Effect of humic acid on the oxidation of phenolic endocrine disrupting chemicals by permanganate

Xiao-Ling Shao, Jun Ma, Jing-Jing Yang, Xu-Chun Li and Gang Wen

ABSTRACT

The effect of dissolved humic acid on the oxidation of phenolic endocrine disrupting chemicals (EDCs) by potassium permanganate was studied. It was found that the degradation of phenolic EDCs is promoted to various extents by the addition of humic acid. Results show that the removal rate of estrone by permanganate within 3 min of reaction time is increased from approximately 10% in control experiments to 68% when 0.08 mg l^{-1} of humic acid is present in the reaction system. The oxidation experiment of nine types of phenolic EDC by permanganate confirms that the promotion induced by the addition of humic acid varies in the cases of different EDCS. Results also indicate that the promotion induced by the presence of humic acid takes effect under acidic and neutral pH conditions, while the effect of pH plays a dominant role for the degradation of phenolic EDCs under alkaline conditions. Additionally, it was found that the oxidation of estrone by permanganate is promoted through the addition of humic acid to natural waters.

Key words | humic acid, permanganate, pH, phenolic endocrine disrupting chemicals

Xiao-Ling Shao
Jun Ma (corresponding author)
Jing-Jing Yang
Xu-Chun Li
Gang Wen
State Key Laboratory of Water Resource and Environment,
National Engineering Research Center of Urban Water Resources,
Harbin Institute of Technology,
202 Haihe Road,
Harbin 150090,
China
Tel.: +86 451 86282292
Fax: +86 451 82368074
E-mail: *majun@hit.edu.cn*

INTRODUCTION

Endocrine disrupting chemicals (EDCs) are a type of micropollutant that will elicit adverse effects on endocrine systems of humans and wildlife. They have been implicated in a number of reproductive and sexual abnormalities observed in wildlife (Guillette *et al.* 1994; Facemire *et al.* 1995; Jobling *et al.* 1998) and reduced sperm counts in human males (Carlsen *et al.* 1992). These compounds may travel along the water pathway from wastewater treatment plants to the raw water used for drinking water production (Desbrow *et al.* 1998; Jobling *et al.* 1998; Kolpin *et al.* 2002). Studies indicate that mixtures of various EDCs are prevalent in most natural waters (Kolpin *et al.* 2002). Some of these contaminants are highly refractory to conventional physicochemical water treatments (e.g. coagulation/sedimentation, filtration) and may enter drinking water distribution systems (Boyd *et al.* 2003; Westerhoff *et al.* 2005; Chen *et al.* 2007). Phenolic EDCs including natural steroid estrogens have been verified as the dominant form of estrogenic activity in surface waters (Snyder *et al.* 2001). Studies indicate that these chemicals, even at extremely low concentrations, will cause significant health problems for wildlife and/or humans when they experience long-term exposure to mixtures of them (Jobling *et al.* 1998; Silva *et al.* 2002; Campbell *et al.* 2006; Brian *et al.* 2007).

Chemical oxidation can convert hazardous contaminants to non-hazardous or less toxic compounds, and may be a good choice to eliminate EDCs in natural waters. Among those commonly used oxidants in waterworks (e.g. chlorine, ozone, UV photolysis, monochloramine, chlorine dioxide, etc.), permanganate has been verified as an inexpensive, operationally easy and effective oxidant for the control or decomposition of iron, manganese, taste and odour and also many types of organic contaminant (Herrera-Melian *et al.* 2000; Kao *et al.* 2007; Rodriguez *et al.* 2007; Bastos *et al.* 2008; Urynowicz 2008). However,

doi: 10.2166/aqua.2010.015

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

permanganate has received relatively little attention to date compared with ozone, partly because of its perceived relatively inferior oxidation strength to ozone and also concern about residual manganese, as metallic ions should also be controlled in drinking water. Therefore, the use of permanganate to abate pollutants occurs mainly where the residual manganese can be removed easily by conventional water treatment plants. Up till now, permanganate oxidation has been used in drinking water treatment processes in many waterworks of Chinese cities such as Beijing, Shanghai, Nanjing, Wuxi, Jiaxing and Guangzhou.

The success of permanganate application largely depends on several parameters besides its ability to degrade target contaminants. One of the determining factors is natural organic matter (NOM), as NOM can also react with permanganate and will exert a negative effect on the oxidation of target compounds (Mumford *et al.* 2004, 2005; Urynowicz *et al.* 2008). The concentration of NOM was reported to be approximately 10 mg l^{-1} which consisted up to 90% of dissolved organic carbon (DOC) in surface waters (Gjessing *et al.* 1998). Therefore, the extent of oxidant demand from NOM might be many times greater than that from target contaminants. Urynowicz (2008) reported that humic acid (HA) competes with trichloroethene for available permanganate which reduces the rate of trichloroethene degradation and the mass degraded. Siegrist *et al.* (1999) also found that the addition of humic acid could substantially increase the reaction half-lives of trichloroethene. As a result, the effect of NOM must be taken into account when evaluating permanganate oxidation as a potential approach for the control of EDCs.

As little work has been carried out specifically on the oxidation of estrogenic phenolic EDCs by permanganate and the effect of NOM on their degradation in aqueous systems, the primary objectives of this study are: (1) to evaluate the oxidation of phenolic EDCs by potassium permanganate; (2) to assess the effect of humic acid on the degradation of phenolic EDCs both in ultra-pure water and in natural waters; (3) to estimate roughly the extent of the influence of humic acid on the oxidation by permanganate of different kinds of phenolic EDC under similar conditions; and (4) to evaluate the effect of pH on the decay of phenolic EDCs in both the presence and the absence of humic acid.

MATERIALS AND METHODS

Chemicals

Estrone (E1), 17β-estradiol (E2), 17α-ethynylestradiol (EE2), estriol (E3), diethylstilbestrol (DES), bisphenol A (BPA), 4-*n*-nonylphenol (*n*-NP), NP (mixture of *p*-isomers with branched side chain) and 4-*tert*-octylphenol (OP) are all Sigma-Aldrich reagents. Other chemicals including potassium permanganate ($KMnO_4$), hydrochloric acid (HCl), sodium hydroxide (NaOH) and ascorbic acid are of analytical grade and used without further purification.

Ultra-pure water used in the experiment was Milli-Q water, 18.2 MΩcm. The natural water used was taken from Songhua River, situated in northern Harbin, China. The natural water sample was filtered through glass fibre filters of 1 μm pore size (Whatman) to remove suspended solids and then stored at 4°C. The main water quality parameters of the filtered natural water are: DOC, 3.6 mg l^{-1}; conductivity, 210 μS cm^{-1}; pH 7.8; turbidity, 0.6 NTU.

The EDCs working solutions were prepared daily in Milli-Q water or natural water and stored in amber glass bottles at ambient temperature. Potassium permanganate working solution (1 g l^{-1}), ascorbic acid working solution (1g l^{-1}) and other reagents were also freshly prepared in Milli-Q water every four to seven days and stored in dark bottles to avoid light exposure.

A commercially available humic acid (CHA, Shanghai Chemicals Reagent Co. Ltd, China) was used in this experiment. The humic acid was characterized in previous studies (Guo & Ma 2006; Ma *et al.* 2007). The humic acid was firstly dissolved in NaOH solution (0.01 mol l^{-1}), and then filtered through a cellulose acetate membrane of 0.45 μm pore size, and then diluted to approximately 400 mg l^{-1} of total organic carbon (TOC) and finally conditioned with HCl solution to neutral pH. Exact TOC value of the humic acid solution was measured using a Multi N/C 3100 TOC analyzer (Analytik Jena, Germany).

Analytical methods

High performance liquid chromatograph equipped with a Waters 1,500 series binary pump was used for the analysis, in which a Waters Symmetry C18 column (ID = 4.6 mm,

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

length = 150 mm, 5 μm particle, made in Ireland), a Waters 717 plus auto-injector and a Waters 2487 dual λ UV detector were employed. The mobile phase was run in an isocratic mode, with Milli-Q water being used as the mobile phase A and methanol (Dikma, USA) as the mobile phase B. The proportions of A/B were 25/75, 25/75, 25/75, 40/60, 25/75, 30/70, 5/95, 8/92 and 10/90 for the detection of E1, E2, EE2, E3, DES, BPA, *n*-NP, NP and OP, respectively. The injection volume was 100 μl for each sample. The wavelengths selected for the quantification were 280 and 224 nm. The total flow rate of mobile phase A and B was 1.0 ml min^{-1}.

The analytes were quantified by the external standard quantification procedure. The system was calibrated using standard solutions prepared in methanol at six concentration levels by serial dilutions from stock solutions (100 mg l^{-1}). For each analyte, the peak area vs. injected amount chart was obtained as a standard curve with a correlation coefficient over 0.99. The detection limit was 5 μg l^{-1} for those phenolic EDCs.

Permanganate oxidation experiments

The EDCs solutions placed in cylindrical glass reactors were immersed in a thermostatic water bath to perform batch oxidation experiments. A magnetic stirrer was used under the water bath. The temperature of reaction systems was maintained at 25°C except for the experiment conducted in natural water. The pH of water samples was adjusted directly by the addition of HCl or NaOH solution (0.1 mol l^{-1}). All pH values were measured by a pHs-3C pH meter with glass electrode that was pre-calibrated with standard buffer solutions (Leici, Shanghai, China). A volume of humic acid solution was added to water samples while stirring with a Teflon-coated magnetic bar. The reaction was initiated by an injection of $KMnO_4$ working solution. Samples were collected at several time intervals, and quenched immediately with ascorbic acid solution. The residual EDCs concentrations were analysed directly by HPLC without further pretreatment. Each experiment was performed in duplicate.

Measurement of permanganate concentration

Because there are two representative peaks for permanganate ion at 526 and 546 nm, permanganate ion can, therefore, always be detected at approximately 526 nm (Mumford *et al.* 2005; Kao *et al.* 2007). Thus, the concentration of permanganate was determined using a Shimadzu UV-2550 spectrophotometer by absorbance at 526 nm. The spectrophotometer was zeroed each time using a control sample to correct for the presence of humic acid.

RESULTS AND DISCUSSION

Effect of humic acid on estrone degradation

The effect of humic acid concentration on the degradation of estrone was conducted with humic acid concentration ranging from 0.08 to 15.32 mg l^{-1} (counted as TOC) at natural pH (about 5.8).

Figure 1 shows the percentage of estrone remaining ($[E1]/[E1]_0$ = remaining estrone concentration/initial estrone concentration) versus time under the condition of various humic acid concentrations. As can be observed, the removal of estrone within 3 min of reaction time is promoted from approximately 10% in control tests to 68% when 0.08 mg l^{-1} of humic acid is present in the reaction system. The removal efficiency is increased to 84% with the concentration of humic acid increased to 0.19 mg l^{-1}. However, the increase in the concentration of humic acid from 0.19 to 15.32 mg l^{-1} cannot further enhance the

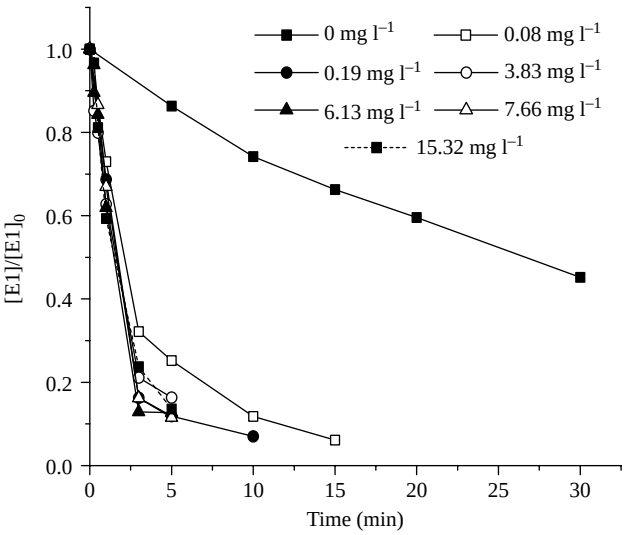


Figure 1 | Effect of humic acid concentration on the degradation of estrone by permanganate; $[E1]_0 = 1.26 \pm 0.06$ μmol l^{-1}, $[KMnO_4]_0 = 12.66$ μmol l^{-1}, temperature, 25°C.

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

degradation of estrone. This means that the promotion induced by humic acid is independent of humic acid concentration at a higher level, at least in the studied range. The result is quite different from the previous reports that humic acid has a negative effect on the degradation of trichloroethene during permanganate oxidation (Siegrist *et al.* 1999; Urynowicz 2008). However, our present research result is similar to those obtained in our previous study (Ma & Graham 1999) for the enhanced degradation of atrazine in the presence of humic substances, and to those of Rivera-Utrilla *et al.* (2008) who also found that the presence of humic acid can increase the degradation of sodium dodecylbenzenesulfonate by O_3 and O_3-based advanced oxidation processes. In their experiments, humic acid was confirmed to act as an initiator of ozone transformation into HO· radicals.

It should be noted that humic acid solution was added to water samples and stirred for about 10 to 15 min before the reaction was initiated. The first sample (initial concentration) was collected before the addition of $KMnO_4$ working solution. Comparing all these first samples with and without the presence of humic acid, it was found that there is no obvious difference in their initial concentrations. The tiny difference between different additions of humic acids is just within the range of error permission (5%). samples were also collected at several time intervals from the moment of humic acid addition without the addition of permanganate. These samples were detected immediately by HPLC after sampling. It was found that there was virtually no variation in concentrations of estrone with the contact time of estrone with humic acid (0–60 min). Thus, it can be concluded that humic acid itself has no important adsorption or other effect on estrone. Besides, the MnO_2 produced in the process of permanganate oxidation was reduced to Mn^{2+} by ascorbic acid at the end of the reaction, so the amount of estrone adsorbed by MnO_2 is negligible in the study. This indicates that the rapid removal of estrone may be entirely due to the oxidation by permanganate.

Similar to the present study, Zahonyi-Budo & Simandi (1992) found that the oxidation of phosphorus (III) by permanganate was induced in the presence of arsenite(III), while the direct oxidation of phosphorus (III) by MnO_4^- was negligible. The behaviour was explained by the formation of reactive Mn(V) intermediates in the reaction of As(III) with MnO_4^-, which was selectively reduced by P(III). The presence of reactive manganese species, Mn(V), Mn(III), Mn(IV) and Mn(VI) was verified by stop-flow technique or spectrophotometry in the oxidation of organic or inorganic compounds by permanganate. Among them, Mn(V) intermediates formation is always believed to be a result of the direct reduction of MnO_4^- in the early reaction stages and plays an important role in the decomposition of target compounds (Zahonyi-Budo & Simandi 1992; Wiberg & Freeman 2000; Shaker 2001; Jaky & Simon-Trompler 2002; Wiberg *et al.* 2006; Ahmed *et al.* 2007; Rodriguez *et al.* 2007).

Thus, the authors tentatively suggest here a similar mechanism for the reaction of estrone with permanganate; however, this requires further studies. Humic acid acts as initiating agent involved in the permanganate transformation into Mn(V) or other reactive manganese species in the initial reaction stages. Then those produced intermediates may selectively react with estrone, which results in the rapid degradation of estrone. This can be partially confirmed by the consumption of permanganate (Figure 2).

When both humic acid and estrone are present in the reaction system, permanganate was consumed in excess of the total amount (the dotted line in Figure 2) used up by estrone and by humic acid which reacted individually with

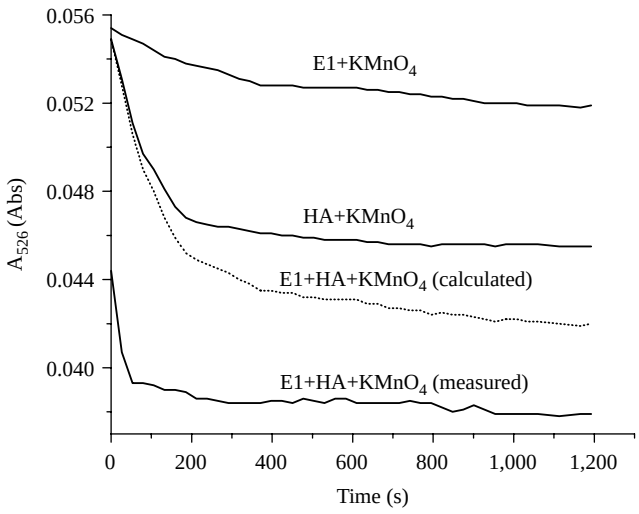


Figure 2 | Absorbance of permanganate ion as a function of time at constant wavelength of 526 nm. Solid lines represent measured results and the dotted line represents the calculated result; $[E1]_0 = 1.26 \pm 0.06\ \mu mol\ l^{-1}$, $[KMnO_4]_0 = 12.66\ \mu mol\ l^{-1}$, $[HA] = 0.77\ mg\ l^{-1}$, ambient temperature, $24 \pm 2°C$.

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

permanganate. Because of the higher reactivity in the initial stages and a few-second time delay caused by manual operation, the initial absorbance value ($t = 0$) measured at 526 nm is 20% lower than the actual value for the reaction of estrone with permanganate in the presence of humic acid. Thus the over-consumption of permanganate encountered here is probably due to an induced degradation of estrone, involving an intermediates-estrone reaction. On the other hand, the produced reactive intermediates in the reaction of permanganate with humic acid can be further reduced to lower valence of manganese species either by estrone or by humic acid, or may undergo disproportionation or oxidation by MnO_4^- to other oxidation states of manganese (Jaky & Simon-Trompler 2002; Wiberg *et al.* 2006; Ahmed *et al.* 2007). However, it is possible that the selective reaction between estrone and those reactive species may cause the decrease of estrone concencetration correspondingly. In addition, it might be due to the formation of those short-lived reactive species, the estrone is degraded rapidly in the initial stages. However, lower reactivity is observed after 3 min of reaction.

With increasing concentration of humic acid but fixed permanganate concentration, the amount of reactive manganese species produced might reach a constant value and the degradation rate of estrone is therefore no longer increased. Further work will therefore be conducted to verify the existence of these intermediates by means of the stop-flow technique together with spectrophotometry. In addition to humic acid, other reductive species such as Mn^{2+}, Fe^{2+}, NO_2^- and SO_3^{2-} will be evaluated in future experiments to establish their influence on the oxidation, in order to observe whether there will be a similar enhanced effect on the oxidation of estrone by permanganate.

Effect of pH on estrone degradation

The normalized concentration of estrone versus time in the experiments performed at various initial pH values (pH 2.0, 3.0, 4.5, 6.0, 7.0, 8.4 and 9.1) with and without the presence of humic acid is presented in Figure 3(a, b), respectively.

Figure 3(a) presents the estrone degradation trends under acidic conditions which are very similar, suggesting that the oxidation is independent of pH over the range of pH 2–6. Additionally, there is a lag time of about 1 min at the beginning of the reaction under acidic conditions. This can be explained by the formation and accumulation of reactive intermediates in the reaction of humic acid with permanganate in the initial stages. This can also be confirmed by the rapid consumption of permanganate (Figure 2) within the initial 1 min of reaction time. Figure 3(a) also reveals that estrone is degraded substantially from the moment the reaction started under alkaline conditions. Estrone is completely degraded in less than 1 min at pH 9.1. The minimum removal rate of estrone was observed at pH 7.0 in this group of experiments.

When it comes to the control groups (Figure 3(b)), the reactions are somewhat different from those in the presence of humic acid (Figure 3(a)). The reaction rate is first

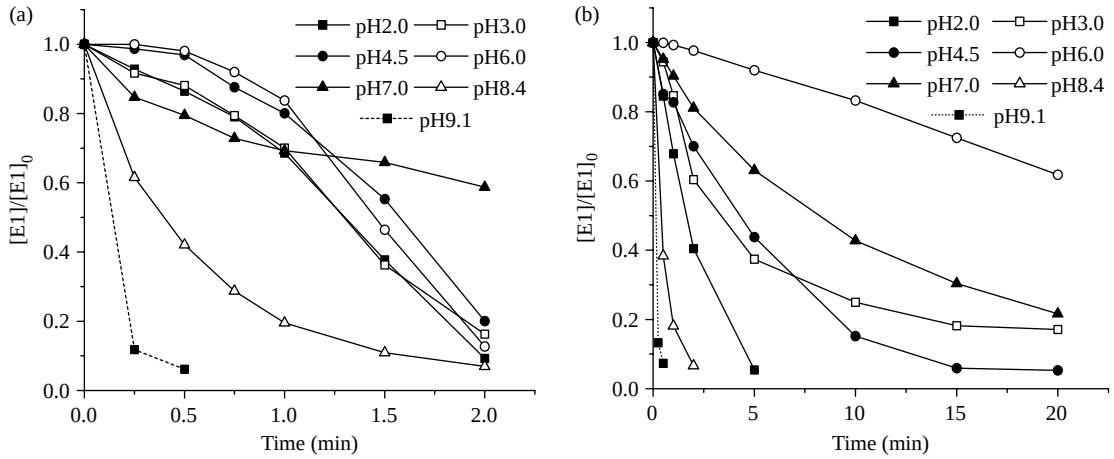


Figure 3 | Effect of pH on the oxidation of estrone by permanganate (a) in the presence of 0.15 mg l^{-1} humic acid, and (b) without the presence of humic acid; $[E1]_0 = 1.28 \pm 0.08\ \mu mol\ l^{-1}$, $[KMnO_4]_0 = 12.66\ \mu mol\ l^{-1}$, [HA] = 0.15 mg l^{-1}, temperature, 25°C.

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

decreased with the increase in pH values and then is increased with the increase in pH values. The minimum degradation rate of estrone takes place at pH 6.0, with higher reactivity at higher or lower pH values.

Compared with the control experiments (Figure 3(b)), the decay rates of estrone are accelerated both under acidic and neutral pH conditions (pH 2.0–7.0) when humic acid is present in the reaction system. The removal efficiencies are increased by 31.2, 44.0, 50.0, 87.0 and 22.4% within 2 min of reaction time in the presence of humic acid under pH 2.0, 3.0, 4.5, 6.0 and 7.0, respectively. The maximum promotion takes place at pH 6.0. However, the reaction of estrone with permanganate is not affected by the addition of humic acid both at pH 8.4 and pH 9.1. The above results lead to the conclusion that the oxidation promotion induced by the addition of humic acid plays a role under acidic and neutral pH conditions. However, the effect of pH plays a dominant role on the degradation of estrone under alkaline conditions.

With regard to the rapid degradation of estrone under alkaline conditions, this might be due to the deprotonation of estrone which facilitates the attack by permanganate. Ladbury & Cullis (1958) reported that the ionized organic compounds, especially phenoxy groups, are easily attacked by MnO_4^-. Because of the pK_a of estrone of 10.3–10.8 (Campbell *et al.* 2006), the pH adopted is close to the pK_a, where a higher percentage of estrone will be dissociated. As a result, the degradation rate is rapid under alkaline conditions. The result agrees with those obtained by Bastos *et al.* (2008) who found that brominated phenols with lower pK_a values reacted faster with $KMnO_4$ at pH 7.6.

Degradation of estrone in natural water

In order to assess the applicability of permanganate oxidation in actual water treatment, estrone was spiked directly into the filtered natural water mentioned above. The background concentration of estrone in the filtered natural water was at the low ng l^{-1} level and was therefore ignored in the experiment. Experiments were performed at ambient temperature (28 ± 1°C) under two different permanganate concentrations, 1 and 2 mg l^{-1}. A comparison study was also conducted in ultra-pure water system at the same pH without the addition of humic acid.

As shown in Figure 4, the degradation rate of estrone in filtered natural water is obviously faster than that in the ultra-pure water system within 10 min of reaction time. An increase in permanganate concentration resulted in an increase of the degradation rate of estrone in the natural water. As expected, the addition of a lower level of 0.08 mg l^{-1} humic acid to a filtered natural surface water spiked with a certain level of estrone also promoted estrone removal compared with those achieved in ultra-pure water, indicating that the characteristics of natural water did not change the mechanism of permanganate oxidation for estrone. This means that the presence of humic acid, even at lower levels in natural water is helpful for the removal of estrone or other phenolic EDCs during permanganate oxidation. Besides, a deliberate addition of an amount of humic acid to natural water would also enhance the removal of these phenolic EDCs. The results might also have implications for the remediation of NOM-containing underground water.

Natural organic matter is present in all surface waters with a world mean concentration of organic carbon of about 5 mg l^{-1} (Gjessing *et al.* 1998). Therefore, according to the present results, permanganate oxidation may be

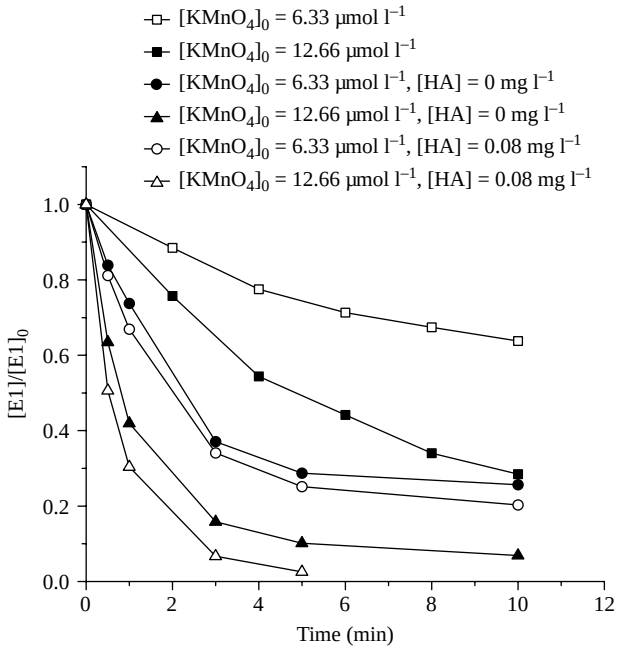


Figure 4 | Degradation of estrone in a filtered natural water with and without humic acid at ambient temperature of 28 ± 1°C; comparison experiments were also conducted in an ultra-pure water system; $[E1]_0 = 1.25 \pm 0.01$ μmol l^{-1}.

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

a good option for the removal of estrone or other estrogenic phenolic EDCs in natural waters prior to coagulation-sedimentation treatment. In addition, permanganate pre-oxidation may be useful in enhancing the subsequent coagulation and filtration processes (Ma & Li 1993; Ma *et al.* 1997) and controlling the formation of trihalomethanes and other disinfection by-products (DBPs) (Ma & Graham 1996). The MnO_2 produced during permanganate oxidation can be easily removed by coagulation-sedimentation- filtration processes.

Care was also taken over the residual manganese ion in the natural water experiments. The concentrations of manganese ion were measured by a Perkin Elmer Optima 5300 DV ICP-AES instrument after the filtration of water samples with cellulose acetate membranes of 0.45 μm pore size. The background concentration of manganese ion was below the limit of detection (0.005 mg l^{-1}) in the filtered natural water. As the contact time of permanganate pre-oxidation in actual water treatment always ranges from 30 min to several hours, manganese ion was therefore measured after 30 min of the reaction mentioned above between estrone and permanganate in the filtered natural water. Results show that the concentrations of manganese ion are 0.05 and 0.16 mg l^{-1} for the reaction with initial permanganate concentration of 1 and 2 mg l^{-1}, respectively. The latter value can be reduced through the direct pre-oxidation of source water, or extended contact time, or other follow-up traditional treatment processes to below the guideline value of 0.1 mg l^{-1} proposed by the Ministry of Health of the People's Republic of China (MOH 2006) and the World Health Organization (WHO 2004). Thus, it is indicated that an added concentration of permanganate is acceptable up to 2 mg l^{-1} during drinking water treatment processes.

Oxidation of different types of phenolic EDC by permanganate

From the above results, it can be expected that the promotion induced by humic acid may also take effect on other phenolic EDCs when they are oxidized by permanganate. In addition, the extent of the promotion may be different for different kinds of phenolic EDC. Therefore, a series of oxidation experiments were conducted with nine types of phenolic EDC individually in an ultra-pure water system. The concentrations of humic acid and permanganate were 0.15 and 2 mg l^{-1}, respectively. The initial concentrations of these nine types of EDC varied in a range of 1.0–2.0 μmol l^{-1}. The control experiments ([HA] = 0 mg l^{-1}) were also conducted in parallel.

Figure 5 shows the plots of residual EDCs proportion ([EDCs]/[EDCs]$_0$) versus reaction time. As can be observed, the reactions of all nine phenolic EDCs with permanganate are accelerated to a certain extent when humic acid is added to the reaction systems. Estriol, 17α-ethynylestradiol and estrone were degraded faster in the presence of humic acid, whereas the promotion effect induced for the degradation of two types of nonylphenol by permanganate was very weak.

It is difficult to quantify the extent of promotion on EDCs oxidation enhanced by the presence of humic acid through comparing their rate constants. The reason is that the reaction order is hard to determine because of the complexity of the reaction system in the presence of humic acid. The degradation of these EDCs is neither first order nor second order when humic acid is present. In comparison with rate constants, half-lives are easier to use to estimate the enhancement of organic oxidation through the simulation of the reaction curves revealed in Figure 5. Thus, the ratio of half-lives is used in the study to characterize roughly the extent of promotion induced by the presence of humic acid and can be expressed by Equation (1).

$$f = \frac{t_{1/2}}{t_{1/2}'} \tag{1}$$

where f is the promotion factor and $t_{1/2}'$ and $t_{1/2}$ are the half-lives of EDC decay with and without the presence of humic acid, respectively.

The oxidation of nine types of EDC by permanganate in control groups is assumed to be the same order for the convenience of comparison between the reaction rates. The pseudo-first-order rate constants (k_{obs}) ($r^2 = 0.9827 \pm 0.0358$) and half-lives ($t_{1/2}$) were calculated accordingly (see Table 1). It can be seen that the species reacting fastest with permanganate is estriol with a half-life of 714 s. Diethylstilbestrol reacts slightly slower than estriol, whereas 4-*tert*-octylphenol is the slowest EDC to react with permanganate.

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

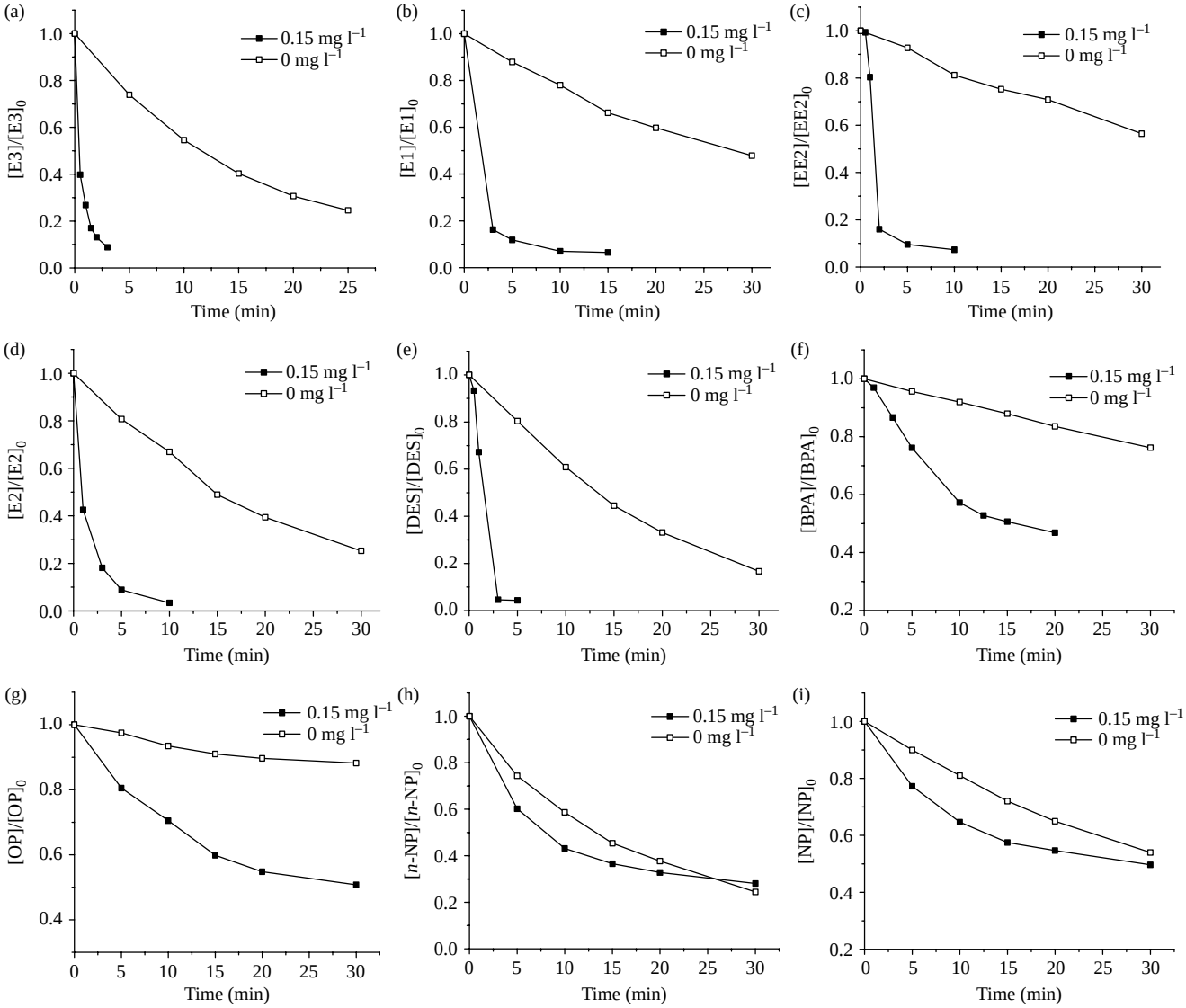


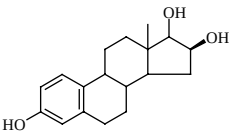
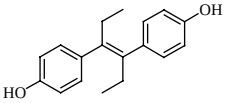
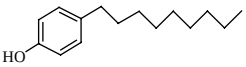
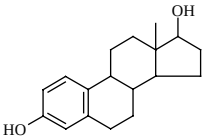
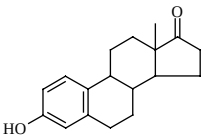
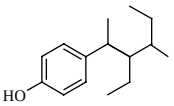
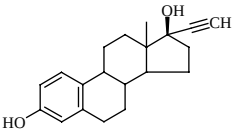
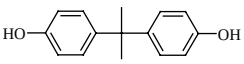
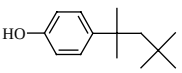
Figure 5 | Degradation of (a) estriol, (b) estrone, (c) 17α-ethynylestradiol, (d) 17β-estradiol, (e) diethylstilbestrol, (f) bisphenol A, (g) 4-*tert*-octylphenol, (h) 4-*n*-nonylphenol, and (i) branched *p*-nonylphenol by permanganate in the presence of 0.15 mg l^{-1} humic acid at 25°C.

The half-lives of EDCs ($t_{1/2}'$) in the experiments conducted in the presence of humic acid were roughly estimated using polynomial regression. The promotion factor (f) for each EDC was computed according to Equation (1). Table 1 shows that the half-lives of these EDCs are clearly shortened from the range of 714–8,663 s to the range of 18–1,800 s when 0.15 mg l^{-1} of humic acid was added to the reaction systems between EDCs and permanganate. The promotion of the degradation of estriol is the strongest among these EDCs with a half-life 39 times lower than that for the reaction without the presence of humic acid. In the case of estrone, the extent of promotion in degradation is slightly lower than for estriol with a promotion factor of 37.5, followed by 17α-ethynylestradiol and 17β-estradiol with a promotion factor of 25.7 and 19.6, respectively. The promotion of degradation for the two nonylphenols is in the same range and is the weakest of all the EDCs, whereas diethylstilbestrol, bisphenol A and 4- *tert*-octylphenol are in a medium range.

It is interesting to note that the five types of EDCs have the highest promotion factors. They have very similar

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

Table 1 | Pseudo-first-order rate constants (k_{obs}), half-lives of investigated EDCs in reaction with permanganate in the presence of humic acid ($t_{1/2}'$) and without the presence of humic acid ($t_{1/2}$) and their promotion factors (f)

Chemical	Molecular structure	$k_{obs} \times 10^{-4}$ (s^{-1})	$t_{1/2}$ (s)	$t_{1/2}'$ (s)	f
Estriol		9.7	714	18	39.7
Diethylstilbestrol		9.5	729	78	9.4
4-*n*-nonylphenol		8.1	856	451	1.9
17β-estradiol		7.7	900	46	19.6
Estrone		4.2	1,650	44	37.5
Branched *p*-nonylphenol		3.5	1,980	1,686	1.2
17α-ethynylestradiol		3.1	2,235	87	25.7
Bisphenol A		1.5	4,620	906	5.1
4-*tert*-octylphenol		0.8	8,663	1,800	4.8

molecular structures (Table 1). Previous studies reported that these estrogens have higher estrogenic potency and constitute the main components of estrogenic activity in natural waters (Legler *et al.* 2002; Campbell *et al.* 2006). Among them, estriol, 17β-estradiol and estrone are natural estrogens excreted by animals and human beings. 17α-ethynylestradiol and diethylstilbestrol are man-made compounds used as pharmaceuticals in contraceptive pills or growth promoters for livestock. Figure 5 reveals that these estrogens are removed quickly and more than 80% of them are degraded within 3 min of reaction, indicating that they are readily degraded by permanganate, especially in the presence of humic acid.

It should be noted that the concentrations of phenolic EDCs are in the ng l^{-1} or low μg l^{-1} range in actual environmental samples (Kolpin *et al.* 2002). Therefore, further work is needed to understand the real application of permanganate in potable water treatment, the mechanism of humic acid enhancement of the oxidation of phenolic organics by permanganate, and also the possible formation of by-products associated with these phenolic EDCs and their estrogenic activities during permanganate oxidation.

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

CONCLUSIONS

Natural organic matter is the main component of DOC in surface waters and can react with most oxidants used in water treatment. Therefore, NOM would exert an important effect on the removal of organic or inorganic contaminants in drinking water treatment. Some previous research reported that the presence of humic acid has a negative impact on the degradation of target contaminants. However, our results are just the opposite in the case of the oxidation of phenolic EDCs by permanganate. The presence of humic acid was found to be useful for the degradation of estrogenic phenolic EDCs by permanganate. The reaction between estrone and permanganate is substantially stimulated by the addition of humic acid.

Surprisingly, estrone removal by permanganate oxidation is more efficient in natural water than in an ultra-pure water system, and it can also be enhanced when humic acid is added to a filtered actual surface water. Of course, the promotion induced by the presence of humic acid is different for different types of phenolic EDC. Among nine types of phenolic EDC, experimental results indicate that the promotion of the degradation of estriol is the strongest while that of branched nonylphenol is the weakest one under similar reaction conditions. With respect to the promotion mechanism of permanganate oxidation, humic acid might act as an initiating agent of permanganate transformation into reactive manganese intermediates which may be responsible for the observed enhanced oxidation effects. Thus, it seems that permanganate oxidation is a feasible choice for the removal of estrogenic phenolic EDCs in natural water prior to coagulation-sedimentation treatment.

ACKNOWLEDGEMENTS

The work was supported by the Ministry of Education of China (705013), the National Key Special Founding for Water Pollution Control and Management (Number 2009ZX07424-005), and the State Key Laboratory of Urban Resource and Environment (2008DX06).

REFERENCES

Ahmed, G. A., Fawzy, A. & Hassan, R. M. 2007 Spectrophotometric evidence for the formation of short-lived hypomanganate (V) and manganate (VI) transient species during the oxidation of K-carrageenan by alkaline permanganate. *Carbohydr. Res.* **342**(10), 1382–1386.

Bastos, P. M., Eriksson, J., Green, N. & Bergman, A. 2008 A standardized method for assessment of oxidative transformations of brominated phenols in water. *Chemosphere* **70**(7), 1196–1202.

Boyd, G. R., Reemtsma, H., Grimm, D. A. & Mitra, S. 2003 Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. *Sci. Total Environ.* **311**(1–3), 135–149.

Brian, J. V., Harris, C. A., Scholze, M., Kortenkamp, M., Booy, P., Lamoree, M., Pojana, G., Jonkers, N., Marcomini, A. & Sumpter, J. P. 2007 Evidence of estrogenic mixture effects on the reproductive performance of fish. *Environ. Sci. Technol.* **41**(1), 337–344.

Campbell, C. G., Borglin, S. E., Green, F. B., Grayson, A., Wozei, E. & Stringfellow, W. T. 2006 Biologically directed environmental monitoring, fate, and transport of estrogenic endocrine disrupting compounds in water: a review. *Chemosphere* **65**(8), 1265–1280.

Carlsen, E., Giwercman, A., Keiding, N. & Skakkebaek, N. E. 1992 Evidence for decreasing quality of semen during past 50 years. *Br. Med. J.* **305**(6854), 609–613.

Chen, C. Y., Wen, T. Y., Wang, G. S., Cheng, H. W., Lin, Y. H. & Lien, G. W. 2007 Determining estrogenic steroids in Taipei waters and removal in drinking water treatment using high-flow solid-phase extraction and liquid chromatography/tandem mass spectrometry. *Sci. Total Environ.* **378**(3), 352–365.

Desbrow, C., Routledge, E. J., Brighty, G. C., Sumpter, J. P. & Waldock, M. 1998 Identification of estrogenic chemicals in STW effluent 1. Chemical fractionation and in vitro biological screening. *Environ. Sci. Technol.* **32**(11), 1549–1558.

Facemire, C. F., Gross, T. S. & Guillette, L. J. 1995 Reproductive impairment in the Florida panther: nature or nurture? *Environ. Health Perspect.* **103**(suppl 4), 79–86.

Gjessing, E. T., Alberts, J. J., Bruchet, A., Egeberg, P. K., Lydersen, E., Mcgown, L. B., Mored, J. J., Munster, U., Pempkowiak, J., Perdue, M., Ratnawerra, H., Rybacki, D., Takacs, M. & Abbt-Braun, G. 1998 Multi-method characterisation of natural organic matter isolated from water: Characterisation of reverse osmosis-isolates from water of two semi-identical dystrophic lakes basing in Norway. *Water Res.* **32**(10), 3108–3124.

Guillette, L. J., Gross, T. S., Masson, G. R., Matter, J. M., Percival, H. F. & Woodward, A. R. 1994 Developmental abnormalities of the gonad and abnormal sex hormone concentrations in juvenile alligators from contaminated and control lakes in Florida. *Environ. Health Perspect.* **102**(8), 680–688.

Guo, J. & Ma, J. 2006 AFM study on the sorbed NOM and its fractions isolated from River Songhua. *Water Res.* **40**(10), 1975–1984.

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest

Herrera-Melian, J. A., Tello Rendon, E., Dona Rodriguez, J. M., Viera Suarez, A., Valdes Do Campo, C., Perez Pena, J. & Arana Mesa, J. 2000 Incidence of pretreatment by potassium permanganate on hazardous laboratory wastes photodegradability. *Water Res.* **34**(16), 3967–3976.

Jaky, M. & Simon-Trompler, E. 2002 Permanganate oxidation of unsaturated alcohols in alkaline media. *Int. J. Chem. Kinet.* **34**(9), 561–567.

Jobling, S., Nolan, M., Tyler, C. R., Brighty, G. & Sumpter, J. P. 1998 Widespread sexual disruption in wild fish. *Environ. Sci. Technol.* **32**(17), 2498–2506.

Kao, C. M., Huang, K. D., Wang, J. Y., Chen, T. Y. & Chien, H. Y. 2007 Application of potassium permanganate as an oxidant for *in situ* oxidation of trichloroethylene-contaminated groundwater: a laboratory and kinetics study. *J. Hazard. Mater.* **153**(3), 919–927.

Kolpin, D. W., Furlong, E. T., Meyer, M. T., Thurman, E. M., Zauqq, S. D., Barbe, L. B. & Buxton, H. T. 2002 Pharmaceuticals, hormones, and other organic wastewater contaminants in U.S. streams, 1999–2000: a national reconnaissance. *Environ. Sci. Technol.* **36**(6), 1202–1211.

Ladbury, J. W. & Cullis, C. F. 1958 Kinetics and mechanism of oxidation by permanganate. *Chem. Rev.* **58**(4), 403–439.

Legler, J., Zeinstra, L. M., Schuitemaker, F., Lanser, P. H., Bogerd, J., Brouwer, A., Vethaak, A. D., Voogt, P. D., Murk, A. J. & Burg, B. V. D. 2002 Comparison of *in vivo* and *in vitro* reporter gene assays for short-term screening of estrogenic activity. *Environ. Sci. Technol.* **36**(20), 4410–4415.

Ma, J. & Graham, N. 1996 Controlling the formation of chloroform by permanganate preoxidation-destruction of precursors. *J. Water Suppl. Res. Technol.–AQUA* **45**(6), 308–315.

Ma, J. & Graham, N. J. D. 1999 Manganese-catalysed ozonation for the destruction of atrazine: effect of humic substances. *Water Res.* **33**(3), 785–793.

Ma, J. & Li, G. B. 1993 Laboratory and full-scale plant studies of permanganate oxidation as an aid to the coagulation. *Water Sci. Technol.* **27**(11), 47–54.

Ma, J., Graham, N. & Li, G. B. 1997 Effect of permanganate preoxidation in enhancing the coagulation of surface waters-laboratory case studies. *J. Water Suppl. Res. Technol.–AQUA* **46**(1), 1–10.

Ma, J., Jiang, J., Pang, S. Y. & Guo, J. 2007 Adsorptive fractionation of humic acid at air-water interfaces. *Environ. Sci. Technol.* **41**(14), 4959–4964.

MOH 2006 *Standards for Drinking Water Quality*. GB5749-2006, Ministry of Health of the People's Republic of China, Beijing (in Chinese).

Mumford, K. G., Lamarche, C. S. & Thomson, N. R. 2004 Natural oxidant demand of aquifer materials using the push-pull technique. *J. Environ. Eng.* **130**(10), 1139–1146.

Mumford, K. G., Thomson, N. R. & Allen-King, R. M. 2005 Bench-scale investigation of permanganate natural oxidant demand kinetics. *Environ. Sci. Technol.* **39**(8), 2835–2840.

Rivera-Utrilla, J., Sanchez-Polo, M., Mendez-Diaz, J. D., Ferro-Garcia, M. A. & Bautista-Toledo, M. I. 2008 Behavior of two different constituents of natural organic matter in the removal of sodium dodecylbenzenesulfonate by O_3 and O_3-based advanced oxidation processes. *J. Colloid Interface Sci.* **325**(2), 432–439.

Rodriguez, E., Majado, M. E., Meriluoto, J. & Acero, J. L. 2007 Oxidation of microcystins by permanganate: reaction kinetics and implications for water treatment. *Water Res.* **41**(1), 102–110.

Shaker, A. M. 2001 Kinetics and mechanism of formation of manganate (VI) and hypomanganate (V) coordination polymer intermediates during the base-catalyzed oxidation of carboxymethyl cellulose polymer by permanganate. *Int. J. Chem. Kinet.* **33**(10), 605–611.

Siegrist, R. L., Urynowicz, M. A. & West, O. R. 1999 An overview of *in situ* chemical oxidation technology features and applications. In: *Proceedings of the Conference on Abiotic In Situ Technologies for Groundwater Remediation*. Dallas, Texas, 31 August–2 September 1999.

Silva, E., Japakse, N. & Kortenkamp, A. 2002 Something from 'nothing': eight weak estrogenic chemicals combined at concentrations below NOECs produce significant mixture effects. *Environ. Sci. Technol.* **36**(8), 1751–1756.

Snyder, S. A., Villeneuve, D. L., Snyder, E. M. & Giesy, J. P. 2001 Identification and quantification of estrogen receptor agonists in wastewater effluents. *Environ. Sci. Technol.* **35**(18), 3620–3625.

Urynowicz, M. A. 2008 *In situ* chemical oxidation with permanganate: assessing the competitive interactions between target and nontarget compounds. *Soil Sediment. Contam.* **17**(1), 53–62.

Urynowicz, M. A., Balu, B. & Udayasankar, U. 2008 Kinetics of natural oxidant demand by permanganate in aquifer solids. *J. Contam. Hydrol.* **96**(1–4), 187–194.

Westerhoff, P., Yoon, Y., Snyder, S. & Wert, E. 2005 Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes. *Environ. Sci. Technol.* **39**(17), 6649–6663.

WHO 2004 *Guidelines for Drinking-water Quality*, 3rd edition. (Vol. 1). World Health Organization, Geneva.

Wiberg, K. B. & Freeman, F. 2000 Kinetics of the base-catalyzed permanganate oxidation of benzaldehyde. *J. Org. Chem.* **65**(2), 573–576.

Wiberg, K. B., Wang, Y., Sklenak, S., Deutsch, C. & Trucks, G. 2006 Permanganate oxidation of alkenes, substituent and solvent effects. Difficulties with MP2 calculations. *J. Am. Chem. Soc.* **128**(35), 11537–11544.

Zahonyi-Budo, E. & Simandi, L. I. 1992 Induced oxidation of phosphorus (III) by a short-lived manganate (V) intermediate in the permanganate oxidation of arsenite (III). *Inorg. Chim. Acta* **191**(1), 1–2.

First received 26 February 2009; accepted in revised form 26 January 2010

Downloaded from https://iwaponline.com/aqua/article-pdf/59/5/324/401616/324.pdf
by guest