</td>
<td>3.01</td>
<td>17,860</td>
<td>22.1</td>
<td>-</td>
<td>23</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>Real wastewater 6#</td>
<td>1.70</td>
<td>35,288</td>
<td>41.5</td>
<td>683</td>
<td>319</td>
<td>75</td>
<td>244</td>
</tr>
<tr>
<td>CWO effluent 6#</td>
<td>2.75</td>
<td>31,050</td>
<td>38.5</td>
<td>-</td>
<td>284</td>
<td>265</td>
<td>19</td>
</tr>
</tbody>
</table>
time zero of the CWO experiments. At the end of the CWO experiment, the reactor was cooled by water to r.t., and the pressure was relieved to atmospheric pressure by a relief valve. The suspension was then filtered, and the effluent was analyzed in time.

**Lime-catalyzed formose reaction**

The CWO effluent was further treated by the lime-catalyzed formose reaction to remove \( \text{CH}_2\text{O} \) and \( \text{PO}_4^{3-} \), and 50 mL of CWO effluent was added to a 250 mL four-neck flask equipped with mechanical stirring, a condenser, a thermometer, and a feed opening. The effluent was heated to 60–90 °C with stirring at 300 rpm. Once the set temperature was reached, lime was added to the flask, and this was considered time zero for the reaction. Due to the autocatalytic nature of the lime-catalyzed formose reaction, there was an abrupt change in the \( \text{CH}_2\text{O} \) elimination along with an abrupt change in the suspension color from white to yellow or to red. The elimination of \( \text{CH}_2\text{O} \) was almost unchanged once the suspension color changed (Moussavi et al. 2002; Kopetzki & Antonietti 2011). Therefore, the abrupt change of the suspension color was considered the end point \( (t_{\text{yellow}}) \) of the lime-catalyzed formose reaction. At the end of the formose reaction, the suspension was cooled to room temperature and filtered using quantitative filter paper. The percolate was then analyzed, and the sludge was dried at 120 °C for 8 h.

**Analytical methods**

The concentration of PMG was analyzed following the Chinese standard method (GB 12686-2004, China), and the concentrations of TP and \( \text{PO}_4^{3-} \) were measured according to the standard methods (GB 11893-89, China). The concentration of TP minus the concentration of \( \text{PO}_4^{3-} \) equaled the concentration of OP in this study. Chemical oxygen demand (COD) was analyzed by sealed catalytic digestion-colorimetric method (HJ/T, 399-2007) using a Hach DR1010 COD analyzer. The presence of \( \text{CH}_2\text{O} \) was measured using a specific colorimetric method (GB 12686-2004). Biochemical oxygen demand for 5 days (BOD\(_5\)) was analyzed by the standard methods (HJ 505–2009). The pH of the wastewater was measured with a pH meter (PHS-3C, SPSIC China).

---

**RESULTS AND DISCUSSION**

**Catalytic performances of the modified ACs**

The catalytic activities of the parent AC of LXBT, the oxidized AC of LXBT-O, and the melamine-modified ACs of LXBT-M and LXBT-OM were evaluated under mild reaction conditions \( (T=120 \, ^\circ \text{C}, \, P=1.0 \, \text{MPa}, \, m \text{ (cat.})/m \text{ (wastewater)} = 3\%, \, \text{reaction time} = 2 \, \text{h}) \). Each catalyst was evaluated twice, and the experimental errors in the measured OP and \( \text{PO}_4^{3-} \) concentrations were evaluated in the range of ±10 mg/L (Figure 2). TP in the effluents was almost the same, indicating that the absorption effect of the ACs can be neglected. Compared with the parent AC, the melamine-modified ACs showed higher catalytic activities for the removal of OP (LXBT-M: 90.2%, LXBT-OM: 94.7%). The enhanced catalytic activity observed in other catalytic oxidation reactions with nitrogen-doped AC (Cao et al. 2014; Messele et al. 2014; Rocha et al. 2015) was caused by the changes of the porous structure and surface chemistry of the ACs.

The results of the texture characterization of the AC catalysts are given in Table S1 (Supplementary Material, available with the online version of this paper). The parent AC, LXBT, presented a high specific surface area (SSA_{BET}, 1,472 m\(^2\)/g), and a high percentage of mesoporous structure (40% for \( V_{\text{meso}} \)). Oxidation and/or melamine modification decreased the SSA_{meso} and \( V_{\text{meso}} \) by 5%–15%. This is likely due to the destruction of pore walls and the blocking of some pores by functional groups. It is worth noting that no major changes were observed in the microporous structure.

---

**Figure 1** | The preparation process of modified ACs.
However, while the modification decreased the specific surface area and pore volume, the catalytic activity increased.

Therefore, the enhanced catalytic activity should result from the change of the surface chemistry. The surface elemental composition characterized by XPS and the fitted O 1 s and N 1 s XP spectra are shown in Table 2 and Figure S1 (Supplementary Material, available with the online version of this paper). For the O 1 s peaks, the binding energies of 530.8–531.5 eV, 532.4–532.8 eV, 533.4–534.0 eV, and 535.0–535.8 eV represent quinone or pyrone type groups (O-1), C=O like ether groups and/or –OH phenol groups (O-2), O–C=O like lactone or carboxylic groups (O-3), and chemisorbed O 2 or H 2 O (O-4), respectively (Biniak et al. 1997; Figueiredo et al. 1999). The N 1 s peaks are fitted into four types of nitrogen species, and these are assigned to pyridinic nitrogen (N-6, 398.4–398.8 eV), pyrrolic and/or pyridonic nitrogen (N-5, 400–400.4 eV), graphitic nitrogen (N-Q, 401.3–401.7 eV), and pyridine-N-oxide (N-O, 403.5–403.9 eV) (Biniak et al. 1997; Bagreev et al. 2004).

Pre-oxidation with H 2 O 2 increased the number of oxygen-containing functional groups, especially for acidic groups like O-3. More acidic groups were favored for introducing more nitrogen-containing functional groups (Bagreev et al. 2004). This was verified by the results of doping the ACs (without and with oxidation treatment) by melamine. The pre-oxidation and melamine-treated carbon, LXBT-OM, was doped with up to 2.52 at.% of nitrogen.

LXBT and LXBT-O (without nitrogen-containing functional groups), also exhibited high OP removal (81.2%, 84.3%). This may be related to the presence of basic oxygen-containing functional groups like O-1, which have been considered in previous works to play an important role in the catalytic oxidation with AC (Figueiredo et al. 1999; Aguilar et al. 2003). Additionally, the catalyst of LXBT-OM contained more nitrogen-containing functional groups like N-6, N-5, and N-Q, which are considered to be the origin of the positive effect of N-doped AC. This has been reported in previous studies for some catalytic oxidation reactions with nitrogen-doped materials (Sousa et al. 2010; Sousa et al. 2012; Rocha et al. 2015). The presence of more basic groups in N-doped AC can enhance the interaction of oxygen molecules with the AC surface and more active oxygen species that can be generated (Figueiredo et al. 1999; Strelko et al. 2004; Pollak et al. 2006; Rocha et al. 2015), which can degrade organic pollutants.

**Effect of operating conditions of CWO**

As discussed above, LXBT-OM showed high activity for OP removal, and so it was necessary to investigate the effects of the operating conditions on OP removal (Figure 3). Specifically, the operating conditions investigated were pressure, temperature, reaction time, and amount of catalyst. The results showed that the higher the pressure was, the higher the OP removal was. With an increase in air pressure, the liquid phase oxygen concentration increased, which was beneficial for OP removal. However, there were no significant differences when the pressure was over 1 MPa. The effect of pressure is minimized at high pressure because oxygen is not the limiting reactant at high pressure (Guo & Al-Dahhan 2005).

Longer reaction times led to higher OP removal. However, OP removal did not continue to increase when the reaction time was more than 2.0 h. Temperature was found to be a crucial factor for OP conversion, and OP removal was higher when the temperature was increased. When more catalyst was added, more OP degraded. However, excessive catalyst increased the absorption of OP over the AC catalyst, which affected the activity of the AC catalyst. Thus the optimal operating conditions were T = 150 °C, P = 1.0 MPa, reaction time = 2 h, and 3% catalyst.

At the optimal conditions, six different kinds of real PMG wastewaters were treated by LXBT-OM, and the results are listed in Table 1. In the real wastewaters, the PMG and OP amounts varied considerably from 213 to 2,560 mg/L and from 51 to 474 mg/L, respectively. The PMG removals reached over 99%, and the OP removals reached over 90%, suggesting that LXBT-OM has high effectiveness.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>O-1</th>
<th>O-2</th>
<th>O-3</th>
<th>O-4</th>
<th>N-6</th>
<th>N-5</th>
<th>N-Q</th>
<th>N-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>LXBT</td>
<td>87.07</td>
<td>12.95</td>
<td>0.00</td>
<td>0.80</td>
<td>5.18</td>
<td>4.19</td>
<td>2.77</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LXBT-O</td>
<td>85.96</td>
<td>14.04</td>
<td>0.00</td>
<td>1.16</td>
<td>4.71</td>
<td>4.82</td>
<td>3.35</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>LXBT-M</td>
<td>85.84</td>
<td>12.21</td>
<td>1.96</td>
<td>0.91</td>
<td>4.29</td>
<td>3.83</td>
<td>3.17</td>
<td>0.95</td>
<td>0.42</td>
<td>0.59</td>
<td>0</td>
</tr>
<tr>
<td>LXBT-OM</td>
<td>85.13</td>
<td>12.35</td>
<td>2.52</td>
<td>1.03</td>
<td>4.59</td>
<td>3.52</td>
<td>3.22</td>
<td>1.20</td>
<td>0.47</td>
<td>0.42</td>
<td>0.43</td>
</tr>
<tr>
<td>LXBT-OM-U</td>
<td>82.81</td>
<td>14.87</td>
<td>2.31</td>
<td>0.98</td>
<td>5.21</td>
<td>4.86</td>
<td>3.82</td>
<td>1.07</td>
<td>0.41</td>
<td>0.35</td>
<td>0.48</td>
</tr>
</tbody>
</table>
catalytic activity for the real glyphosate wastewaters regardless of the concentrations of PMG and OP. The OP in the CWO effluents was as low as 5–19 mg/L. Additionally, the catalyst also showed catalytic activity for the removal of CH$_2$O and COD.

Durability of the N-doped AC

Consecutive CWO runs with real wastewater 2# (Table 1) were performed to test the durability of the AC catalyst under the optimal operating conditions (T = 130 °C, P = 1.0 MPa, reaction time = 2 h, and 3% catalyst). The results are presented in Figure 4. Compared with higher OP removal (91%) and COD removal (64.3%) in CWO, the OP removal (13.5%) and COD removal (12.5%) in wet oxidation (WO) without catalyst were significantly less. This is indicative of the catalytic roles of the nitrogen-doped AC catalyst. A slight loss of catalytic activity (an OP removal decrease from 91% to 87%) was observed when LXBT-OM was reused 20 times, which indicated that it exhibited good durability for the conversion of OP. Furthermore, LXBT-OM also exhibited stability for the conversion of CH$_2$O. The increase of COD and the decrease of pH, however, suggested that the catalytic performance for acid refractory compounds like formic acid was weakened with successive reuse. Compared to the fresh catalyst, the micropore surface area and volume of the used catalyst (LXBT-OM-U) declined and more mesopores were created because of the oxidation effect in CWO after 20 runs (Table S1). The
surface nitrogen leached slightly from 2.52 at.% to 2.31 at.% (Table 2), suggesting that the nitrogen groups of LXBT-OM were stable during the CWO process. The amount of N-6, N-5, and N-Q decreased, while the amount of N-O increased, indicating that only a small amount of N-6 was oxidized to pyridine-N-oxide. Thus, the excellent durability of the nitrogen-doped AC provided a potential industrial application for the OP removal in PMG wastewater.

Post-treatment of CWO effluents by the lime-catalyzed formose reaction

The high concentrations of CH\textsubscript{2}O and phosphorus left in the CWO effluents were treated using the lime-catalyzed formose reaction. Lime was added to adjust the pH of the solution to 10.5–12.5, acting as a catalyst of the formose reaction and as a precipitating agent for TP (Moussavi et al. 2002; Kopetzki & Antonietti 2011). Since PO\textsubscript{4}\textsuperscript{3–} was easier to remove by lime precipitation than formaldehyde was by the formose reaction, the main judgment was the formaldehyde removal, the secondary judgment was the TP removal, and the tertiary judgment was the amount of sludge produced. Thus the lime concentration was a crucial factor for the formose reaction. The CWO effluent 6# (Table 1) was treated by lime with different formaldehyde-to-lime molar ratios (F/L) at the same temperature (80 °C) and pH (no adjustment, 2.75). With an increase in the lime concentration, the conversion of CH\textsubscript{2}O was accelerated, with the shorter t\textsubscript{yellow} representing the end point time of the formose reaction (Table 3). However, excessive lime caused more sludge to be produced. There was a balance between t\textsubscript{yellow}, sludge production, and CH\textsubscript{2}O removal efficiency. The suitable lime concentration for CH\textsubscript{2}O removal was at F/L of 5, where the CH\textsubscript{2}O and TP removals were 99.9% and 96.2%, respectively.

In order to reduce sludge at 80 °C and F/L of 5, the pH adjustment of the CWO effluent 6# prior to the formose reaction was accomplished by adding the required amount

Table 3 | Effect of lime concentration on formaldehyde and phosphorus removal

<table>
<thead>
<tr>
<th>F/L Molar ratio</th>
<th>t\textsubscript{yellow} min</th>
<th>CH\textsubscript{2}O mg/L</th>
<th>PO\textsubscript{4}\textsuperscript{3–} mg/L</th>
<th>TP mg/L</th>
<th>Sludge m(sludge)/m(wastewater)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWO effluent 6#</td>
<td>–</td>
<td>31,050</td>
<td>245</td>
<td>284</td>
<td>–</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>15</td>
<td>~0</td>
<td>7.8</td>
<td>4.01%</td>
</tr>
<tr>
<td>1.25</td>
<td>1</td>
<td>19</td>
<td>~0</td>
<td>8.6</td>
<td>3.57%</td>
</tr>
<tr>
<td>2.5</td>
<td>5</td>
<td>21</td>
<td>~0</td>
<td>9.4</td>
<td>3.24%</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>28</td>
<td>0.3</td>
<td>10.8</td>
<td>1.78%</td>
</tr>
<tr>
<td>10</td>
<td>&gt;120\textsuperscript{a}</td>
<td>21,506</td>
<td>0.7</td>
<td>15.6</td>
<td>0.34%</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Means that the time reaching the end point was over 120 min and the reaction was stopped at 120 min, then the effluent was analyzed in this study.

Table 4 | Effect of temperature on formaldehyde and phosphorus removal

<table>
<thead>
<tr>
<th>T °C</th>
<th>t\textsubscript{yellow} min</th>
<th>CH\textsubscript{2}O mg/L</th>
<th>PO\textsubscript{4}\textsuperscript{3–} mg/L</th>
<th>TP mg/L</th>
<th>Sludge m(sludge)/m(wastewater)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWO effluent 6#</td>
<td>–</td>
<td>31,050</td>
<td>245</td>
<td>284</td>
<td>–</td>
</tr>
<tr>
<td>60</td>
<td>115</td>
<td>64</td>
<td>0.4</td>
<td>8.9</td>
<td>1.32%</td>
</tr>
<tr>
<td>70</td>
<td>80</td>
<td>45</td>
<td>0.5</td>
<td>9.8</td>
<td>1.54%</td>
</tr>
<tr>
<td>80</td>
<td>15</td>
<td>28</td>
<td>0.3</td>
<td>10.8</td>
<td>1.78%</td>
</tr>
<tr>
<td>90</td>
<td>9</td>
<td>32</td>
<td>0.4</td>
<td>11.5</td>
<td>2.04%</td>
</tr>
</tbody>
</table>
of 6 M NaOH. This reduced the consumption of lime by adjusting the solution pH to the range of 10.5–12.5. The effect of pH on formaldehyde and phosphorus removals and on the sludge amount is shown in Table 5. The value of t\text{yellow} decreased with an increase in pH when F/L was 10. At the same time, the sludge decreased from 1.78% to 0.36%. Thus, adjusting the pH of the CWO effluent 6# to 7.0 was useful for reducing sludge. Under the optimal formose reaction conditions (F/L = 10, reaction temperature = 80 ° C, and pH of the CWO effluent = 7), the CWO effluents 5# and 5# (Table 1) were treated, and the results are listed in Table 5. The lime-catalyzed formose reaction exhibited high CH₂O and TP removal efficiency for the different CWO effluents of the real wastewaters. A higher concentration of CH₂O reached a higher removal efficiency.

In order to confirm the necessity of CWO for the removal of TP by the lime-catalyzed formose reaction, the real wastewater 6# was treated directly with lime (without CWO). PO₄³⁻ was removed completely, but the OP removal was only 11.9% (Table 5). This indicated that CWO pretreatment is necessary for the complete removal of TP. Furthermore, the direct treatment of the real wastewater 6# showed lower CH₂O removal, and the effluent from the formose reaction still contained 205 mg/L. This may be related to the promoting effect of the phosphate buffer (contained in the CWO effluent) on the lime-catalyzed formose reaction as observed by Kopetzki (Kopetzki & Antonietti 2011).

### Biodegradability of lime-catalyzed formose reaction effluents

High concentrations of OP and CH₂O in PMG wastewater were treated by CWO and the lime-catalyzed formose reaction. The final effluents only contained 0.5–12 mg/L TP and 20–60 mg/L CH₂O, which meant biological treatment was a possibility. The biodegradability was evaluated by the BOD₅/COD ratio. BOD₅/COD ratios for the final effluents were in the range of 0.31 to 0.41, suggesting good biodegradability (Table 6). However, the BOD₅/COD ratio for the effluent of the direct formose reaction for the real wastewater 6# was 0.20, implying a negative effect of OP on the biodegradability.

### CONCLUSIONS

Introduction of nitrogen-containing functional groups to AC enhanced the catalytic performance for the degradation of OP by CWO. The AC modified by H₂O₂ and melamine showed the highest catalytic activity and excellent stability in consecutive CWO runs for 20 times with mild reaction conditions (T = 130 ° C and P = 1.0 MPa). The further treatment of the CWO effluent using lime exhibited high CH₂O and TP removal efficiency at suitable reaction conditions (F/L = 10, reaction temperature = 80 ° C, and pH of the CWO effluent = 7). The final effluents only contained 0.5–12 mg/L TP and 20–60 mg/L CH₂O, and showed good

### Table 5  Effect of pH on formaldehyde and phosphorus removal

<table>
<thead>
<tr>
<th>pH</th>
<th>F/L Molar ratio</th>
<th>t\text{yellow} min</th>
<th>CH₂O mg/L</th>
<th>PO₄³⁻ mg/L</th>
<th>TP mg/L</th>
<th>Sludge m(sludge)/m(wastewater)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CWO effluent 6#</td>
<td>–</td>
<td>–</td>
<td>31,050</td>
<td>245</td>
<td>284</td>
<td>–</td>
</tr>
<tr>
<td>2.75</td>
<td>5</td>
<td>15</td>
<td>&gt;120⁸</td>
<td>28</td>
<td>0.3</td>
<td>10.8</td>
</tr>
<tr>
<td>2.75</td>
<td>10</td>
<td>&gt;120⁸</td>
<td>21,506</td>
<td>0.7</td>
<td>15.6</td>
<td>0.34%</td>
</tr>
<tr>
<td>5.02</td>
<td>10</td>
<td>22</td>
<td>31</td>
<td>0.9</td>
<td>12.6</td>
<td>0.32%</td>
</tr>
<tr>
<td>7.06</td>
<td>10</td>
<td>13</td>
<td>22</td>
<td>0.8</td>
<td>11.5</td>
<td>0.36%</td>
</tr>
<tr>
<td>9.12</td>
<td>10</td>
<td>16</td>
<td>21</td>
<td>0.7</td>
<td>11.0</td>
<td>0.45%</td>
</tr>
<tr>
<td>CWO effluent 5#</td>
<td>–</td>
<td>–</td>
<td>7,895</td>
<td>35</td>
<td>40</td>
<td>–</td>
</tr>
<tr>
<td>7.10</td>
<td>10</td>
<td>20</td>
<td>60</td>
<td>0.4</td>
<td>2</td>
<td>–</td>
</tr>
<tr>
<td>CWO effluent 5#</td>
<td>–</td>
<td>–</td>
<td>17,860</td>
<td>21</td>
<td>23</td>
<td>–</td>
</tr>
<tr>
<td>7.08</td>
<td>10</td>
<td>18</td>
<td>38</td>
<td>0.3</td>
<td>0.8</td>
<td>–</td>
</tr>
<tr>
<td>Real wastewater 6#</td>
<td>–</td>
<td>–</td>
<td>35,288</td>
<td>75</td>
<td>319</td>
<td>–</td>
</tr>
<tr>
<td>7.18</td>
<td>10</td>
<td>15</td>
<td>205</td>
<td>0.6</td>
<td>215</td>
<td>–</td>
</tr>
</tbody>
</table>

*Means that the time reaching the end point was over 120 min and the reaction was stopped at 120 min then the effluent was analyzed.

---

1396  B. Xing et al. | Pretreatment of glyphosate wastewater by CWO and lime  Water Science & Technology | 75.6 | 2017

Downloaded from https://iwaponline.com/wst/article-pdf/75/6/1390/454471/wst075061390.pdf by guest on 26 January 2020
biodegradability with a BOD₃/COD ratio of 0.31–0.41. This research provided a feasible method for the removal of high concentrations of OP and formaldehyde in glyphosate wastewater by CWO using nitrogen-doped AC as the catalyst and lime-catalyzed formose reaction.

ACKNOWLEDGEMENTS

This work was funded by the Sichuan Province Science and Technology Support Program 2015GZ0169 and the Chengdu Top Innovation Team Project.

REFERENCES


First received 21 June 2016; accepted in revised form 14 December 2016. Available online 2 January 2017.