Removal of glyphosate from water by electrochemically assisted MnO_2 oxidation process

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ABSTRACT

Glyphosate, one of the organophosphate herbicides, has been widely used in the world. The removal of glyphosate was comparatively investigated by MnO_2 oxidation, electrochemical oxidation, and electrochemically assisted MnO_2 oxidation (electro- MnO_2) processes. The effects of MnO_2 dosage, current density, and solution pH on glyphosate removal and Mn^{2+} release were examined. The results indicated that the removal of glyphosate by MnO_2 oxidation favored acidic pH conditions and a large portion of Mn^{2+} ions were released from MnO_2 . With the electro- MnO_2 process using $\text{RuO}_2/\text{TiO}_2$ coated titanium mesh as both anode and cathode, glyphosate removal was significantly promoted and most of the released Mn^{2+} ions were oxidatively reverted to MnO_2 , which in turn enhanced the removal of glyphosate. Solution pH exerted an insignificant effect on glyphosate removal in the electro- MnO_2 process. Major reaction intermediates including sarcosine, glycine, and PO_4^{3-} were identified in the initial phase of the MnO_2 oxidation and electro- MnO_2 processes. Glycine was further decomposed to glycolic acid and $\text{NH}_3\text{-N}$ in the MnO_2 oxidation process; in contrast, glycine was oxidized into oxamic acid, glycolic acid and N-contained intermediates, and N-contained intermediates could be finally oxidized into acetic acid, $\text{NH}_3\text{-N}$ and $\text{NO}_3\text{-N}$ in the electro- MnO_2 process.

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1. Introduction

Glyphosate is a non-selective, post-emergence, broad-spectrum, and commonly applied organophosphate herbicide. It can be used on non-crop lands as well as on a numbers of crops [1]. The occurrence of glyphosate and its metabolite aminomethylphosphonic acid (AMPA) in surface and ground waters worldwide has been reported frequently [2,3].

Chlorination was found to be an efficient method for glyphosate removal [4], however, it brought about new risks of producing other hazardous metabolites [5]. The removal of glyphosate by adsorption on activated carbon, Mg/Al-layered double hydroxides, and goethite has been suggested [6,7]. The degradation of glyphosate by microbial process was also investigated [8].

Advanced oxidation processes (AOPs) seem to be potential options to reduce organic contaminants to acceptable limits. The major active species in such systems is the hydroxyl radical. Studies dealing with the degradation of glyphosate in water with AOPs have been reported, including photocatalysis with TiO_2 , $\text{H}_2\text{O}_2/\text{UV}$,

and $\text{Fe(III)}/\text{H}_2\text{O}_2/\text{UV}$ [9–12]. The combination of H_2O_2 and UV radiation could be a simple and convenient process for the treatment of this type of pollutants. The electrochemical oxidation of glyphosate on dimensionally stable anode (DSA) electrodes was also investigated under galvanostatic conditions [13], which indicated that the influence of the oxide composition on glyphosate elimination was significant in the absence of chloride. However, after 4 h of electrolysis, only 32% of glyphosate removal was observed for the best anode at 50 mA cm^{-2} . This low oxidation rate was a consequence of the competition between O_2 evolution and organic compound oxidation.

It has been reported that both glyphosate and AMPA could be degraded in dilute aqueous suspensions of birnessite, a manganese oxide common in soils, as evidenced by the accumulation of orthophosphate in solution [14,15]. In the oxidation of glyphosate using MnO_2 , the oxidation efficiency was low and a large portion of Mn^{2+} ions were released [16]. Application of modified electro-Fenton process to degrade glyphosate in an aqueous solutions has been assessed with Mn^{2+} and other metal ions to overcome the problems caused by some stable metal ion complexes of phosphonate herbicides; bulk electrolysis with a carbon-felt cathode and a Pt anode was performed in an undivided cell under galvanostatic conditions

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to study the effect of the applied current as well as Mn^{2+} and glyphosate concentrations [17]. Herein, a combined process of electrochemically assisted MnO_2 oxidation (electro- MnO_2) process in degrading glyphosate was investigated, which achieved a fast removal of glyphosate. The sole MnO_2 oxidation and electrochemical oxidation processes were also tested for the purpose of comparison. Different degradation intermediates were identified to establish possible reaction pathways.

2. Experimental section

2.1. Chemicals

Glyphosate (purity 99.6%) was purchased from Sigma Company. P-toluenesulfonyl chloride was chemically pure, purchased from Beijing Chemical Reagent Company. Acetonitrile was of HPLC grade and purchased from J&K. All of other reagents were of analytic grade.

2.2. Experimental procedure

Experiment were performed in an electrochemical reaction cell (Fig. 1). The anode and cathode were both made of DSA with an area of 30 cm^2 and an electrode gap of 30 mm. The power was provided by a DC power supply source (DH1718E-4, Dahua Instrument Co., Beijing). The reaction solution (400 mL) contained 0.1 M Na_2SO_4 as electrolyte. At given times, samples were taken and filtrated through $0.45\text{ }\mu\text{m}$ membrane for analysis. The pH of reaction solution was adjusted by 0.10 M NaOH and H_2SO_4 solutions.

2.3. Analytic methods

Glyphosate was analyzed by ion chromatography with an Ion PacAG19-HC ($4\text{ mm} \times 250\text{ mm}$) guard column, an AS19A-HC ($4\text{ mm} \times 50\text{ mm}$) separating column, and an ion self-regenerating suppressor (Alltech DS-Plus). KOH solution (30 mM) was used as eluent at a flow rate of 1.2 mL/min [18]. The injection volume was $25\text{ }\mu\text{L}$ with a suppress current of 90 mA.

Glycine was measured by pre-column derivatization and HPLC (HPLC-1260, Agilent, USA) analysis at 240 nm with a hypersil gold

column ($250\text{ mm} \times 4.6\text{ mm}$, i.d. $5\text{ }\mu\text{m}$, Thermo, USA). Specifically, 1.5 mL of sample was mixed with 0.5 mL of 0.05 M sodium borate solution ($\text{pH} = 9.0$) and 1.0 mL of an acetonitrile solution of toluenesulfonyl chloride (1.0 g/L) at room temperature in sequence. The mixture was allowed to stand overnight (to complete the derivatization), and then filtered through $0.45\text{ }\mu\text{m}$ membrane for HPLC analysis [19]. A mixture of acetonitrile/ammonium acetate (50 mM) ($v/v = 20/80$) was used as the mobile phase with a flow rate of 1.0 mL/min . The concentration of phosphate was determined by molybdenum antimony anti-spectrophotometric method.

3. Results and discussion

3.1. Performance of electro- MnO_2 process for glyphosate removal

The removal of glyphosate and Mn^{2+} release in the individual MnO_2 oxidation, single electrochemical oxidation and electro- MnO_2 processes were compared. Fig. 2 shows that glyphosate was gradually degraded by MnO_2 and single electrochemical processes, and at 120 min, nearly 40% glyphosate was removed. This is consistent with that reported by Barrett and McBride [14]. Moreover, the release of Mn^{2+} continued as the MnO_2 oxidation reaction proceeded. In contrast, the removal of glyphosate was obviously increased, reaching up to 80% at 120 min in the electro- MnO_2 process. It is noted that the concentration of Mn^{2+} increased rapidly in the first 30 min, and thereafter, decreased gradually till the end of reaction. It suggested that in the electro- MnO_2 process, the released Mn^{2+} ions were timely reverted to MnO_2 particles at anode, which enhanced the removal of glyphosate.

3.2. Effect of current density

The removal of glyphosate under various current densities with a constant MnO_2 dosage was tested in the electro- MnO_2 process. As shown in Fig. 3a, the removal rate of glyphosate significantly increased with the increasing current density. At a current density of 10 mA/cm^2 , about 80% glyphosate was removed at a reaction time of 120 min. Meantime, Mn^{2+} release also increased with the increasing current density in the first 30 min, and afterwards, the concentration of Mn^{2+} ions decreased quickly (Fig. 3b). This result further confirms the electrochemical oxidation of Mn^{2+} ions in the later phase of the electro- MnO_2 process.

Fig. 1. The experimental setup for glyphosate removal by electro- MnO_2 process.

Fig. 2. Removal of glyphosate and release of Mn^{2+} in the MnO_2 , electrochemical and electro- MnO_2 processes ($C_0 = 0.1\text{ mM}$, MnO_2 dosage = 0.25 mM , current density = 10 mA/cm^2 , $\text{pH} = 5.0$).

Fig. 3. Effect of current density on: (a) glyphosate removal in the electro- MnO_2 process, and (b) Mn^{2+} release in the MnO_2 oxidation and electro- MnO_2 processes ($C_0 = 0.1$ mM, pH = 5.0).

3.3. Effect of pH

The effect of pH on glyphosate removal was examined at different initial pH values (i.e., 3.0, 5.0, 7.0 and 9.0) when maintaining the initial glyphosate concentration and the current density constant. Fig. 4 shows that an acidic pH was more favored for glyphosate removal in the MnO_2 oxidation process than in the electro- MnO_2 process. However, pH had a negligible effect in the individual electrochemical process.

The concentrations of released Mn^{2+} ions in the MnO_2 oxidation and electro- MnO_2 processes were measured. In the MnO_2 oxidation process, no significant difference was observed from pH 9.0–5.0, but the Mn^{2+} concentration increased rapidly at pH 3.0 (Fig. 4b). A similar trend was observed in the first 30 min of the electro- MnO_2 process, and then Mn^{2+} ions were oxidized back to MnO_2 (Fig. 4c).

3.4. Intermediates identification

Major intermediates such as glycine and oxamic, glycolic, acetic and formic acids were identified. The concentration variation of these intermediates with reaction time in the MnO_2 oxidation, electrochemical and electro- MnO_2 processes were comparatively presented.

It can be seen from Fig. 5a that the concentration of generated glycine in the electrochemical process was about to 0.5 mg/L at 360 min. In contrast, the concentration of generated glycine in the MnO_2 oxidation and electro- MnO_2 processes increased to 2.5 and 1.0 mg/L, respectively. A similar variation trend was observed for glycolic acid in the three processes, although the maximum concentration of glycolic acid was as low as 0.6 mg/L (Fig. 5b).

Fig. 5c shows that oxamic acid was generated at a low concentration in the MnO_2 oxidation process. The concentration of oxamic acid obviously increased in the electrochemical and electro- MnO_2

Fig. 4. (a) Effect of pH on glyphosate removal by the MnO_2 oxidation, electrochemical and electro- MnO_2 processes; (b) release of Mn^{2+} ions in the MnO_2 oxidation process at various pH values; (c) release of Mn^{2+} ions in the electro- MnO_2 process at various pH values ($C_0 = 0.1$ mM, MnO_2 dosage = 0.25 mM, current density = 10 mA/cm², pH = 5.0).

processes. Similar trend was observed for the variation of acetic acids. Furthermore, an obvious difference in the generation and variation of formic acid in the three processes were observed. In the electro- MnO_2 and electrochemical process, the concentration of formic acid increased with the time before 120 min. After that, the concentration of formic acid decrease with the reaction time. In contrast, the concentration of formic acid increased with the reaction time in individual MnO_2 process.

Furthermore, the evolution of PO_4^{3-} , NH_3-N and NO_3^-N with reaction time was given in Fig. 6. As shown in Fig. 6a, there was only slight difference in PO_4^{3-} generation among the three processes. However, much more NH_3-N was generated in the MnO_2

Fig. 5. The concentration variation of identified intermediates during glyphosate degradation in the MnO₂ oxidation, electrochemical oxidation and electro-MnO₂ processes: (a) glycine; (b) glycolic acid; and (c) oxamic acid (C₀ = 0.1 mM, MnO₂ dosage = 0.25 mM, current density = 10 mA/cm², pH = 5.0).

oxidation process than in other two processes (Fig. 6b). The concentration of NH₃-N in the electrochemical process increased slightly with the reaction time. In the electro-MnO₂ process, the concentration of NH₃-N increased with reaction time before 120 min and then decreased slightly. In contrast, the concentration of NH₃-N kept increasing in the MnO₂ oxidation process. Correspondingly, an opposite trend was observed for the variation of NO₃⁻-N concentration in the three processes (Fig. 6c). The NO₃⁻-N concentration was always below 0.03 mg/L in the MnO₂ oxidation process; by contrast, it increased to 0.3 mg/L in both electrochemical and electro-MnO₂ processes.

3.5. Proposed reaction pathways

In the MnO₂ oxidation process, the C–P bond tended to break first, leading to the generation of sarcosine and PO₄³⁻. Sarcosine could be further oxidized to glycine and formic acid. The continuous oxidation of glycine produced glycolic acid and NH₃-N. Meanwhile, Mn²⁺ ions were released into the aqueous solution. Similar intermediates (i.e., sarcosine, glycine, and formic acid) were

Fig. 6. The concentration variation of (a) PO₄³⁻, (b) NH₃-N, and (c) NO₃⁻-N during glyphosate degradation in the MnO₂ oxidation, electrochemical oxidation and electro-MnO₂ processes (C₀ = 0.1 mM, MnO₂ dosage = 0.25 mM, current density = 10 mA/cm², pH = 5.0).

observed in the degradation of glyphosate by using manganese oxide [14].

In the electro-MnO₂ process, sarcosine, glycine and PO₄³⁻ were also identified in the initial phase of reaction. After that, glycine was oxidized to oxamic, glycolic acid and N-contained intermediates, and N-contained intermediates can be further oxidized to acetic acid, NH₃-N and NO₃⁻. At the meantime, Mn²⁺ was oxidized back to MnO₂. The assisted electrochemical process could oxidize not only Mn²⁺ but also glyphosate and its intermediates, which led to the different pathways of glyphosate degradation in the MnO₂ oxidation and electro-MnO₂ processes. In a Fe(III)/H₂O₂/UV process, two degradation pathways were proposed [10]. The cleavage of the C–N and C–P bonds was attributed to the attack of hydroxyl radicals. When the C–P bond was broken, glyphosate was decomposed to AMPA and acetic acid; when the C–N bond was broken, sarcosine and phosphoric acid were produced [10]. In a photocatalytic process, two possible pathways for glyphosate degradation were proposed under acidic (i.e., sarcosine formation) and basic (i.e., direct generation of glycine) pH conditions, respectively

Fig. 7. Proposed pathways for glyphosate degradation in the MnO_2 oxidation and electro- MnO_2 processes.

[20]. Therefore, the hydroxyl radicals generated in the electrochemical process may be responsible for a different pathway of glyphosate degradation in the electro- MnO_2 process. The pathways of glyphosate degradation in the MnO_2 oxidation and electro- MnO_2 processes were comparatively illustrated in Fig. 7.

4. Conclusions

This work comparatively investigated the removal of glyphosate from water by the MnO_2 oxidation, electrochemical oxidation, and electrochemically assisted MnO_2 oxidation (electro- MnO_2) processes. Based on the obtained results, the following conclusions are drawn:

- The electro- MnO_2 process exhibited a higher efficiency for glyphosate removal than the MnO_2 oxidation process. Because the released Mn^{2+} could be timely reverted to MnO_2 by the electrochemical process.
- The removal efficiency of glyphosate increased with the current density. pH had a insignificant effect on glyphosate removal.
- Similar intermediates such as sarcosine, glycine and PO_4^{3-} are identified in the initial phase of the MnO_2 oxidation and electro- MnO_2 processes. Thereafter, glycine was oxidized to glycolic acid and $\text{NH}_3\text{-N}$ in the MnO_2 process; while in the electro- MnO_2 process, glycine was oxidized into oxamic acid, glycolic acid and N-contained intermediates, and N-contained intermediates could be finally oxidized into acetic acid, $\text{NH}_3\text{-N}$ and $\text{NO}_3^-\text{-N}$.

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