Investigation of heavy oil refinery wastewater treatment by integrated ozone and activated carbon-supported manganese oxides

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The activated carbon-supported manganese oxides (MnOx/GAC) was utilized for catalytic ozonation of heavy oil refinery wastewater (HORW). MnOx/GAC was characterized by XRD, SEM & EDS and N2-adsorption-desorption. The effects of reaction parameters on HORW treatment were investigated. COD, BOD5, TOC, biodegradability, toxicity, and simulated activated sludge processes and ESI-FT-ICR MS analysis were used to analyze HORW samples. MnOx/GAC exhibited greater COD reduction efficiency in the catalytic ozonation of HORW than did GAC. The dominant mechanism of HORW catalytic ozonation was oxidation via hydroxyl radicals over MnOx/GAC. The results suggested that big molecular pollutants with high toxicity and low biodegradability were first degraded to small molecular oxidation products with low toxicity and high biodegradability, afterward which small molecular pollutants and oxidation products further oxidized or mineralized. The investigation uncovered the industrial potential of MnOx/GAC for ozonation treatment of refinery wastewater.

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1. Introduction

Heavy oil refinery wastewater (HORW) produced in heavy crude oil mining and processing can cause serious water pollution and endanger physical health. In fact, the pressure is mounting on society to address the necessity and difficulty of treating HORW. However, traditional treatment processes have been unable to remove pollutants efficiently due to its complicated components, high-concentration organic pollution, acute toxicity and poor biodegradability [1–5]. It was even difficult to degrade effectively by chemical oxidation because of sensitive pollutant selectivity of targeted oxidants Cl2, ClO2, H2O2, KMnO4 and O3 [6–8]. Fortunately, catalytic ozonation process (COP) with heterogeneous catalysts has thrown light on the removal of recalcitrant organic pollutants, which can overcome the slow reaction rate of the single ozonation process (SOP) [9,10]. Moreover, a great deal of effort has been devoted to offer high-efficiency removal of target organic pollutants aiming at developing diverse heterogeneous catalysts such as MnO2, TiO2, Al2O3 and mixed metal oxides [11–14].

The predominant role of heterogeneous catalysts in a COP is activating ozone to more active oxidant species over the active functional groups of the catalyst surface and adsorbing the targeted pollutants to react with the dissolved zone [15–17]. Nevertheless, most of catalysts synthesized have been cost-intensive, which limits their application in full-scale systems. A major trend that addresses this issue is the development of increasingly stringent requirements for the efficiency and cost of COP catalysts. A potentially feasible approach to meet these requirements is to develop COP catalysts based on cheap materials. The activated carbon has given rise to great interests in wastewater ozonation treatment owing to its low cost and abundant reserves [18–25]. Besides, a comprehensive study has revealed that manganese oxide, either independently or supported by other materials as a catalyst, can play a positive role in COP [26–28]. Some investigation has focused on the integrated ozone and activated carbon-supported manganese oxide system for single pollutant wastewater treatment such as p-chlorobenzoate, oxalic acid and nitrobenzene [29–31]. The system of ozone and the activated carbon-supported manganese oxides can effectively degrade pollutants, in which activated carbon-supported manganese oxides were of low cost and simple preparation. However, to the best of our knowledge, the function of integrated ozone and activated carbon-supported manganese oxide system has not well investigated in real wastewater treatment, which could provide more instructive for industrial application.

The objective of this study was to investigate HORW treatment by integrated ozone and activated carbon-supported manganese oxides. The catalyst was characterized by XRD, SEM & EDS, TGA and N2-adsorption-desorption. HORW samples were analyzed by COD (Chemical Oxygen Demand), BOD5 (Biochemical Oxygen Demand), TOC (Total Organic...
2. Materials and methods

2.1. HORW samples and reagents

HORW samples with the characteristics listed in Table 1 were obtained from Liaohé Petrochemical Branch Company (LPBC) of PetroChina Inc. The activated carbon (average diameter 2.0–4.0 mm, density 0.45–0.55 g/g) was purchased from ChengDe North Activated Carbon Company, China. Mn(NO₃)₂ was purchased from Beijing Chemical Reagents Company, China.

2.2. Catalyst preparation

The activated carbon (GAC) was first washed sequentially with 10 m% NaOH solution, 1:1 (v/v) H₂SO₄ solution for 12 h, respectively and distilled water until pH about 7 to remove the associated debris, and air-dried at room temperature for 2 days. The washed GAC was dried at 393 K for 4 h and the resulted GAC was finally used in the experiments.

MnOₓ/GAC was prepared by impregnation as follows: 10 g GAC was added to 20 mL Mn(NO₃)₂ solution with various concentrations on a shaker at 303 K for 24 h, respectively and the resulted samples were named as MnOₓ/GAC-1, MnOₓ/GAC-2 and MnOₓ/GAC-3 correspondingly.

2.3. Experimental system

The experimental system was consisted of an oxygen machine, an ozone generator, a column reactor, and an exhaust bottle (shown in Fig. 1a). The column reactor (shown in Fig. 1b) made of tubular quartz glass was 60 mm in inner diameter, 500 mm in height and 1.41 L working volume, which was equipped with an ozone gas input port, an exhaust gas port, a sampling port, some porous supporting plates and catalyst porous plates. The capacity of the ozone generator on CF-G20 (SMSM Enviro-tech, Beijing, China) was 10 g/h. The flow rate range of L2B-3W flow meter (SHX Rotermoter Inc., Beijing, China) was 20–140 L/h. Here, the volume of treated HORW was 1 L and the initial pH of HORW was adjusted by 1:2 (v/v) H₂SO₄ or 20 m% NaOH solution.

In the experiment, the HOPW sample was continuously degraded by the same catalyst in order to eliminate the influence of the catalyst carrier on the adsorption of pollutants. The duration of each run was 80 min for wastewater treatment except when the influence of treatment time on the pollutant reduction was studied. The treated HORW sample obtained periodically was analyzed after it was added 0.5 mL Na₂S₂O₃ (0.1 mol/L) to quench the oxidative reaction and then filtered by microfiltration. Meanwhile, the mixed exhaust gas was absorbed and measured by 2 L absorber with 2 mol/L Na₂S₂O₃.

2.4. Analytical methods

COD of HORW sample was measured by 5B-6 COD speed meter (LianHua, China) and BOD₅ was determined by OxiTo system (WTW Co., Germany). TOC of HORW sample was analyzed by Aurora 1030 TOC meter (OI analytical Co., USA). The conductivity and pH for HORW sample were measured by PHS-3C pH meter (LeiCi, China) and DDSJ-308A conductivity meter (LeiCi, China), respectively. The ozone concentration in the gas was determined by iodometric titration method [33]. The acute toxicity test of the wastewater (TU) was analyzed by the Vibrio Fischeri method [34] and meanwhile related analytical meters, materials, cold Vibrio Fischeri and analysis software were provided by Azur Environmental Company, USA. The data shown in this paper were the average of three individual measurements. Phenol concentration of HORW sample was measured by a direct spectrophotometric method of 4-aminantipyrine over a 7230G-visible spectrophotometer according to GB 7490-87. UV–visible absorption spectroscopy analysis was performed for HORW quality analysis.

The simulative activated sludge (SAS) test was as follows: the active sludge suspension (concentration 3–4 g/L and SV 15–35%) obtained from the wastewater treatment plant of LPBC of PetroChina Inc. was first aerated overnight in order to remove organic substrate; the resulting mixture was further treated by sedimentation for 2 h, in which the supernatant liquids were removed and the left ones were used for subsequent experiments; the wastewater was diluted to avoid high sludge loading and then added into the prepared activated sludge along with aeration. The COD of the wastewater samples was measured at certain time intervals.

The X-ray diffraction of the catalyst sample was analyzed by a Shimadzu XRD-6000 powder diffraction instrument (Shimadzu, Japan) with 40.0 kV working voltage and 40.0 mA electric current of the cube target X-ray tube. Surface area and pore size distribution of the catalyst were measured by the N₂ adsorption-desorption method on QUADRASORB SI Micrometrics instrument (Quantachrome, USA). The scanning electron microscopy (SEM) was used for the crystal morphology analysis in the QUANTA 200F (FEI, Netherlands) and the energy dispersive X-ray spectroscopy (EDS) was applied for the surface elements in Genesis XM4 (EDAX, USA). TGA (Thermogravimetric Analysis) was used to measure the bulk mass percentage. The pH of Zero Point Charge (pH_{ZPC}) for catalyst was measured by a zeta electric potential method, where the net charge of catalyst surface was zero. The acid–base stability of the catalyst was characterized by the concentration of manganese ions of 2 g catalyst dissolved in the solutions of 20 mL acidic, neutral and alkaline conditions by potassium periodate spectrophotometric method.

ESI–FT–ICR MS was used to quantitatively analyzed HORW operated in the negative–ion mode on an Apex–ultra FT–ICR MS (Bruker Daltonics, USA) with a 9.4 T actively shielded magnet. Ions were generated from a micro–electrospray source along with a 50 μm i.d. fused silica–capillary. The operation condition is as follows: flow rate of HORW samples 180 μl/h, mass to charge ratio (m/z) scanning 115–1000 and signal to noise (S/N) > 4. Each mass spectrum was overlapped by 64 scan spectra in order to reduce S/N and increase resolution. Moreover, 1 mL wastewater sample was added with 20 μl 30% (v/v) NH₄OH to accelerate the deprotonation of acidic compounds in ion ESI [35]. The data was acquired on the software of XMass version 6.0 (Bruker Daltonics, USA) and analyzed by the Kendrick method.

Table 1

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<th>Value</th>
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</table>
3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of MnOx/GAC and GAC were shown in Fig. 2. GAC displayed a typical amorphous structure and the diffraction pattern of about 26° may be attributed to a slight impurity peak. No obvious manganese oxide peaks were detected for MnOx/GAC, indicating that the formed MnOx was amorphous [36]. The difference of the surface crystal structure and microstructure area composition was further revealed by SEM & EDS spectra for MnOx/GAC and GAC in Fig. 3. The surface of MnOx/GAC was lightly smoother in contrast to that of GAC from 5000 times magnification SEM photograph. Table 2 listed the element mass ratio in microstructure area for GAC and MnOx/GAC from EDS. Clearly, there was a gradual increase of Mn and O elements and a decrease of C element with increased MnOx loading. The mass percentage of Mn for MnOx/GAC-2 was 7.38% by EDS. The bulk mass percentage of MnOx for MnOx/GAC-2 was about 4.8% according to TGA analysis in air (shown in Fig. 2b). The result suggested manganese oxides covering the surface of coarse GAC. Besides, MnOx/GAC-2 had the highest sum of surface Al, Si and Ca element mass ratio among three MnOx/GAC catalysts. It is noted that most of the metal oxides may probably be a potential catalytic active center in the ozonation process [37].

Surface areas and pore properties of GAC and MnOx/GAC were shown in Table 3 by the N2 adsorption–desorption method. Compared to GAC, MnOx/GAC showed the decrease of surface areas, pore volume and average pore diameter, suggesting that manganese oxides are occupying and blocking the surface of GAC to some extent. Moreover, more manganese oxide loading, more declining of surface areas, pore volume and average pore diameter. To sum up, the surface feature of MnOx/GAC was as follows: MnOx/GAC-1 high surface areas and low manganese loading, MnOx/GAC-3 had low surface areas and high manganese loading and MnOx/GAC-2 owned medium surface areas and medium manganese loading. The difference among the above catalysts will closely influence adsorption, catalysis or both according to previous reports [38].

3.2. Pollutant removal of HORW

3.2.1. Influence of manganese loading

In order to eliminate the influence of the catalyst carrier on the adsorption of pollutants in the experiment, the HOPW sample was continuously degraded by the same catalyst in 2.025 g/h O3 dose, 5 g catalyst, 7.36 pH, 333 K and 80 min duration (total of 10 runs) for each run. Fig. 4a exhibited COD reduction efficiency for various runs according to O3 alone, O3 + GAC, and O3 + MnOx/GAC systems. Clearly, increasing reaction run can lead to the decrease of COD reduction efficiency. For run 1, the COD reduction efficiency for single O3, O3 + GAC, O3 + MnOx/GAC-1, O3 + MnOx/GAC-2 and O3 + MnOx/GAC-3 was 37.2%, 75.1%, 72.9%, 73.3% and 68.8%, respectively. The adsorption of GAC on COD reduction was studied in Fig. 4b for run 1. The COD reduction efficiency for single GAC and single MnOx/GAC-2 was 21.3% and 19.0%, respectively. The adsorption of MnOx/GAC-2 on COD reduction was a little lower than that of single GAC, which was related to decreased surface areas. It can be seen that the role of single adsorption or single ozonation on COD reduction was pronounced. From Fig. 4b, O3 + MnOx/GAC-2 and O3 + GAC displayed higher COD reduction efficiency than single O3, single GAC and single MnOx/GAC-2, respectively, which identified the role of catalytic oxidation for O3 + GAC or O3 + MnOx/GAC-2 system.

For run 2, the highest COD reduction efficiency (67.4%) for HORW was obtained for O3 + MnOx/GAC-2 system among O3 (36.8%), O3 + GAC (63.4%), O3 + MnOx/GAC-1 (64.6%) and O3 + MnOx/GAC-3 (60.5%).
The result may be probably assigned to the combined role of catalytic oxidation and adsorption–desorption on COD reduction. Increasing run will decrease the adsorption of catalyst on COD reduction efficiency. The high COD reduction efficiency over MnOx/GAC-2 for HORW at run 2 may be due to improved catalytic oxidation combined with still maintaining relative high adsorption performance in the system. For run 10, COD reduction efficiency for O3 + GAC, O3 + MnOx/GAC-1, O3 + MnOx/GAC-2 and O3 + MnOx/GAC-3 systems was 42.4%, 46.3%, 51.3% and 44.2%, respectively. The promoted COD reduction efficiency over MnOx/GAC may dominantly be attributed to enhanced catalytic oxidation performance as opposed to that over GAC in catalytic ozonation system because of adsorption saturation attained at that time.

It is widely accepted that GAC can accelerate O3 decomposition and the generation of hydroxyl radicals and consequently improve the degradation of pollutant in O3 + GAC system [15,16]. Therefore, the promoted catalytic oxidation performance of O3 + MnOx/GAC system can be assigned to improved generation of hydroxyl radicals over the surface of MnOx/GAC in contrast to single GAC for ozonation system.

The increased COD reduction efficiency for O3 + MnOx/GAC-2 among three O3 + MnOx/GAC systems may be probably assigned to high catalytic active sites over the catalyst surface. MnOx loading can increase the amount of surface active sites over GAC and however excessive MnOx loading could cover part of initial surface active sites over GAC. So, further investigation was based on the O3 + MnOx/GAC-2 system.

3.2.2 Influence of catalyst dose and ozone dose

The COD reduction efficiency of 47.1% (28.2%), 51.3% (35.4%), 52.6% (39.8%) and 53.8% (42.3%) was obtained over MnOx/GAC-2 catalyst of 2.5, 5.0, 7.5 and 10.0 g, respectively in 2.025 g/h O3 dose, 333 K, and 7.36 pH for 80 (40) min treatment. Clearly, it was on a rise for COD reduction efficiency along with catalyst rising for 80 or 40 min treatment, which was probably due to more surface active sites for more catalyst dose. A pronounced increase of COD reduction efficiency was achieved with the catalyst dose increasing from 2.5 to 5.0 g, whether it was for 80 or 40 min treatment time. As thus, further investigation was according to 5.0 g catalyst.

<table>
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<tr>
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<tr>
<td>C</td>
<td>74.01</td>
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<tr>
<td>MnOx/GAC-1</td>
<td>74.25</td>
</tr>
<tr>
<td>MnOx/GAC-2</td>
<td>68.73</td>
</tr>
<tr>
<td>MnOx/GAC-3</td>
<td>63.44</td>
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Table 2
The element mass ratio in microstructure area for GAC and MnOx/GAC from EDS.

<table>
<thead>
<tr>
<th>Items</th>
<th>S BET (m²/g)</th>
<th>Vp (cm³/g)</th>
<th>dstr (nm)</th>
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<tr>
<td>GAC</td>
<td>1143.3</td>
<td>0.72</td>
<td>3.18</td>
</tr>
<tr>
<td>MnOx/GAC-1</td>
<td>1029.7</td>
<td>0.66</td>
<td>3.05</td>
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<tr>
<td>MnOx/GAC-2</td>
<td>975.6</td>
<td>0.58</td>
<td>2.84</td>
</tr>
<tr>
<td>MnOx/GAC-3</td>
<td>899.4</td>
<td>0.50</td>
<td>2.92</td>
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</table>

Table 3
The texture properties of GAC and MnOx/GAC.

Fig. 3. SEM photographs and EDS spectra (a, GAC; b, MnOx/GAC-1; c, MnOx/GAC-2; d, MnOx/GAC-3).
Fig. 5 depicted the influence of ozone dose of 0.795, 2.02 and 3.150 g/h on the COD reduction efficiency. The low intake flow of ozone at 0.795 g/h can lead to channeling phenomenon during the experiments, indicating insufficiently fluidized state of catalyst. Certainly, adding ozone can benefit for the increase of COD reduction efficiency due to sufficient fluidizing of catalyst, enough contact between gas–liquid–solid and high ozone mass transfer rate from gas to liquid water phase. However, ozone utilization was relatively low at high ozone flow because of ozone saturation in wastewater. As such, 2.025 g/h ozone dose was determined considering the ozone utilization and COD reduction efficiency.

3.2.3. Influence of reaction temperature and initial pH

The low temperature can favor ozone dissolution and high temperature may accelerate ozone decomposition and reaction rate. Herein, the influence of temperature was surveyed and the results were listed in Table 4. High COD and TOC reduction efficiency was obtained at 313 K in the system. There was a little decrease of COD and TOC reduction efficiency at 333 K of original wastewater temperature compared to that at 313 K. However, it was feasible to treat HORW at the original 333 K in the commercialization without decreasing temperature to 313 K.

Table 5 presented COD and TOC reduction efficiency at various initial pHs in the system. The COD and TOC reduction efficiency was high about at weak acidic and neutral condition, while it would be low in strong acidic or alkaline condition. According to the acid–base stability of MnOx/GAC-2, Mn was found to easily leach out from the surface of catalyst at pH less than 4, whereas it was stable at pH 6–9. As thus, the low pollutant reduction in strong acidic condition may be deduced to catalytic active sites lost due to the manganese oxide desorption from GAC. At strong alkaline condition, low COD and TOC removal might probably be due to carbonate and bicarbonate formed from organic mineralization, which is the typical \( \cdot \)OH radical scavengers [8]. In addition, the surface hydroxyl groups in neutral state on the heterogeneous catalyst surface can play a great positive role in the decomposition of ozone to attain relative high catalytic performance. Meanwhile, the surface hydroxyl group in the neutral state is dominant only when the pH value of the solution is at about pH\(_{pzc}\) [17]. Here, the highest COD and TOC reduction was obtained at pH 6.03, near to the pH\(_{pzc}\) of MnOx/GAC-2 (6.34). At pH 7.35 of original wastewater, the relative high COD and TOC removal efficiency was achieved. Thence, it was acceptable and easily operated at pH 7.35 without adjustment.

3.2.4. Influence of treatment time

Fig. 6 illustrated the influence of treatment time on the COD, BOD\(_5\), TOC and BOD\(_5\)/COD ratio. The concentration of COD and TOC was on the decline along with extended treatment time. As for BOD\(_5\), it first decreased, then increased and last decreased again with prolonged treatment time. BOD\(_5\)/COD ratio changed with lengthened treatment time as follows: slowly rising from 0.10 to 0.11 during initial 20 min, then quickly increasing to 0.31 at 100 min and last gradually declining to 0.30 at 140 min. The changing trend for BOD\(_5\)/COD ratio with treatment time indicated organic pollutants’ main transformation at various stages: a part of organic pollutants with high biodegradability oxidized to the transitional pollutants with low biodegradability at the initial stage, then the refractory transitional pollutants further oxidized to easily degradable organic pollutants and the biodegradable organic pollutants were further degraded at the final stage.
mineralization at late stage. The BOD5/COD for 80 min treatment HORW was about 0.30, which indicated that the biodegradability for treated HORW was markedly improved in spite of no maximum. Fig. 6b showed the UV–visible absorption spectroscopy changes for HORW during treatment time. The middle strong adsorption band (B adsorption band) was observed in the range of 230–270 nm for original HORW, indicating the presence of a large number of aromatic pollutants. However, the absorbance of band was greatly decreased for treated HORW, suggesting that part of benzene ring of organics was oxidized via ring opening by hydroxyl radicals.

Besides, phenol concentration was 30.5 mg/L and phenol reduction efficiency can be up to 71.2% for 80 min treatment HORW according to direct spectrophotometric method of 4-aminoantipyrine.

### 3.3. Biodegradability analysis of HORW

The biodegradability analysis of HORW treated by integrated O3 and MnOx/GAC-2 was studied according to biodegradability stability by BOD5/COD change at continuity test, toxicity bioassay test and simulative activated sludge test (Fig. 7). As depicted in Fig. 7a, BOD5/COD ratio for treated HORW was in the range of 0.28–0.33, bigger than that for original one, which indicated high biodegradability and stability for treated wastewater. The toxicity bioassay at various treatment times showed (in Fig. 7b) that the TU (toxicity unit) of treated HORW lightly
increased for the first 20 min, then quickly decreased until at 80 min and afterward slowly went down. There was about 70.3% TU decreasing rate obtained for 80 min treatment of HORW. The changing trend of TU revealed that high biological toxicity pollutants were formed at initial 20 min and then further converted to low biological toxicity organic pollutants.

In the simulative activated sludge test, the COD variation with the time was analyzed according to original wastewater and two kinds of treated HORW by O3 + MnOx/GAC-2 for 20 min and 80 min respectively (in Fig. 7c). The COD reduction efficiency for HORW during 20 min treatment was lower than that for initial HORW (0 min treatment) during SAS process, revealing the poor biodegradable and high toxic intermediates produced in ozonation catalytic process for 20 min treatment. The result was similar to that of BOD5/COD ratio variation and TU test for 20 min treatment and thus the reverse side of O3 + MnOx/GAC-2 system for HORW treatment was discovered in the initial stage, but it can be avoided by controlled reaction time. The highest COD reduction efficiency during SAS processes for the treated HORW during 80 min treatment, indicating its improved biodegradability among the three kinds of wastewater. To sum up, the wastewater after 80 min treatment by O3 + MnOx/GAC-2 can more benefit for subsequent biochemical treatment process.

3.4. Influence of TBA on pollutant removal

The COD reduction efficiency of wastewater was displayed in Fig. 8 according to TBA (tert-butyl alcohol) addition, a typical of hydroxyl radical (•OH) inhibitor, in the system. It was a pronounced decrease of COD reduction efficiency for treated HORW due to TBA introduction. For 80 min treatment, the COD reduction efficiency with TBA introduction was 17.3%, lower than that of 51.4% without TBA. As thus it clearly identified hydroxyl radical reaction mechanism in O3 + MnOx/GAC-2.

3.5. ESI FT-ICR MS analysis

ESI FT-ICR MS analysis can identify petroleum-wide organic pollutants and correlate their properties and behavior from sufficiently complete characterization of the organic composition in petroleum [39]. Here, negative-ion ESI FT-ICR MS analysis was applied to characterize organic pollutants of HORW before and after 80 min treatment by O3 + MnOx/GAC-2 system (shown in Fig. 9). In each spectrum, there were more than 9000 peaks detected with 175 < m/z < 520 and S/N > 6 at an average mass resolving power of more than 100,000. Obviously, there was a pronounced change of the molecular weight distribution of polar organic pollutants before and after treatment. Besides, the relative peak intensity of pollutants, particularly in molecular weight fraction with 350 < m/z < 520, was markedly decreased for 80 min treatment wastewater compared to that for the original HORW. Besides, there was a wide variety of NSO compounds detected in the mass spectra of the two kinds of wastewater. However, the most changes happened on oxygen containing compounds (O-compounds) for HORW before and after treatment.

Fig. 10 illustrated the two-dimensional modified van Krevelen diagrams for O-compounds, by which the changing trends of H/C and O/C atomic ratio for each identified molecule derived from mass spectra and relative abundance of various hetero-aromatic compounds and Z-distributions (molecular hydrogen loss index) [40] were obtained. An obvious increase of H/C and O/C atomic ratio in the organic pollutants was found and the pollutants with Z < −20 were degraded due to the treated process. The increased H/C was dominantly ascribed to C element decrease because of little capability of H element increase in the molecular during the ozonation catalytic reaction. The results indicated that the ring opening and chain scission of the big C–C and C=CC chain happened, which was converted to relative small ones. On the other
van Krevelen diagram (a: raw sample, b: treated sample) (2643. However, the number of Ox compounds increased from 847 to 973 during the treatment, which was consisted with that of O/C atomic ratio changing. The activation of HOPW than did GAC. The dominant mechanism of HOPW catalytic ozonation was oxidation via hydroxyl radicals over MnOx/GAC. The system of MnOx/GAC-2 combined with ozone can promote COD reduction efficiency, improve biodegradability and decrease TU for HORW in the conditions of 333 K, 80 min treatment, 2.025 g/h O2.

4. Conclusions

The activated carbon-supported manganese oxide (MnOx/GAC) combined with ozone system was developed to treat HORW. MnOx/GAC exhibited greater COD reduction efficiency in the catalytic ozonation of HORW than did GAC. The dominant mechanism of HOPW catalytic ozonation was oxidation via hydroxyl radicals over MnOx/GAC.

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Table 6

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