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An integrated permanganate and ozone process for the treatment of textile dyeing wastewater: Efficiency and mechanism



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ABSTRACT

Textile dyeing effluent has been the focus of considerable research because of its adverse effects on aquatic biota. Here, we present the first comprehensive study of a combined permanganate and ozone $(KMnO_4 - O_3)$ technique to treat different kinds of textile dyeing wastewater. We investigated the effects of process parameters on TOC and COD removal and the toxicity of the wastewater after KMnO₄-O₃ treatment. The synergistic mechanism involved in the KMnO₄-O₃ process is also discussed. The results indicate that $KMnO_4-O_3$ treatment is efficient in treating many kinds of textile dyeing wastewater. The TOC, COD, and toxicity were reduced by approximately 70%, 80%, and 34.4–95.5%, respectively, using a KMnO₄ dosage of 1.5 mM, an O₃ dosage of 10 mg/L, a pH value of 7, and a reaction time of 30 min. Furthermore, biodegradability was increased to 0.33-0.68. The combined use of KMnO₄ and O₃ provided synergetic and complementary advantages. On the one hand, oxidation of pollutants on suspended solid surfaces and in the aqueous phase was enhanced by the stirring action of O_3 molecule bubbles. On the other hand, small molecular organic compounds and fine particles were coagulated by KMnO4 and its intermediate oxidations. X-ray photoelectron spectroscopy results indicate that the valence state of manganese changed after $KMnO_4-O_3$ treatment, and the manganese intermediate catalysing O_3 process contributed to the removal of 20% of COD and 19% of TOC. It was therefore determined that the KMnO₄-O₃ treatment is a promising method for use in the treatment of textile dyeing wastewater.

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1. Introduction

Approximately 1.84 billion tons of textile dyeing wastewater was generated in China during 2015, making textile dyeing the third largest industrial wastewater contributor in China, according to the China Environment Statistical Yearbook (2015). Textile dyeing wastewater has a dark colour, variable pH, high total organic carbon (TOC) content and chemical oxygen demand (COD), and contains numerous small particles (Rajoriya et al., 2018) and carcinogenic pollutants that are extremely harmful and toxic to animals and human beings (Liang et al., 2017). Conventional biological processes are not effective in removing these refractory organics, as most are bio-recalcitrant; therefore, it is necessary to develop an eco-friendly technique for treating textile dyeing wastewater prior to it being discharged into aquatic environments.

In recent years, various integrated methods, involving chemical,

biological, and physical oxidation treatments, have been employed to treat textile dyeing secondary effluent (Dasgupta et al., 2015; Fan et al., 2016; Morali et al., 2016). In particular, ozone (O₃) has been proven effective in oxidising dyes and refractory organic pollutants (He et al., 2018). O₃ targets electrophilic compounds that contain amine groups, aromatic structures, or double bonds (Nakada et al., 2007), and although the oxidation products may not be completely mineralised, they are more susceptible to biodegradation (Wilt et al., 2018). Therefore, O₃ treatment typically provides a high removal efficiency for pollutants (Mohapatra et al., 2014), and an increase in the biodegradability of recalcitrant compounds. However, toxic by-products may also be formed during O₃ treatment (Yan et al., 2016), and it is therefore necessary to develop a technique that combines O₃ treatment with other methods and identifies the toxicity of the wastewater. Currently, many catalysts (e.g. carbon aerogel and mesoporous carbon aerogel supported copper oxide catalysts) (Hu et al., 2016a, 2016b) and physical methods (e.g. ultrasound) (Benli and Bahtiyari, 2015) have been studied to catalyse O_3 , producing more OH, and these methods are efficient. However, the disadvantages of these integrated methods are their





Abbreviation list

Potassium permanganate KMnO ₄
Ozone O ₃
Permanganate combined with ozone KMnO ₄ -O ₃
Total organic carbon TOC
Chemical oxygen demand COD
Manganese dioxide MnO ₂
Textile dyeing plants TDPs
Biochemical oxygen demand BOD
Desmodesmus subspicatus D. subspicatus
Vibrio fischeri V. fischeri
Scanning electron microscope SEM
X-ray photoelectron spectroscopy XPS

high energy consumption and the complex preparation processes required for the catalysts.

In this respect, the use of potassium permanganate (KMnO₄) is a very promising technology for the advanced treatment of wastewater. It has many advantages, such as a high oxidation potential $(E_0 = 1.68 \text{ V})$, high stability span, wide pH scope, and it is comparatively simple and cheap to operate. In addition, it does not produce brominated or chlorinated by-products (Jiang et al., 2014a). Furthermore, it can oxidise a series of organic compounds in the presence of manganese dioxide (MnO₂), which is an insoluble reduction product of KMnO₄ (Jiang et al., 2014b). KMnO₄ principally removes contaminants via electron transfer, and enables the abstraction of hydride, hydrogen, and double bonds (Ding et al., 2018). However, an unpleasant colour is produced when large doses of KMnO₄ are used, limiting its use. Additionally, the oxidising capability of KMnO₄ cannot completely mineralise organic pollutants, especially pollutants without electron-rich moieties. Therefore, developing a KMnO₄ integrated technique would enable exploitation of its superior removal efficiency while avoiding its limitations.

Previous studies demonstrated that MnO₂ can cause O₃ to generate additional OH, which is advantageous for the removal of organic pollutants from wastewater (Liu et al., 2010). A study by Dong et al. (2010) conducted on drinking water reported a decrease in bromate formation of 26% after $KMnO_4$ and O_3 treatment (KMnO₄-O₃). The authors speculated that this result was related to intermediate products of KMnO₄ facilitating the decomposition of O₃ in water, and the low state of intermediate manganese oxidations that competed with bromide and consumed O_3 , thereby resulting in less bromate formation. Although KMnO₄–O₃ could provide an alternative process to enhance the removal of organic pollutants from textile dyeing wastewater, to date, no research has been conducted in this area. In addition, few researchers have studied whether the pollutant removal efficiency is consistent when different textile dyeing wastewaters with various compositions are involved, and the mechanism involved in KMnO₄-O₃ treatment and the toxicity of wastewater after treatment have not yet been fully confirmed. Prior to its application on an industrial scale, it is therefore necessary to confirm the efficiency and mechanism involved in KMnO₄-O₃ treatment of real textile dyeing effluents.

Therefore, in this research, $KMnO_4-O_3$ treatment was employed for the first time to treat different textile dyeing wastewaters with various compositions at four textile dyeing plants (TDPs). The effects of process parameters, including $KMnO_4$ dosage, O_3 dosage, reaction time, and pH conditions, on TOC and COD removal were examined and compared using O_3 treatment, $KMnO_4$ treatment, and integrated $KMnO_4-O_3$ treatment. The toxicities of the wastewaters after $KMnO_4-O_3$ treatment were also investigated, and the synergistic mechanism involved in $KMnO_4-O_3$ treatment was determined using modern analytical techniques. This study provides useful advice for the development of an advanced oxidation process that removes organic pollutants from textile dyeing wastewater.

2. Materials and methods

2.1. Wastewater sampling

To gain an understanding of the differences between wastewaters from various TDPs in Guangdong Province, China, four typical plants (located in Guangzhou, Dongguan, and Zhongshan) were studied. Basic information relating to the four TDPs is presented in Table 1 (including conventional indicators and the type of wastewater treatment processes, dyes, and textile materials used).

Samples were collected from secondary effluent on July 24, 2017. Ladle samplers were scheduled to sample 200 mL textile dyeing secondary effluent every 2 h during normal operation, to account for any variability of the effluent. The wastewater composite was placed in empty 5-L bottles, which were then completely filled with wastewater. After sampling, the bottles were sealed and transported to the laboratory at 277 K, where they were subsequently analysed.

2.2. Experiments using KMnO₄, O₃, and KMnO₄–O₃ treatment

Flowcharts for the different wastewater treatments are shown in Fig. 1. KMnO₄ crystals were dissolved in deionised water to prepare a stock KMnO₄ solution, and the sodium oxalate titration method was used to standardise the KMnO₄ solution (Wang et al., 2015). A sequence of experiments was conducted to test KMnO₄ oxidation in 1-L beakers, and the impacts of pH (2–7) and KMnO₄ dosages (0, 0.5, 1.0, 1.5, and 2.0 mM) on the removal of COD and TOC were evaluated. The solution was stirred continuously for 30 min (Jaafarzadeh et al., 2017). Subsequently, 20 mL of the supernatant, quenched with hydroxylamine, was extracted for TOC analysis, while samples for COD determination were analysed without quenching.

O₃ gas was prepared using a generator (Guangzhou Zeao Ozone Equipment Co., Ltd), producing O₃ through high-pressure ionisation of high-purity oxygen gas (99.7%). To generate the saturated O₃ solution, the O₃ gas was first pumped via Milli-Q water at a speed of 100 mL/min for 1 h. Once the solution had stabilised, O₃ was fed into a 1-L borosilicate glass reactor with 1 L of wastewater. The concentration of saturated O₃ solution was determined by indigo disulphonate spectrophotometry. Exhausts were adsorbed with 0.1 M sodium sulphite solution. Fig. S1 shows a schematic representation of the experimental design. Reactions were conducted under different conditions, including pH levels ranging from 3 to 11, reaction times of 0, 5, 10, 15, 20, 25, and 30 min, and O3 concentrations of 0, 5, 10, 15, and 20 mg/L. After each treatment, 20 mL of the supernatant, quenched with hydroxylamine, was used for TOC analysis, while the samples for COD determination were analysed without quenching.

According to the results of the experiments described above, 10 mg/L of O_3 , 1.5 mM of KMnO₄, and a reaction time of 30 min were used in KMnO₄–O₃ treatment. The reaction pH was set to 7 to prevent the treated effluent from neutralising prior to discharge. COD, TOC, biochemical oxygen demand (BOD), and toxicity were analysed, and two radical scavengers were added to the wastewater samples (benzoquinone and 2-propanol for $O_2 \cdot -/HO_2 \cdot -$ and OH, respectively) to investigate the oxidant species during KMnO₄–O₃

Table 1

Basic information about the four TDPs and different textile	dyeing wastewater treatments used.
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TDPs	TDP1	TDP2	TDP3	TDP4
Operating capacity (m ³ /d)	13,000	14,000	11,000	13,000
Main dyes	Disperse dyes	Mix dyes	Ionic dye, disperse dyes	Ionic dye, acid dye
Textile material	Cotton	Cotton	Cotton	Chemical fiber
Wastewater treatment process	PC-AD-AB-SF	AD-AB-MF	AD-AB-SB-SF	PC-AD-AB-BSB-
				ESB-BAF
pH	7.88 ± 0.02	6.65 ± 0.01	7.50 ± 0.00	7.48 ± 0.00
Colour	145	200	180	160
MLVSS (mg/L)	754 ± 21	776 ± 34	1668 ± 32	1890 ± 38
MLSS (mg/L)	53 ± 8	124 ± 12	618 ± 10	1140 ± 21
COD (mg/L)	192 ± 9	358 ± 25	328 ± 28	480 ± 20
TOC (mg/L)	42 ± 2	147 ± 2	111±3	82 ± 2
$BOD_5 (mg/L)$	24 ± 1	24 ± 3	28 ± 3	24 ± 1
EC50 to V. fischeri	4.7 ± 0.2	240.0 ± 4	72.0 ± 3	97.0 ± 4
EC50 to D. subspicatus	3.9 ± 0.8	4.9 ± 0.0	4.7 ± 0.2	3.2 ± 0.2

PC: primary clarifier; AD: aeration digester; AB: aeration basin; SF: sand-filtration; BSB: biochemical sedimentation basin; ESB: end sedimentation; BAF: biological aerated-filtration; MF: membrane filtration; SB: sedimentation basin.



Fig. 1. Flowcharts for different wastewater treatments.

treatment (Cheng et al., 2016). The alga *Desmodesmus subspicatus* (*D. subspicatus*) and the bacterium *Vibrio fischeri* (*V. fischeri*) were used to assess the toxicity of wastewater after treatment with KMnO₄, O₃, and KMnO₄–O₃. There were minimum changes in the pH value during this process, and the reaction temperatures of all experiments were controlled to room temperature (Nasuhoglu et al., 2018) (which was approximately $298 \pm 2 \text{ K}$) to avoid the need for a temperature regulating device. All experiments were conducted in triplicate.

2.3. Analytical method

A digital pH meter (pHS-3C, Leici, China) was used to measure pH; the potassium dichromate method was used to measure COD concentrations; mixed liquor volatile suspended solid (MLVSS) and mixed liquor suspended solids (MLSS) measurements were conducted using standard methods (APHA, 1998); TOC in the sample filtrate was determined using a TOC-VCPH analyser (Shimadzu, Japan); the concentration of BOD₅ was determined by the five-day cultivation method ($293 \pm 1 \text{ K}$); colour was determined using the dilution method; and the KMnO₄ concentration in the wastewater

was measured via UV detection at 525 nm after filtration using a 0.45 µm membrane. Atomic absorption spectrometry (AAS, Z-2000, Hitachi) was employed to determine the Mn content in sludge; a scanning electron microscope (SEM) (S-3400N, Hitachi, Japan) was used to view sludge surface morphologies; a laser particle size analyser (Eye Tech, Ankersmid, Netherlands) was used to examine the sludge particle sizes; infrared spectra were acquired using a Nicolet 6700 FT-IR spectrophotometer (Thermo Fisher, USA); X-ray photoelectron spectroscopy (XPS) (ESCALAB250, Thermo Fisher Inc.) was used to determine the valence states of Mn; and the binding energy was calibrated using the C1s peak at 284.8 eV.

2.4. Toxicity tests

Two different organisms, the alga *D. subspicatus* and the bacterium *V. fischeri*, were used to assess the toxicity of textile dyeing wastewater after different treatments. As the samples used for toxicity analysis had been quenched with hydroxylamine, there was no notable toxicity caused by oxidants. Toxicity for *V. fischeri* was determined according to GB/T15441-1995 using a Microtox Model DXY-2 Toxicity Analyser (Nanjing, China), and the ability of

wastewater to inhibit the bioluminescence of *V. fischeri* within 15 min of exposure was evaluated. A further toxicity test was conducted using *D. subspicatus*, following the GB/T 21805-2008 guidance. Samples and blank solutions were tested after 72 h of exposure, and toxicity was spectrophotometrically expressed via UV detection at 680 nm. Toxicity experiments were conducted in triplicate. EC_{50} (the concentration of wastewater that inhibits bioluminescence of *V. fischeri* within 15 min, or *D. subspicatus* growth by 50% after 72 h) was analysed using the linear interpolation method. EC_{50} was calculated as a dilution factor (x% of effluent), and the toxicity of each sample was further expressed in toxic units, TU (unitless), according to Eq. (1) (Raptis et al., 2014):

$$TU = 100/EC_{50}.$$
 (1)

3. Results and discussion

3.1. Performance of KMnO₄ treatment

As KMnO₄ exhibits a very high oxidation potential under acidic conditions, the effect of pH, within a range of 2–7, on the removal of TOC and COD by KMnO₄ was investigated (results are presented in Fig. 2a and b). As the pH increased, there was a significant decrease in the removal of TOC and COD; in contrast, the lowest TOC and COD concentrations were obtained at pH 2 for TDPs 1–4 (16, 78, 42, and 28 mg/L, and 60, 230, 130, and 126 mg/L, respectively). It was also determined that the concentrations at pH 3 were very close to those at pH 2. Electron exchange was determined using the aqueous pH of the reaction system. Under neutral and alkaline conditions, the oxidation potential of KMnO₄ was lower (Aleboyeh et al., 2009), and therefore, acidic conditions promoted the removal

of TOC and COD by KMnO₄ treatment.

Fig. 2c and d presents the impacts of KMnO₄ dosage on the removal of TOC and COD at pH 3 for 30 min. When the KMnO4 dosage increased from 0.13 to 2 mM, the concentrations of TOC and COD decreased to 16, 75, 41, and 28 mg/L and 61, 230, 128, and 126 mg/L. in TDP1-4, respectively. At high KMnO₄ dosages, more organic pollutants were oxidised and suspended matter was flocculated, which reduced the TOC and COD concentrations. However, TOC and COD's values at a KMnO₄ dosage of 2 mM were only marginally lower than those at a dosage of 1.5 mM. This can be attributed to the fact that Mn(III) or Mn(IV) intermediates were produced when the KMnO₄ dosage was excessive, hindering the reaction (Jiang et al., 2010). On average, 59% of TOC and 57% of COD were removed when the pH value was 3.0 and the KMnO₄ dosage was 1.5 mM. The removal of COD was higher than for pulp and paper wastewater treatment (which saw COD removal rates of only 43.8%) under the same conditions (Jaafarzadeh et al., 2017). However, the acidic conditions during the KMnO₄ treatment were inappropriate to treat textile dyeing wastewater.

3.2. Performance of O₃ treatment

Different influential factors were investigated during O_3 treatment. Concentrations of TOC and COD decreased as the pH increased from 3 to 9, but increased slightly as the pH increased from 9 to 11 (Fig. S2a-b). The lowest TOC and COD concentrations were obtained at pH 9 for TDPs 1–4 (23, 96, 95, and 46 mg/L, and 132, 232, 232, and 184 mg/L, respectively). The O_3 decomposition rate increased as the concentration of hydroxide ions increased because these ions react with O_3 molecules and produce OH (Ershov and Morozov, 2009). OH has a stronger oxidation potential (2.86 V) than O_3 (2.07 V), which elevates pH levels and reduces the



Fig. 2. Effects of pH and KMnO₄ dosage on TOC and COD removal by KMnO₄ for 30 min, with a KMnO₄ dosage of 1.5 mM at pH 3.

 O_3 concentration, but produces more radical species (Asghar et al., 2015). Although this is advantageous for TOC and COD removal, an excessive amount of OH can cause chain reactions between OH and \cdot OH or HO₂ ⁻, which reduces organic pollutant removal.

TOC and COD concentrations also decreased as the reaction time (Fig. S2c–d) and O_3 dosage (Fig. S2e–f) increased. However, there were almost no noticeable differences between the TOC and COD concentrations at O_3 dosages of 10 and 20 mg/L. On average, 35% of TOC and 39% of COD were removed at a pH of 9.0 and an O_3 dosage of 10 mg/L. Less TOC and COD were removed by O_3 under alkaline conditions than by KMnO₄ under acidic conditions; this is considered to be related to the intense oxidative ability of KMnO₄ and the high adsorption potential of MnO₂ for several organic pollutants (Liu et al., 2010). Owing to the extreme conditions required for O_3 (pH 9) and KMnO₄ (pH 3) treatment and the low removal efficiencies for TOC and COD, development of a more appropriate method is required. Combined O_3 and KMnO₄ treatment is thought to be a suitable method.

3.3. Performance of KMnO₄–O₃ treatment

KMnO₄-O₃ treatment was assessed in terms of TOC and COD removal (results are illustrated in Fig. 3a and b) and was found to be effective in treating different kinds of textile dyeing wastewater. Under neutral conditions, O₃ treatment was more effective than KMnO₄ at removing TOC, whereas KMnO₄ was more effective at removing COD. The concentrations of TOC and COD were lowered to 11, 62, 30, and 20 mg/L, and 24, 86, 90, and 76 mg/L, in TDP 1-4, respectively, after KMnO₄–O₃ treatment for 30 min. The removal efficiencies for TOC and COD (70% and 80%, on average) were better than for KMnO₄ alone (21% and 27%, on average) or O₃ alone (30% and 23%, on average). In addition, the KMnO₄-O₃ treatment under neutral conditions was even more effective than KMnO₄ treatment under strongly acidic conditions or O₃ under strongly alkaline conditions. Therefore, KMnO₄-O₃ treatment provided the combined advantages of both KMnO₄ and O₃ treatments. We consider that these results relate to the strong oxidative ability of KMnO₄ and O₃ and the insoluble reduction product (MnO₂) produced from



Fig. 3. Effects of different treatments at a KMnO₄ dosage of 1.5 mM and an O₃ dosage of 10 mg/L at pH 7 for 30 min.

KMnO₄, which significantly facilitates the oxidation kinetics of O₃ and adsorbs suspended organic matter. Ma and Graham (1999) also identified that dissolved Mn, present as either Mn(II) or Mn(IV) formed in-situ, catalyses O₃ to produce more OH. A further advantage is that the colour was almost completely removed following KMnO₄–O₃ treatment (Fig. S3).

As shown in Fig. 3c-d, the BOD/COD values for raw secondary effluent were 0.13, 0.26, 0.27, and 0.11 for TDPs 1-4, respectively. which indicates poor biodegradability. However, the KMnO₄-O₃ treatment considerably increased the biodegradability of the wastewater: BOD/COD values reached 0.68, 0.47, 0.43, and 0.33, respectively, which indicates that the wastewater was biodegradable following KMnO₄-O₃ treatment. We consider that organic pollutants with large molecular weights may have been broken down into compounds with smaller molecular weights that were more biodegradable, thereby resulting in the higher BOD/COD values (Jaafarzadeh et al., 2017). In the toxicity analysis (Fig. 3e and f), the initial values of TU for V. fischeri and D. subspicatus for TDPs 1-4 were 4.7, 240.0, 72.0, and 97.0 and 3.9, 4.9, 4.7, and 3.2, respectively. After KMnO₄–O₃ treatment, approximately 34.4–95.5% of the toxicity was removed; therefore, KMnO₄–O₃ was also shown to be effective in detoxifying wastewater. It should be noted that the different toxicities for V. fischeri and D. subspicatus after the KMnO₄, O₃, and KMnO₄–O₃ treatments can be attributed to the different toxicities of the degradation products used; however, these degradation products could not be identified in the complex mixtures.

3.4. Pollutant removal mechanism for KMnO₄–O₃ treatment

3.4.1. Morphology analysis of suspended solids

TDP 2 was chosen to study the pollutant removal mechanism for serious pollution. SEM images of sludge after different treatment processes are presented in Fig. 4a. Floc clusters were found to be aggregated in the raw suspended solid, and only a small amount of the suspended solid was crushed after individual KMnO₄ and O₃ treatments; therefore, these separate treatments had little effect on the suspended solid. However, there was a significant change in the morphology of the suspended solid after KMnO₄–O₃ treatment (compared with the raw suspended solid), and the suspended solid floc was almost completely broken down. Similar results can be seen from the particle size distribution of the suspended solid (Fig. 4b): after KMnO₄ $-O_3$ treatment (d50 = 132 µm), the suspended solid particles were smaller than those in the raw suspended solid ($d50 = 344 \,\mu m$). We consider that these results relate to enhanced oxidation of pollutants on the suspended solid surface and in the aqueous phase due to the strong oxidation ability of KMnO₄ and O₃. In this respect, the suspended solid was easily disturbed by the stirring action of O₃ molecule bubbles. Furthermore, KMnO₄ flocculated the fine particles of suspended solids and organic pollutants, resulting in a proportion of floc matter remaining in the sludge (Liu et al., 2010; Li et al., 2013).

3.4.2. XPS analysis

According to our experiment, 12.34% of Mn remained in the sludge, 5.30% existed in the wastewater, and an amount exceeding 80% was fully utilised during the KMnO₄–O₃ treatment. Therefore, XPS spectra of the suspended solid after KMnO₄ and KMnO₄–O₃ treatment were used to determine the MnO_x catalytic mechanism. Table 2 presents the binding energies and relative intensities based on deconvolution of the Mn 2p XPS spectra. A spin-orbit doublet of Mn 2p_{1/2} and Mn 2p_{3/2} was found in the Mn 2p spectrum (Fig. 5), with a binding energy gap of 11.7 ± 0.1 eV. Three peaks could be seen in the deconvoluted Mn 2p_{3/2} spectrum, with binding energies of 640.6, 641.7, and 642.7, corresponding to Mn(II), Mn(III), and





Fig. 4. (a) SEM images of the sludge and (b) particle size distribution of the sludge for the following reaction conditions: $[KMnO_4] = 1.5 \text{ mM}$, $[O_3] = 10 \text{ mg/L}$, pH = 7, and reaction time = 30 min.

Mn(IV), respectively (Tang et al., 2014; Huang et al., 2017). Following the KMnO₄–O₃ reaction, considerable changes were observed in the relative intensities of Mn(II), Mn(III), and Mn(IV), which became 26:30:44; more Mn(II) and Mn(IV) remained in the suspended solid, catalysing O₃ to produce further reactive oxygen species. Mn(VII), OH, $O_2 \cdot -/HO_2 \cdot -$, and O_3 were the main reactive oxygen species in the KMnO₄-O₃ treatment, and Mn(VII) was the most influential species. Individual KMnO₄ treatment contributed to the removal of 27% of COD and 21% of TOC, while individual O₃ treatment removed 23% of COD and 30% of TOC. Quenching experiments showed (see Fig. 6a) that after extraction of OH, the $O_2 \cdot - /HO_2 \cdot -$ contribution was caused by O_3 alone, and that OH contributed to the removal of 14% of COD and 15% of TOC, whereas $O_2 \cdot - /HO_2 \cdot -$ contributed to the removal of 6% of COD and 4% of TOC. These results show that the manganese intermediate catalysing O₃ process contributes to the removal of more than 20% and 19% of COD and TOC respectively.

3.4.3. Fourier transform infrared spectroscopy (FTIR) analysis

FTIR was used to analyse the sludge both before and after $KMnO_4-O_3$ treatment (results are shown in Fig. 6b). A sharp peak was observed at 1042 cm⁻¹ corresponding to C–O (Pavia et al., 2008) and related to carboxylic acid, alcohols, and esters, which

Table 2	
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XPS results for Mn 2p_{3/2} in sludge samples.

Sludge	Mn 2p _{3/2} binding	g energy (eV)	Relative intensity Mn(II)/Mn(III)/Mn(IV)	
	Mn(II)	Mn(III)	Mn(IV)	
KMnO ₄ treatment KMnO ₄ -O ₃ treatment	640.6 640.6	641.7 641.7	642.7 642.7	16:46:38 26:30:44

70

60

1042



Fig. 5. Mn 2p regions of XPS spectra for the sludge after (a) KMnO₄ treatment and (b) $KMnO_4 - O_3$ treatment. Reaction conditions: $[KMnO_4] = 1.5 \text{ mM}, [O_3] = 10 \text{ mg/L}, \text{ pH} = 7$, and reaction time = 30 min.

indicates that these organic pollutants were removed successfully by the $KMnO_4-O_3$ treatment. A peak was also observed at 1644 cm⁻¹, corresponding to C–O stretching vibrations (amide I) (Chon et al., 2012), indicating that compounds containing an amide functional group can be coagulated by KMnO₄–O₃ treatment. A C–H band at 2923 cm⁻¹ was also determined, corresponding to the alkanes group (Ngamlerdpokin et al., 2011). The -OH group and Hbonded group found between 3200 and 3400 relate to metal hydroxides, amines, and carboxylic acid (Pavia et al., 2008). The complexity of the textile dyeing sludge was therefore confirmed by the various functional groups present in the FTIR spectra.

The presence of various functional groups in the sludge revealed that the coagulation mechanism of KMnO₄ may contribute to the removal of organic compounds. Liu et al. (2010) also found that MnO₂ made a substantial contribution of 65% to the removal of dissolved organic carbon. Our result also supports the findings of Li et al. (2013), who observed that KMnO₄ greatly enhanced coagulation for the removal of dissolved organic carbon from the biotreated effluents of textile dyeing wastewater.

3.5. Application prospects

Currently, O₃ is used to treat wastewater in many large-scale and industrial applications. However, the efficiency limit of this technique has been reached. If KMnO₄ were added during this process, the pollutant removal efficiency could be significantly improved. the toxicity of wastewater could be reduced, and the biodegradability could be considerably increased. Moreover, post-treatment adjustments to the wastewater would not be needed because the KMnO₄-O₃ treatment is efficient under neutral conditions. The wastewater processing costs could also be greatly reduced. However, to obtain the appropriate engineering costs, future research would need to include large-scale field studies. Therefore, the KMnO₄–O₃ integrated method will hopefully be employed in largescale and industrial applications.

4. Conclusions

KMnO₄-O₃ treatment was performed to treat different textile dyeing wastewaters with various compositions at four TDPs. The effects of process parameters on TOC and COD removal and the



1000 2000 2500 3000 3500 500 1500 Wave number (cm⁻¹) Fig. 6. (a) Average removal efficiencies for TOC and COD at four TDPs after quenching OH and $O_2 \cdot /HO_2 \cdot$ radicals during O_3 and KMnO₄-O₃ treatments. (b) FTIR analyses of the sludge. Reaction conditions: [KMnO₄] = 1.5 mM, [O₃] = 10 mg/L, pH = 7, and reaction time = 30 min.

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synergistic mechanism involved in KMnO₄-O₃ treatment were examined. The toxicity of the wastewater was also investigated. This study represents the first report showing that KMnO₄-O₃ treatment under neutral conditions is more effective (i.e. reductions of 70% and 80% for TOC and COD, respectively) than KMnO₄ treatment under strongly acidic conditions (21% and 27% reductions, respectively) or O₃ treatment under a strongly alkaline conditions (30% and 23% reductions, respectively). Therefore, the integrated KMnO₄ and O₃ treatment was found to have synergetic and complementary advantages for removing organic pollutants. Moreover, 34.4-95.5% of the toxicity was removed and the biodegradability was considerably increased (to 0.33-0.68) after KMnO₄-O₃ treatment.

SEM, particle size, and FTIR results indicate that the oxidation of pollutants on suspended solid surfaces and aqueous phases was increased under the stirring action from O_3 molecule bubbles, and KMnO₄ and its intermediate oxidations enhanced coagulation to remove fine particle sizes from suspended solid and organic compounds. Furthermore, XPS results indicate that the valence state of manganese changed after KMnO₄–O₃ treatment, suggesting that manganese oxides catalyse O_3 to produce more reactive oxygen species, which is favourable for degrading pollutants in textile dyeing wastewater. The quenching experiment also indicates that the manganese oxides catalyse the O_3 process, contributing to the removal of 20% of COD and 19% of TOC. Therefore, KMnO₄–O₃ treatment was shown to be a promising advanced oxidation process for the treatment of textile dyeing wastewater.

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