Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.896288

54 (2015) 2252–2258
May

Taylor & Francis
Taylor & Francis Group

Photocatalytic decolorization of methyl orange solution with KIO_3

Jianzhang Li, Junbo Zhong*, Tao Wang, Jun Zeng, Jinjin He, Minjiao Li

Key Laboratory of Green Catalysis of Higher Education Institutes of Sichuan, College of Chemistry and Pharmaceutical Engineering, Sichuan University of Science and Engineering, Zigong 643000, P.R. China, Tel./Fax: +86 813 5505601; email: junbozhong@163.com

Received 19 June 2013; Accepted 15 February 2014

ABSTRACT

The use of azo dyes must be controlled and the sewage must be properly treated before being released into the environment. Thus, it is crucial to develop processes that can destroy these azo dyes completely. It has been reported that a methyl orange (MO) aqueous solution can be effectively decolorized in KIO_3 homogeneous system under UV light irradiation. In this study, the kinetics and effects of KIO_4, H_2O_2, $K_2S_2O_8$, and $KBrO_3$ on the decolorization of MO with KIO_3 under UV light irradiation were investigated in detail. The results show the decolorization reaction is a zero-order reaction when the concentration of MO is above 25 mg/L. IO_4^-, $S_2O_8^{2-}$, BrO_3^-, and H_2O_2 can greatly inhibit the photocatalytic decolorization reaction of MO. Several observations indicate the photocatalytic decolorization of MO with KIO_3 under UV irradiation occurs by $\cdot O_2^-$ attack only. A more detailed mechanism of KIO_3 photocatalysis will be further investigated in the near future.

Keywords: KIO_3; Decolorization; Methyl orange; Inorganic additives; Mechanism

1. Introduction

Azo dyes are widely used synthetic colored organic compounds that contain one or more azo bonds (–N=N–) as chromophore groups linked to aromatic structures with functional groups such as OH and SO_3H [1,2]. Azo dyes effluents are a threat to the surrounding ecosystems and can pose the environmental pollution. For example, the toxicity and potentially carcinogenic nature of azo dyes and their manufacturing precursors represent an increasing danger in aquatic life [3]. Therefore, the azo dyes in sewage must be readily treated before being released into the environment. Conventional water treatment technologies, such as activated sludge-based biological processes, coagulation/flocculation, adsorption, and ion exchange, have been developed and used widely for the azo dyes treatment [4]. However, these methods cannot eliminate the color completely [5,6], so it is crucial to develop processes that can destroy these dyes completely.

Among the before mentioned approaches for azo dyes treatment, photocatalysis has attracted increasing attention in recent years [7–12]. Due to its capability to treat extremely low concentration of organic pollutants at room temperature and it is environmental friendly, photocatalysis has been widely employed in the treatment of all kinds of organic contaminants [13]. Generally, photocatalytic systems are categorized as either homogeneous or heterogeneous. Polyoxometalates are mostly used as photocatalysts in homogeneous systems, in which their photochemical behavior has been studied [14]. In heterogeneous systems, the main photocatalyst is

---

*Corresponding author.

semiconductor-based materials. TiO_2 and ZnO have been used in heterogeneous photocatalysis for various environmental-related applications.

Previous studies have demonstrated that H_2O_2, Na_2BO_3, $K_2S_2O_8$, $KBrO_3$, KIO_3, and KIO_4 in TiO_2, ZnO, CdO, Fe_2O_3, CuO, ZnS, and Nb_2O_5 system under UV can enhance the degradation of the substrate [15,16]. Choy and coworker reported that oxyhalogens (ClO_3^-, BrO_3^-, and IO_3^-) can significantly improve the o-Chloroaniline decay in the UV/TiO_2/oxyhalogens process. Faster decay of o-Chloroaniline was observed in the order of $IO_3^- > BrO_3^- > ClO_3^-$ [17,18]. As inorganic oxidants, oxyanions can capture the electrons ejected from TiO_2; therefore, the probability of electron-hole recombination will decrease, causing an increase in the half-life of h^+ in the solution, which in turn benefits the photocatalytic reaction [19]. Cotton et al. suggested the overall reaction of iodate reduction, yielding iodide as the end product [20], $TiO_2 + h\upsilon \rightarrow e^- + h^+, IO_3^- + 6H^+ + 6e^- \leftrightarrow [IO_2^-, HOI] \leftrightarrow I^- + 3H_2O$. On the other hand, Weavers et al. have outlined that the reduction pathway of IO_3^- under the UV illumination [21]. During the process, radical species such as $IO_2^\bullet$ and $HIO_3^{-\bullet}$ would be generated, yielding I^- as the end product.

KIO_3 is widely used in analytical chemistry and as an additive in the food industry. KIO_3 is extremely irritating and injurious to tissues especially those of the optic nerves. The concentration of KIO_3 in the wastewater released by analytical laboratories and the food industry is relative high. Thus, we wonder whether or not KIO_3 released in the wastewater can photocatalytically oxidize the organic pollutants in waters. If this is feasible, then the potential use of photoactivated potassium bromate at ambient temperature is of interest, realizing the self-purification of water to some extent. Our previous studies have demonstrated that a methyl orange (MO) aqueous solution can be effectively decolorized in KIO_3 homogeneous system under UV light irradiation [22]. However, more studies are needed to better understand this process, especially the effects of several reagents on the IO_3^- homogeneous systems and the underlying photocatalytic mechanism of IO_3^- under UV light irradiation. The influence of the several reagents must be accurately examined before application as some of them may affect the degradation adversely at specific conditions. In this paper, MO, a water soluble azo dye widely used in the textile industry, was chosen as the model azo dye.

2. Experimental

2.1. Materials and instruments

All chemicals (analytical grade reagents) were purchased from Chengdu Kelong Chemical Reagent Factory and used as received. All the studies were done using double-distilled water. A 756 PC spectrophotometer, a quartz beaker with 100 mL volume, and a 30 W medical violet lamp (Philips, with maximum emission at 254 nm) were used in the experiments.

2.2. Procedures

The procedures for photocatalytic reaction have been described in Ref. [22]. The reactor consisted of a 100 mL ($\varphi = 5.4$ cm) quartz beaker placed in a constant temperature water bath. In a dark room, a 100 mL MO aqueous solution containing 50 mg KIO_3 was introduced into the reactor, and the mixture was placed under UV illumination. The distance from the lamp to the solution was 15 cm, and the intensity of UV irradiation was 380 μw/cm^2. The mixture was magnetically stirred. The decolorization reaction was carried out at 298 K and $HClO_4$ and NaOH solutions were used to adjust the pH. The additional reagents were added into the reaction system separately, and the mixture was then irradiated as the procedure mentioned above. At regular intervals, samples were withdrawn for analysis. The concentration of MO was measured with a spectrophotometer using Lambert–Beer law. Experiments were carried out under two conditions: one with illumination but no KIO_3 (I) and the other with KIO_3 but no irradiation (II).

In this paper, the decolorization efficiency of MO was calculated by $(C_0-C)/C_0$, where C is the concentration of the MO after irradiation, C_0 the initial concentration of MO before the irradiation in the presence of KIO_3. All data were the average values of three parallel determinations.

3. Results and discussion

3.1. Blank experiments

The results of blank experiments show that the concentration of MO aqueous solution (10 mg/L) under condition I during 1 h period changes so little that can be ignored. The concentration of MO solution (10 mg/L) under condition II during 1 d time period keeps the same, indicating that KIO_3 cannot decolorize MO directly without UV irradiation. The results fit

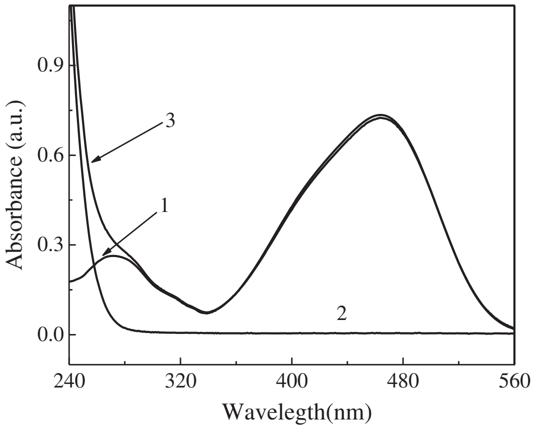

Fig. 1. Spectrum of MO and KIO_3: (1) MO (pH 7.0); (2) KIO_3 (pH 7.0); (3) MO + KIO_3 (pH 7.0); the concentration of MO was 10 mg/L; the concentration of KIO_3 was 0.5 g/L; the volume of solution was 100 mL; pH was adjusted at 7.0 with $HClO_4$ and NaOH.

well with the results reported by Choy and coworker [17]. The results are shown in Fig. 1. As shown in Fig. 1, the spectrum of MO in the mixed solution (MO and KIO_3) after 1 d is almost the same as that of initial MO, the results further demonstrate that no new absorption appears from 320 to 560 nm when MO and KIO_3 coexist in the solution, which demonstrates that the presence of KIO_3 will not interfere with the measurement of MO at 460 nm. The results of blank tests show that decolorization of MO with KIO_3 under UV illumination is due to photocatalysis.

3.2. Kinetics investigation

Our previous studies have demonstrated that the decolorization rates of MO with KIO_3 under UV light irradiation fit a first-order model for initial low concentrations (≤10 mg/L) [22]. Fig. 2 is a plot of normalized concentrations vs. irradiation time for MO at three relative high initial concentrations (≥25 mg/L), it is clear that C_t vs. t is in linear form, which shows that the decolorization rates fit a zero-order model, that is, $C_t = C_0 - k_0 t$ describes the tendency well, where C_0 and C_t are the concentration of MO at time 0 and t, respectively, and k_0 is the observed zero-order rate constant. To make the further mathematic inferences clear, all the relating kinetic parameters, such as the reaction rate constants (k_0), half-life ($t_{0.5}$), and interrelated coefficients (R^2), are all presented in Table 1. In the decolorization reaction process, the higher initial concentration is, the more intermediates appear, and the negative effects become stronger on the apparent reaction rate constant. As to the negative effect of high initial concentration, it can be speculated to be caused by the limited dosage of oxidants which is fixed in our case because the intermediates would compete with MO for active species. On the other hand, higher concentration of the dye decreases the light penetrability in the dye solution and diminishes the amount of light required for the formation of active species owing to the fact that the dye molecules may absorb a significant amount of light [23].

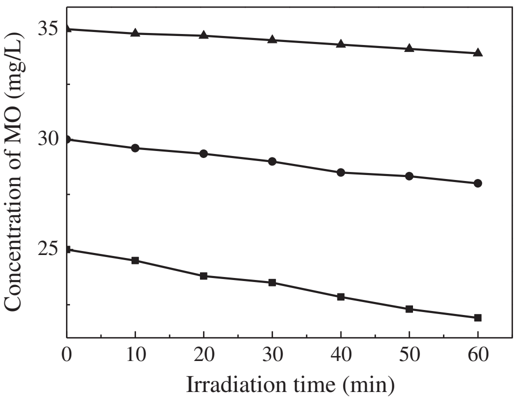

Fig. 2. Plot of photocatalytic decolorization of MO vs. irradiation time.

3.3. Effect of inorganic additives

The influence of some inorganic additives must be accurately examined before their application due to possible negative effects depending on experimental parameters. Previous studies have shown that the presence of periodate (IO_4^-) can degrade some toxic organic compounds significantly under UV and near sunlight wavelengths [21,24], the reaction mechanism is summarized as below:

$$IO_4^- + h\upsilon \rightarrow IO_3^{\cdot} + O^{\cdot -} \quad (1)$$

$$O^{\cdot -} + H^+ \leftrightarrow OH^{\cdot} \quad (2)$$

$$OH^{\cdot} + IO_4^- \rightarrow OH^- + IO_4^{\cdot} \quad (3)$$

$$2\ OH^{\cdot} \rightarrow H_2O_2 \quad (4)$$

$$2\ IO_4^{\cdot} \leftrightarrow I_2O_8 \quad (5)$$

$$I_2O_8 + H_2O \rightarrow IO_3^- + IO_4^- + 2H^+ + O_2 \quad (6)$$

$$2IO_3^{\cdot} \leftrightarrow I_2O_6 \quad (7)$$

$$I_2O_6 + H_2O \rightarrow IO_3^- + IO_4^- + 2H^+ \quad (8)$$

Table 1
Parameter and reaction kinetic equation for different initial concentration

C_0 (mg/L)	Reaction kinetic equation	Rate constant (k_0) (mg/L min^{-1})	$t_{0.5}$ (min)	R^2
25	$C_t = 24.98 - 0.0523t$	0.0523	238.81	0.9952
30	$C_t = 29.98 - 0.0335t$	0.0335	447.46	0.9920
35	$C_t = 35.02 - 0.0182t$	0.0182	962.08	0.9943

$$IO_4^- + h\upsilon \rightarrow IO_3^{\cdot} + O(^3P) \tag{9}$$

$$O_2 + O(^3P) \rightarrow O_3 \tag{10}$$

$$O_3 + IHO_3^{\cdot} \rightarrow IO_4^{\cdot} + O_2 \tag{11}$$

$S_2O_8^{2-}$ [25] and BrO_3^- [26] can also be used to degrade some organic substrates under UV illumination. The thermal or photochemical activated decomposition of $S_2O_8^{2-}$ ion to $SO_4^{\cdot -}$ radical has been proposed as a method of accelerating the process [25], as summarized in the following reactions:

$$S_2O_8^{2-} + \text{photons or heat} \rightarrow 2SO_4^{\cdot -} \tag{12}$$

$$SO_4^{\cdot -} + RH_2 \rightarrow SO_4^{2-} + H^+ + RH^{\cdot} \tag{13}$$

$$RH^{\cdot} + S^2O_8^{2-} \rightarrow R + SO_4^{2-} + H^+ + SO_4^{\cdot -} \tag{14}$$

$$SO_4^{\cdot -} + RH \rightarrow R^{\cdot} + SO_4^{2-} + H^+ \tag{15}$$

$$2R^{\cdot} \rightarrow RR\,(\text{dimer}) \tag{16}$$

H_2O_2 is a commonly used oxidant, its degradation mechanism only involving $^{\cdot}OH$ attack under UV irradiation [27].

$$H_2O_2 + h\upsilon \xrightarrow{\lambda < 380\,\text{nm}} 2HO^{\cdot}$$

$$^{\cdot}OH + H_2O_2 \longrightarrow H_2O + HO_2^{\cdot}$$

$$HO_2^{\cdot} + H_2O_2 \longrightarrow H_2O + O_2 + {}^{\cdot}OH$$

When the concentration of MO aqueous solution (10 mg/L) and other conditions were fixed, the effects of IO_4^-, $S_2O_8^{2-}$, BrO_3^-, and H_2O_2 on the decolorization reaction of MO with KIO_3 under UV illumination are shown in Table 2.

As shown in Table 2, interestingly for processes 6–9, the photocatalytic decolorization of MO is greatly inhibited, the first-order rate constants being 0.0333 min^{-1} (K_6), 0.0274 min^{-1} (K_7), 0.008 min^{-1} (K_8) and 0.0108 min^{-1} (K_9), respectively. These results indicate that IO_4^-, $S_2O_8^{2-}$, BrO_3^-, H_2O_2, and KIO_3 have an inhibition which leads to the low decolorization rate of MO, but the presence of IO_4^-, $S_2O_8^{2-}$, BrO_3^-, and H_2O_2 cannot alter the kinetic model of the reaction as demonstrated by the results, since the photocatalytic decolorization reaction is still pseudo-first-order. Furthermore, $K_6 \approx K_1 – K_5$ illustrates that the inhibition between KIO_4 and KIO_3 is not very strong. $K_6 > K_2 – K_5$ shows that the inhibition between $K_2S_2O_8$ and KIO_3 is not very strong. $K_8 < K_3 – K_5$ indicates that the inhibition between H_2O_2 and KIO_3 is very strong, while $K_9 > K_4 – K_5$ suggests that the inhibition between $KBrO_3$ and KIO_3 is not very strong. It is possible that these results are caused by the nature of the oxidants and the mechanism of the photocatalysis by these oxidants, but the specific interaction mechanisms between these oxidants under UV illumination are not clear, remaining to be studied in near future. For process 8, the photocatalytic decolorization rate constant is the lowest among the experimental conditions. As a weak

Table 2
Kinetic parameter for MO with different oxidant

Process	Oxidant	K (min^{-1})	$t_{0.5}$ (min)	R^2
1	50 mg KIO_4	0.0409	16.95	0.9998
2	50 mg $K_2S_2O_8$	0.0296	23.18	0.9993
3	50 mg H_2O_2	0.0181	38.30	0.9997
4	50 mg $KBrO_3$	0.0150	46.21	0.9994
5	50 mg KIO_3	0.0079	89.15	0.9982
6	50 mg KIO_4 + 50 mg KIO_3	0.0333	20.81	0.9948
7	50 mg $K_2S_2O_8$ + 50 mg KIO_3	0.0274	25.30	0.9991
8	50 mg H_2O_2 + 50 mg KIO_3	0.0080	86.64	0.9905
9	50 mg $KBrO_3$ + 50 mg KIO_3	0.0108	64.18	0.9992

reductant, H_2O_2 can react with the strong oxidant (KIO_3); thus, the photocatalytic decolorization rate constant is slow.

3.4. Photocatalytic mechanism

H_2O_2 was employed as a standard for comparison in the degradation mechanism with KIO_3 based on the fact that the two reaction systems are both homogeneous reaction system. If the photocatalytic mechanism of KIO_3 only concerns hydroxyl radical attack as that of H_2O_2, the spectral changes recorded during the MO photocatalytic decolorization by H_2O_2 and KIO_3 would follow the same spectral changes. The spectral changes recorded during MO photocatalytic decolorization are shown in Fig. 3. As shown in Fig. 3, the intermediates formed from MO photocatalytic decolorization by KIO_3 appear different from that of H_2O_2. In H_2O_2 photocatalysis, the intermediates have a broad band in the range of about 313–555 nm, the absorbance in the range of about 244–313 nm decreases with the irradiation time. However, the products formed from KIO_3 photocatalysis exhibit a broader band in about 350–543 nm, while the absorbance in the range of about 293–350 and 543–600 nm increases with the irradiation time (KIO_3 absorption at $\lambda < 300$ nm overlaps with MO). Thus, the intermediates were found to experience further degradation in situ with irradiation time. These results illustrate that the degradation mechanism of MO with KIO_3 under UV irradiation is greatly different from that of MO with H_2O_2, but the result here cannot exclude that the degradation of MO with KIO_3 involves the attack of $^{\cdot}OH$ radicals.

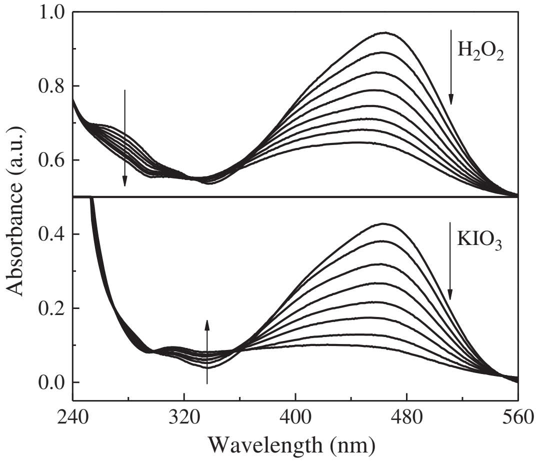

Fig. 3. The spectral changes recorded during MO photodegradation by H_2O_2 and KIO_3 at reaction time of 0, 10, 20, 30, 40, 50, 60, and 70 min, respectively. The amount of H_2O_2 and KIO_3 was 0.5 g/L and pH of MO solution (6 mg/L) was 5.6.

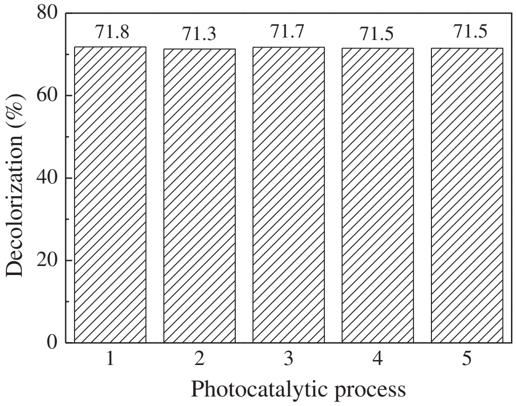

Fig. 4. Effects of scavengers on the photocatalytic decolorization efficiency of MO: (1) KIO_3; (2) KIO_3 + methanol (about 1% by volume); (3) KIO_3 + ethanol (about 1% by volume); (4) KIO_3 + t-BuOH (about 1% by volume); (5) KIO_3 + AO (0.2 mM); the concentration of MO was 6 mg/L; the amount KIO_3 was 0.5 g/L.

In order to better understand the photocatalytic mechanism, the effects of different scavengers on the decolorization efficiency of MO were investigated. The scavengers used in this study are ethanol for $^{\cdot}OH$ [28] (99.9%, 1 mL), methanol for $^{\cdot}OH$ [29] (99.9%, 1 mL), and t-BuOH for $^{\cdot}OH$. T-BuOH is an effective hydroxyl radicals scavenger, which reacts quickly with hydroxyl radicals with a rate constant of $6.0 \times 10^8\,M^{-1}\,s^{-1}$ [30]. Ammonium oxalate (AO) is a scavenger for h^+ [31]. As shown in Fig. 4, the presence of these scavengers has no influence on the decolorization efficiency of MO. The evidence obtained here supports that $^{\cdot}OH$ and h^+ are not involved in the degradation of MO by KIO_3 photocatalysis. However, when 0.4

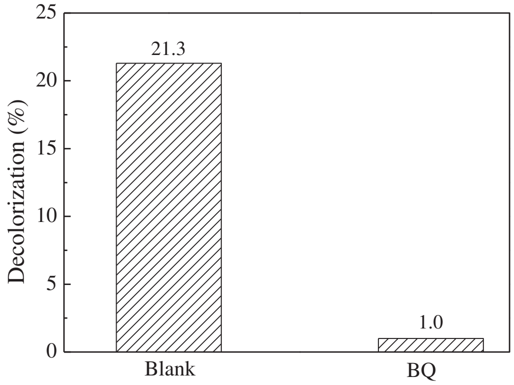

Fig. 5. Effect of BQ on the photocatalytic efficiency of MO; the concentration of MO was 10 mg/L, the amount KIO_3 was 0.5 g/L, the concentration of BQ was 0.4 mmol/L, the reaction time was 1 h.

mmol/L benzoquinone (BQ), an $\cdot O_2^-$ scavenger [32], was added, it is interesting that the photocatalytic reaction was totally retarded (Fig. 5). The result here indicates that the photocatalytic mechanism of MO with KIO_3 under UV irradiation involves the attack of $\cdot O_2^-$. However, the formation of $\cdot O_2^-$ is not clear, remaining for further study.

4. Conclusion

This paper demonstrates that the decolorization reaction of MO is a zero-order reaction when the concentration is above 25 mg/L and organic compounds such as IO_4^-, $S_2O_8^{2-}$, BrO_3^-, and H_2O_2 can greatly inhibit the photocatalytic decolorization of MO. Although there is a lack of direct evidence for the presence of $\cdot O_2^-$, several observations indicate that $\cdot O_2^-$ radicals are involved in the photocatalytic decolorization of MO with KIO_3 under UV irradiation. Furthermore, a more detailed mechanism needs to be further investigated.

Acknowledgments

This project was supported financially by the program of Science and Technology Department of Sichuan province (No. 2013JY0080), the program of Education Department of Sichuan province (No. 11ZA27), Research Fund Projects of Sichuan University of Science and Engineering (Y201216), Construct program of the Discipline in Sichuan University of Science and Engineering, the Project of Zigong city (2012X07), and the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of High Education (No. LZJ1202).

References

[1] S. Garcia-Segura, S. Dosta, J.M. Guilemany, E. Brillas, Solar photoelectrocatalytic degradation of Acid Orange 7 azo dye using a highly stable TiO_2 photoanode synthesized by atmospheric plasma spray, Appl. Catal., B: Environ. 132–133 (2013) 142–150.

[2] C.A. Martínez-Huitle, E. Brillas, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review, Appl. Catal., B: Environ. 87 (2009) 105–145.

[3] Z.P. Xing, D.Z. Sun, Treatment of antibiotic fermentation wastewater by combined polyferric sulfate coagulation, Fenton and sedimentation process, J. Hazard. Mater. 168 (2009) 1264–1268.

[4] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Mariñas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (2008) 301–310.

[5] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations, Appl. Catal., B: Environ. 49 (2004) 1–14.

[6] A. Nezamzadeh-Ejhieh, M. Khorsandi, Heterogeneous photodecolorization of eriochrome black T using Ni/P zeolite catalyst, Desalination 262 (2010) 79–85.

[7] G. Subramanian, P. Parakh, H. Prakash, Photodegradation of methyl orange and photoinactivation of bacteria by visible light activation of persulphate using a tris(2,2′-bipyridyl)ruthenium(II) complex, Photochem. Photobiol. Sci. 12 (2013) 456–466.

[8] L.I. Doumic, P.M. Haure, M.C. Cassanello, M.A. Ayude, Mineralization and efficiency in the homogeneous Fenton Orange G oxidation, Appl. Catal., B: Environ. 142–143 (2013) 214–221.

[9] R. Daghrir, P. Drogui, D. Robert, Modified TiO_2 for environmental photocatalytic applications: A review, Ind. Eng. Chem. Res. 52 (2013) 3581–3599.

[10] C.T. Fragoso, R. Battisti, C. Miranda, P.C. de Jesus, Kinetic of the degradation of C.I. Food Yellow 3 and C.I. Food Yellow 4 azo dyes by the oxidation with hydrogen peroxide, J. Mol. Catal. A: Chem. 301 (2009) 93–97.

[11] M. Sun, G.D. Chen, Y.K. Zhang, Q. Wei, Z.M. Ma, B. Du, Efficient degradation of azo dyes over Sb_2S_3/TiO_2 heterojunction under visible light irradiation, Ind. Eng. Chem. Res. 51 (2012) 2897–2903.

[12] A. Nezamzadeh-Ejhieh, M. Karimi-Shamsabadi, Decolorization of a binary azo dyes mixture using CuO incorporated nanozeolite-X as a heterogeneous catalyst and solar irradiation, Chem. Eng. J. 228 (2013) 631–641.

[13] Y.Q. Qu, X.F. Duan, Progress, challenge and perspective of heterogeneous photocatalysts, Chem. Soc. Rev. 42 (2013) 2568–2580.

[14] F. Chai, L.J. Wang, L.L. Xu, X.H. Wang, J.G. Huang, Degradation of dye on polyoxotungstate nanotube under molecular oxygen, Dyes Pigm. 76 (2008) 113–117.

[15] C. Karunakaran, R. Dhanalakshmi, P. Gomathisankar, G. Manikandan, Enhanced phenol-photodegradation by particulate semiconductor mixtures: Interparticle electron-jump, J. Hazard. Mater. 176 (2010) 799–806.

[16] A. Nezamzadeh-Ejhieh, N. Moazzeni, Sunlight photodecolorization of a mixture of methyl orange and bromocresol green by CuS incorporated in a clinoptilolite zeolite as a heterogeneous catalyst, J. Ind. Eng. Chem. 19 (2013) 1433–1442.

[17] W.K. Choy, W. Chu, The use of oxyhalogen in photocatalytic reaction to remove o-chloroaniline in TiO_2 dispersion, Chemosphere 66 (2007) 2106–2113.

[18] W.K. Choy, W. Chu, Photo-oxidation of o-chloroaniline in the presence of TiO_2 and IO_3^-: A study of photo-intermediates and successive IO_3^- dose, Chem. Eng. J. 136 (2008) 180–187.

[19] W.K. Choy, W. Chu, Semiconductor-catalyzed photodegradation of o-chloroaniline: Products study and iodate effect, Ind. Eng. Chem. Res. 46 (2007) 4740–4746.

[20] F.A. Cotton, G. Wilkinson, P.L. Gaus, The halogens: Fluorine, chlorine, bromine, iodine, and astatine, in: Basic Inorganic Chemistry, 3rd ed., Wiley, New York, NY, 1995, pp. 471–482.

[21] L.K. Weavers, I. Hua, M.R. Hoffmann, Degradation of triethanolamine and chemical oxygen demand reduction in wastewater by photoactivated periodate, Water Environ. Res. 69 (1997) 1112–1119.

[22] T. Wang, X.Y. He, J.Z. Li, J.B. Zhong, F.C. Zeng, W. Hu, Decolorisation of methyl orange solution with KIO_3 under UV irradiation, Appl. Mech. Mater. 178–181 (2012) 653–656.

[23] N. Sobana, K. Selvam, M. Swaminathan, Optimization of photocatalytic degradation conditions of direct red 23 using nano-Ag doped TiO_2, Sep. Purif. Technol. 62 (2008) 648–653.

[24] D. Robert, Industrial and environmental applications of photocatalysis, Int. J. Photoenergy 5 (2003) 43–197 (special issue).

[25] J.B. Zhong, D. Ma, H. Zhao, A. Lian, M.J. Li, S.T. Huang, J.Z. Li, Photocatalytic decolorization of methyl orange solution with potassium peroxydisulfate, Cent. Eur. J. Chem. 6 (2008) 245–252.

[26] J.B. Zhong, X.Y. He, J.Z. Li, J. Zeng, W. Hu, Decolorization of methyl orange solution with potassium bromate under UV irradiation, J. Adv. Oxid. Technol. 15 (2012) 183–187.

[27] S. Antonaraki, E. Androulaki, D. Dimotikali, A. Hiskia, E. Papaconstantinou, Photolytic degradation of all chlorophenols with polyoxometallates and H_2O_2, J. Photochem. Photobiol., A: Chem. 148 (2002) 191–197.

[28] M.Q. Hu, Y.M. Xu, Photocatalytic degradation of textile dye X3B by heteropolyoxometalate acids, Chemosphere 54 (2004) 431–434.

[29] D.F. Ollis, E. Pelizzetti, N. Serpone, Destruction of water contaminants, Environ. Sci. Technol. 9 (1991) 1523–1529.

[30] L.H. Chia, X.M. Tang, L. Weavers, Kinetics and mechanism of photoactivated periodate reaction with 4-chlorophenol in acidic solution, Environ. Sci. Technol. 38 (2004) 6875–6880.

[31] S.G. Meng, D.Z. Li, M. Sun, W.J. Li, J.X. Wang, J. Chen, X.Z. Fu, G.C. Xiao, Sonochemical synthesis, characterization and photocatalytic properties of a novel cube-shaped $CaSn(OH)_6$, Catal. Commun. 12 (2011) 972–975.

[32] M.C. Yin, Z.S. Li, J.H. Kou, Z.G. Zou, Mechanism investigation of visible light-induced degradation in a heterogeneous TiO_2/eosin Y/rhodamine B system, Environ. Sci. Technol. 43 (2009) 8361–8366.