Desalination and Water Treatment
www.deswater.com

22 (2010) 111–116
October

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doi: 10/5004/dwt.2010.1633

Removal of phosphorus in municipal landfill leachate by photochemical oxidation combined with ferrate pre-treatment

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Received 12 November 2009; Accepted 28 March 2010

ABSTRACT

Removal of phosphorus in municipal landfill leachate by photochemical oxidation processes combined with ferrate pre-treatment was investigated in this study. Removal effect of phosphorus in the five systems, Fe(VI)/UV, Fe(VI)/TiO_2/UV, Fe(III)/UV, TiO_2/UV and UV, were evaluated. The results show that ferrate pre-treatment removes 78% of total phosphorus by using 0.16 mM ferrate dealing with 500 mL municipal landfill leachate at pH 5. Among the five systems, Fe(VI)/TiO_2/UV is the most efficient process for total phosphorus removal (almost 100%).

Keywords: Landfill leachate; Phosphorus; Ferrate; Photochemical oxidation

1. Introduction

Phosphorus is one of essential nutrient for the growth of organisms, and it caused detrimental eutrophication in aquatic environments. In order to lower the discharge this nutrient into the environment various technologies have been investigated. Including conventional treatment such as precipitation, adsorption, ion exchange and biological treatment, and novel treatments have also been investigated such as reverse osmosis and electrodialysis [1].

Landfilling of municipal waste is a very important and indispensable part of the waste management system worldwide. One of the most severe environmental pollutions related to landfilling is the generation of leachates. The landfill leachate is an effluent produced by the garbage in the process of its filling and burying by fermentation, rain washing, and soaking of surface water and underground water. Leachate migration from the landfill is a potential source of surface and groundwater contaminations. The landfill leachate contains high concentrations of organic matters, ammonia nitrogen, toxic metals, chlorides and phosphorus. Physical-chemical processes are promising processes used for the removal of contaminants in landfill leachate. Kim et al. have studied the enhancing struvite precipitation potential for ammonia nitrogen removal in municipal landfill leachate [2]. Fenton treatment for organic contaminants in mature municipal landfill leachate has been also reported [3]. Anodic oxidation has been shown to be effective for ammonium removal from landfill leachate [4]. COD in landfill leachate reductions of up to 48% were achieved after treatment with O_3/H_2O_2 system as reported by Tizaoui et al. [5]. In the past few years, the photochemical process has been widely applied for treating the landfill leachate because this process can degrade the pollutants in a very short period of time. The mechanism of photochemical process generates active radicals ($^{\bullet}OH$) with extra-high oxidizing capacity (E^0=2.8 V) that can oxidize, degrade or even mineralize organic matters [6].

Extensive efforts have been made on treating the landfill leachate by the photochemical process in the past 20 y. Various studies have been made on treating

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the landfill leachate in UV/oxidant system (UV/H_2O_2, UV/O_3, UV/H_2O_2/O_3) [7,8]. Photo-Fenton reaction for treating the landfill leachate can remove 70% of COD and 83% of TOC [9].The UV/TiO_2 system can also remove 70% of TOC from the landfill leachate [10]. Furthermore, the application of solar energy in treating the landfill leachate has been reported [11].

Ferrate(VI) ion has the molecular formula, FeO_4^{2-}, and is a very strong oxidant. Under acidic conditions, the redox potential of ferrate(VI) ions is the highest among all the oxidants/disinfectants practically used for water and wastewater treatment [12]. A range of studies have shown that various types of organic impurities can be oxidized by ferrate(VI) effectively. The organic compounds investigated include phenol [13], hydroxylamine [14], thiourea [15], and algae [16]. During the oxidation process of organic matters and microorganisms in water, ferrate(VI) ions will be reduced to Fe(III) ions or ferric hydroxide, which generates a coagulant and photocatalysis property in the process simultaneously [14]. Gray [17] and Solo's studies [18] showed that the residual turbidity in treated water with ferrate was less than that with ferrous sulphate and ferric nitrate. Ferrate can destabilize the colloidal particles within 1 min, while ferric and ferrous salts can only achieve the destabilization after 30 min of mixing [19].

Landfill leachate treatment by a coagulation—photooxidation process with Fe(III) ions was reported in the previous study [19]. The coagulation process is effective for removing high concentration of organic pollutants. Furthermore, there is a large quantity of hydrolytic iron(III) in the effluent of coagulation treatment process under acidic conditions, which is an abundant source of active radicals for advanced photooxidation treatment.

It is well known that in the pH range ≤5 at least four different low-molecular-weight Fe(III) ions coexist in aqueous solution: Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^+$ and the dimer $Fe_2(OH)_2^{4+}$. The corresponding hydrolysis equilibriums are presented as Eqs. (1)–(3) [20,21,22].

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+ \qquad K_1 = 2.7 \times 10^{-3}\ M \tag{1}$$

$$Fe^{3+} + 2H_2O \rightarrow Fe(OH)_2^{+} + 2H^+ \qquad K_2 = 1.3 \times 10^{-8}\ M \tag{2}$$

$$Fe^{3+} + 2H_2O \rightarrow Fe_2(OH)_2^{4+} + 2H^+ \qquad K_3 = 6 \times 10^{-4}\ M \tag{3}$$

In aqueous solution at the pH range of 2.5–5, $Fe(OH)^{2+}$ is the dominant monomeric Fe(III)-hydroxy complex based on equilibrium constants for Fe(III)-hydroxy complexes in Eqs. (1)–(3). According to Weschler, the charge transfer band of $Fe(OH)^{2+}$ overlaps the solar UV spectrum (290–400 nm) [23]. Faust et al. reported that quantum efficiencies for the photolysis of $Fe(OH)^{2+}$ are 0.04 ± 0.04 at 313 nm and 0.017 ± 0.003 at 360 nm (293 K, ionic strength = 0.03 M) [23]. Moreover, the quantum yield of $^\bullet OH$ produced from the photolysis of $Fe(OH)^{2+}$ is much higher than that of the other two species $Fe(H_2O)_6^{3+}$ and $Fe_2(OH)_2^{4+}$ [25]. Therefore, $Fe(OH)^{2+}$ is the dominant photoreactive species in the solution at the pH range of 2.5–5. The photolysis of $Fe(OH)^{2+}$ to produce $^\bullet OH$ radicals can be expressed as Eq. (4):

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + {}^\bullet OH \tag{4}$$

Moreover, the photolysis of Fe(III) also leads to the production of $^\bullet OH$ radicals as shown in Eq. (5) [24,25].

$$Fe^{3+} + hv \rightarrow Fe^{2+} + {}^\bullet OH \tag{5}$$

Ferrate(VI) salt has unique properties such as strong oxidizing potential; simultaneous generation of ferric coagulating and photocatalytic species [14]. Photochemical oxidation combined with ferrate pre-treatment can remove the phosphorus in the landfill leachate more effectively compared with the biological and pure chemical methods. Accordingly, it was a promising alternative treatment method for the phosphorus removal. In this work, ferrate pre-oxidization combined with the photochemical process was designed for landfill leachate treatment. The ferrate pre-oxidation process was investigated by varying the following operating parameters: (i) initial pH; (ii) initial ferrate concentration in pretreatment in this study. The removal efficiency of total phosphorus (total-P) removal from landfill leachate was also investigated in the following combined photocatalytic system: Fe(VI)/UV, Fe(VI)/TiO_2/UV, Fe(III)/UV, TiO_2/UV, and UV.

2. Materials and methods

2.1. Leachate

The leachate was collected from Wuhan Liufang landfill (landfill age of approximately 15 y), and the characteristics of raw leachate quality is shown as follow: COD: 1300 mg·l^{-1}, BOD_5: 38 mg·l^{-1}, NH_3–N: 820 mg·l^{-1}, total phosphorus: 15.1 mg·l^{-1}, organic phosphorus: 10.2 mg · l^{-1}, inorganic phosphorus: 3.9 mg·l^{-1}. The sample was collected by plastic container and stored at 4 °C before experiments in the refrigerator.

2.2. Analysis

Phosphorus was determined by the standard methods [26]; pH was determined by pH meter (model: pHS-3; manufacturer: LEI-CI equipment Co., Ltd (Shanghai, P. R. China)). All other chemicals were analytical grade and the

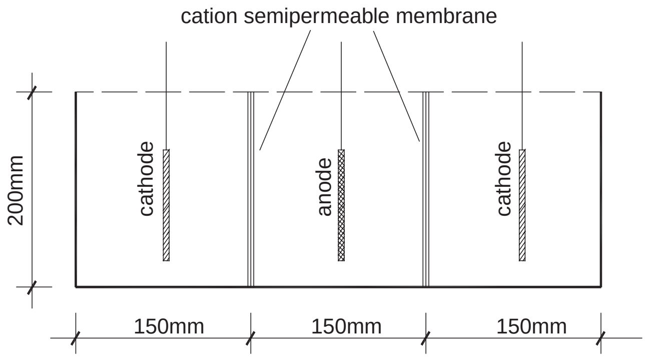

Fig. 1. Scheme of electrolytic bath.

water used in this study was doubly distilled water. The errors all through the experiments are less than 5%.

2.3. Ferrate

Ferrate was prepared through electrolysis onsite. The material of the electrolytic bath was unplasticized polyvinyl chloride, and the structure and size were shown in Fig. 1. The anode was made of gray cast iron, and the double cathodes were made of nickel sheet. For each electrode, the area was 20 cm^2. Saturated aqueous NaOH solution was used as electrolyte and separated by cationic semi-permeable membrane. Direct current stabilized voltage supply (RXN-3010A, Zhaoxin, PR China) was used and the electrolytic voltage was maintained between 5–10 V. The concentration of ferrate prepared by electrolysis was measured using UV-visible spectrophotometer (Model: CARY 50 Probe; Manufacturer: Varian Corporation (Palo Alto, USA)) [27].

2.4. Experimental procedures

The experiments were carried out in a Pyrex batch photoreactor (Fig. 2). The effective volume of the photoreactor (length = 410 mm, O.D. = 69 mm and wall thickness = 1 mm) was 600 mL. Low-pressure UV lamp (254 nm, 15 W, light intensity = 48.4 $\mu W/cm^2$) was used. In low-pressure lamp, about 81.7% UV radiation is emitted at the wavelength of 254 nm. This lamp was obtained from Changsha Yuelu Xinhui Electric Company (Changsha, P. R. China). An immersion well made of high purity quartz was placed inside the glass reactor fitted with a standard joint at the top. The UV lamp was kept inside the immersion well. Water was passed through the thin annular zone of the immersion well to prevent overheating of the reaction mixture. In order to achieve a stabilized radiation emission, the lamp was always switched on for 30 min before being fitted into the reactor. Air was bubbled in the reacting mixture to homogenize the liquid solution throughout the experiments.

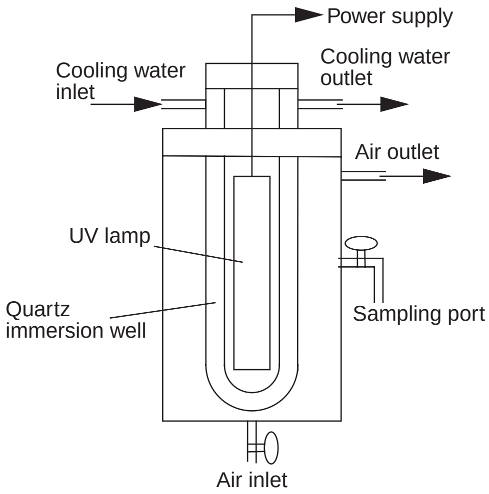

Fig. 2. The diagram of the photocatalytic reactor.

All of the solution was prepared with distilled water. NaOH (saturated solution) and H_2SO_4 (0.005 mol/l) were used to adjust the initial pH values of the reaction solutions. The reaction solutions are all 500 ml. The ferrate concentration was 16.0 $mmol \cdot l^{-1}$, TiO_2 concentration was 2 $g \cdot l^{-1}$, $FeCl_3 \cdot 6H_2O$ concentration was 500 $mg \cdot l^{-1}$, glyphosate concentration was 2 $mg \cdot l^{-1}$. Samples were taken from the irradiated solutions at predetermined time intervals before analysis. All experiments were carried out at room temperature.

3. Results and discussion

3.1. Effect of pH on the removal of total-P by ferrate pretreatment

Fig. 3 shows the effect of pH on total-P removal in leachate treatment by ferrate pretreatment. The lower the pH value, the higher the concentration of •OH produced by ferrate and the greater the oxidizing capacity. The removal of phosphorus (about 78% at pH 5) is mainly due to the oxidization of organic phosphorus by

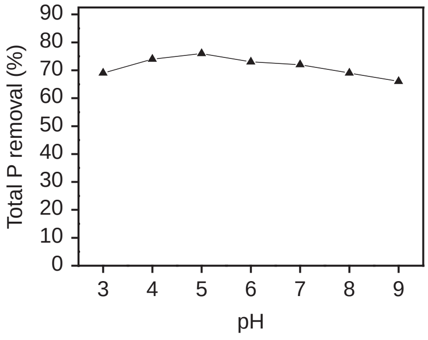

Fig. 3. Effect of pH on the removal of total-P by ferrate pretreatment: ferrate concentration 16.0 $mmol \cdot l^{-1}$, ferrate dosage 10 ml.

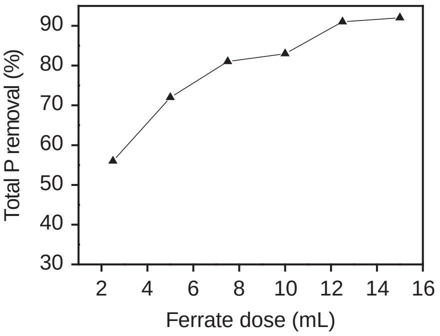

Fig. 4. Effect of ferrate dosage on the removal of total-P by ferrate pretreatment: ferrate concentration 16.0 mmol·l^{-1}, pH 5.

ferrate under acidic condition. In addition, $Fe(OH)_3$ can also removal inorganic phosphorus (phosphates mainly) by coagulation. In consideration of cost and convenient, pH 5 was set the optimal pH value in the experiment.

3.2. *Effect of ferrate dosage on the removal of total-P by ferrate pretreatment*

Fig. 4 shows the removal efficiency of total phosphorus for 500 mL leachate with different ferrate dosages at pH 5. Total phosphorus removal increased with the ferrate dosage. When the dosage of ferrate reached 12.5 mL, the 91% removal efficiency of total-P was achieved. However, little total-P was removed with more dosage. Accordingly, the optimum ferrate dosage was 12.5 mL for considering cost. Phosphorus removal by ferrate is due to the fact that $^{\bullet}OH$ generated by hydrolysis of ferrate would oxidize organic phosphorus and transform it to low-molecular organic acids and phosphates [28]. Thus, the phosphates formed and the original inorganic phosphorus in the solution may be further removed by flocculation and sedimentation of $Fe(OH)_3$.

3.3. *The removal of total-P in different combined UV systems*

Fig. 5 shows total phosphorus concentration versus irradiation time in different combined UV systems. 78% of total phosphorus was removed after ferrate oxidation. Over 90% of total phosphorus removal efficiency was achieved in Fe(VI)/TiO_2/UV, Fe(III)/UV and Fe(VI)/UV system. It can be concluded that $Fe(OH)_3$ coagulation has significant effect on total phosphorus removal. Among these systems, Fe(VI)/TiO_2/UV system had the maximum removal efficiency (almost 100%). Phosphorus removal was attributed to the oxidization of $^{\bullet}OH$ generated by photochemical reaction of Fe(VI) and coagulation of $Fe(OH)_3$. In contrast, only 37% and 25% of total phosphorus was removed in TiO_2/UV and UV system, respectively. The addition of TiO_2 in the UV system caused the decrease of the phosphorus removal. This was predominantly due to the light scattering and screening effect by the granular TiO_2. In the same experimental conditions, we also studied the COD removal. There was a best effect (about 55.3%) after 4 h′ light in Fe(VI)/TiO_2/UV system, and 50.4% of COD was removed in Fe(VI) /UV system. However, in the UV system only 6.9% of COD was removed.

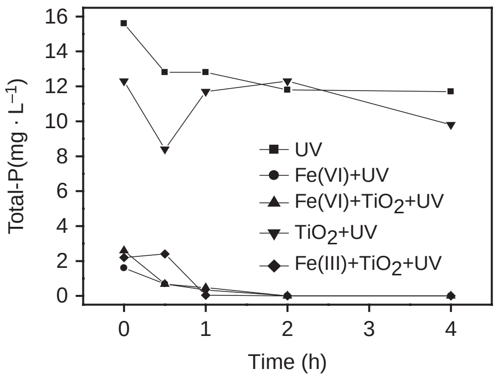

Fig. 5. Total-P concentration versus irradiation time in different combined UV system: ferrate concentration 16.0 mmol · l^{-1}, pH 5, TiO_2 concentration 2 g·l^{-1}, $FeCl_3·6H_2O$ concentration 500 mg· L^{-1}, irradiation wavelength 254 nm, light intensity = 48.4 μW/cm^2.

4. Mechanism of photocatalytic removal of phosphorus

Phosphorus in landfill leachate includes organic phosphorus and inorganic phosphorus. In order to understand the mechanism of photocatalytic removal of phosphorus, photochemical transformation of glyphosate (organic phosphorus, an herbicide, abundant in landfill leachate) by ferrate pre-treatment was investigated. As shown in Fig. 6, glyphosate was all removed after 30 min irradiation with ferrate pre-treatment. Most of organic phosphorus was

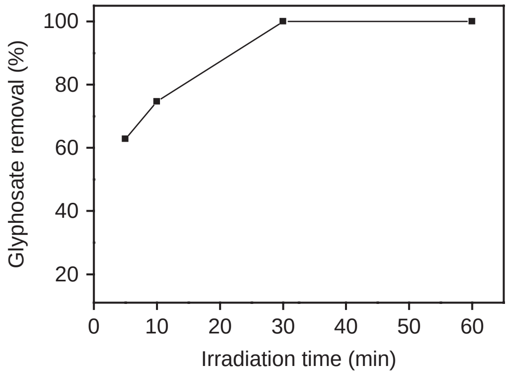

Fig. 6. Photochemical degradation of glyphosate by ferrate pre-treatment: ferrate concentration 16.0 mmol·l^{-1}, pH 5, glyphosate concentration 2 mg·l^{-1}, irradiation wavelength 254 nm, light intensity = 48.4 μW/cm^2.

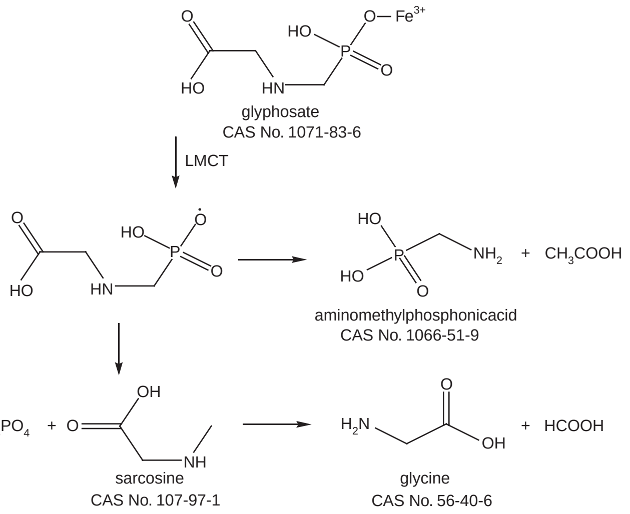

Fig. 7. The possible mechanism of glyphosate photochemical degradation.

oxidized to inorganic phosphorus with ferrate pre-treatment. Organic phosphorus in leachate after ferrate pre-treatment was removed in the subsequent photochemical process. Inorganic phosphorus was then removed by flocculation and sedimentation of Fe(OH)$_3$. The mechanism of photochemical degradation of glyphosate was shown in Fig. 7 [29,30]. In the region where glyphosate was widely used, aminomethylphosphonic acid was detected in surface water. Thus, it can be interpreted that two types of bond cleavage, C–P and C–N exist in photochemical degradation.

5. Conclusions

Degradation of phosphorus in municipal landfill leachate by photochemical oxidation combined with ferrate pre-treatment was effective, and the following conclusions have been achieved:

1. The pH value has effect on the ferrate pretreatment. The maximum removal efficiency of total phosphorus was observed at pH 5.
2. The optimal ferrate dosage was 0.2 mM in ferrate pretreatment at pH 5.
3. Among the systems studied, Fe(VI)/TiO$_2$/UV system is optimal for the degradation of phosphorus. Total phosphorus removal efficiency was almost 100% in Fe(VI)/TiO$_2$/UV system. The cost of phosphorus removal is approximately 10 times the cost of chemical phosphorus removal by using ferrate pre-oxidization combined with the photochemical process. However, the phosphorus removal efficiency of this method is 100%, which is unlikely to be achieved by chemical phosphorus removal.
4. The possible mechanism of phosphorus in landfill leachate degradation was proposed. Organic phosphorus in landfill leachate was oxidized to inorganic phosphorus by $^{\bullet}$OH generated by photochemical process and ferrate. Inorganic phosphorus was then removed by flocculation and sedimentation of Fe(OH)$_3$.

Symbols

BOD$_5$	—	5-day biochemical oxygen demand
COD	—	Chemical oxygen demand
Fe(VI)/TiO$_2$/UV system	—	Fe(VI) pre-oxidization combined with TiO$_2$ photocatalytic oxidation
Fe (VI)/UV system	—	Fe(VI) pre-oxidization combined with UV radiation
Fe(III)/UV system	—	Fe(III) coagulation combined with UV radiation
Fe(III)/TiO$_2$/UV system	—	Fe(III) coagulation combined with TiO$_2$ photocatalytic oxidation
NH$_3$–N	—	Ammonia nitrogen
TiO$_2$/UV system	—	using TiO$_2$ as catalyst in UV radiation
UV system	—	direct UV radiation

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