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Research paper

Degradation of bisphenol A by nano-sized manganese dioxide synthesized using montmorillonite as templates

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ABSTRACT

A new method was developed to synthesize nanoscale manganese dioxide (MnO_2) using natural montmorillonite as the template. When the exchangeable Mn^{2+} cations reacted with $KMnO_4$, the unique structure of montmorillonite effectively prevented the agglomeration of MnO_2 resulting in the formation of nano-sized MnO_2 particles. The clay mineral-templated MnO_2 showed higher reactivity compared to nano-MnO_2 prepared by conventional method as indicated by the oxidation of bisphenol A (BPA). Over 90% of BPA could be degraded within 10 min at pH 4.0 containing 250 mg L^{-1} montmorillonite (109 μM MnO_2) and 21.9 μM BPA. The presence of humic acid showed significant enhancement on BPA removal under acidic condition, while slight inhibition under alkaline condition. Due to the ubiquitous distribution of montmorillonite in natural environment, montmorillonite templated MnO_2 would offer the potential for in situ remediation of many organic contaminants.

1. Introduction

Manganese dioxide (MnO_2) is one of the mostly studied strong oxidants for degradation of various organic pollutants, e.g., steroid estrogens (Xu et al., 2008), oxytetracycline (Rubert and Pedersen, 2010) and lincosamide (Chen et al., 2010). Due to the smaller particle size and higher specific surface area, nanoscale MnO_2 has drawn considerable attentions and has been utilized to degrade organic pollutants in green infrastructure and water treatment (Remucal and Ginder-Vogel, 2014). Various synthesis methods for nano-MnO_2 have been developed, such as sol-gel process (Giraldo et al., 2000), hydrothermal synthesis (Subramanian et al., 2005) and thermal decomposition (Lamaita et al., 2005). However, during the process of synthesis, MnO_2 nanoparticles prone to cause agglomeration resulting in larger particles with reduced activity (Lin et al., 2009; Zhao et al., 2006). Therefore, many strategies have been tested to stabilize the synthesized nano-MnO_2 to prevent further aggregation. Activated carbon fibers were used as stabilizer to increase MnO_2 particles dispersion, which enhanced the catalytic oxidation efficiency to convert NO into NO_2 remarkably (Wang et al., 2014). Moreover, bovine serum albumin stabilized MnO_2 nanoparticles exhibited high peroxidase-, oxidase-, and catalase-like activities (Liu et al., 2012). MnO_2 nanosheets using grapheme oxide as the template exhibited high activity for the degradation of methylene blue (Zhao et al., 2013).

Montmorillonites are ubiquitous in subsoils, sediments and soils. Depending on the exchangeable cations, the layer spacings of montmorillonites generally vary from 1 to 1.8 nm, and the width is in the range between a few tens and a few hundreds nanometers. The specific surface area of montmorillonites is 800 m^2 g^{-1} (Schoonheydt, 2002). Hence, montmorillonite can be considered as a natural nanomaterial. Because of isomorphic substitution, montmorillonites possess structural negative charges, which are compensated by exchangeable cations in the interlayer. Our previous studies showed that montmorillonite could be used as a template to synthesize subnano-sized zero valent iron (ZVI) (Gu et al., 2010; Zhang et al., 2015). Due to the special structure of montmorillonite, ZVIs could be synthesized in interlayer region of montmorillonite with the average size of 0.5 nm (Gu et al., 2010). The montmorillonite templated ZVI exhibits higher efficiency than ZVIs synthesized from traditional methods as indicated by the reductive degradation of nitrobenzene (Gu et al., 2010). With the protection of montmorillonite, the montmorillonite-templated ZVIs also maintain a greater stability (Gu et al., 2010). Here, we hypothesize that nano-MnO_2 could also be formed in clay mineral interlayer by initially saturating montmorillonite with Mn^{2+}, then via oxidation by addition of MnO_4^-.

Bisphenol A (BPA) is widely used for the production of polycarbonates and other plastics, and has been frequently detected in soils, sediments, air, municipal waste and biota samples (Huang et al., 2012). It has been reported that the concentration of BPA in bottled water could even reach 568 ng L^{-1} (Li et al., 2006). Recent studies showed that BPA could act as an estrogen agonist or antagonist to disrupt cell function (Wozniak et al., 2005; Lee et al., 2003), which may

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potentially lead to breast cancer (EFSA, 2006). Hence it is greatly needed to develop an environmental-friendly and inexpensive technique to effectively degrade BPA.

The objectives of this study were to develop a new highly reactive montmorillonite based nano-MnO_2 and to investigate the degradation process of BPA by montmorillonite supported MnO_2. Our results clearly demonstrated that the isolated distribution of exchangeable Mn^{2+} effectively prevents the agglomeration of formed MnO_2 particles upon reaction with MnO_4^-, and the degradation of BPA by montmorillonite templated MnO_2 is significantly enhanced compared to MnO_2 prepared by conventional method. Furthermore, the effects of pH and humic acid on the oxidation of BPA were also evaluated.

2. Experimental part

2.1. Materials

Analytical grade manganese chloride ($MnCl_2$), potassium acetate, 2-(cyclohexylamino) ethanesulfonic acid (CHES), potassium permanganate ($KMnO_4$), BPA, 4-morpholinepropanesulfonic acid (MOPS), L-ascorbic acid, silylation reagent *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) were purchased from Sigma-Aldrich and the purities of the chemicals were >98%. Aldrich humic acid was used as the reference humic acid and purchased from Sigma-Aldrich. Acetonitrile and methanol were HPLC grade from Tedia Inc.

2.2. Preparation of montmorillonite templated MnO_2 and δ-MnO2

Mn^{2+} saturated montmorillonite (Mn^{2+}-montmorillonite) was prepared according to the method of Arroyo et al. (2005). The montmorillonite was supplied from Fenghong Chemical Co. (Zhejiang, China). The carbonate impurities in montmorillonite were removed by titrating the clay mineral dispersion to pH 6.8 using pH 5.0 acetic acid-sodium acetate buffer (0.5 M), then the montmorillonite dispersion was centrifuged at 60*g* for 6 min to obtain clay mineral sized particles (<2 μm). The montmorillonite fraction was redispersed in 0.1 M $MnCl_2$ solution for 8 h and centrifuged at 3500*g* for 15 min. To ensure full saturation of montmorillonite by Mn^{2+}, this procedure was repeated five more times. The resultant Mn^{2+}-montmorillonite was washed by deionized water until a negative chloride test using $AgNO_3$, then stored at 4 °C as aqueous dispersion for further use. The manganese content in Mn^{2+}-montmorillonite was determined through HCl-HNO_3-HF digestion and then analyzed by atomic absorption spectrophotometer (AAS) (PerkinElmerPinAAcle900T, Shelton, CT). Synthesis of montmorillonite templated MnO_2 was based on the redox reaction of Mn^{2+} ion with potassium permanganate. Briefly, 4 L of 25 g L^{-1} Mn^{2+}-montmorillonite dispersion was purged with nitrogen and constantly stirred, followed by a dropwise addition of 100 mL aqueous solution containing 4.6 g $KMnO_4$ and 2.3 g NaOH (molar ratio of $KMnO_4/Mn^{2+}$ = 2:3). The formed montmorillonite/MnO_2 dispersion was centrifuged. The montmorillonite dispersion was washed with fresh Milli-Q water until the conductivity of supernatant was below 2 μS cm^{-1}. The montmorillonite templated manganese dioxide was stored in aqueous dispersion at 4 °C.

Manganese dioxide (δ-MnO_2) was synthesized following the method of Murray (1974). Briefly, 80 mL of 0.1 M $KMnO_4$ and 160 mL of 0.1 M NaOH were mixed with 1640 mL of nitrogen-purged water, then 120 mL of 0.1 M $MnCl_2$ was added dropwisely. The formed MnO2 particles were allowed to settle down by gravity, then washed with Milli-Q water until the conductivity of supernatant was below 2 μS cm^{-1}.

2.3. Characterization of montmorillonite templated MnO_2

X-ray diffraction (XRD) analysis was employed to determine the clay mineral basal spacings. The X-ray diffractometer (Bruker AXS, Germany) was equipped with crystal graphite monochromator and CuKα radiation (λ = 1.5418 Å), operating at 40 mA and 40 kV. X-ray photoelectron spectroscopy (XPS) (UIVAC-PHI Physical Electronics PHI 5000 Versa Probe) was employed to confirm the transformation of Mn^{2+} to Mn^{4+} upon the reaction with MnO_4^-. The X-ray photoelectron spectroscopy equipped with a monochromatic Al X-ray source operated at 20 mA and 30 kV.

Aniline was used as the probe molecule to determine the reaction efficiency of synthesized montmorillonite/MnO_2. Prior studies have demonstrated that during the oxidation of aniline by manganese dioxide, aniline is considered as a 2-equivalent reductants (Laha and Luthy, 1990). The kinetic experiments were performed in 8 mL glass vials. 5 μL of aniline stock solution was added to 5 mL acetate buffer (pH = 4) containing 2.468 g L^{-1} montmorillonite/MnO_2 to obtain an initial aniline concentration of 1.074 mM. The experiment was performed in an anaerobic chamber and all water used in the experiment was fully deoxygenated. At predetermined time intervals, 5 μL of L-ascorbic acid solution (50 g L^{-1}) was added to terminate the reaction and the vial was immediately vortexed for 30 s, followed by addition of 3 mL methanol and 10 min of vortex to extract the aniline adsorbed on montmorillonite. The concentration of aniline was analyzed separately by a high performance liquid chromatography (HPLC) (Waters Alliance 2695, Milford, MA) monitored at 254 nm using a photodiode array detector. A 4.6 × 250 mm Waters XBridge Shield C_{18} column was employed for the separation. The isocratic mobile phase consisted of 50% acetonitrile and 50% 0.05 M ammonium acetate. The flow rate is 1.0 mL min^{-1} and the injection volume was 10 μL.

2.4. Kinetic experiments for oxidation of BPA

The degradation experiment was conducted in a 150 mL glass Erlenmeyer flask at room temperature (23 °C), which was covered with aluminum foil to avoid direct light irradiation. Reaction mixture (100 mL) was constantly stirred with a magnetic stir bar at 480 rpm. Reaction solution was maintained at constant pH buffered with 10 mM acetic acid (pH 4–6), MOPS (pH 7–8), or CHES (pH 9) and the corresponding potassium conjugate bases. Reaction was initiated by adding 50 μL of BPA methanol stock solution (43.80 mM) into a continuously stirred 100 mL buffer solution containing 250 mg L^{-1} montmorillonite (109 μM MnO_2) with the initial BPA concentration of 21.9 μM. The volume fraction of methanol in reaction solution was <0.1% to minimize the effect of organic solvent on the degradation process. At predetermined time intervals, aliquot of 0.5 mL of reaction mixture was withdrawn, transferred to 8 mL glass tubes containing 0.5 μL of L-ascorbic acid solution (50 g L^{-1}) and vortexed for 30 s, followed by addition of 1 mL methanol and 10 min of vortex to extract the BPA adsorbed on montmorillonite. After extraction, sample of the montmorillonite dispersion was filtered through 0.45 μm regenerated cellulose syringe filters. All samples were analyzed within 24 h. Control experiments confirmed that BPA was stable in the presence of L-ascorbic acid and the efficiency of the extraction method for the adsorbed BPA was nearly 100%, there was no measureable adsorption of BPA in methanol/water mixture by the membrane filters. For comparison, similar experiments were also conducted for δ-MnO_2 prepared by conventional method at pH 4. The initial concentrations of δ-MnO_2 and BPA were 109 μM and 21.9 μM, respectively. The concentrations of BPA were determined using the same HPLC system as described above with the UV absorbance at 200 nm. The isocratic mobile phase consisted of 50% acetonitrile and 50% water. The flow rate is 1.0 mL min^{-1} and the injection volume was 25 μL. The released Mn^{2+} concentration in solution during the reaction was also analyzed by AAS.

For reaction product identification, the reaction mixture was extracted by 100 mL methylene chloride using a rotary shaker at a rate of 250 rpm for 3 h, then silylated by adding BSTFA + TMCS (99:1) and analyzed by the Thermo gas chromatograph fitted with a mass spectrometer (GC–MS) on full scan mode. Helium was the carrier gas at a flow rate of 1 mL min^{-1}. The oven temperature was set from 60 °C

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