Retention–oxidation–adsorption process for emergent treatment of organic liquid spills

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ABSTRACT

The feasibility and effectiveness of retention–oxidation–adsorption process (ROA) for the elimination of organic contaminants induced by chemical accidents were investigated in this study. Organobentonites (DTMA-, TTA-, CTMA- and OTMA-bentonite), potassium ferrate (Fe(VI)), ozone and granular activated carbon (GAC) were used as rapid and efficient materials in the treatment and recovery of organic liquid spills. Results indicated that the retention capacities of organobentonites (especially CTMA-bentonite) were much higher than that of natural bentonite towards the chosen organic compounds. Additionally, pH, oxidant dosage, initial concentration of contaminant and chemical structure had significant influences on the effectiveness of the oxidation process. In a pilot-scale experiment, the ferrate/GAC (F/G) and ozone/GAC (O/G) processes made a comparatively good performance in the treatment of wastewater containing aniline or nitrobenzene, with the removal efficiencies of the contaminants greater than 80%. Overall, the ROA process showed a high efficiency and steady operation in the removal of hazardous organic liquids and subsequent clean up of the contaminated site.

1. Introduction

In recent years, there has been growing concern in China about the widespread occurrence of chemical incidents in industry and road transport [1]. Every year, sudden and unexpected contamination events (accidental leakage, spills, explosions, etc.) put large numbers of the public in the danger of exposure to hazardous organic pollutants (benzene, nitrobenzene, petroleum, etc.), which account for about 34% of the total involved pollutants [2]. Since the accident scenes and contaminants varied, the systematic study of remediation technologies and processes seems to be very difficult and necessary, especially in China.

When chemical incidents take place accidently, response actions must be quick and accurate to minimize the impact of the contaminants [3]. The method of retention is considered to be one of the most common processes for the removal of hazardous organic liquids and subsequent cleanup of the contaminated site, and many types of sorbents are developed accordingly. Among them, organobentonites, normally synthesized by cationic surfactants and bentonite with cationic exchanging, are widely used as effective sorbents for organic contaminants and numerous stud-

ies have investigated their mechanisms in the past decades [4–6]. Ozonation [7–10] and ferrate oxidation [11–16] have also shown their own advantages in removal of a wide range of organic pollutants both in wastewater and drinking water. Meanwhile, activated carbon has proven to be one of the most effective adsorbent materials, which is widely used in the elimination and recovery of hazardous organic pollutants [17–19]. However, more information remains to be gathered to evaluate their application in organic contamination treatment.

Considering the ideas addressed above, this research chose eight organic compounds as representative pollutants on the basis of their predominant occurrence in chemical accidents, including aromatics (benzene, toluene, *o*-xylene, nitrobenzene, chlorobenzene, aniline) and chlorophenols (2,4-dichlorophenol, 2,4,6-trichlorophenol), and introduced an effective retention–oxidation–adsorption process for the emergent treatment of organic liquid spills induced by chemical accidents. The present study was conducted to investigate the effectiveness and the influence factors (sorbent material, solution pH, oxidant dosage, initial concentration of contaminant, chemical structure, etc.) of retention–oxidation–adsorption process, and to try to develop a mobile treatment system based on the ROA process for environmental emergency management departments, corporations that deal with organic chemicals, etc., which could be applied for the treatment of chemical incidents that occur in industry and road transport.

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2. Experimental

2.1. Chemicals

Benzene, toluene, o-xylene, nitrobenzene, chlorobenzene, aniline, 2,4-dichlorophenol, 2,4,6-trichlorophenol were purchased from Sinopharm Chemical Reagent Co. (China) and were of 99% purity or higher. Dodecyltrimethylammonium bromide (DTMAB), tetradecyltrimethylammonium bromide (TTAB), cetyltrimethylammonium bromide (CTMAB) and octadecytrimethylammonium bromide (OTMAB) of analytical grade were obtained from Shanghai Chemical Co., China.

The natural bentonite composed primarily of Ca^{2+}-montmorillonite was obtained from Inner Mongolia, China. The bentonite BET-N_2 surface area, organic carbon content, and cation exchanged capacity (CEC) was $73.3 \, m^2 \, g^{-1}$, 0.17%, and $108 \, cmol \, kg^{-1}$, respectively.

Potassium ferrate (97%) was purchased from Sigma–Aldrich Co., USA. Ozone was generated from oxygen by an ozone generator (NPL5W, Green Continent Co., China) with a maximum ozone production rate of $5 \, g \, h^{-1}$. All other chemicals were of reagent grade, and used as received. Doubly distilled water was used throughout the study except in the pilot-scale experiment.

2.2. Batch retention experiment

In this investigation, DTMA-bentonite, TTA-bentonite, CTMA-bentonite, OTMA-bentonite and natural bentonite were chosen as sorbents. The organobentonites were synthesized with the following procedure [20]: 30.0 g natural bentonite was mixed with 500 mL of an aqueous solution containing 9.99 g DTMAB, 10.9 g TTAB, 11.8 g CTMAB or 12.7 g OTMAB, respectively, equal to 100% of bentonite's CEC. The mixture was stirred at 60 °C for 4 h. The product was separated from water by vacuum filtration and washed with distilled water six times, then dried at 70 °C for 12 h. Finally, the organobentonite was grounded to pass a 100 mesh sieve.

The retention capacity measurements were undertaken as follows [21]: 200 mL of pure pollutant liquid was poured into a 250 mL pyrex glass beaker. 5.0 g of sorbent was weighed and the value recorded. The sorbent material was spread evenly on a filter paper, placed into a circular brass wire mesh ($2 \, mm^2$) basket (Φ $5.0 \times 8.0 \, cm$), and then lowered into the beaker so that the sorbent was completely covered by the liquid. After 15 min of immersion,

the basket with the sorbent was hung up for about 5 min to allow the excess liquid to be drained off. Then, the saturated sorbent was transferred to a suitable pre-weighed dish and weighed. Additionally, to evaluate the effect of retention time between the chosen pollutants and sorbents, the experiments were conducted with the same procedure other than the volume of pure organic liquid was reduced to 25 mL and the contact time varied from 1 to 30 min. All tests were carried out in triplicate.

The retention capacity of the sorbents and the retention rate of organic liquids on a weight basis were calculated as follows: retention capacity $(g \, g^{-1}) = (S_1 - S_0)/S_0$, retention rate $(\%) = (S_1 - S_0)/S_2 \times 100$, where S_0 is the initial dry weight of sorbent, S_1 is the weight of the saturated sorbent, S_2 is the weight of the pure organic liquid.

2.3. Degradation by ozonation and ferrate oxidation

The experimental set-up used for wastewater treatment by ozonation consisted of a pressurized oxygen gas cylinder, an ozone generator, a gas flow meter, and a reaction vessel (Φ $5 \times 50 \, cm$) of about 1 L in volume. The reactor was equipped with a gas diffuser at the bottom to sparge the ozone/oxygen stream into the water. The exhaust gas vented from the top of the reactor was captured in a pair of adsorption bottles containing 2% (w/v) KI solution. 500 mL of a solution that contained different contaminants at various concentrations was adjusted to the desired pH value by using either sulfuric acid or sodium hydroxide, and added to the reactor before the ozone bubbled. In this work, the ozone dosage added into the system was controlled between $5.59 \, mg \, min^{-1}$ and $35.1 \, mg \, min^{-1}$ by a gas flow meter. Samples were collected at fixed intervals and $1.0 \, mol \, L^{-1} \, Na_2SO_3$ was added to remove the residual ozone and organic radicals prior to analysis.

Batch Fe(VI) oxidation experiments were conducted in 100 mL conical flasks in which 50 mL of a solution was stirred vigorously by magnetic stirrer. $1.0 \, mol \, L^{-1} \, Na_2SO_3$ was added into the samples immediately to stop any further reaction. After the quenching, samples were centrifuged at 8000 rpm for 10 min, and then filtered with 0.45 μm filters before analysis.

All the experiments were conducted in triplicate at room temperature (23 ± 2 °C). The elimination of the target pollutant through volatilization was evaluated and deducted. Removal is defined as $(\%) = (C_0 - C)/C_0 \times 100$, where C_0 is the initial contaminant concentration or TOC.
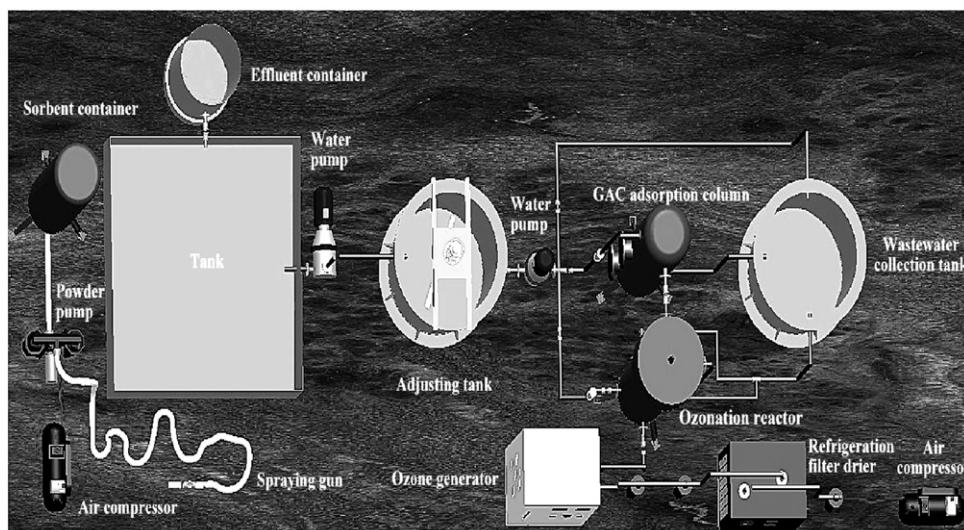

Fig. 1. The schematic diagram of the retention–oxidation–adsorption system.

2.4. Pilot-scale experiment

According to the results of the lab experiment, a pilot-scale experiment was performed to simulate the treatment and recovery of an accidental organic liquid spill. The indoor temperature was about $20 \pm 2\,^\circ C$ during the period of the experiment. Fig. 1 shows the schematic diagram of the retention–oxidation–adsorption system used in this study.

The pilot-scale retention experiments were conducted in a tank $(2 \times 2 \times 0.5\,m)$ made of polyurethane. With the consideration of environment protection, a certain concentration (about $50\,g\,L^{-1}$ with most of the pollutant remained undissolved) of effluent containing the chosen pollutant (aniline or nitrobenzene) was used as the treatment target instead of pure organic liquid. When all the effluent stored in a polyurethane cylinder ($\Phi\ 0.5 \times 0.5\,m$, working volume 20 L) was gradually released through a needle valve into the tank, and spread over most of the closed area, the CTMA-bentonite was quickly transferred through a plastic flexible pipe from its container, a stainless steel cylinder ($\Phi\ 1.0 \times 2\,m$), and spread evenly across the polluted area by an air-operated powder pump (650780-X, Ingersoll Rand Company, USA). The consumed weight of CTMA-bentonite was calculated by the product of jet velocity ($kg\,min^{-1}$) and handling time (min).

After that, the waste solid was removed for final disposal and tap water was used to flush the contaminated site. All the wastewater was pumped directly into an adjusting tank ($\Phi\ 2.0 \times 1.0\,m$), mixed with tap water for a working volume of $2.0\,m^3$ and conditioned by agitation (300 rpm) for 4 h. Before further treatment, a small sample was withdrawn and the concentration of the pollutant was measured subsequently. Then, the wastewater was treated by Fe(VI) oxidation or ozonation. In Fe(VI) oxidation, an optimal amount of potassium ferrate was added directly into the adjusting tank, reacting with the contaminant in the condition of agitation (300 rpm) for 20 min. The ozonation system consisted of an air compressor, a refrigeration filter drier, and an ozone generator (maximum ozone output: $100\,g\,h^{-1}$) supplied by Shandong Zhiwei Science and Technology Co., China. The wastewater with a flow rate of $1\,m^3\,h^{-1}$ was pumped into a stainless steel reactor ($\Phi\ 0.5 \times 2\,m$) which was a magnification of the lab-scale reactor. The effective volume of the reactor and the actual ozone production were approximately 300 L and $76\,g\,h^{-1}$, respectively.

Both of the oxidation processes were followed by an activated carbon adsorption process since most of the pollutants could not be completely degraded. The GAC adsorption column ($\Phi\ 0.5 \times 1.5\,m$) consisted of a 30 cm high gravel layer in the bottom and a 100 cm carbon layer above the gravel layer. The flow rate of the effluent in the packed bed was fixed at $1.0\,m^3\,h^{-1}$. The pollutant concentration was measured at the inlet and outlet of each reactor by the methods mentioned below.

2.5. Analytical methods

The concentration of Fe(VI) in the aqueous solution was determined by monitoring the absorbance at 510 nm using a GBC Cintra 303 spectrophotometer (Australia) [22]. The ozone concentration in the inlet and outlet gas was determined by a standard iodometry method [23]. The dissolved ozone in solution was measured by the indigo method [24]. TOC was measured by a TOC analyzer (Shimadzu TOC-V$_{CPH}$, Japan) and pH was measured by a PHSJ-3 F instrument (Shanghai Precision & Scientific Instrument Co., China). The determination of benzene, toluene and o-xylene was carried out by a gas chromatograph (FULI 9790, Fuli Analytical Instrument Co., China) equipped with a SE-30 capillary column (30 m × 0.32 mm, 0.33 μm film), a headspace sampler DK3001A (Zhongxinghuili Science and Technology Development Co., China), and an ECD detector according to the method
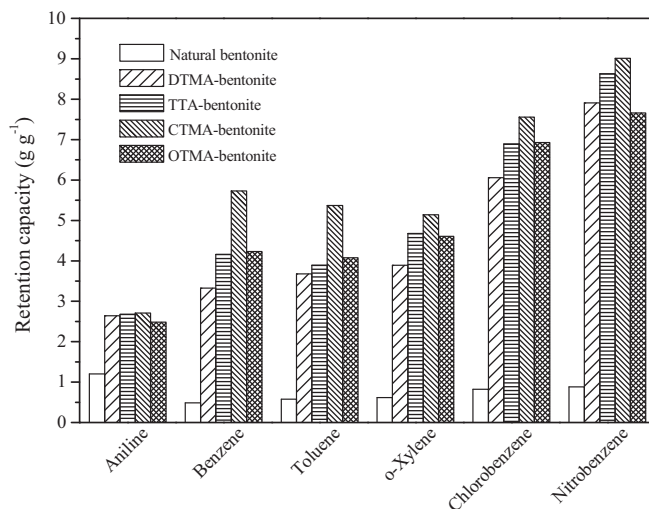

Fig. 2. The retention capacity ($g\,g^{-1}$) of natural bentonite and organobentonites towards the chosen pollutants.

reported by Menendez et al. [25]. The other compounds were measured by high performance liquid chromatography (HPLC) using an Agilent instrument (1200 series, Agilent, USA) equipped with an Eclipse XDB-C18 column (25 μm particle size, 250 × 4.6 mm i.d.). The proportions of the specific mobile phase and UV detection wavelength used for each compound by HPLC were as follows: nitrobenzene, methanol/water-70/30 (v/v), UV-262 nm; chlorobenzene, methanol/water-80/20 (v/v), UV-212 nm; aniline, methanol/water-40/60 (v/v), UV-280 nm; 2,4-dichlorophenol, methanol/water-80/20 (v/v), UV-280 nm; 2,4,6-trichlorophenol, methanol/water-80/20 (v/v), UV-295 nm. The flow rate was $1\,mL\,min^{-1}$, and injection volume was $20\,\mu L$.

3. Results and discussion

3.1. Retention by organobentonites

3.1.1. Retention capacity of organobentonites

As shown in Fig. 2, the retention capacities of organobentonites were much higher than that of natural bentonite towards the chosen organic compounds, and compared with other three organobentonites (DTMA-, TTA- and OTMA-bentonite), CTMA-bentonite stood out as the best performing sorbent. As for CTMA-bentonite, benzene, toluene, o-xylene and chlorobenzene showed similar retention capacities (5.14–5.73 $g\,g^{-1}$), while aniline (2.71 $g\,g^{-1}$) and nitrobenzene (9.01 $g\,g^{-1}$) showed the lowest and highest retention capacities, respectively. This trend coincides with the hydrophobicity of the chemicals and may be greatly influenced by the viscosity and other factors [5].

3.1.2. Effect of retention time

Based on the retention capacity test, the effect of retention time between toxic chemicals and CTMA-bentonite was investigated. The simulated leakage volume of organic liquid was 25 mL and the dosage of CTMA-bentonite was fixed at 200 $g\,L^{-1}$, which was more than the theoretical optimal value.

As shown in Fig. 3, the CTMA-bentonite adsorbed the pollutants (aniline, benzene, chlorobenzene and nitrobenzene) very quickly, and the retention rates were all over 80% within 4 min and changed little after 6 min. It was noticeable that about 50% of the hazardous chemicals were retained in 1 min, which indicates the CTMA-bentonite could be used as a rapid and efficient material for preventing the dispersal of hazardous organic liquids.
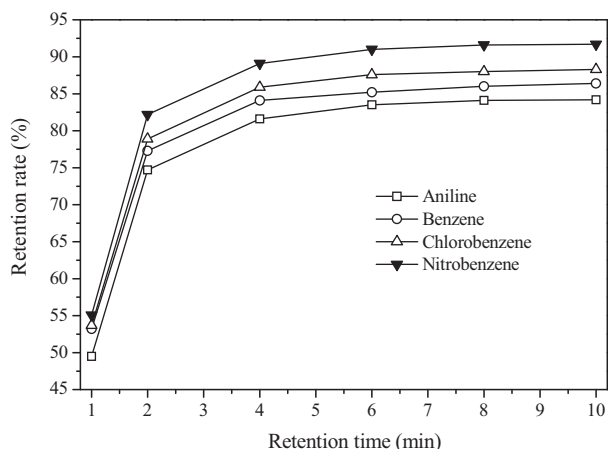
Fig. 3. Effect of retention time on the retention rate of organic liquid by CTMA-bentonite.

3.2. Ozonation and ferrate oxidation

3.2.1. Effect of initial pH value

Effect of initial pH values of the aqueous solution on the degradation of aniline was investigated at different pH in the range of 3.0–11.0 with aniline initial concentration of 10.7 mM. The ozone dosage was kept constant at 26.5 mg min^{-1}. As shown in Fig. 4(a), there was an increase in 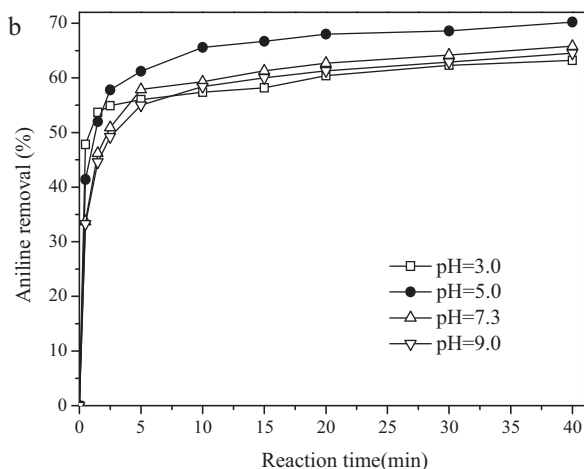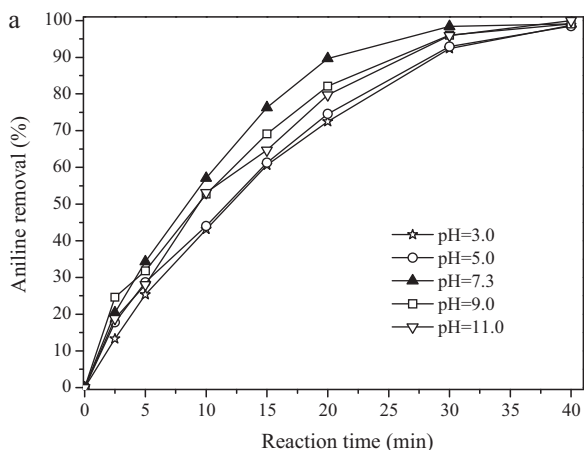the degradation efficiency with an increasing pH value in the range of 3.0–7.3 (after which a decrease was observed). When the pH value was 7.3 (the initial pH value without adjustment), the degradation of aniline reached 90% within 20 min. The intermediate products can also influence the reactions by consuming ozone and •OH [26]. Sarasa et al. [27] have confirmed that nitrobenzene is the major aromatic by-product formed after ozonation of aniline, which is one of the target compounds for remove in this study. Under the conditions of this experiment, nitrobenzene was gradually accumulated in solution, and was detected in higher concentrations at acidic conditions. The final concentrations of nitrobenzene during the reactions at pH 3.0, 5.0, 7.3, 9.0 and 11.0 were 3.2×10^{-2}, 2.1×10^{-2}, 1.1×10^{-2}, 5.3×10^{-3} and 1.2×10^{-2} mM, respectively. Meanwhile, the TOC removal in 40 min at pH 3.0, 5.0, 7.3, 9.0 and 11.0 was 16%, 25%, 34%, 41% and 28%, respectively. It can be seen that a considerable high pH (pH 7.3) of the solution can benefit the mineralization of aniline.

The influence of pH on the Fe(VI) oxidation process for aniline degradation was investigated with potassium ferrate concentration of 15.1 mM. As presented in Fig. 4(b), the degradation efficiencies of aniline at different pH values showed no significant differences. When the pH value was 3.0, 5.0, 7.3 and 9.0, the degradation efficiency of aniline after 20 min of treatment was 61%, 68%, 62% and 60%, respectively. At the same time, the TOC removal at pH 3.0, 5.0, 7.3 and 9.0 was found to be 27%, 31%, 22% and 20%, respectively. Nitrobenzene was also detected as a by-product during the ferrate oxidation of aniline, and its concentration increased quickly in the first 10–20 min, then decreased slowly in the residual time. For example, when the initial pH value was 5.0, the nitrobenzene concentration reached its maximum value (4.2×10^{-2} mM) in the first 15 min, and its final concentration after 40 min of treatment was 3.0×10^{-2} mM. The solution pH also played an important part in the formation and degradation of nitrobenzene. The final concentrations of nitrobenzene at pH 3.0, 7.3 and 9.0 were 4.4×10^{-3}, 1.5×10^{-2} and 3.7×10^{-2} mM, respectively. As for Fe(VI), its reactivity with reactants varies significantly with pH [28]. It is highly unstable but more powerful at pH < 6. In contrast, it becomes more chemically stable but has a weaker oxidizing ability at pH > 9 [29]. In these experiments, the final decomposition rates of ferrate at pH 3.0, 5.0, 7.3 and 9.0 were 87%, 72%, 48% and 44%, respectively. Since the removal of aniline showed no significant difference between pH 5.0 and 7.3, a pH of 7.3 was chosen as the optimal pH for Fe(VI) oxidation of aniline in this study. By avoiding the pH regulation there is a considerable saving of time and money, which is very important for wastewater treatment in cases of emergency.

3.2.2. Effect of oxidant dose

The dosage of oxidant was found to be the most important factor in achieving better degradation of aniline. To evaluate the effect of ozone dose on the degradation of aniline, experiments were conducted over a range of ozone doses of 5.59–35.1 mg min^{-1} under the condition of optimal pH 7.3 and the results were shown in Fig. 5(a). It was clear that the degradation efficiency of aniline increased with the increasing ozone dosage. When the ozone dosages were 5.59, 21.6, 26.5, 31.1 and 35.1 mg min^{-1}, the aniline removal in 20 min was found to be 33%, 75%, 90%, 96% and 98%, respectively. The TOC removal was 8.8%, 17%, 20%, 33% and 36%, respectively. During the reaction time, the average ozone fluxes in the outlet gas were about 0.024, 0.24, 1.0, 2.3 and 4.7 mg min^{-1}, so the utilization rate of ozone decreased with the increasing ozone dosage. It was also found that the final nitrobenzene concentration in solution decreased when ozone dosage was higher than 21.6 mg min^{-1}, though its maximum concentration during the reaction increased with the increasing ozone dosage. The final nitrobenzene concentrations with the ozone dosages of 21.6, 26.5, 31.1 and 35.1 mg min^{-1} were 1.1×10^{-2}, 1.5×10^{-2}, 4.2×10^{-3}, 3.7×10^{-3} mM, respectively. Therefore it can be concluded that

Fig. 4. Effect of initial pH on the degradation efficiency of aniline by ozone (a) and ferrate (b). [aniline] = 10.7 mM, [ozone] = 26.5 mg min^{-1}, [ferrate] = 15.1 mM.
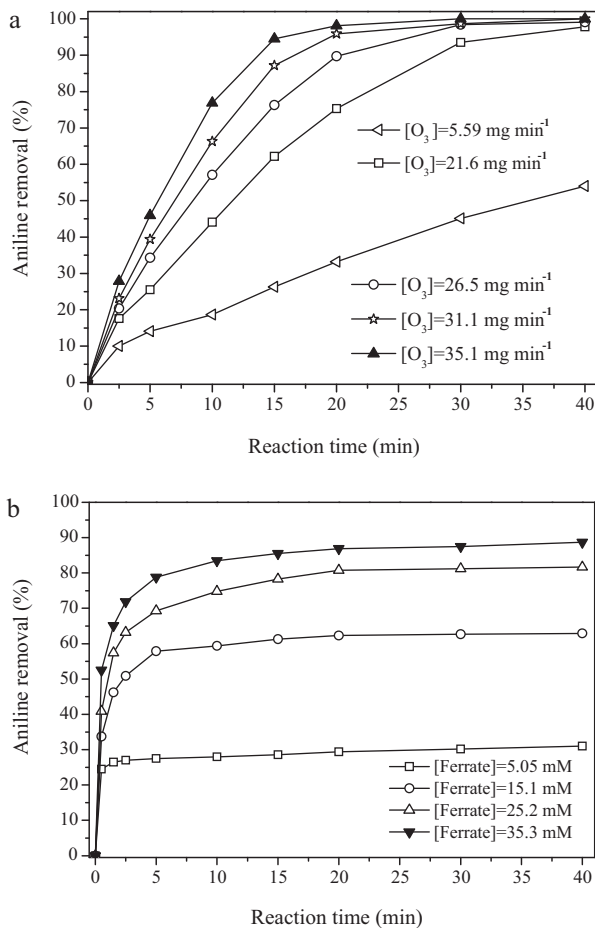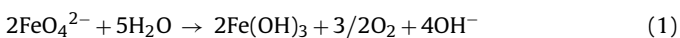
Fig. 5. Effect of oxidant dosage on the degradation efficiency of aniline by ozone (a) and ferrate (b). [aniline] = 10.7 mM, pH = 7.3.

Fig. 6. Effect of initial contaminant concentration on the degradation efficiency of aniline by ozone (a) and ferrate (b). pH = 6.9–7.3, [ozone] = 31.1 mg min^{-1}, [ferrate] = 25.2 mM.

an appropriate ozone dosage can accelerate the reaction rate of ozonation and shorten the overall reaction time.

The degradation efficiencies with different dosages of Fe(VI) were also tested under the condition of optimal pH 7.3. As shown in Fig. 5(b), the aniline degradation efficiency increased by increasing the Fe(VI) dosage. When the Fe(VI) dosage was 25.2 mM, 81% of aniline was degraded after 20 min. The degradation efficiency of aniline changed little after 20 min and about 69% of aniline was degraded during the first 5 min. It was found that the decomposition rates of Fe(VI) in 5, 20 and 40 min were 45%, 56% and 65%, respectively. However, when the Fe(VI) dosage was 35.3 mM, the degradation efficiency of aniline after 20 min of treatment was 87%, and the decomposition rates of Fe(VI) in 5, 20 and 40 min were 47%, 66% and 79%, respectively. In this experiment, the final nitrobenzene concentration and TOC removal both increased slightly with the increasing of Fe(VI) dosage. With a Fe(VI) dosage of 5.05, 15.1, 25.2 and 35.3 mM, the final nitrobenzene concentrations were 4.1×10^{-3}, 3.0×10^{-2}, 3.5×10^{-2}, 4.9×10^{-2} mM, while the TOC removals after 40 min of treatment were 16%, 22%, 27% and 33%, respectively. This can be explained by the kinetics of Fe(VI) ion reactions in aqueous solutions. In general, the Fe(VI) ion decrease is caused by its reaction with organic compounds and by its self-decay. The spontaneous decomposition of Fe(VI) in an aqueous solution is described by the following reaction (Eq. (1)) [30].

$$2FeO_4{}^{2-} + 5H_2O \rightarrow 2Fe(OH)_3 + 3/2O_2 + 4OH^- \tag{1}$$

The decomposition rate of Fe(VI) is dependent upon pH, initial Fe(VI) concentration, co-existing ions and temperature [31,32]. The iron(III) hydroxide formed upon decomposition (reaction (1))
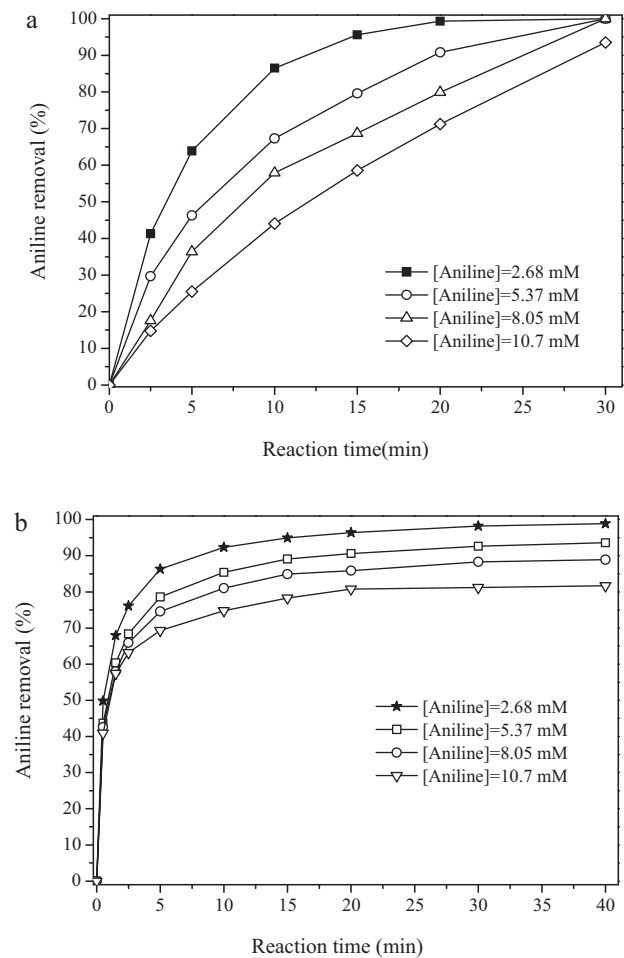
also controls the decomposition of Fe(VI) [33]. When the concentration of Fe(VI) is higher than the optimal dose, its reaction with water cannot be neglected [14]. Considering economic and technical issues, the optimal dose of Fe(VI) to be added into the aniline solution with the concentration of 10.7 mM was 25.2 mM (the molar ratio of Fe(VI) to aniline = 2.4).

3.2.3. Effect of initial contaminant concentration

The effects of the initial contaminant concentrations on the oxidation processes were investigated. In these experiments, the initial pH values varied in the range of 6.9–7.3 due to different aniline concentrations. Considering the mass transfer and economic efficiency, ozone dosage was fixed at 31.1 mg min^{-1}. Fig. 6(a) shows the results of aniline degradation by ozonation for various initial aniline concentrations. Clearly, a higher initial concentration of aniline in the range of 2.68–10.7 mM resulted in a lower degradation efficiency and TOC removal in 30 min of oxidation. However, as the initial aniline concentration increased, the ozone utilization rate and final nitrobenzene concentration in solution increased significantly. When the initial aniline concentration increased from 2.68 to 10.7 mM, the average ozone flux in the outlet gas decreased from 6.8 to 2.3 mg min^{-1}, and the final nitrobenzene concentration in 30 min increased from 0 to 2.9×10^{-2} mM.

As shown in Fig. 6(b), when the Fe(VI) dosage was 25.2 mM there was a small increase in degradation efficiency as the initial concentration of aniline decreased. The degradation efficiency of aniline with an initial concentration of 2.68 mM was 96%, while 81% of

Table 1
Half life and pseudo-first-order rate constant for selected target compounds by ozonation.

Compound	pH	$t_{1/2}$ (min)	Observed 1st order reaction rate constant, k (min^{-1})	R^2
Nitrobenzene	5.7	5.1	0.136	0.992
Chlorobenzene	6.1	4.4	0.158	0.996
Toluene	5.6	4.3	0.160	0.991
Benzene	5.8	2.1	0.331	0.998
o-Xylene	5.6	2.0	0.353	0.999
2,4-Dichlorophenol	5.4	1.3	0.522	0.997
Aniline	6.6	1.1	0.643	0.997
2,4,6-Trichlorophenol	4.5	0.9	0.791	0.995

Table 2
The optimal molar ratio of ferrate to contaminant and its corresponding degradation efficiency by ferrate oxidation.

Compound	pH	The optimal molar ratio of ferrate to contaminant	Degradation efficiency (%)
Benzene	5.8	0.10	82
Chlorobenzene	6.1	0.23	84
Toluene	5.6	0.47	88
o-Xylene	5.6	0.54	83
Aniline	6.6	3.0	83
Nitrobenzene	5.7	3.1	47
2,4-Dichlorophenol	5.4	5.6	57
2,4,6-Trichlorophenol	4.5	12	31

aniline was degraded as the initial concentration increased to 10.7 mM in 20 min. The final nitrobenzene concentration with an initial aniline concentration of 2.68, 5.37, 8.05 and 10.7 mM was 1.6×10^{-2}, 3.8×10^{-2}, 4.1×10^{-2} and 3.5×10^{-2} mM, respectively.

3.2.4. Effect of chemical structure

The kinetics of ozone reactions with organic and inorganic compounds are typically second order [34], and can be described by

$$-\frac{d[M]}{dt} = (k_{O_3}[O_3] + k_{\bullet OH}[\bullet OH])[M] \qquad (2)$$

Here [M] is the target compound, [O$_3$] and [•OH] are concentrations (mol L^{-1}) of dissolved ozone and hydroxyl radical, t is time (s), k_{O_3} and $k_{\bullet OH}$ represent reaction rate constants for molecular ozone and the hydroxyl radical. The ozone concentration in water is limited by its solubility and is influenced by intermediates and final products that may be formed during the ozonation of a contaminant [35]. It was observed that the ozone concentration in the liquid phase increased slowly with reaction time. For example, with a pH of 7.3, aniline concentration of 10.7 mM, and ozone dosage of 31.1 mg min^{-1}, the dissolved ozone in 2.5, 5 and 10 min was 6.1, 7.7 and 10.5 mg L^{-1}, respectively. However, for specific processing of the system and gas phase ozone concentration, the dissolved ozone still could be estimated as fixed values in a very short reaction time.

Therefore the reaction kinetics can be treated as a pseudo-first-order reaction (the influence of the hydroxyl radical was negligible at neutral and acidic conditions) and the integration of Eq. (2) is simplified as follows:

$$-\ln\left(\frac{[M]_t}{[M]_0}\right) = kt \qquad (3)$$

As shown in Table 1, the time for 50% contaminant removal and observed first-order reaction rate constants are used to evaluate the degradation efficiency for selected contaminants without pH adjustment. In this set of experiments, contaminants with 100 mg L^{-1} initial concentration were degraded with the ozone dosage of 31.1 mg min^{-1}. Among the selected compounds, nitrobenzene, chlorobenzene and toluene were shown to be more difficult to degrade by ozone. The observed first-order rate constants for degradation of these compounds were about only 17–20% of 2,4,6-trichlorophenol. In this study, we found aniline and chlorophenols were easy and fast to eliminate by ozonation, while benzene and o-xylene had a moderate reaction rate. Moreover, the degradation of 2,4,6-trichlorophenol was faster than that of 2,4-dichlorophenol, since the presence of chlorine enhanced the dechlorination step. This finding is generally in accordance with previous established literatures [36–38]. According to the above results, it can be seen that the chemical structures of the compounds have a dominant influence on the oxidation process.

The kinetic studies for the reaction of Fe(VI) with a large number of organic compounds were reported to be first order with respect to both reactants [39]:

$$\frac{-d[Fe(VI)]}{dt} = k[Fe(VI)][M] \qquad (4)$$

The values of second-order rate constant (k) for the reaction of Fe(VI) with aniline were determined as a function of pH in a few studies [40–42]. For example, with a Fe(VI) concentration of 90 μM at pH 7.0 (25 °C), the second-order rate constant (k) and half-life ($t_{1/2}$) of this reaction was reported to be 6.6×10^3 M^{-1} s^{-1}, 2.1 s, respectively [42]. Potassium ferrate has shown an appreciable reactivity with a variety of compounds. Most of the half-lives for reactions of Fe(VI) with possible contaminants under excess Fe(VI) conditions are reported to be in seconds to minutes [39], and a similar result was obtained in this study.

As observed in Fig. 5(b), the degradation efficiency increased with the molar ratio of Fe(VI) to contaminant, and further increases in the extent of contaminant degradation were likely to be minor at molar ratios greater than optimal. This behavior was repeated for all of the compounds studied. Table 2 shows the optimal molar ratios of Fe(VI) to contaminants, and the corresponding degradation efficiencies of the selected compounds with 100 mg L^{-1} initial concentration after 20 min of treatment. Considering the dosage of Fe(VI) and the oxidative elimination, the results clearly show that the oxidation reactivity increases in the order of benzene > chlorobenzene > toluene > o-xylene > aniline. Nitrobenzene and chlorophenols were found to be hard to degrade in acidic and neutral conditions. The electron attracting effect of nitro-substituting groups and chlorine atoms is believed to make the compound more electronically stable [29], and hence, less reactive. For chlorophenols, the electronegativity of the molecule increases with the degree of chlorine substitution, and thus the degradation of 2,4,6-trichlorophenol is much more difficult than 2,4-dichlorophenol, even at a higher molar ratio of Fe(VI) to contaminant, as shown in Table 2.

3.3. Simulated treatment by ROA process

In the pilot experiment, the amounts of CTMA-bentonite consumed were flexible due to operational factors. Approximately 26 kg and 21 kg of CTMA-bentonite were used in the retention of wastewater containing aniline or nitrobenzene, respectively. Meanwhile, the concentrations of aniline and nitrobenzene in the adjusting tank were found to be 72 mg L^{-1} and 43 mg L^{-1}, respectively. Therefore more than 85% of the pollutants were removed by the retention process. The results of pollutant and TOC removal in each treatment unit of the experimental system are shown in Fig. 7(a) and (b).

With the methods of Fe(VI) oxidation, ozonation and GAC adsorption, aniline removal efficiencies could reach 78%, 62% and 55%, respectively. However, the TOC removal efficiencies were
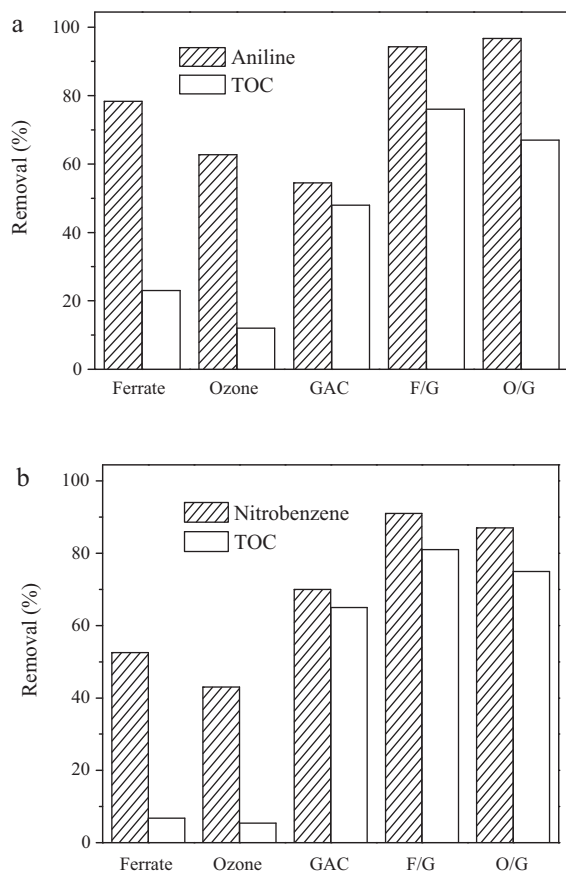
Fig. 7. The removal of pollutant and TOC in each treatment unit. [ozone] = 76 g h^{-1}, the molar ratio of ferrate to contaminant = 5.0, pH = 6.8–7.0. (a) [aniline] = 0.773 mM, [TOC] = 64.4 mg L^{-1}. (b) [nitrobenzene] = 0.406 mM, [TOC] = 31.5 mg L^{-1}.

only 23%, 12% and 48%, respectively. The degradation efficiency of ozonation was restricted to the mass transfer and the hydraulic retention time, which is beyond the scope of this paper. It is noticeable that there was a great improvement in aniline and TOC removal efficiencies with the Fe(VI) oxidation/GAC adsorption treatment processes, as well as the ozonation/GAC adsorption processes.

In the lab-scale study, it was observed that nitrobenzene was hard to degrade by Fe(VI) oxidation and ozonation. However, activated carbon has proven to be an effective sorbent for nitrobenzene elimination in many publications [43,44]. In this study, using GAC adsorption, the nitrobenzene and TOC removal efficiencies were as high as 70%, 65%, respectively, and with the treatment of F/G and O/G processes, nitrobenzene removal efficiencies were both over 80%.

4. Conclusions

In the present study, we introduce a retention–oxidation–adsorption process to remedy the contaminated environment caused by organic spills. The results showed that the retention capacities of organobentonites were much higher than that of natural bentonite with respect to the chosen organic compounds. CTMA-bentonite was successfully used as a rapid and efficient material for preventing the dispersal of hazardous liquids in the pilot scale experiment. As a subsequent treatment, ozonation and Fe(VI) oxidation have proven to be efficient, rapid processes for the elimination of selected pollutants in wastewater. The results indicated that pH, oxidant dosage, initial concentration of contaminant, and chemical structure had significant influences on the effectiveness of degradation.

Additionally, compared with ozonation, the advantage of the Fe(VI) treatment is its easy adaptation to variations in wastewater quality and quantity. Ozonation also shows its advantage over Fe(VI) oxidation in the treatment of chlorophenols, and if given sufficient time, complete degradation is possible. In the pilot-scale experiment, The F/G and O/G processes made a comparatively good performance in the treatment of wastewater containing aniline or nitrobenzene, with the removal efficiencies of the contaminants greater than 80%. Further research is needed to enhance the removal efficiency and cost effectiveness of these processes. Meanwhile, much work should be carried out to assess the feasibility and application of the combined processes in pilot or full-scale emergent treatment of organic liquid spills.

References

[1] J. Yang, F.Y. Li, J.B. Zhou, L. Zhang, L. Huang, J. Bi, A survey on hazardous materials accidents during road transport in China from 2000 to 2008, J. Hazard. Mater. 184 (2010) 647–653.
[2] Y. Hou, T.Z. Zhang, Evaluation of major polluting accidents in China-results and perspectives, J. Hazard. Mater. 168 (2009) 670–673.
[3] L. Alfonso, A. Jonoski, D. Solomatine, Multiobjective optimization of operational responses for contaminant flushing in water distribution networks, J. Water Res. Pl.-ASCE 136 (2010) 48–58.
[4] J.A. Smith, P.R. Jaffe, Benzene transport through landfill liners containing organophilic bentonite, J. Environ. Eng.-ASCE 120 (1994) 1559–1577.
[5] L.Z. Zhu, B.L. Chen, X.Y. Shen, Sorption of phenol, p-nitrophenol, and aniline to dual-cation organobentonites from water, Environ. Sci. Technol. 34 (2000) 468–475.
[6] R. Koswojo, R.P. Utomo, Y.H. Ju, A. Ayucitra, F.E. Soetaredjo, J. Sunarso, S. Ismadji, Acid green 25 removal from wastewater by organo-bentonite from Pacitan, Appl. Clay Sci. 48 (2010) 81–86.
[7] W.R. Zhao, F.F. Liu, Y. Yang, M. Tan, D.Y. Zhao, Ozonation of cationic Red X-GRL in aqueous solution: kinetics and modeling, J. Hazard. Mater. 187 (2011) 526–533.
[8] A.H. Konsowa, M.E. Ossman, Y.S. Chen, J.C. Crittenden, Decolorization of industrial wastewater by ozonation followed by adsorption on activated carbon, J. Hazard. Mater. 176 (2010) 181–185.
[9] R. Broseus, S. Vincent, K. Aboulfadl, A. Daneshvar, S. Sauve, B. Barbeau, M. Prevost, Ozone oxidation of pharmaceuticals, endocrine disruptors and pesticides during drinking water treatment, Water Res. 43 (2009) 4707–4717.
[10] K. Ikehata, M. Gamal El-Din, S.A. Snyder, Ozonation and advanced oxidation treatment of emerging organic pollutants in water and wastewater, Ozone Sci. Eng. 30 (2008) 21–26.
[11] B. Yang, G.G. Ying, L.J. Zhang, L.J. Zhou, S. Liu, Y.X. Fang, Kinetics modeling and reaction mechanism of ferrate(VI) oxidation of benzotriazoles, Water Res. 45 (2011) 2261–2269.
[12] V.K. Sharma, G.W. Luther III, F.J. Millero, Mechanisms of oxidation of organosulfur compounds by ferrate(VI), Chemosphere 82 (2011) 1083–1089.
[13] I. Ciabatti, F. Tognotti, L. Lombardi, Treatment and reuse of dyeing effluents by potassium ferrate, Desalination 250 (2010) 222–228.
[14] N. Noorhasan, B. Patel, V.K. Sharma, Ferrate(VI) oxidation of glycine and glycylglycine: kinetics and products, Water Res. 44 (2010) 927–935.
[15] V.K. Sharma, Oxidation of nitrogen-containing pollutants by novel ferrate(VI) technology: a review, J. Environ. Sci. Health A 45 (2010) 645–667.
[16] Y.Y. Eng, V.K. Sharma, A.K. Ray, Ferrate(VI): green chemistry oxidant for degradation of cationic surfactant, Chemosphere 63 (2006) 1785–1790.
[17] L.Y. Huang, Z.D. Yang, B.J. Li, J.A. Hu, W. Zhang, W.C. Ying, Granular activated carbon adsorption process for removing trichloroethylene from groundwater, AlChE J. 57 (2011) 542–550.
[18] S.J. Zhang, T. Shao, H.S. Kose, T. Karanfil, Adsorption of aromatic compounds by carbonaceous adsorbents: a comparative study on granular activated carbon, activated carbon fiber, and carbon nanotubes, Environ. Sci. Technol. 44 (2010) 6377–6383.
[19] A. Dabrowski, P. Podkoscielny, Z. Hubicki, M. Barczak, Adsorption of phenolic compounds by activated carbon—a critical review, Chemosphere 58 (2005) 1049–1070.
[20] B.L. Chen, W.H. Huang, J.F. Mao, S.F. Lv, Enhanced sorption of naphthalene and nitroaromatic compounds to bentonite by potassium and cetyltrimethylammonium cations, J. Hazard. Mater. 158 (2008) 116–123.

[21] O. Carmody, R. Frost, Y.F. Xi, S. Kokot, Adsorption of hydrocarbons on organo-clays-implications for oil spill remediation, J. Colloid Interface Sci. 305 (2007) 17–24.

[22] Y. Lee, J. Yoon, U.V. Gunten, Spectrophotometric determination of ferrate (Fe(VI)) in water by ABTS, Water Res. 39 (2005) 1946–1953.

[23] K. Rakness, G. Gordon, B. Langlais, W. Masschelein, N. Matsumoto, Y. Richard, C.M. Robson, I. Somiya, Guideline for measurement of ozone concentration in the process gas from an ozone generator, Ozone Sci. Eng. 18 (1996) 209–229.

[24] H. Bader, J. Hoigne, Determination of ozone in water by the indigo method, Water Res. 15 (1981) 449–456.

[25] J.C.F. Menendez, M.L.F. Sanchez, J.E.S. Uria, E.F. Martinez, A. Sanz-Medel, Static headspace, solid-phase microextraction and headspace solid-phase microextraction for BTEX determination in aqueous samples by gas chromatography, Anal. Chim. Acta 415 (2000) 9–20.

[26] F.J. Beltran, J. Rivas, P.M. Alvarez, M.A. Alonso, A kinetic model for advanced oxidation processes of aromatic hydrocarbons in water: application to phenanthrene and nitrobenznene, Ind. Eng. Chem. Res. 38 (1999) 4189–4199.

[27] J. Sarasa, S. Cortes, P. Ormad, R. Gracia, J.L. Ovelleiro, Study of the aromatic by-products formed from ozonation of anilines in aqueous solution, Water Res. 36 (2002) 3035–3044.

[28] K. Osathaphan, P. Tiyanont, R.A. Yngard, V.K. Sharma, Removal of cyanide in Ni(II)–cyanide, Ni(II)–cyanide–EDTA, and electroplating rinse wastewater by ferrate(VI), Water Air Soil Pollut. 219 (2011) 527–534.

[29] N. Graham, C.C. Jiang, X.Z. Li, J.Q. Jiang, J. Ma, The influence of pH on the degradation of phenol and chlorophenols by potassium ferrate, Chemosphere 56 (2004) 949–956.

[30] R.H. Wood, The heat, free energy and entropy of the ferrate(VI) ion, J. Am. Chem. Soc. 80 (1958) 2038–2041.

[31] T. Schink, T.D. Waite, Inactivation of F2 virus with ferrate(VI), Water Res. 14 (1980) 1705–1717.

[32] M.D. Johnson, K.D. Sharma, Kinetics and mechanism of the reduction of ferrate by one-electron reductants, Inorg. Chim. Acta 293 (1999) 229–233.

[33] V.K. Sharma, Oxidation of inorganic contaminants by ferrates (VI, V, and IV) kinetics and mechanisms: a review, J. Environ. Manage. 92 (2011) 1051–1073.

[34] M.M. Huber, S. Canonica, G.Y. Park, U. Von Gunten, Oxidation of pharmaceuticals during ozonation and advanced oxidation processes, Environ. Sci. Technol. 37 (2003) 1016–1024.

[35] E. Kusvurana, O. Gulnazb, A. Samilc, O. Yildirima, Decolorization of malachite green, decolorization kinetics and stoichiometry of ozone-malachite green and removal of antibacterial activity with ozonation processes, J. Hazard. Mater. 186 (2011) 133–143.

[36] J. Hoigne, H. Bader, Rate constants of reactions of ozone with organic and inorganic-compounds in water. 1. Non-dissociating organic-compounds, Water Res. 17 (1983) 173–183.

[37] J. Hoigne, H. Bader, Rate constants of reactions of ozone with organic and inorganic-compounds in water. 2. Dissociating organic-compounds, Water Res. 17 (1983) 185–194.

[38] F.J. Benitez, J. Beltran-Heredia, J.L. Acero, F.J. Rubio, Rate constants for the reactions of ozone with chlorophenols in aqueous solutions, J. Hazard. Mater. 79 (2000) 271–285.

[39] V.K. Sharma, Potassium ferrate(VI): an environmentally friendly oxidant, Adv. Environ. Res. 6 (2002) 143–156.

[40] V.K. Sharma, S. Hollyfield, Ferrate(VI) oxidation of aniline and substituted anilines, Abstr. Pap. Am. Chem. Soc. 210 (1995) 186.

[41] H. Huang, D. Sommerfeld, B.C. Dunn, C.R. Lloyd, E.M. Eyring, Ferrate(VI) oxidation of aniline, J. Chem. Soc. Dalton Trans. (2001) 1301–1305.

[42] Y. Lee, S.G. Zimmermann, A.T. Kieu, U. Von Gunten, Ferrate (Fe(VI)) application for municipal wastewater treatment: a novel process for simultaneous micropollutant oxidation and phosphate removal, Environ. Sci. Technol. 43 (2009) 3831–3838.

[43] M. Chen, L. Cui, C.H. Li, G.W. Diao, Adsorption, desorption and condensation of nitrobenzene solution from active carbon: a comparison of two cyclodextrins and two surfactants, J. Hazard. Mater. 162 (2009) 23–28.

[44] S.X. Liu, R. Wang, Modified activated carbon with an enhanced nitrobenzene adsorption capacity, J. Porous Mater. 18 (2011) 99–106.