PHOTODEGRADATION OF THE IODINATED X-RAY CONTRACT MEDIUM IOPROMIDE USING COMBINED OXIDANTS OF S2O82- AND H2O2 PROMOTED BY UV IRRADIATION

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ABSTRACT

In the present study, the degradation of the iodinated X-ray contract medium (ICM) iopromide in aqueous solution by the combined oxidants of $S_2O_8^{2-}$ and H_2O_2 with UV irradiation has been investigated. All experiments were carried out on a laboratory scale set-up. The effects of various parameters including different wavelengths of UV irradiation, numbers of UV lamps, and initial solution pH on the degradation efficiency have been evaluated. In addition, the presence of certain organic matters such as glucose and humic acid on the influence of the process performance was also assessed. Experimental results show that the wavelength of 254 nm exhibits best decay of ICM among the three tested wavelengths (254, 300 and 350 nm). ICM photo-decay rate linearly increases with the number of UV lamps. For the effect of solution pH, optimum performance was observed to be pH=4.34. Additionally, the sequential addition of $S_2O_8^{2-}$ and H_2O_2 was also studied and the degradation efficiency was ranked in the following order: $UV/S_2O_8^{2-}/H_2O_2 > UV/H_2O_2 + S_2O_8^{2-} > UV/S_2O_8^{2-} + H_2O_2$. Furthermore, test results indicate that ICM photodecay rate by $UV/S_2O_8^{2-}/H_2O_2$ process is significantly inhibited in the presence of glucose or/and humic acid, suggesting certain pre-treatment measures should be taken to abate their negative effect upon real application.

KEYWORDS

Iopromide, Persulfate, Advanced oxidation process, Sulfate radical, Hydroxyl radical.

INTRODUCTION

In recent years, the release of pharmaceutical compounds into the environment due to their extensive use and incomplete removal during wastewater treatment processes has gained significant concern. Pharmaceutical substances were considered as environmental microcontaminants by previous researchers (Richardson and Bowron, 1985). Iodinated X-ray contrast medium compounds (ICMs) are among the identified pharmaceuticals in domestic and hospital wastewaters, the aquatic environment, and even in drinking water supplies. ICMs have been widely applied as diagnostic pharmaceuticals to enhance the contrast of structures or fluids within the body in medical imaging. It is estimated that approximately 3.5×10^3 tons of ICMs are consumed annually world-wide. ICMs can not be effectively removed by conventional wastewater treatment processes due to their biological inertness, high polarity and stability and therefore they are commonly detected in the aquatic environment at concentrations up to the low microgram per liter range (Schulz et al., 2008). Additionally, it is found that the presence of ICMs contributes to the burden of absorbable organic halogens (AOX) in hospital sewage water and municipal waste waters (Gartiser et al., 1996), which further encourages the need of developing alternative treatment technologies to effectively degrade these compounds.

The findings on the elimination of ICMs from drinking water and wastewaters by direct photolysis, ozonation, and advanced oxidation processes (AOPs) have been reported. However, the ICMs degradation effectiveness of these technologies is still a debate. It was reported that only a partial oxidation of ICMs can be achieved by ozonation, while the photocatalytic activity of TiO_2 did not lead

to complete mineralization of iomeprol. Thus, it is useful to further investigate the degradation performance of ICMs by these processes. Among the reported ICMs treatment technologies, AOPs have shown great potential to degrade bio-refractory organics and recalcitrant compounds. In terms of ICMs, findings on the treatment of ICMs by AOPs such as UV/H_2O_2, $UV/S_2O_8^{2-}$ and O_3/H_2O_2 have been reported. It is obvious that these processes mainly employed sole hydroxyl radicals or sulfate radicals as the oxidizing species. Information related to utilizing both of hydroxyl and sulfate radicals as the powerful oxidants for the attacks of ICMs is yet limited.

Therefore, the degradation of ICMs using iopromide as a model substance by the combined oxidants of $S_2O_8^{2-}$ and H_2O_2 with UV irradiation was investigated in this work. Effects of different wavelengths of UV irradiation, numbers of UV lamps, and initial solution pH on the degradation efficiency have been explored. The findings of this study could be useful for the treatment of ICMs-contaminated water.

EXPERIMENTAL
Chemicals and Materials

Highly purified iopromide was obtained from Schering (Pty) Ltd. Its physiochemical characteristics are listed in Table 1. Potassium persulfate ($K_2S_2O_8$, 99.5%) and Hydrogen peroxide (H_2O_2, 30% solution) were purchased from International Laboratory (IL, USA) and VWR International Ltd, respectively. Glucose ($CH_2OH(CHOH)_4CHO \cdot H_2O$) and Humic acid (50-60%) were supplied by UNI-CHEM chemical Ltd., and ACROS Organics Ltd., respectively. All chemicals are analytical reagent grade and all solvents are HPLC-grade and used as received without further purification. For pH adjustment, 0.1 M sulfuric acid and/or 0.1 M sodium hydroxide were used. All stock and working solutions were prepared in deionized and distilled water with resistivity of 18.2 MΩ obtained from a Bamstead NANOpure water treatment system (Thermo Fisher Scientific Inc., USA).

Table 1 Physiochemical characteristics of iopromide.

Chemical structure of iopromide	Molecular formula	MW (g mol^{-1})	λ_{max} (nm)
	$C_{18}H_{24}I_3N_3O_8$	791.12	238

Experimental procedure

All the preparations and experiments were carried out in an air-conditioned laboratory at 23±2°C. The tests were duplicated and average values were used in presenting the results. KPS and H_2O_2 solutions were freshly prepared before use to minimize variations in concentration caused by self-decomposition. For the photodegradation experiments, 250 mL 0.15 mM ICM was added into a 300 mL (56 mm i.d. × 125 mm H) quartz beaker and mixed by a magnetic stirrer to ensure the complete homogeneity during reaction. The beaker was placed in the center of a Rayonet™ RPR-200 photoreactor (Southern New England Ultraviolet Co.) equipped with a cooling fan. Two phosphor-coated low pressure mercury lamps, emitting 253.7 nm monochromatic UV at a light intensity of 1.5×10^{-6} Einstein L^{-1}s^{-1} for each lamp, were symmetrically equipped in the photoreactor and employed as the source of UV irradiation. The lamps were warmed up for 10 min prior to reaction to obtain constant output. The reaction was initiated by adding predetermined amounts of $S_2O_8^{2-}$ and/or H_2O_2 and simultaneously switching on the UV lamps. Samples of 1 mL withdrawn at specific time intervals were mixed with the same volume of 1 mM sodium nitride to quench the reaction before the quantification of ICM.

Analytical methods

The concentration of ICM in aqueous solutions was analyzed by high-performance liquid chromatography (HPLC), which consisted of a Waters 515 HPLC pump, Waters 2487 Dual λ Absorbance Detector, and a reverse-phase column (Grace Smart RP 18 column, 5 μm, 4.6mm i.d ×250 mm long). The mobile phase was composed of 5% acetonitrile and 95% distilled-deionized water (V/V) with pH value adjusted to 2.8 by using 0.1 mM formic acid, while the flow rate of mobile phase was set as 1 mLmin^{-1}. Detection was performed with detector set at 238 nm which was pre-determined to be the maximum adsorption wavelength (λ_{max}) of ICM by a UV/Vis spectrophotometer. To measure the

solution pH, a CD510 digital pH meter was used in this study.

RESULTS AND DISCUSSIONS
Comparison of ICM degradation under various processes

Preliminary experiments were conducted to choose the optimum process. Considering the conditions with or without the addition of oxidants (2 mM $S_2O_8^{2-}$ and/or 2 mM H_2O_2) with or without two 254 nm UV lamps irradiation, five processes including $S_2O_8^{2-}/H_2O_2$, sole-UV, $UV/S_2O_8^{2-}$, UV/H_2O_2, and $UV/S_2O_8^{2-}/H_2O_2$ were assessed for the degradation of 0.15 mM ICM. It was found that negligible degradation was observed in the $S_2O_8^{2-}/H_2O_2$ process within 30 minutes, which was in agreement with previous studies that reactions of H_2O_2 or persulfate with organic pollutants in water are generally slow at ambient temperature (Mendez-Arriaga et al., 2010, Xu and Li, 2010). In contrast, the latter four processes all showed considerable decrease in the concentration of ICM. For the direct photolysis, almost 63% removal of ICM was achieved within 30 minutes. Experimental results show that ICM degradation performance could be improved by the addition of persulfate and/or H_2O_2. This enhancement is due to the powerful radicals generated from the homolysis of the peroxide bond of $S_2O_8^{2-}$ or H_2O_2 upon UV irradiation as illustrated in Eqs. 1 and 2.

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{-\bullet} \tag{1}$$

$$H_2O_2 + hv \rightarrow 2HO^{\bullet} \tag{2}$$

Additionally, the degradation of ICM by these four processes were found to follow pseudo first-order kinetics with correlation coefficients R^2 all higher than 0.99. The ICM decay rate constant increases from 0.038 to 0.054 min^{-1}, ranking in the order of $UV<UV/S_2O_8^{2-}<UV/H_2O_2 < UV/S_2O_8^{2-}/H_2O_2$. It can be noted that the formation of oxidizing radicals in UV-assisted persulfate and/or H_2O_2 system leads to a more rapid ICM degradation, suggesting the proposed $UV/S_2O_8^{2-}/H_2O_2$ is a promising process.

ICM degradation under different UV wavelengths

The photodegradation of 0.15 mM ICM in aqueous solution by $UV/S_2O_8^{2-}/H_2O_2$ process under different wavelengths is compared in Fig. 1. No ICM degradation is observed in the absence of UV irradiation. For the photodegradation processes, ICM removal efficiency at UV 350 nm and UV 300 nm irradiation is 12% and 44%, respectively, while more 84% degradation of ICM is observed at UV 254 nm irradiation. This significant increment of ICM degradation is apparently resulted from the high rate of homolytic cleavage of $S_2O_8^{2-}$ and H_2O_2 into sulphate and hydroxyl radicals upon high energy UV irradiation. Furthermore, all the photodegradations are found to follow pseudo first-order kinetics with decay rate constants increasing from 0.0043, 0.0208 to 0.058 min^{-1} as wavelength decreases. It can be noted that the kinetic rate constant of UV 254 nm irradiation is around 2.8 and 13.5 times of those of UV 300 nm and UV 350 nm, respectively. These significant performance differences under various UV wavelengths can be rationalized from the absorption characteristics of $S_2O_8^{2-}$, H_2O_2 and ICP. The absorption of $S_2O_8^{2-}$ sharply decreases from the deep-UV region (<220 nm) to ~350 nm. The extinction coefficients of $S_2O_8^{2-}$ at 248, 308 and 351 nm were reported to be 27.5 ± 1.1, 1.18 ± 0.05, and 0.25 ± 1.01 $M^{-1} \cdot cm^{-1}$, respectively (Herrmann, 2007). Similarly, H_2O_2 mainly absorbs in the UV range of <250 nm and has a maximum absorbance at 210-230 nm. It can be concluded that both $S_2O_8^{2-}$ and H_2O_2 have highest absorbance at 254 nm among the three investigated UV wavelengths. Thus, the relative strong absorptivity of $S_2O_8^{2-}$ and H_2O_2 at 254 nm results in a faster generation of $SO_4^{-\bullet}$ and $HO^{\bullet}$, thereby leading to a more rapid decay of ICM. Moreover, the maximum absorption wavelength of ICM was observed at 238 nm, suggesting the direct-photolysis of ICM is also favored at 254 nm compared with the other two wavelengths in the test. As a result, wavelength of 254 nm was chosen as the light source for the rest of this study.
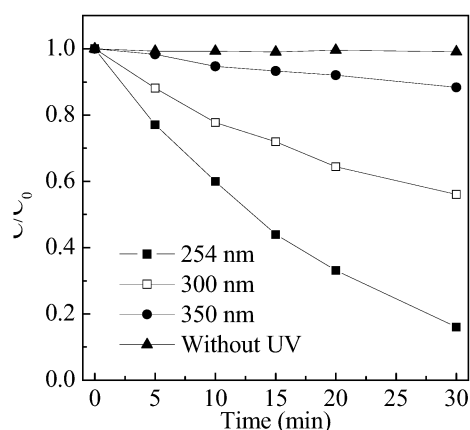
Figure 1 Photodegradation of 0.15 mM ICM in presence of 2 mM $S_2O_8^{2-}$ and 2 mM H_2O_2 under different UV wavelengths. pH=4.3

Effect of UV light intensity

The effect of UV light intensity was investigated by varying the number of UV 254 nm lamps from 1 to 10 (~1.5 to 15× 10^{-6} Einstein $L^{-1}s^{-1}$) with other parameters unchanged. The test results are depicted in Fig. 2. When the UV light intensity varies from 1.5 to 3.0, 6.0, 9.0 and 15× 10^{-6} Einstein $L^{-1}s^{-1}$, the efficiency of ICM degradation within 30 min reaction is increased from 27 to 56, 78.5, 88 and 98% as illustrated in Fig.2. Additionally, the pseudo first-order kinetics model is used to describe the photodegradation of ICM by UV/$S_2O_8^{2-}$/H_2O_2 process under various UV light intensities. Calculation results show that all the data are well fitted by the pseudo first-order kinetics model. The plot of pseudo first-order rate constant with respect to the number of UV 254 nm lamps is shown in Fig.3. It can be seen that the photodecay rate constant is linearly increased with the increase of UV light intensity. It was reported that the decomposition of $S_2O_8^{2-}$ and H_2O_2 depends mainly on the intensity of the light source (Neppolian et al., 2008). An increase in the number of lamps accelerates the hemolytic cleavage of $S_2O_8^{2-}$ and H_2O_2, thus generating more oxidizing radicals. On the other hand, for direct photolysis, ICM degradation rate is reported to be directly proportional to the light intensity. As a result, when the UV lamps are increased, the generation of radical species as well as the direct photolysis decay rate of ICM increases, thereby resulting in an enhanced total ICM decay rate. Considering that (1) the photodecay rate constant is linearly dependent on the UV light intensity and (2) the optimal ICM removal efficiency per each lamp is achieved when the number of UV 254 nm lamps is fixed at two, two UV 254 nm lamps emitting totally light intensity of 3.0 × 10^{-6} Einstein $L^{-1}s^{-1}$ were therefore used for the rest of this study.
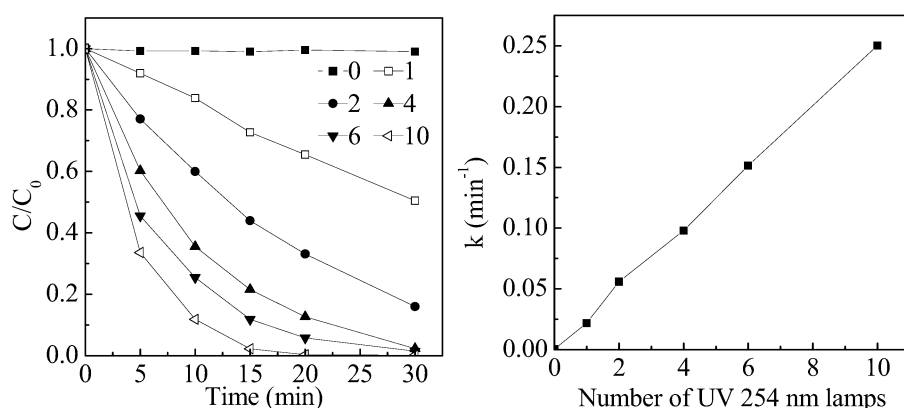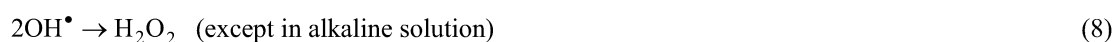

Left-Figure 2 Photodegradation of ICM under various UV light intensities ([ICM]= 0.15 mM, [$S_2O_8^{2-}$] = [H_2O_2]=2 mM, pH=4.3)
Right-Figure 3 Plot of the pseudo first-order rate constant for the photodegradation of ICM as a function of the number of UV 254 nm lamps. ([ICM]= 0.15 mM, [$S_2O_8^{2-}$] = [H_2O_2]=2 mM, pH=4.3)

Effect of initial pH

The investigation on the effect of initial pH on the photodegradation of ICM by UV/$S_2O_8^{2-}$/H_2O_2

process was carried out over a wide pH range of 2.24-12.06. As indicated in Fig. 4, the reaction is observed to be dependent on the initial pH. The ICM removal efficiency is first increased from 78 to 84% and then decreased to 45% as solution pH increases from 2.24 to 4.34 and 12.06, respectively. The first-order kinetic rate constants at different pH levels were also determined as shown in the inset of Fig. 4. The highest decay rate was achieved at pH 4.34 and it decreases at lower and higher pH levels. The pH dependency on the ICM photodegradation can be explained by the following reasons. Firstly, from the H_2O_2 point of view, (1) at a very low pH level, it was reported that the scavenging effect of hydroxyl radicals by hydrogen ions becomes significant, resulting in a limited contaminant decay rate (Huang et al., 2009, Masomboon et al., 2009). (2) At alkaline pH levels, the self-decomposition rate of H_2O_2 is increased with the increment of solution pH as explained by Eq. 3, which results in a low availability of H_2O_2 in the solution and leands to a lower production of $OH^\bullet$; meantime, the following reactions (Eqs. 4-8) are also enhanced at elevated pH level:

$$H_2O_2 \rightarrow H_2O + O_2 \tag{3}$$

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{4}$$

$$HO_2^- + H_2O_2 \rightarrow H_2O + O_2 + OH^- \tag{5}$$

$$OH^\bullet + HO_2^- \rightarrow H_2O + O_2^{-\bullet} \tag{6}$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \tag{7}$$

$$2OH^\bullet \rightarrow H_2O_2 \quad \text{(except in alkaline solution)} \tag{8}$$

It can be seen from Eqs. (4-7) that these reactions lead to an invalid depletion of H_2O_2 as well as hydroxyl radicals. In addition, the reaction products of $O_2^{-\bullet}$ (superoxide radical) and $HO_2^\bullet$ exhibit much less reactive toward organic compounds as compared to hydroxyl radicals. Secondly, from the $S_2O_8^{2-}$ point of view, (1) in acidic conditions (pH 3), the formation of ineffectual anions or weaker oxidants such as $HS_2O_8^-$, H_2SO_5, SO_4 and HSO_4^- rather than sulfate radicals are reported to be dominant. Furthermore, it was reported that the reaction (Eq. 9) of $SO_4^{-\bullet}$ with $S_2O_8^{2-}$ to convert to SO_4^{2-} and $S_2O_8^{\bullet-}$ with a rate constant of 5.5×10^5 $M^{-1}s^{-1}$ under acidic conditions (pH 2) also lead to the scavenging of sulfate radicals (Yu et al., 2004).

$$SO_4^{-\bullet} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \quad k=6.22 \times 10^5 \ M^{-1}s^{-1} \tag{9}$$
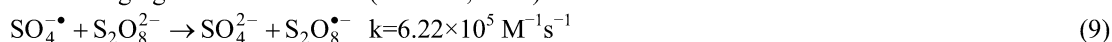
Therefore, the decrease in the photodecay rate of ICM is observed when the initial solution pH is acidified from 4.34 to 2.24. (2) At alkaline pHs, sulfate radicals can undergo reactions with OH^- to transform into $OH^\bullet$ according to Eq. (10)

Alkaline pH: $SO_4^{-\bullet} + OH^- \rightarrow SO_4^{2-} + OH^\bullet$ $k=1.4 - 7.3 \times 10^7 \ M^{-1}s^{-1}$ $\tag{10}$
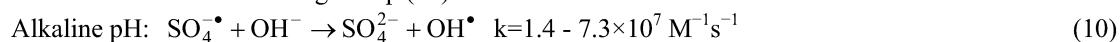
This sulfate radical scavenging reaction becomes significant at the initial pH > 8.5. This reaction as well as the formation of $OH^\bullet$ is considered to be predominant for solution pH higher than ~10.5 (Yang et al.).
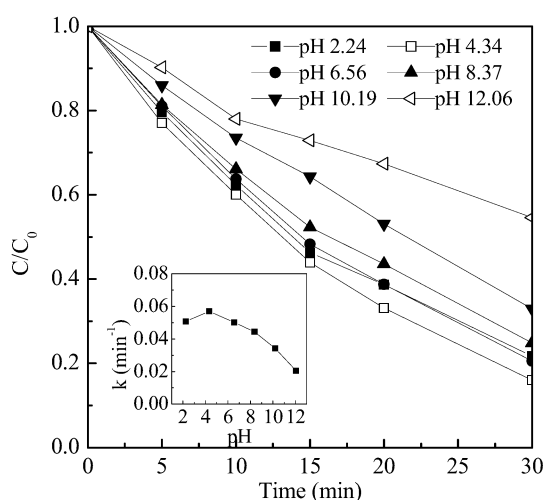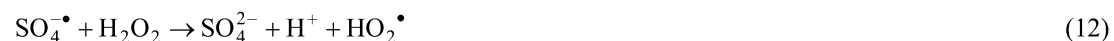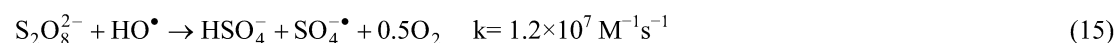

Fig. 4. Photodegradation of ICM at varied pH level. (Plot of the pseudo first-order rate constant as a function of pH level. [ICM]= 0.15 mM, $[S_2O_8^{2-}] = [H_2O_2]$=2 mM pH=4.3)

Comparison of different oxidant dosing sequence

A set of experiments were conducted to investigate the effect of oxidant dosing sequence on the photodegradatin of ICM. Three different dosing sequences including UV/$S_2O_8^{2-}$+H_2O_2 (the addition of H_2O_2 into UV/$S_2O_8^{2-}$ system), UV/H_2O_2+$S_2O_8^{2-}$ (the addition of $S_2O_8^{2-}$ in to UV/H_2O_2 system) and UV/$S_2O_8^{2-}$/H_2O_2 process (simultaneous addition of H_2O_2 and $S_2O_8^{2-}$ as well as turning on the lamps immediately) are compared in Fig. 5. As illustrated in Fig. 5, the photodegradation efficiencies of ICM by the tested three processes are in the sequence of UV/$S_2O_8^{2-}$+H_2O_2<UV/H_2O_2+$S_2O_8^{2-}$< UV/$S_2O_8^{2-}$/H_2O_2. The observed result can be explained on the basis of oxidizing radical-scavenging effect caused by the different oxidant addition sequence. In the case of UV/$S_2O_8^{2-}$+H_2O_2 process, the sulfate radicals already existed in the system due to the photolysis of $S_2O_8^{2}$ may suffer from radical-scavenging reactions (Eqs. 12 and 13) with the newly added H_2O_2, leading to the consumption of $SO_4^{-\bullet}$.

$$SO_4^{-\bullet} + H_2O_2 \rightarrow SO_4^{2-} + H^+ + HO_2^{\bullet} \tag{12}$$

$$SO_4^{-\bullet} + HO_2^{\bullet} \rightarrow SO_4^{2-} + H^+ + O_2 \tag{13}$$

On the contrary, for the UV/H_2O_2+ $S_2O_8^{2-}$ process, the $S_2O_8^{2-}$ ions can undergo reactions with the previously generated $OH^{\bullet}$ through Eqs. 14 and 15 (Chu et al., 2006).

$$S_2O_8^{2-} + HO^{\bullet} \rightarrow S_2O_8^{\bullet-} + OH^- \tag{14}$$

$$S_2O_8^{2-} + HO^{\bullet} \rightarrow HSO_4^- + SO_4^{\bullet-} + 0.5O_2 \quad k= 1.2 \times 10^7 \, M^{-1}s^{-1} \tag{15}$$

It can be noted that Eq. 14 results in a depletion of hydroxyl radicals as well as the formation of less reactive species of $S_2O_8^{\bullet-}$. As for Eq. 15, the reaction between 1 mol $S_2O_8^{2-}$ ions and 1 mol $OH^{\bullet}$ only contributes to the generation of 1 mol $SO_4^{-\bullet}$, which is much less as compared to the production of 2 mol $SO_4^{-\bullet}$ by the photolysis of $S_2O_8^{2-}$.

Generally, these reactions lead to either the scavenging of valuable powerful radicals or the invalid consumption of oxidants, and therefore result in the decreased photodecay rate of ICM.
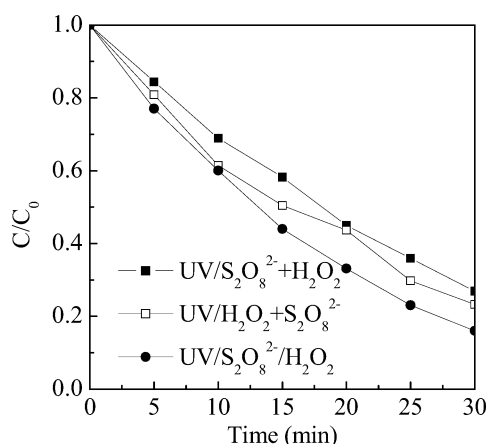

Figure 5 Comparison of ICM photodegradation by different oxidant addition processes. ([ICM]= 0.15 mM, [$S_2O_8^{2-}$] = [H_2O_2]=2 mM, pH=4.3)

Effect of the presence of organic matters

The presence of glucose and humic acid on the effect of ICM photodecay rate by UV/$S_2O_8^{2-}$/H_2O_2 process was examined as natural waters are expected to contain large amounts of these substances. Experimental results indicate that the involvement of organic matters has detrimental effect on the photodegradation process and decreases the extent of probe contaminant degradation. The addition of 50 mg glucose and 50 mg humic acid retarded the process by around 17% and 64% as compared to the process without organic matter addition, respectively. The plots of ln(C/C_0) versus reaction time under different organic matter addition conditions are depicted in Fig. 6. The ICM photodecay rate constants are ranked in the descending order of no addition> 50 mg glucose> 50 mg humic acid> 50 mg glucose & 50 mg humic acid. The rate inhibitory effect by the addition of organic matters likely results from their strong absorption of incident UV light, which retards or blocks the efficient absorption of oxidants and probe compounds. Additionally, the reaction of organic matters with hydroxyl and sulfate radicals can be also contributed to the rate retardation as it is a well-known fact that humic acid acts as a strong

hydroxyl radical scavenger at high concentrations (Gogate and Pandit, 2004). It can be concluded that the presence of certain organic matters can not only affect the efficient absorption of the process but also act as radical scavengers. Therefore, pre-treatment should be considered to reduce the retardation effect due to the presence of certain organic matters upon real application.
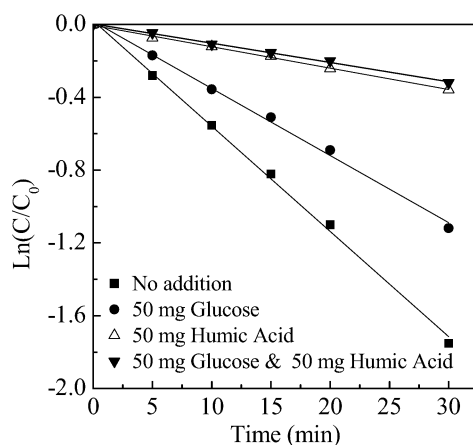

Figure 6 Comparison of ICM photodegradation with or without the presence of organic matters
([ICM]= 0.15 mM, $[S_2O_8^{2-}] = [H_2O_2]$=2 mM, pH=4.3)

CONCLUSIONS

The performance of the proposed $UV/S_2O_8^{2-}/H_2O_2$ process was examined through the photodegradation of ICM under a variety of conditions in aqueous solution. Based on the experimental results, the following conclusions are drawn:
Comparison of ICM degradation by various processes shows that the ICM degradation increases in the order of $UV<UV/S_2O_8^{2-}<UV/H_2O_2 < UV/S_2O_8^{2-}/H_2O_2$, where more than 84% removal of 0.15 M ICM is achieved within 30 min by $UV/S_2O_8^{2-}/H_2O_2$ process. It was found that the photodegradation of ICM follows the pseudo first-order kinetic model. For the effect of different UV wavelength, ICM degradation is favored at 254 nm compared with the other two wavelengths (300 and 350 nm). It was demonstrated that the pseudo first-order photodecay rate constants of ICM is linearly increased with the increment of UV intensity. ICM photodegradation by $UV/S_2O_8^{2-}/H_2O_2$ process was found to be dependency on initial pH and the optimal pH was determined to be 4.34. Studies on the effect of sequential addition of oxidants reveal that simultaneous addition of oxidants is beneficial from the best use of valuable radicals and oxidants point of view. Moreover, the presence of certain organic matters has inhibitory effects on the ICM photodegradation, suggesting pre-treatment measure should be taken for the real application.

ACKNOWLEDGMENTS

REFERENCES

Chu, W., Lau, T.K. and Fung, S.C. (2006) Effects of combined and sequential addition of dual oxidants (H2O2/S2O82-) on the aqueous carbofuran photodegradation. Journal of Agricultural and Food Chemistry 54(26), 10047-10052.

Gartiser, S., Brinker, L., Erbe, T., Kummerer, K. and Willmund, R. (1996) Contamination of hospital wastewater with hazardous compounds as defined by 7a WHG. Acta Hydrochimica Et Hydrobiologica 24(2), 90-97.

Gogate, P.R. and Pandit, A.B. (2004) A review of imperative technologies for wastewater treatment II: hybrid methods. Advances in Environmental Research 8(3-4), 553-597.

Herrmann, H. (2007) On the photolysis of simple anions and neutral molecules as sources of O-/OH, SOx- and Cl in aqueous solution. Physical Chemistry Chemical Physics 9(30), 3935-3964.

Huang, Y.H., Huang, Y.F., Huang, C.I. and Chen, C.Y. (2009) Efficient decolorization of azo dye Reactive Black B involving aromatic fragment degradation in buffered Co2+/PMS oxidative processes with a ppb level dosage of Co2+-catalyst. Journal of Hazardous Materials 170(2-3),

1110-1118.

Masomboon, N., Ratanatamskul, C. and Lu, M.C. (2009) Chemical Oxidation of 2,6-Dimethylaniline in the Fenton Process. Environmental Science & Technology 43(22), 8629-8634.

Mendez-Arriaga, F., Esplugas, S. and Gimenez, J. (2010) Degradation of the emerging contaminant ibuprofen in water by photo-Fenton. Water Research 44(2), 589-595.

Neppolian, B., Celik, E. and Choi, H. (2008) Photochemical oxidation of arsenic(III) to arsenic(V) using peroxydisulfate ions as an oxidizing agent. Environmental Science & Technology 42(16), 6179-6184.

Richardson, M.L. and Bowron, J.M. (1985) The fate of pharmaceutical chemicals in the aquatic environment. J. Pharm. Pharmacol. 37, 1-12.

Schulz, M., Loffler, D., Wagner, M. and Ternes, T.A. (2008) Transformation of the X-ray contrast medium Iopromide in soil and biological wastewater treatment. Environmental Science & Technology 42(19), 7207-7217.

Xu, X.R. and Li, X.Z. (2010) Degradation of azo dye Orange G in aqueous solutions by persulfate with ferrous ion. Separation and Purification Technology 72(1), 105-111.

Yang, S.Y., Wang, P., Yang, X., Shan, L., Zhang, W.Y., Shao, X.T. and Niu, R. Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide. Journal of Hazardous Materials 179(1-3), 552-558.

Yu, X.Y., Bao, Z.C. and Barker, J.R. (2004) Free radical reactions involving Cl-center dot, Cl-2(-center dot), and SO4-center dot in the 248 nm photolysis of aqueous solutions containing $S_2O_8^{2-}$ and Cl. Journal of Physical Chemistry A 108(2), 295-308.