In-situ degradation of soil-sorbed 17 β -estradiol using carboxymethyl cellulose stabilized manganese oxide nanoparticles: Column studies

Bing Han^{a, b}, Man Zhang^a, Dongye Zhao^{a,*}

^a Environmental Engineering Program, Department of Civil Engineering, Auburn University,
Auburn, AL 36849, USA

Institute of Environmental Science, Taiyuan University of Science and Technology, Taiyuan,
Shanxi 030024, China

^b Department of Ocean Science and Technology, Shanghai Ocean University, Shanghai 201306,
China

* Corresponding author: Phone: (334) 844 6277; Fax: (334) 844 6290; E-mail:
zhaodon@auburn.edu

ABSTRACT:

This work tested a new remediation technology for in-situ degradation of estrogens by delivering a new class of stabilized manganese oxide (MnO_2) nanoparticles in contaminated soils. The nanoparticles were prepared using a food-grade carboxymethyl cellulose (CMC) as a stabilizer, which was able to facilitate particle delivery into soil. The effectiveness of the technology was tested using 17β -estradiol (E2) as a model estrogen and three sandy loams (SL1, SL2, and SL3) as model soils. Column transport tests showed that the nanoparticles can be delivered in the three soils, though retention of the nanoparticles varied. The nanoparticle retention is strongly dependent on the injection pore velocity. The treatment effectiveness is highly dependent upon the mass transfer rates of both the nanoparticles and contaminants. When the E2-laden soils were treated with 22-130 pore volumes of a 0.174 g/L MnO_2 nanoparticle suspension, up to 88% of water leachable E2 was degraded. The nanoparticles were more effective for soils that offer moderate desorption rates of E2. Decreasing injection velocity or increasing MnO_2 concentration facilitate E2 degradation. The nanoparticles-based technology appears promising for in-situ oxidation of endocrine disruptors in groundwater.

Keywords: Endocrine disrupter; Emerging contaminant; Nanoparticle; Soil remediation; Manganese dioxide

1. Introduction

Steroidal hormones are a class of endocrine disrupting chemicals (EDCs). Exposure to even ng/L levels of the chemicals can adversely affect wildlife and humans via interactions with the endocrine systems, leading to abnormal development, reproductive disorders, and even cancers (Colborn et al., 1993; Diamanti-Kandarakis et al., 2009). Over the last decade or so, numerous endogenous and synthetic hormones have been detected in sewage treatment effluents, septic system effluents, surface waters, groundwater, and soil worldwide (Desbrow et al., 1998; Drewes et al., 2003; Finlay-Moore et al., 2000; Kolpin et al., 2002; Shore and Shemesh, 2003; Ternes et al., 1999). Land application of animal wastes (e.g., manure and feces) as fertilizer releases significant amounts of endogenous hormones into soil, which can then leach into groundwater (Shore and Shemesh, 2003). Finlay-Moore et al. (2000) reported that land application of broiler litter increased the 17 β -estradiol (E2) concentration in soil from a background value of 55 ng/kg to 675 ng/kg. Shore and Shemesh (2003) reported that chicken manure stockpiles leachate contained 730 ng/L of estrogen. In general, estrogens are subjected to adsorption by soil. As a result, their concentrations in groundwater are lower than in surface waters. However, with rainfall and other runoff, soil-sorbed estrogens can be slowly released into groundwater, causing long-term threat to the ecosystems. E2 was detected at 6.3 ng/L in a monitoring well located downstream of a waste lagoon (Kolodziej et al., 2004), and at up to 0.79 ng/L in >50% of 112 samples from 59 groundwater sites in Austria (Hohenblum et al., 2004). Nichols et al. (1998) reported 1-3 μ g/L of estrogen and testosterone in rainwater runoff. Yet, there has been no suitable in-situ technology available for degrading estrogens in the subsurface.

Conventional manganese oxide (MnO₂) powder has been found effective for oxidizing endocrine disrupters such as E2, tetrabromobisphenol A (TBBPA), and bisphenol A in water

(Jiang et al., 2009; Lin et al., 2009a, 2009b; Xu et al., 2008). Typically, the oxidative transformation process involves an initial rapid adsorption of the contaminants on the particle surface followed by electron transfer. Following this process, E2 is transformed to primary estrone (E1) and 2-hydroxyestradiol (Jiang et al., 2010), which are much less estrogenic than E2, thereby reducing or eliminating the estrogenicity without generating secondary contaminations (Eqs. 1-2) (Jiang et al., 2010; Johnson and Sumpter, 2001; Xu et al., 2008).

However, commercial MnO_2 powder or synthetic aggregated MnO_2 particles are not deliverable in contaminated soil/groundwater systems. To facilitate soil deliverability and in-situ remediation of soil, Han et al. (2015) prepared a new class of stabilized MnO_2 (CMC- MnO_2) nanoparticles using a low-cost, food-grade carboxymethyl cellulose (CMC) as a stabilizer. Preliminary batch tests indicated that the new nanoparticles can effectively degrade E2 in water and soil slurry. However, information remains lacking pertaining to: 1) effectiveness of the nanoparticles when applied in column settings (i.e., under conditions of simulated in-situ soil treatment), 2) detailed transport and deposition behaviors of the nanoparticles in different soils, and 3) key factors affecting the effectiveness of the technology.

Although transport of colloids has been studied for decades (He et al., 2009; Quevedo and Tufenkji, 2012; Wang et al., 2012), our knowledge remains limited on transport of nanoparticles in natural soils. In most transport studies, column breakthrough tests were conducted using artificially modified porous media such as glass beads or pure quartz sand. However, the nanoparticle breakthrough and retention could be much more complex in real soil, and can be strongly affected by soil compositions (e.g., mineral type and content, and organic matter) and

physico-chemical characteristics (e.g., soil geochemical and charge heterogeneity). For example, Basnet et al. (2015) observed notably reduced transport of modified Pd-nZVI nanoparticles in a loamy sand soil than in quartz sand, and they attributed the higher nanoparticle deposition to the heterogeneity created by the clay fraction.

In the last decade or so, application of stabilized nanoparticles for in-situ remediation of soil/groundwater has elicited growing interest. Among various nanoparticles, nanoscale zero valent iron (nZVI) particles have been most extensively studied or employed for in-situ dechlorination of chlorinated solvents in groundwater (Bennett et al., 2010; He et al., 2010; Wei et al., 2010). However, there have been no oxidative nanoparticles reported for in-situ remediation uses.

The overall goal of this study was to test the feasibility of CMC-MnO₂ for in-situ degradation of E2 in soil and groundwater. The specific objectives were to: 1) test and model-simulate the transport behavior of CMC-MnO₂ through 1-D column tests with three model soils of representative properties; 2) determine the effectiveness of CMC-MnO₂ for in-situ degradation of soil-sorbed E2 under the column settings; 3) examine the effects of injection velocity and particle concentration on the treatment effectiveness; and 4) identify the key constraints and optimal conditions for the technology.

2. Materials and methods

2.1 Preparation and characterization of CMC-MnO₂ nanoparticles

CMC-MnO₂ was prepared following a modified redox method using CMC as a stabilizer (Han et al., 2015). Detailed information is provided in Section S1 in the Supplementary Information (SI). The resulting CMC-MnO₂ nanoparticles were aged for one day at room temperature (20±1°C) to allow for full particle growth before all tests. The Transmission electron

microscopy (TEM) and Dynamic light scattering (DLS) analysis method of the nanoparticles have been described by Han et al. (2015).

2.2 Soils and estrogen sorption/desorption tests

Three sandy loam soils (designated as SL1, SL2, and SL3) were obtained from the Bamboo Field, Corn Farm, and Wood Field, respectively, of the E.V. Smith Research Center of Auburn University at Shorter, AL, USA. Before use, the soils were screened through a standard 2 mm sieve, air-dried, thoroughly mixed, and stored at room temperature ($20\pm 1^\circ\text{C}$) for use. The salient physical and chemical properties of the soils and analytical methods are presented in Table S1. The key differences of the soils included the clay content, organic matter (OM), and pH of point of zero charge (pH_{PZC}). The clay content follows the sequence of: SL1 (18%) > SL3 (16%) > SL2 (15%); OM content: SL3 (5.9%) > SL2 (1.3%) > SL1 (0.4%); and pH_{PZC} : SL3 (5.9) > SL1 (5.2) > SL2 (4.5).

E2 was pre-loaded on the soils through soil sorption tests of E2 (Section S2 of SI), which resulted in an E2 loading of 0.0019, 0.0065 and 0.0104 mg/g for SL1, SL2 and SL3, respectively. The E2-spiked soils were then dried under a gentle N_2 atmosphere. The E2 loadings were confirmed through hot methanol extraction (Section S2 of SI), and the overall recovery was determined to be $94.4\pm 3.6\%$, $91.3\pm 3.8\%$ and $85.7\pm 4.1\%$, for SL1, SL2, SL3, respectively. Desorption kinetic tests were carried out following the successive desorption method (Section S2 of SI).

2.3 Column transport tests

The transport behavior of CMC- MnO_2 in the model soils was examined through column breakthrough tests using a glass column (ID = 1 cm, L = 15 cm) with adjustable headspace (Omnifit, Cambridge, England). In each test, a dry mass of 12 grams of a soil was packed in the

column with a constant porosity. Each column was first flushed (0.03 mL/min) with ~10 pore volumes (PVs) of a nitrogen-sparged background solution (0.84 mM NaCl+0.16 mM NaHCO₃, pH=7.5) in the up-flow mode to avoid air entrapment and to achieve complete water saturation. The breakthrough test was then initiated by pumping a suspension of CMC-MnO₂ through the soil bed in the up-flow mode using a High Performance Liquid Chromatography (HPLC) pump (Acuflow series II pump, Lab Alliance, USA) with Teflon tubing. The effluent samples were collected by a fraction collector (Eldex, CA, USA), then each 2 mL of the samples was mixed with 0.5 mL of ascorbic acid (0.05 M) to completely dissolve the nanoparticles, and the CMC-MnO₂ effluent history was then obtained by measuring the total Mn concentration. Following the full breakthrough, the influent reservoir was switched to the background solution to elute the retained nanoparticles. Bromide tracer (Br⁻ as 20 mg/L) tests were conducted under the same conditions to acquire the hydrodynamic parameters. Table S2 in SI summarizes the transport experiment conditions.

To investigate the spatial distribution of the nanoparticles retained in the soil, the soil beds following the transport tests were sectioned into 5 even segments, and the concentration of the nanoparticles in each section was obtained per EPA Method 3050B (acid digestion).

2.4 Simulated in-situ degradation of soil-sorbed E2

Column tests were carried out to simulate in-situ remediation of E2-contaminated soil. In each case, 12 grams of an E2-laden soil were dry-packed in the column with the soil porosity (bed height) being the same as in the transport tests. Column degradation tests were initiated by pumping a CMC-MnO₂ suspension through the column in the up-flow mode at a constant rate, and effluent was collected in a glass tube containing 1 mL of 10 g/L ascorbic acid, which immediately dissolves the MnO₂ particles and terminates the reaction (Xu et al., 2008). Upon

filtration through a 0.22 μm Anotop 10 syringe filter, the filtrate was analyzed by HPLC for E2. Control tests were conducted by pumping a CMC solution of the same concentration (free of particles) through the soil beds under otherwise identical conditions. E2 remaining in the soils after the column treatments was determined through the hot methanol extraction method (S2), which was carried out immediately after each column run.

2.5 Analytical Methods

Bromide concentration was measured using a Dionex Ion Chromatography (DX-120, Dionex, Sunnyvale, CA) (detection limit $<0.05 \text{ mg/L}$). Total manganese was analyzed with a flame atomic-absorption spectrophotometer (AAS) (220FS, Varian, Palo Alto, CA) (detection limit = 0.05 mg/L). E2 was analyzed using an HP Agilent 1260 Infinity HPLC system equipped with a Poroshell 120 EC-C18 column ($4.6 \times 50 \text{ mm}$, $2.7 \mu\text{m}$) and followed the method of Han et al. (2015), giving a detection limit of $5 \times 10^{-8} \text{ M}$.

2.6 Transport modeling

The one-dimensional advection-dispersion equation (ADE) that accounts for advection, dispersion, and solid-phase deposition was used to simulate the breakthrough curves (BTCs) of CMC-MnO₂ through the water-saturated soils (Wang et al., 2008):

$$\frac{\partial C}{\partial t} = \lambda v_p \frac{\partial^2 C}{\partial z^2} - v_p \frac{\partial C}{\partial z} - \frac{\rho_b}{\theta_w} \frac{\partial S}{\partial t} \quad (1)$$

where C and S are the MnO₂ concentration in the aqueous phase (mg/L) and the solid phase (mg/g), respectively, z is the distance from the inlet (cm), t is time (min), λ is the dispersivity (cm), v_p is the average pore velocity (cm/min), ρ_b is the soil bulk density (g/cm^3), and θ_w is the water content, which is equal to porosity. The accumulation rate of CMC-MnO₂ onto the soil is described by the solid-phase deposition equation (Bolster et al., 1999):

$$\frac{\rho_b}{\theta_w} \frac{\partial S}{\partial t} = k_{dep} \psi C - \frac{\rho_b}{\theta_w} k_{det} S \quad (2)$$

where k_{dep} and k_{det} are the first-order deposition and detachment rate constants (min^{-1}), respectively, and ψ is a dimensionless Langmuirian blocking function to describe the change of the available fraction of the surface deposition sites, which is defined as (Adamczyk et al., 1994):

$$\psi = \frac{S_{max} - S}{S_{max}} \quad (3)$$

where S_{max} is the maximum MnO_2 deposition capacity (mg/g). Assuming that the detachment rate of the nanoparticles from sand grains is negligible, i.e., $k_{det} \approx 0$, which was confirmed through the column breakthrough/elution tests, Eqn (2) reduces to an irreversible deposition equation. The HYDRUS-1D code (Simunek et al., 2005) was used to solve Eqns (1)-(3) and data fittings. The longitudinal dispersivity λ was obtained by fitting the classic ADE (without deposition) to the respective tracer BTC. The values of k_{dep} and S_{max} were acquired by fitting the modified ADE (with deposition) to the respective BTC of the nanoparticles.

3. Results and discussion

3.1 Characterization of CMC-stabilized MnO_2 nanoparticles

Fig. S1 shows TEM images of bare and CMC- MnO_2 particles prepared at CMC: MnO_2 molar ratio of 1.39×10^{-3} . The CMC stabilization resulted in fully dispersed, discrete nanoparticles, which remained suspended in water for months. Based on TEM images of 340 CMC- MnO_2 particles, the particle diameter was measured to be 37 ± 10 nm (Mean $\pm$ SD). The DLS measurements gave a mean z-average hydrodynamic diameter of 39.5 ± 0.8 nm, and a zeta potential of -34 ± 2 mV ($\text{MnO}_2 = 0.017$ g/L, pH = 5.1, $I \cong 2.4 \times 10^{-4}$ M). The rather negative zeta potential manifests the strong electrostatic repulsion between the nanoparticles.

[Fig. S1]

3.2 Transport of CMC-MnO₂ in three model soils

Figs. 1a-1c show measured and fitted BTCs of the tracer and CMC-MnO₂ through the three soils (Table S2). Fig. S2 shows the results of duplicate experiments to demonstrate data reproducibility. In all cases, the effluent bromide concentration rapidly reached its influent level at ~1.3 PVs, and then decreased nearly symmetrically to zero when the influent was switched to the background solution. In contrast, the BTCs for CMC-MnO₂ nanoparticles were much more gradual and reached a plateau (calculated as the peak C/C_0 after full breakthrough) that varied remarkably for the three soils. For SL1, the full-breakthrough was reached at ~6 PVs with an average C/C_0 of 0.90, and the plateau exhibited a slightly ascending profile. Based on the BTC, a total of 0.241 mg of MnO₂ was retained in the soil bed in 10 PVs. For SL2, a much sharper breakthrough was observed, with the full-breakthrough occurring at ~3 PVs and a C/C_0 of 0.93. The total retention of MnO₂ nanoparticles in 10 PVs was 0.085 mg. For SL3, a similarly sharp breakthrough was evident with full-breakthrough at ~3 PVs but a much lower peak C/C_0 (0.66), and the total MnO₂ retention in 10 PVs was 0.267 mg. Evidently, CMC-stabilized nanoparticles are deliverable in these soils despite different breakthrough profiles and soil retention. In all cases, the filtration model was able to adequately simulate the experimental BTCs for both the tracer and nanoparticles ($R^2 > 0.98$). Table 1 summarizes the model parameters.

[Table 1]

[Fig. 1]

Fig. 1d shows the vertical retention profiles of the nanoparticles in the soil bed. Both distribution and amount of the retained nanoparticles varied for the three soils. The retention of CMC-MnO₂ in SL2 was about one order magnitude lower than in SL1 and SL3. For SL1 and SL3, the amount of retention and the concentration distribution in the soils were quite similar.

Upon the elution treatments, the mass remaining in SL1, SL2 and SL3 was 39.4 %, 4.3 % and 34.2 % of the total MnO₂ introduced, respectively. Based on the mass extracted from the column and mass eluted from the BTCs, the mass balance of MnO₂ for the three soils ranged from 92.6% to 106.2% (Table 1).

The sharp and immediate breakthrough for SL2 (Fig. 1b) is associated with the low deposition of the particles on the collector. While SL1 and SL3 retained about the same amount of the nanoparticles, the BTCs showed very different patterns: a gradual breakthrough with a high full-breakthrough plateau for SL1, but a sharp BTC with a much lower C/C_0 for SL3. In general, the deposition of nanoparticles in porous media depends on: 1) available surface area (S_{max}^*) of the collectors, which is usually in favor of deposition, and 2) the mass transfer rate of the nanoparticles to the sites (k_{dep}) (Ko and Elimelech, 2000; Sasidharan et al., 2014; Torkzaban et al., 2010). The lower breakthrough plateau for SL3 indicates a higher deposition surface area of the collectors, and the gradual breakthrough for SL1 indicates a faster mass transfer rate of the nanoparticles to the surface sites or a higher particle-collector contact rate. The higher favorable deposition area for SL3 is mainly due to the surface potential of the collectors. Under the prevailing pH (5.1-5.3), the zeta potential for prepared CMC-MnO₂ was -34 mV. The pH_{PZC} for SL1, SL2, and SL3 was 5.2, 4.5, and 5.9, respectively. Therefore, SL2 is likely to be most negatively charged, while SL3 is most positively charged and SL1 is nearly neutral. As such, SL3 would be most favorable for the collision and deposition of the nanoparticles, while SL2 is least favorable. In addition, much higher concentrations of cations (e.g., Ca²⁺, Mg²⁺, Mn²⁺) in SL3 (Table S1) may also contribute to the adsorption of negatively charged MnO₂ nanoparticles through ion pairing and/or surface complexation. Moreover, the larger porosity also promotes the stronger filtration effect of SL3 (Table S2). As the flowrate was kept constant in the transport

experiments (0.05 mL/min), the larger porosity of SL3 (0.42) means a slower pore velocity (0.153 cm/min), which can result in a weaker shear force between the particles and water flow, favoring the deposition. The model-fitted maximum deposition capacity (S_{max}^* , where $S_{max}^* = S_{max}/C_0$) for SL3 ($3.53 \times 10^{-1} \text{ m}^3/\text{g}$) is two orders of magnitude larger than those for SL1 ($1.51 \times 10^{-3} \text{ m}^3/\text{g}$) and SL2 ($1.28 \times 10^{-3} \text{ m}^3/\text{g}$). These findings indicate that the much greater and more favorable surface sites of SL3 are responsible for the observed much lower full-breakthrough plateau ($C/C_0=0.66$).

The gradual breakthrough for SL1 suggested a faster initial MnO_2 deposition (contact) rate, which can be attributed to the faster mass transfer rate of the nanoparticles from solution to the surface sites (Sasidharan et al., 2014; Torkzaban et al., 2010). The k_{dep} value for SL1 (0.252) is about three orders of magnitude larger for SL2 (0.001) and SL3 (0.004). In addition, according to the filtration theory (Tufenkji and Elimelech, 2004; Yao et al., 1971), the single-collector contact efficiency (η_0) for nanoparticles is primarily due to diffusion, and the diffusion coefficient (η_D) is inversely proportional to the ratio of particle diameter (d_p) to spherical collector diameter (d_c). As a result, SL1 gave the highest single-collector contact efficiency due to its larger grain size (0.113 mm), resulting in the most retarded transport of the particles.

To further study the role of particle adsorption in the overall filtration removal of the nanoparticles, batch adsorption kinetic experiments were conducted (Section S3 in SI). The batch tests single out adsorption as the most important particle removal mechanism (i.e., it minimizes other filtration effects as in a column setting). Fig. S3 shows that the initial MnO_2 adsorption is fastest for SL1, however, the equilibrium uptake for SL1 and SL3 is comparable (equilibrium uptake = 0.139, 0.119, and 0.145 mg/g for SL1, SL2, and SL3, respectively). This observation demonstrates that the removal of MnO_2 in SL1 is mainly due to rapid mass transfer from solution

to solid surface, while the larger favorable surface area is the key deposition mechanism for SL3. The batch sorption kinetic profiles of CMC-MnO₂ are quite consistent with the column breakthrough profiles (Fig. 1), where the lowest deposition of CMC-MnO₂ was observed for SL1, and the highest with SL3. The results indicate that sorption plays an important role in the overall filtration removal of the nanoparticles.

In addition, the surface charge heterogeneity on mineral surfaces are considered to play an important role in colloid deposition (Johnson et al., 1996; Rizwan and Bhattacharjee, 2009; Torkzaban et al., 2010). Torkzaban et al. (2010) found that gold nanoparticles can deposit on clay surfaces, but not on sand. They suggested the surface charge heterogeneity on clay particles is the key factor for the deposition of nanoparticles. In our case, the clay contents are 18%, 15%, and 16% for SL1, SL2, and SL3, respectively, suggesting higher surface charge heterogeneity for SL1.

3.3 Effect of pore flow velocity

Fig. 2 shows the BTCs and subsequent elution curves of CMC-MnO₂ nanoparticles under different pore velocities ranging from 0.040 to 0.808 cm/min. Increasing pore velocity from 0.202 to 0.808 cm/min increased the full-breakthrough C/C_0 from 0.93 to nearly 1; and reduced S_{max}^* from 1.28×10^{-3} m³/g to 1.86×10^{-4} m³/g. The lower retention (9.4%) at elevated pore velocity is attributed to the stronger shearing of water flow along the collectors' surface. Conversely, lowering the pore velocity from 0.202 to 0.121 cm/min increased the particle removal to 49.1%, S_{max}^* to 5.75×10^{-1} m³/g, and k_{dep} to 0.003 min⁻¹. At 0.121 cm/min, the initial breakthrough was delayed to ~4 PVs and the full-breakthrough C/C_0 decreased to 0.63. Again, the lower the flow velocity, the less the lift and drag forces acting on the particles near solid surface, and the more particle deposition in the micropores (Bergendahl and Grasso, 2000). The

observation indicates that the particle retention can be manipulated by controlling the pore velocity or injection pressure.

[Fig. 2]

When the pore velocity was further reduced to 0.040 cm/min, the BTC showed a different pattern: rose initially and then fell gradually to zero (Fig. 2). The model failed to simulate the entire BTC, suggesting that the particle removal is beyond the scope of the classic filtration theory. This breakthrough pattern is typical when the particles are unevenly deposited on the upper part of a filter bed, causing blockage of the inlet pores. As more particles accumulate, the soil bed becomes completely clogged, resulting in zero breakthrough. Since most groundwater water flow velocity is in the range of 0.027-2.7 m/d (i.e., 0.00188-0.188 cm/min) (Mackay et al., 1985), this observation shows that while the nanoparticles are deliverable in soil under additional pressure (i.e., elevated pore velocity), the delivered particles will become immobile once the external pressure is released, i.e., the particles will remain in a confined domain under natural groundwater flow conditions, which is desirable for in-situ remediation.

3.4 Effect of nanoparticle concentration

Fig. S4 shows the BTCs and subsequent elution curves of the nanoparticles at MnO₂ concentrations ranging from 0.017 g/L to 0.17 g/L. Despite the 10 times difference in the particle concentration, the BTCs nearly coincided with identical C/C_0 (0.93) values in all cases. From a practical standpoint, this observation indicates that different masses of the nanoparticles can be delivered in a contaminated zone by tuning the influent concentration.

3.5 Degradation of E2 in three model soils

The effectiveness of CMC-MnO₂ nanoparticles for simulated in-situ degradation of E2 in the model soils was investigated through a series of 1-D column experiments. Figs. 3a-3c show the

elution histories of E2 from E2-laden SL1, SL2, and SL3 during the nanoparticle treatments. For comparison, control tests were also carried out using a CMC solution without the nanoparticles under otherwise identical conditions. Duplicate experiments indicated that the experimental data were highly reproducible (Fig.S5), and thus, only one set of data are presented in Fig. 3 for visual clarity. Prior water treatment work (Han et al., 2015) indicated that the MnO₂ nanoparticles effectively transformed E2 to primary estrone (E1), which is much less estrogenic, and the degradation of E2 follows a retarded first-order kinetics. Table 2 gives the E2 degradation efficiency for the three soils. For SL1, the CMC solution eluted ~72% of E2 initially sorbed on the soil, while the nanoparticle suspension eluted ~56% of E2 during the 20 PVs of the column runs (Fig. 3a), i.e., the nanoparticle treatment degraded ~22% of the water leachable E2 (i.e., 0.0003 mg/g-soil). For SL2, the nanoparticle treatment reduced the leachable E2 from ~67% to ~8% (Fig. 3b), i.e., ~88% of the leachable E2 was degraded (i.e., 0.0038 mg/g-soil). E2 on SL3 was least leachable, and the CMC solution and the nanoparticle suspension only leached 8% and 7% of the E2 loaded, respectively (i.e., 0.0001 mg/g-soil was degraded).

[Table 2]

[Fig. 3]

To confirm the overall E2 degradation, E2 remaining in each soil following each treatment was extracted and analyzed. For SL1, ~20% E2 remained following the CMC solution elution and ~17% after the nanoparticle treatment (Table 2). Thus, the total mass percentage of E2 degraded (including E2 in both water and soil) was 21% (i.e., 0.0004 mg/g-soil) (Note: the residual E2 in soil after hot-methanol extraction is assumed not desorbable). For SL2, E2 remaining in the soil was ~24% and ~14% after the CMC solution elution and nanoparticle treatment, respectively, and the total mass degraded reached 76% of the total E2 loaded (i.e.,

0.0045 mg/g-soil). For SL3, the hot-methanol extraction recovered 75% and 61% of residual E2, respectively, following the solution elution and the nanoparticle treatment, namely, 18% of the initial loaded E2 (i.e., 0.0016 mg/g-soil) was degraded. Adding up the E2 mass eluted and remaining in soil, the E2 recovery in the control tests amounted to 92%, 91%, and 83% for SL1, SL2, and SL3. The lower recovery for SL3 may due to the strong adsorption of E2. And the mass balance calculations were based on E2 mass that is recoverable by the hot-methanol extraction method.

Adsorption can limit the chemical availability, and thus, degradability of E2. Of the three soils, SL1 offered the lowest adsorption capacity for E2, with an equilibrium mass loading of 0.0019 mg-E2/g-soil compared to 0.0065 mg/g for SL2 and 0.0104 mg/g for SL3 under identical experimental conditions (Fig. S6a). Figure S6b shows the adsorption isotherms of E2 by the three soils. All the isotherms were adequately fitted with the linear isotherm model, and the E2 distribution coefficients (K_d , L/kg) were then determined to be 7.05 for SL1, 23.20 for SL2 and 33.94 for SL3. Accordingly, the organic carbon-normalized partitioning coefficients ($\log K_{oc}$) were 3.48, 3.51 and 3.00 for the three soils, respectively, which are consistent with values reported by others (Lee et al., 2003). When subjected to successive desorption tests (Figs. S6c-d), SL1 showed the highest desorption rate and extent, with ~50% of E2 desorbed in the first batch, and another 20% in the subsequent desorption; for SL2, ~22% of E2 was desorbed in the first desorption run, and another 18% in the 2nd run; and for SL3, only ~4% of E2 was desorbed after the two desorption runs. The disparate adsorption capacity and reversibility are in accord with the SOM contents (0.4%, 1.3%, and 5.9% for SL1, SL2, and SL3, respectively). The results agree with the assertion that the dominant mechanism for E2 adsorption to soil is hydrophobic interactions (Lee et al., 2003). Consistent with the desorption data, the highest column elution of

E2 was observed for SL1, with a peak concentration of >1 mg/L in the first 2.5 PVs (Fig. 3), indicating the weaker binding of E2 to SL1. In contrast, a much lower E2 elution was found for SL3 (peak concentration = 0.05 mg/L), and a moderate elution for SL2 (peak concentration = 0.43 mg/L).

A close examination of the E2 elution and degradation data (Table 2) reveals that the effectiveness of the nanoparticles is affected by both desorption/mass transfer of E2 and transport of the MnO₂ nanoparticles. In fact, for soil-sorbed E2 to be degraded effectively by the nanoparticles, the following steps are critical: 1) E2 must be desorbed from soil, 2) sufficient nanoparticles must be available, and 3) there must be sufficient contacts and reaction time between E2 and the nanoparticles. Therefore, desorption of E2 and the mass transfer or transport of the nanoparticles in the soil column must in a concerted manner such that the collisions between E2 and nanoparticles are maximized. While E2 in SL1 was rapidly eluted, nanoparticle transport was greatly retarded. Consequently, there exists a time lag between E2 desorption and mass transfer of MnO₂ when the nanoparticle suspension was passed through the soil bed, i.e., the concentration wave front of E2 moves ahead of that of the nanoparticles. As a result, the desorbed E2 was eluted out before contacting with the nanoparticles. In contrast, the extremely slow desorption rate of E2 from SL3 resulted in the very slow degradation rate (i.e., a desorption limited process). The technology appears most effective for SL2, which offers a moderate E2 adsorption capacity, a desorption rate that is compatible with the nanoparticle transport, and less retardation on the nanoparticle transport.

Fig. 3d briefly illustrates the roles of CMC in the transport and reaction of CMC-MnO₂ with soil-sorbed and dissolved E2. Through the electrosteric stabilization mechanism, the CMC molecules adsorbed on the MnO₂ nanoparticles were able to effectively prevent the nanoparticles

from aggregation, assuring the soil deliverability of the nanoparticles. In addition, the CMC coating may also affect deposition of CMC-MnO₂ depending on collector surface potential and may affect the mass transfer of E2 toward the reactive sites of on the MnO₂ surface. Within the microscopic soil pores, soil-sorbed E2 will need to be first desorbed and then diffuse to the reactive sites on CMC-MnO₂, either immobilized on soil grains or suspended in solution, and then degraded. Our prior batch tests in homogeneous systems indicated that the CMC coating had only modest effect on the reactivity of the MnO₂ particles (Han et al., 2015).

3.6 Effect of flow velocity on E2 degradation

The pore water velocity affects contaminant-nanoparticle mass transfer, and thus, the degradation efficacy. Fig. 4 shows elution histories of E2 from SL2 under pore water velocities of 0.202 and 0.808 cm/min. When the velocity was increased from 0.202 to 0.808 cm/min, E2 eluted increased from 8% to 24% of E2 loaded on the soil; accordingly, E2 remaining in the soil increased from 14% to 21%, i.e., the total E2 degradation percentage decreased from 76% to 48% (Table 2). These results indicate that for a given soil the injection flow velocity should be controlled to allow for sufficient nanoparticle retention time. On the other hand, a slower flowrate results in more nanoparticles deposition on the soil surfaces (Fig. 2), which in turn can intercept and degrade more E2 per unit mass of the nanoparticles.

[Fig. 4]

3.7 Effect of nanoparticle concentration on E2 degradation

Fig. 5 shows that when the MnO₂ concentration was decreased from 0.174 to 0.017 g/L, the total E2 degraded decreased from 76% to 29%, and E2 eluted was increased from 8% to 42% within 130 PVs of treatment (Table 2). Our prior work (Han et al., 2015) found that several factors such as soil-MnO₂ interactions and soil-released metals and reductants could inhibit the

oxidation effectiveness. Therefore, a sufficient dosage of MnO_2 is needed to overcome the initial oxidant demand.

[Fig. 5]

4. Conclusions

This work demonstrated the technical effectiveness of stabilized MnO_2 nanoparticles for degradation of a model EDC (E2) in a column configuration simulating in-situ remediation. The technology is most suitable for soils like SL2 that offer moderate E2 desorption rates/extents, and for soils of reasonable particle permeability (i.e., less retardation to the transport of the nanoparticles). In the real world, the scenario like SL1 represents the case of freshly-contaminated and short-lived sites because of the rapid contaminant desorption. In this case, relatively simpler techniques (e.g., water flushing) may be implemented; conversely, E2 in SL3 is barely desorbable, and thus, represents less a concern in terms of bioavailability or human exposure. In fact, many site conditions may fall into the scenario where a soil-sorbed contaminant is affecting the human and environmental health through desorption at a slow but harmful rate as for the case of SL2. Therefore, the technology may offer a powerful alternative for remediation of soil contaminated by EDCs. In addition to soil type, other operating factors, such as particle injection velocity and concentration, may be optimized to accommodate specific site conditions.

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Appendix A. Supporting data

Supporting data was available online.

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Table 1. Model parameters in simulating breakthrough curves of MnO₂ nanoparticles through three model soils.

Soil	v_p^a	C_0^b	Ret. ^c	MR ^d	λ^e	k_{dep}^f	S_{max}^{*g}	R ²
	cm/min	g/L	%	%	cm	min ⁻¹	m ³ /g	
SL1	0.169	0.017	49.0	92.6	0.359	0.252	1.51×10 ⁻³	0.992
SL2	0.202	0.017	20.2	106.2	0.207	0.001	1.28×10 ⁻³	0.991
	0.808	0.017	9.4	-	0.423	0.001	1.86×10 ⁻⁴	0.987
	0.121	0.017	49.1	-	0.070	0.003	5.75×10 ⁻¹	0.995
	0.040	0.017	81.6	-	-	-	-	0.612
	0.202	0.087	20.6	-	0.207	0.001	3.29×10 ⁻³	0.998
SL3	0.202	0.174	21.5	-	0.207	0.001	4.22×10 ⁻³	0.998
	0.153	0.017	48.0	95.1	0.395	0.004	3.53×10 ⁻¹	0.991

^aPore water velocity. ^bInfluent MnO₂ concentration. ^cRetention of CMC-MnO₂, Ret.=1-M_{eff}/M_o, where M_{eff} is the effluent mass of MnO₂ calculated by integrating the BTCs at ~10 PVs, M_o is the total mass of MnO₂ introduced at the same PVs. ^dMass Recovery of MnO₂, obtained by normalizing the sum of eluted particles (based on the BTCs) and soil-retained particles (based on the particle retention profiles) to the total particles introduced. ^eLongitudinal dispersivity. ^fFirst-order deposition rate constant. ^g $S_{max}^*=S_{max}/C_0$, where S_{max} is the maximum MnO₂ deposition concentration.

Table 2. Degradation of E2 pre-sorbed in three soils when treated with MnO₂ nanoparticles.

Soil	M _{E2} ^a	<i>v_p</i> ^b	C ₀ ^c	C _{E2} ^d	S _{E2} ^e		T _{E2} ^f		Deg. of leach. E2 ^g	Deg. of tot. E2 ^h	
	mg	cm/min	g/L	%	%		%		%	%	
				MnO ₂	Control	MnO ₂	Control	MnO ₂	Control	CMC-MnO ₂	CMC-MnO ₂
SL1	0.023	0.169	0.174	56	72	17	20	73	92	22	21
SL2	0.078	0.202	0.174	8	67	14	24	22	91	88	76
	0.078	0.808	0.174	24	59	21	28	45	87	59	48
	0.078	0.202	0.017	42	67	23	24	65	91	37	29
SL3	0.125	0.153	0.174	7	8	61	75	68	83	13	18

^aMass of E2 initially in soil. ^bPore velocity. ^cInfluent MnO₂ concentration. ^dPercentage of E2 eluted. ^ePercentage of E2 remaining in soil. ^fTotal E2 recovered (sum of E2 eluted + E2 extracted from soil). ^gDegradation of water leachable E2 = 1- C_{E2} (control-MnO₂ treated)/C_{E2} (control). ^hDegradation of total E2 =1- T_{E2} (control-MnO₂ treated)/T_{E2}(control).

Fig. 1. Measured and model-fitted breakthrough curves of a KBr tracer and CMC-MnO₂ nanoparticles through three model soils: (a) SL1, (b) SL2, and (c) SL3, and nanoparticle retention profiles (d).

Fig. 2. Breakthrough curves of CMC-stabilized MnO_2 nanoparticles through SL2 at different pore velocities. Symbols: experimental data; Lines: model simulations.

Fig. 3. Elution histories of E2 from three model soils when subjected to a background CMC solution and a suspension of CMC-MnO₂ nanoparticles: (a) SL1, (b) SL2, and (c) SL3; and (d) schematic illustration of CMC-MnO₂ transport and reaction with soil-sorbed and dissolved E2. Experimental conditions: MnO₂ = 0.174 g/L (2×10^{-3} M), CMC = 250 mg/L, inlet flow rate = 0.05 ml/min, soil = 12 g.

Fig. 4. Elution histories of E2 from SL2 at different pore water velocities.

Fig. 5. Elution histories of E2 from SL2 under different MnO₂ concentrations.

Graphical Abstract