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 ($109 \text{ }\mu\text{M MnO}_2$) and $21.9 \text{ }\mu\text{M BPA}$. 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.

Keyword: Clay mineral-templated MnO_2 ; Bisphenol A; Montmorillonite; Humic acid; nanoscale MnO_2

1. Introduction

Manganese dioxide (MnO_2) is one of the mostly studied strong oxidants for degradation of various of 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 and 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 nanometers, and the width is in the range between a few tens and a few hundreds nanometers. The specific surface areas of montmorillonites is $800 \text{ m}^2 \text{ g}^{-1}$ (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 and 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 and Lee et al., 2003), which may 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-MnO₂ and to investigate the degradation process of BPA by montmorillonite supported MnO₂. Our results clearly demonstrated that the isolated distribution of exchangeable Mn²⁺ effectively prevents the agglomeration of formed MnO₂ particles upon reaction with MnO₄⁻, and the degradation of BPA by montmorillonite templated MnO₂ is significantly enhanced compared to MnO₂ 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 (MnCl₂), potassium acetate, 2-(cyclohexylamino) ethanesulfonic acid (CHES), potassium permanganate (KMnO₄), 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 MnO₂ and δ-MnO₂

Mn²⁺ saturated montmorillonite (Mn²⁺-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 ($< 2 \mu\text{m}$). 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 $\text{HCl-HNO}_3\text{-HF}$ 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 $\text{KMnO}_4/\text{Mn}^{2+}=2:3$). 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 $2 \mu\text{S cm}^{-1}$. The montmorillonite templated manganese dioxide was stored in aqueous dispersion at 4°C .

Manganese dioxide ($\delta\text{-MnO}_2$) was synthesized following the method of Murray

(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 MnO_2 particles were allowed to settle down by gravity, then washed with Milli-Q water until the conductivity of supernatant was below $2\ \mu\text{S cm}^{-1}$.

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 monochromater and $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\ \text{\AA}$), 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 ($\text{pH} = 4$) containing $2.468\ \text{g L}^{-1}$ 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 ($50\ \text{g L}^{-1}$) 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 were 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 C₁₈ 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 MnO₂) 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 $\delta\text{-MnO}_2$ prepared by conventional method at pH 4. The initial concentrations of $\delta\text{-MnO}_2$ 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 settled from 60 $^{\circ}\text{C}$ (2 min hold) to 200 $^{\circ}\text{C}$ (20 $^{\circ}\text{C min}^{-1}$, 5 min hold), and then to 300 $^{\circ}\text{C}$ (15 $^{\circ}\text{C min}^{-1}$, 20 min hold).

2.5. Effect of humic acid

The effect of humic acid on the degradation of BPA by montmorillonite/ MnO_2 was investigated at pH 4.0, 7.0 and 9.0 with two humic acid concentrations (5 and 20

mg C L⁻¹) under similar reaction conditions. The adsorption kinetic experiments of aldrich humic acid (5 mg C L⁻¹) on montmorillonite/MnO₂ (250 mg L⁻¹) at different pHs during the reaction period (100 min) were also studied. At designated time, the samples were centrifuged at 3295 g for 5 min and the supernatants were decanted and collected. The concentration of humic acid in supernatants was analyzed by a total organic carbon analyzer (TOC-5000A, Shimadzu Corp, Kyoto, Japan). To test whether humic acid was adsorbed into the interlamellar space of the clay mineral, the samples after adsorption were centrifuged and the clay mineral pastes were collected and freeze-dried for XRD analysis.

3. Results and discussion

3.1. Characterization of montmorillonite templated MnO₂

The manganese content in Mn²⁺-montmorillonite was determined to be 2.4% w/w (Table S1). Addition of KMnO₄ caused the oxidation of Mn²⁺ to Mn⁴⁺, and the negative charges of the montmorillonites became compensated by K⁺ from the added KMnO₄. The formation of MnO₂ from Mn²⁺ proceeds according to the following reaction:

The XRD patterns of Mn²⁺-montmorillonite, K⁺-montmorillonite and montmorillonite/MnO₂ are showed in Figure 1. The basal spacings of Mn²⁺-montmorillonite and K⁺-montmorillonite are 14.8 and 11.3 Å, respectively. During the oxidation of the Mn²⁺-clay mineral with KMnO₄, it is expected that most Mn²⁺ that had previously compensated cation-exchange sites on the montmorillonite

would be replaced by K^+ . After oxidation, due to the XRD peak for montmorillonite occurs at basal spacing greater than 11.3 Å, MnO_2 controls the basal spacing of the oxidized clay mineral system, the basal spacing increased to 12.2 Å. The approximate thickness of a montmorillonite sheet alone is 9.6 Å (Johnson et al. 1988), hence the vertical thickness of formed MnO_2 particles in the clay interlayer is ~ 2.6 Å, which is great smaller than nano- MnO_2 synthesized from traditional methods (Murray, 1974), indicating higher surface area and more active reaction sites, hence exhibiting higher reactivity (Gu et al., 2010 and Zhang et al., 2015).

Based on the XPS spectra reported in the literature (Table S2), the broad peaks of binding energies for Mn^{2+} -montmorillonite ($2p_{1/2} = 653.4$ eV and $2p_{3/2} = 642.1$ eV) indicate that Mn^{2+} has been partially oxidized (Figure 2) (Chen and Hsu, 2014). For montmorillonite/ MnO_2 , the XPS spectrum is consistent with the assignments by other researchers (Subramanian et al., 2005 and Liu et al., 2013), supporting that most of the Mn^{2+} is converted to Mn^{4+} (Figure 2).

Previous studies showed that MnO_2 was active in the oxidative transformation of aromatic amine compounds (Laha and Luthy, 1990 and Henbest and Thomas, 1957). In the reaction of aniline with MnO_2 , the reaction products were Mn^{2+} and azobenzene, and for one aniline two electrons are transferred (Laha and Luthy, 1990). Therefore, the amount of aniline degraded could be used to estimate the reactivity of the synthesized MnO_2 (Laha and Luthy, 1990). To evaluate the reactivity of the MnO_2 in clay mineral interlayer, the initial concentration of aniline (1.074 mM) was equal to the oxidation potential of the total manganese content of the montmorillonite, that is,

a 1:1 molar ratio of aniline/Mn was used. Within ten minutes, ~69% of aniline had been oxidized. After ~30 min, the reaction reached equilibrium with the maximum efficiency of ~80% (Figure S1). This high oxidation efficiency can only be achieved if all of the Mn^{2+} was oxidized to MnO_2 when the $\text{KMnO}_4/\text{Mn(II)}$ molar ratio was 2:3, which implies that the manganese in clay interlayer is predominantly MnO_2 .

3.2. Degradation of BPA by montmorillonite templated MnO_2

Control experiment showed that in the absence of montmorillonite templated MnO_2 , there is negligible degradation of BPA under our experimental conditions. However, as a certain amount of montmorillonite/ MnO_2 was added, BPA was degraded rapidly. A time course of BPA removal by montmorillonite templated MnO_2 is shown in Figure 3. About 90% of BPA could be oxidized in 10 min at pH 4.0, containing 250 mg L^{-1} montmorillonite/ MnO_2 ($109 \text{ }\mu\text{M MnO}_2$) and $21.9 \text{ }\mu\text{M BPA}$. In contrast, only 27% of BPA can be degraded in 100 min in the presence of $109 \text{ }\mu\text{M } \delta\text{-MnO}_2$ and $21.9 \text{ }\mu\text{M BPA}$ under similar reaction conditions. The comparison of reactivity for the oxidation of organic contaminants by different forms of MnO_2 is listed in Table S3, which shows that montmorillonite/ MnO_2 developed in this study is more reactive. The high reactivity of montmorillonite templated MnO_2 could be attributed to the discrete distribution of MnO_2 on the interlayer surfaces of montmorillonite resulting in a much smaller particle size than $\delta\text{-MnO}_2$. Interestingly, only limited release of Mn^{2+} (~4%) during the reaction was observed, it could be explained by the adsorption of Mn^{2+} ion on the surface of clay mineral due to the negative surface charge.

As shown in Figure 4, the degradation of BPA by montmorillonite/MnO₂ is strongly pH-dependent. The estimated pseudo first-order reaction rate constants are 0.174, 0.042, 0.029, 0.024, 0.016 and 0.008 min⁻¹ for pHs of 4.0, 5.0, 6.0, 7.0, 8.0 and 9.0, respectively (Table S4). Overall, the BPA removal rates at different pHs decrease as the increase of pH, suggesting that acidic condition enhances the transformation of BPA. Similar results were also observed for the oxidation of methylene blue (Zhu et al., 2010) and BPA (Lin et al., 2013) by MnO₂. It has been reported that lower pH could increase the reduction potential of manganese dioxide (Lin et al., 2013). As indicated by the following reaction:

protons are essential to reduce MnO₂ to Mn²⁺, which could explain the pH dependence of BPA degradation by montmorillonite/MnO₂.

3.3. Effect of humic acid on BPA degradation

Humic acids are natural macromolecules, which are widely distributed in the environment. Previous studies have shown that the presence of humic acid would significantly affect the oxidation processes of many organic contaminants by MnO₂ (Chen et al. 2010, Zhu et al. 2010). In this research, the effect of humic acid on the oxidation of BPA by montmorillonite templated MnO₂ shows different behavior at different pHs (Figure 5), which might be explained by the interaction between montmorillonite and humic acid. At pH 4, the pseudo first-order reaction rate constants are 0.174, 0.447 and 0.495 min⁻¹ for humic acid concentrations of 0, 5.0 and 20.0 mg C L⁻¹, respectively (Table S5), indicating that under acidic condition (pH = 4),

humic acid could facilitate the degradation of BPA. However, with pH increase (pH = 7 and 9), the presence of humic acid starts to inhibit the oxidation process (Figure 5 and Table S5). Humic acid adsorption from water by MnO₂-clay mineral at several pH values is presented in Figure 6. In general, adsorption decreases as the increase of clay mineral dispersion pH. It is well known that humic acid carries a variety of functional groups, such as phenolic groups and carboxylic. At low pH (below pK_a of the functional groups), humic acid gets protonated so that it becomes a neutral more or less hydrophobic molecule. Such polymeric molecules can be more easily adsorbed into the interlayer of clay minerals (Schnitze and Kodama, 1966 and Martinez and Rodriguez, 1969), it is also supported from our XRD results (Table S6). At pH 4, after the adsorption of humic acid onto montmorillonite, the d-spacing increases from 12.2 Å to 13.7 Å (Table S6). Humic acids are generally considered as the strong chelating agents for metals (e.g. Cu, Pb and Cd) (Christl et al., 2001 and Liu and Gonzalez, 2000), and the phenolic and carboxylic groups are mainly the active binding sites (Liu and Gonzalez, 2000). During the oxidation process, as MnO₂ is converted to Mn²⁺, it is expected that the humic acid molecules in the interlayer would complex with Mn²⁺ to prevent the accumulation of Mn²⁺ on MnO₂ surfaces and make the reactive sites more accessible (Xu et al., 2008 and Kang et al., 2004), which could explain the positive effect of humic acid at low pH. With the increase of pH (neutral or alkaline), the phenolic groups and carboxylic of humic acid dissociate, causing the repulsion between the negatively charged clay mineral and humic acid molecules. In this case, humic acid is mainly associated with montmorillonite on the external surface of the

mineral, it is also consistent with our experimental observation and the XRD results, no increase of d-spacing was observed at pH 7 and 9 (Table S6). The humic acid on the external surface might block the edge of clay mineral and decrease the possibility of BPA entering the internal surface to react with MnO₂.

3.4. Reaction intermediates

The reaction products were identified by GC-MS after the samples were extracted by methylene chloride and subsequent silylation. Only two major reaction products were detected, and other minor coupling products were also identified. The GC chromatogram and mass spectra of the major reaction products are shown in Figure S2. Products B and C correspond to the same molecule, depending on the extent of silylation. Both of the two reaction products (products A and B) are from the decomposition of BPA. Product D could be considered as the oxidation product of L-ascorbic. The oxidative degradation of L-ascorbic could form two major intermediates, L-xylonic acid and L-lyxonic acid (Yamabe et al., 2015), so we speculate that product D was formed via coupling of the intermediates. The products observed in this study were consistent with the oxidative transformation of BPA by MnO₂ dispersion, and the detailed reaction pathway had been proposed by Lin et al. (Lin et al., 2009).

4. Conclusions

In this research, a novel method was developed to synthesize MnO₂ using montmorillonite as template. As montmorillonite surface serves as the support, small isolated regions of MnO₂ have been formed when Mn²⁺-clay mineral is oxidized by

KMnO₄ due to the discrete distribution of negative charge sites on montmorillonite. The enhanced oxidation efficiency and high reactivity of montmorillonite-templated MnO₂ compared to pure δ -MnO₂ provide the evidence for the small size of MnO₂. Aniline oxidation experiments indicate that ~80% of the MnO₂ reactivity can be retained. The newly formed clay mineral templated MnO₂ also demonstrated a high reactivity when BPA was used as the model compound.

Montmorillonites are natural environmental materials and the montmorillonite-templated MnO₂ could be potentially utilized for *in situ* treatment of variable contaminants, such as steroid estrogens and antibiotics via oxidation by MnO₂. In addition, since most of Mn²⁺ converted from MnO₂ during the reaction is retained by montmorillonite clay mineral, it not only prevents the toxic effect of released Mn²⁺, but also makes possible to reuse Mn²⁺ by simply addition of KMnO₄ to regenerate montmorillonite/MnO₂.

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Appendix A. Supplementary data

The following are the supplementary data related to this article.

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Figure 1. X-ray diffraction patterns of Mn²⁺-montmorillonite, K⁺-montmorillonite, and montmorillonite/MnO₂. Two Theta represents the diffracted angle relative to the incident X-ray beam.

Figure 2. X-ray photoelectron spectra of Mn^{2+} -montmorillonite and montmorillonite/ MnO_2 .

Figure 3. Degradation of BPA by montmorillonite clay templated MnO₂ and pure δ -MnO₂ at pH 4. Experimental conditions: initial bisphenol A, clay, and interlayer MnO₂ concentrations of 21.9 μ M, 0.25 g L⁻¹ and 109 μ M, respectively; initial BPA and pure δ -MnO₂ concentrations of 21.9 μ M and 109 μ M, respectively. Error bars are the standard deviations of triplicate analyses.

Figure 4. Effect of pH on BPA removal by montmorillonite clay templated MnO_2 . Experimental conditions: initial BPA, montmorillonite and MnO_2 concentrations of $21.9 \mu\text{M}$, 0.25 g L^{-1} and $109 \mu\text{M}$, respectively. Error bars are the standard deviations of triplicate analyses.

Figure 5. Effect of humic acid on BPA removal by montmorillonite clay templated MnO_2 . Experimental conditions: initial BPA, montmorillonite and MnO_2 concentrations of $21.9 \mu\text{M}$, 0.25 g L^{-1} and $109 \mu\text{M}$, respectively. Error bars are the standard deviations of triplicate analyses.

Figure 6. Adsorption of humic acid on montmorillonite/MnO₂ as a function of time at different pHs. Experimental conditions: initial humic acid and montmorillonite concentrations of 5 mg C L⁻¹ and 0.25 g L⁻¹ respectively. Error bars are the standard deviations of triplicate analyses.

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