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Response to Comment on “Reinvestigation of the Role of Humic Acid in the Oxidation of Phenols by Permanganate”

We gratefully appreciate the interest of Pang et al. in our recent article¹ and welcome the opportunity to respond.

We never made an effort to clarify and to rule out the contribution of soluble manganese intermediates such as Mn(III) to the oxidation of phenolic compounds by permanganate in the presence of phosphate, polyphosphate, NTA and EDTA.^{2,3} The formation of Mn(INT)_{aq} species was identified by Jiang et al. based on the online scanning of UV-vis spectra at 350–700 nm during the course of oxidation of phenolic compounds by permanganate in the absence or presence of pyrophosphate or EDTA.² These authors also showed that humic acid (HA) and preformed MnO₂ had similar effect on phenolic compounds oxidation by permanganate as phosphate, polyphosphate, and EDTA.⁴ However, without demonstrating the influence of HA on manganese oxide formation, the authors concluded that the influence of HA on phenolic compound oxidation by permanganate was also ascribed to the effects of identified Mn(III) complexes.⁴

We had no evidence to exclude the contribution of Mn(III) complexes to the oxidation of phenolic compounds by permanganate in the presence of HA. However, we highlighted the role of HA as moderate reductant and complexing agent in the process of degrading phenolic compounds by permanganate.¹ Our viewpoints were supported by the following evidence including the UV-vis analysis:

- (1) The nonspecific absorbance at <500 nm and the linear relationship between absorbance at 418 and 526 nm suggested the generation of colloidal MnO₂.⁵
- (2) The UV-vis spectra showed that the formation of MnO₂ was strongly promoted at pH 5.0–9.0 in the presence of HA, which was definitely very different from those collected in the presence of pyrophosphate or EDTA.^{1,2}
- (3) The preformed MnO₂ oxidized phenol at a much greater rate than permanganate at pH 5.0, supporting that HA may enhance the oxidation of phenols by promoting the formation MnO₂, but it was much inert than permanganate at pH ≥ 6.0.
- (4) The positive effects of HA on oxidation of phenol by permanganate at pH 5.0 were depressed after preoxidation by ozone.
- (5) HA could only enhance the oxidation of phenols, oxidizable by preformed MnO₂, by permanganate at pH 5.0. There was a good correlation between the pseudo-first-order rate constants of the oxidation of phenols by preformed MnO₂ and the difference in the pseudo-first-order rate constants of the oxidation of phenols by permanganate in the presence or absence of HA at pH 5.0.
- (6) Comparing the influences of Na₂S₂O₃ and HA on phenol oxidation by permanganate further supported that HA induced the continuous generation of fresh MnO₂ and thus accelerated the oxidation of phenols by permanganate at pH ≤ 7.0.

Thank Jiang et al. for their comments on our ultrafiltration experiment, which was employed to show the binding of phenol to HA in our previous study.¹ We had performed the ultrafiltration experiment again with great caution and found that we did overestimate the binding of phenol to HA because we neglected the phenol sorption to the filterpaper. Fortunately, the mistake did not influence our conclusions. Several evidence indicated that there was binding of phenol to HA:

- (1) Although Na₂S₂O₃ resulted in the generation of more MnO₂ in the process of phenol oxidation by permanganate than that of HA under alkaline conditions, it did not induce an enhancement in phenol oxidation in the initial reaction stage.
- (2) The presence of HA with concentration up to 10 mg L⁻¹ did not accelerate the oxidation of 2,6-DCP by permanganate at pH 9.0 in the initial reaction stage. The different influences of HA on phenol and 2,6-DCP oxidation by permanganate at pH 9.0 should be mainly associated with the different pK_a values of phenol and 2,6-DCP. About 90% of phenol (pK_a = 9.99) is nondissociated at pH 9.0 while 2,6-DCP is completely dissociated at pH 9.0 (pK_a = 6.78). Therefore, the interaction between HA and nondissociated phenols contribute to the acceleration of the oxidation of phenols by permanganate in the initial stage under alkaline conditions.⁶
- (3) The ultrafiltration behaviors of phenol with and without HA were different (not shown), indicative of the binding of phenol with HA.

Since HA accelerated the oxidation of phenols by permanganate under acidic conditions mainly by promoting the formation MnO₂, we compared the formation of MnO₂ in the process of phenol oxidation by permanganate in the presence of pristine HA or HA preoxidized by ozone. It should be notified that the reaction conditions, under which ozonation experiments were carried out, were identical to those presented in our previous study.¹ Compared to the pristine HA, less MnO₂ was generated in the process of phenol oxidation by permanganate in the presence of HA preoxidized by ozone, confirming that the oxidizable moieties in HA and MnO₂ generated *in situ* were crucial for the influence of HA on the oxidation of phenols by permanganate. The results of this experiment also verified that ozonation under the reaction conditions employed in our study did cause the change of HA chemical properties.

We had never examined the influence of MnO₂ on the oxidation of refractory nitrophenols by permanganate at acidic pH. The catalytic effect of preformed MnO₂ on phenol oxidation by permanganate was excluded because the kinetics of oxidation of phenol by permanganate in the presence of

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preformed MnO_2 was almost equal to but slightly slower than the sum of the kinetics of oxidation of phenol by permanganate and that by preformed MnO_2 at pH 5.0–9.0 (Figure S3 in our previous paper).¹ Thus, we concluded that preformed MnO_2 mainly worked as an oxidant in the oxidation of phenol by permanganate. Furthermore, we found that preformed MnO_2 could not oxidize 2- NO_2 -Phenol and HA could not enhance the oxidation of 2- NO_2 -Phenol by permanganate, in agreement with our speculation that HA worked as a reductant and induced the formation of MnO_2 in the process of the oxidation of phenols by permanganate.

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The authors declare no competing financial interest.

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