Enhanced abatement of various phenols by integrated permanganate and activated carbon process: role of quinones and phenolic acids

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ABSTRACT

Enhanced degradation of phenols by integrated permanganate and activated carbon (Mn(VII)/AC) process was investigated. Quantitative experiments for phenol removal were performed in view of various phenols, pH, and activated carbon (AC) dosage. With respect to the oxygen-containing functionalities on AC surface, the influence of quinones and phenolic acids on phenol degradation by permanganate was studied. Synergistic effect for the degradation of various phenols is observed for integrated Mn(VII)/AC process, which can achieve significant abatement of phenols with a concomitant release of chloride ions from chlorophenols. Lower pH (4.0–6.0) is more favorable for the enhancement of phenol degradation due to significant formation of manganese dioxide on AC surface. The presence of model quinones and phenolic acids also enhances phenol abatement by permanganate from 26% to 50% to 70% at pH 6.0. pH exerts a similar effect as AC on phenol degradation by permanganate in the presence of quinones and phenolic acids. An increase of the apparent second-order rate constant for phenol abatement is significantly enhanced with the decrease of pH, which is due to the newly formed manganese dioxide catalyzing permanganate to manganese dioxide.

Keywords: Permanganate; Activated carbon; Quinones; Phenolic acids; Phenols

1. Introduction

Carbon materials have been widely used in various areas as adsorbents [1–4]. Among the carbon materials, activated carbon (AC) has been considered as an effective adsorbent in removing micropollutants in water treatment operations. In addition to being used as an adsorbent, AC has also found great applications in combined processes [5–8]. Combined ozone oxidation and AC adsorption are well-established processes for the removal of organic compounds [9]. High surface area and basic property of AC are found to play an important role in ozone decomposition and the corresponding formation of highly reactive radical species [10]. In addition to catalytic ozonation, AC is also found to catalyze persulfate to form sulfate radical, thus accelerating the transformation of azo dye acid orange 7 [11,12].

Nowadays, the simultaneous application of permanganate and AC has found wide application in China. Integrated permanganate oxidation and powdered AC adsorption processes are effective for reducing the formation of a series of carbonaceous and nitrogenous disinfection by-products by removing or transforming their precursors [13]. Effectiveness of permanganate pre-oxidation followed by coagulant addition with powdered AC for eliminating microcystin-LR has been demonstrated [14]. It could be postulated from previous reports that AC, as a reducing agent, could accelerate the degradation of pollutants from water bodies by permanganate [15,16]. In our previous work, a synergistic enhancement of phenols and aniline removal is found for integrated permanganate multiwalled carbon nanotube (MWCNT) process [17]. The formation of manganese dioxide induced

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by the reaction between permanganate and carbon nanotubes (CNTs) mainly contributes to the enhancement of phenol oxidation. Previous reports have demonstrated that the reducing property of AC can lead to the formation of manganese dioxide [18,19].

Surface functional groups on AC will exert a significant influence on the efficacy of various oxidation processes. It has been previously reported that quinone groups and carboxylic groups are the major oxygen-containing functional groups on AC [20]. It has been demonstrated that quinones and phenolic acids can enhance pentachlorophenol degradation in Fenton system, in which the quinones transfer electrons from HO adduct of the starting aromatic compound to Fe(III) [21]. Activation of persulfate by quinones is also reported, and it is found that quinone and hydroquinone (HQ) comproportionate to form semiquinone radical, thus activating persulfate ion to produce SO_4^- [22]. However, there has been little information with respect to the enhanced degradation of phenols by integrated permanganate and activated carbon (Mn(VII)/AC) process and the surface functional groups (quinones or phenolic acids) on the oxidation of phenols by permanganate. Therefore, to understand the role of AC in the oxidation of target organic compounds by permanganate, it is of crucial significance to elucidate the functionalities that contribute to the facilitation.

The objectives of this study were (i) to evaluate the efficacy of phenol degradation by integrated Mn(VII)/AC process, (ii) to compare the influence of pH on phenol abatement for three reaction systems including permanganate oxidation, AC adsorption, and integrated Mn(VII)/AC process, (iii) to assess the effect of AC dosage on phenol abatement, (iv) to investigate the effect of model quinones and phenolic acids in the transformation of phenol by permanganate in terms of various model compounds and pH, and (v) to elucidate the role of model quinones and phenolic acids in phenol oxidation by permanganate.

2. Materials and methods

2.1. Materials

Phenol (purity \geq 99%), 2-CP (2-chlorophenol, purity \geq 99%), 4-CP (4-chlorophenol, purity \geq 99%), 2,4-DCP (2,4-dichlorophenol, purity ≥ 99%), 2,4,6-TCP (2,4,6-trichlorophenol, purity \ge 98%), and BPA (bisphenol A, purity \ge 99%) were obtained from Sigma-Aldrich, Beijing, China. 1,4-benzoquinone (BQ, purity \geq 98%), HQ (*p*-HQ and *o*-HQ, purity \geq 99%), lawsone (2-NQ, purity 97%), and 9,10-anthraquinone-2sulfonic acid sodium salt monohydrate (AQ, purity 97%) were also purchased from Sigma-Aldrich, Beijing, China. Gallic acid (GA, purity 98%), tannic acid (TA), and ferulic acid (FA, purity 99%) were provided by China National Pharmaceutical Group Corporation, Beijing, China. All reagents were used without further purification. AC was purchased from Aladdin, Shanghai, China. Before use, AC was washed with deionized water until the solution pH is constant and then dried for 24 h. All reaction solutions were prepared using 18.2 MΩ cm Milli-Q water from Millipore System, USA. Stock solution of permanganate was prepared by dissolving 3.2 g permanganate crystals to 1.0 L Milli-Q water.

2.2. Kinetic experiments

Kinetic experiments were performed according to the following procedure: permanganate and AC particles were simultaneously added to 100 mL pH-buffered solutions containing phenols which were maintained at 23° C ± 1°C and agitated by magnetic stirrer. At predetermined time intervals, appropriate amount of solution was withdrawn from the reaction solution, filtered through 0.70 µm glass fiber filter, and immediately quenched by 10 µL of hydroxylamine hydrochloride to determine the residual concentration of phenols. When considering the influence of pH, sodium acetate and borate were adopted as the buffer for pH 4.0–6.0 and 7.0–9.0, respectively.

With respect to the influence of quinones and phenolic acids, batch experiments were conducted with the reaction solution maintained at 23°C ± 1°C and agitated by magnetic stirrer. The influence of solution pH and various model compounds on phenol degradation by permanganate was investigated. The detailed procedure was that 250 µL of 20 mM permanganate stock solution was added to 100 mL reaction solutions containing 5 µM phenol, buffer solution, and model compounds (quinones or phenolic acids). Then, at different intervals, 1 mL sample was withdrawn from the reaction solution and immediately quenched by 10 μ L of 0.2 M hydroxylamine hydrochloride to determine the residual concentration of phenol. When investigating the effect of different model compounds on phenol degradation by permanganate, the ultraviolet (UV)-vis absorbance was measured as a function of time. All experiments were performed in duplicates, and the data in the figures were the mean value.

2.3. Analyses

The concentration of permanganate in solution was determined by ABTS method (2,2-azinobis(3-ethylbenzothiazoline)-6-sulfonic acid diammonium salt) [23]. Highperformance liquid chromatography (HPLC) with photodiode array detection was used for the determination of the concentrations of phenol and chlorophenols. One-hundred microliters of the withdrawn solution was injected into HPLC system equipped with a Waters symmetry C18 column (4.6 mm × 150 mm, 5 µm particle size), a Waters 717 autosampler, and a Waters 2487 dual λ detector. The mobile phase consisted of methanol and 0.1% aqueous acetic acid. The flow rate of the mobile phase was controlled at 1 mL/min. The online UV-vis scanning was performed with a Cary 300 spectrometer.

The release of chloride ion was measured by ion chromatography (IC) (Dionex ICS-3000). Before the measurement of chloride ion, the samples after quenching were filtered with a Dionex OnGuard II H Cartridge, which can efficiently remove Mn(II) by ion exchange from the sample matrices in order to prevent the precipitation of manganese oxides on the IC column under the basic conditions of the effluent. The acetate buffer and borate buffer can affect the IC measurement because of their high buffer capacity. Therefore, pH of the samples was adjusted to the value same as the pH of the effluent before the IC injection. The procedure is as follows: 1 mL sample was withdrawn and added to a 2-mL plastic vial and then pH of the sample was adjusted to 11.0–12.0 by sodium hydroxide. This pH range can guarantee that solution pH was as same as the eluent in IC measurements. The mobile phase was in a gradient mode from 2–175 mM NaOH.

3. Results and discussion

3.1. Enhanced phenol abatement by integrated Mn(VII)/AC process

To elucidate the enhancement of phenol degradation by integrated Mn(VII)/AC process, efficacy of phenol abatement for three reaction systems of permanganate oxidation, AC adsorption, and integrated Mn(VII)/AC process is compared. Fig. 1 shows the abatement of various phenols including phenol, 2-CP, 4-CP, 2,4-DCP, 2,4,6-TCP, and BPA as a function of time for the above three processes.

As shown in Fig. 1, a significant increase of the abatement for the selected phenols is observed in integrated Mn(VII)/AC process compared with permanganate oxidation and AC adsorption. Taking BPA as an example, the removal efficiencies of BPA in samples containing 20 mg/L AC or 50 μ M permanganate alone are 32% and 72%, respectively. Whereas 100% of BPA degradation is observed for integrated Mn(VII)/AC process. Similar phenomenon occurs to other phenols. Experimental results clearly indicate that integrated Mn(VII)/AC process shows synergistic effect for phenol degradation. This effect of promotion is observed, to different extent, for different phenols tested in this study.

The enhanced phenol degradation by integrated Mn(VII)/AC process is, to some extent, similar to the system of AC adsorption under oxic conditions, in which the adsorption capacity of *o*-cresol and 2-methylphenol increases 2.6-fold and 2.5-fold compared with that of anoxic environment [24–27]. Exposure to oxygen can induce phenols

undergo oxidative coupling on AC surface, leading to the polymerization of phenols. This process can make phenols difficult to desorb from AC surface and result in irreversible adsorption. The experiment in this study was conducted under oxic conditions according to the definition described by Suidan [24]. AC shows significant uptake of phenol. From the perspective of permanganate oxidation, the presence of AC significantly promotes the degradation of phenol and its substitutes. It is possible that permanganate may play a similar role as oxygen in the irreversible adsorption of phenol on AC. On the other hand, regarding the redox reaction of permanganate and AC, AC will serve as a sacrificial reductant to reduce permanganate to colloidal manganese dioxide, which contributes to the enhancement of phenol degradation [17].

Chlorophenol degradation is accompanied with the concomitant chloride release during the process of oxidative coupling [28]. In terms of dechlorination of chlorophenol oxidation by permanganate, the transformation efficiency of these phenols is much lower and is not discussed here. The experimental dechlorination number (DN), representing the amount of the degraded chlorophenol molecules per one released chloride ion, is calculated according to the following equation [29]. The transformation efficiency and DN values of 2-CP, 4-CP, and 2,4-DCP for AC adsorption and integrated Mn(VII)/AC process are illustrated in Table 1.

$$DN = \frac{\left[CP\right]_{0} - \left[CP\right]_{t}}{\left[Cl^{-}\right]}$$

where $[CP]_0$ and $[CP]_t$ represent the initial and the residual concentration of chlorophenols, respectively. [CI-] is the concentration of the released chloride ion.



Fig. 1. Abatement of various phenols by integrated Mn(VII)/AC process. Experimental conditions: [AC] = 20 mg/L, $[phenols] = 5 \mu M$, $[Mn(VII)] = 50 \mu M$, pH 6.0, Temperature = $23^{\circ}C \pm 1^{\circ}C$.

Chlorophenols	Transfo	ormation percentage	Released chloride ion/µM		DN	
	AC (%)	Mn(VII)/AC (%)	AC	Mn(VII)/AC	AC	Mn(VII)/AC
2-CP	59	100	0.9	2.0	3.2	2.5
4-CP	74	100	1.1	2.2	3.0	2.3
2,4-DCP	78	100	1.2	2.8	2.5	1.8

Table 1 Dechlorination numbers (DN) of chlorophenols by AC adsorption and integrated Mn(VII)/AC process at pH 6.0

As shown in Table 1, a significant transformation is achieved for both integrated Mn(VII)/AC process and AC adsorption process, whereas the released chloride ions are in the range of 2.0-2.8 and 0.9-1.2 µM, respectively. As illustrated in Table 1, although DN values of these three phenols for integrated Mn(VII)/AC process are comparatively higher than that for AC adsorption process, both processes can achieve significant dechlorination. AC shows negligible adsorption of chloride ion. The discrepancies of DN values for the two processes are not significant, and thus, the addition of permanganate would not change the mechanism of the AC adsorption process, and the reduced dehalogenation for the AC adsorption process is probably due to the direct adsorption of some reactive intermediates on AC surface. Oxidation of phenols by permanganate leads to the formation of the quinone intermediates or free radicals, and subsequent nucleophilic attack results in the release of chloride ion.

3.2. Effect of reaction conditions on phenol degradation by integrated Mn(VII)/AC process

3.2.1. Effect of pH

The influence of pH on the performance of integrated Mn(VII)/AC process was studied using phenol as the model

compound (Fig. 2). Adsorption by AC could not be omitted due to its significant phenol uptake. Integrated Mn(VII)/AC process can achieve efficient removal of phenol in the pH range of 4.0–8.0, and a synergistic effect is observed for permanganate and AC. At pH 7.0, the removal efficiencies of phenol for permanganate oxidation, AC adsorption and integrated Mn(VII)/AC process are 30%, 41%, and 100%, respectively. With the further increase of pH to 9.0, phenol decay in the presence of AC tends to coincide with the oxidation kinetics by permanganate, and there is no enhancement of phenol degradation by AC. Therefore, the synergistic effect is much favorable for lower pH conditions.

Permanganate decay for the integrated Mn(VII)/AC process in the absence of phenol was also monitored for differing pH values, which is listed in Table 2. It could be clearly seen that the permanganate decay rate was higher for lower pH values (Table 2). As for pH 4.0 and 5.0, permanganate decay was the most significant. With increasing pH, the rate of permanganate decay decreased greatly. This indicates that the reaction between permanganate and AC exerts an effect on phenol removal. For lower pH values, the synergistic effect is much favorable due to the fact that manganese dioxide formation from reaction between permanganate and AC with high reaction rate contributes to phenol abatement.



Fig. 2. Effect of solution pH on phenol abatement by integrated Mn(VII)/AC process. Experimental conditions: [AC] = 20 mg/L, $[phenol] = 5 \mu M$, $[Mn(VII)] = 50 \mu M$, Temperature = $23^{\circ}C \pm 1^{\circ}C$.

рН	Pseudo-first-order rate constant/(min ⁻¹)	Residual Mn(VII)/Mn(IV) concentration/(µM)
4.0	0.124	22
5.0	0.075	30
6.0	0.046	36
7.0	0.046	41
8.0	0.047	41
9.0	0.046	42

Table 2 Permanganate decay for the integrated Mn(VII)/AC process in the absence of phenol

For higher pH values (8.0–9.0), phenol abatement induced by oxidation is significant and contribution of manganese dioxide can be negligible. To quantitatively evaluate the formation of manganese dioxide on AC surfaces, the total manganese concentration in aqueous solution was measured (Table 2). The amount of manganese dioxide on AC surface was 28 μ M at pH 4.0, which was decreased with increasing pH. This phenomenon is consistent with the enhanced phenol abatement in the integrated Mn(VII)/AC process.

Phenol degradation by integrated Mn(VII)/AC process is a complicated process, in which manganese dioxide functions as illustrated in our previous study [17]. Oxidative coupling of phenols in the process of oxidation may also be a factor due to the presence of AC. However, oxidative coupling of phenol is more facile under higher pH values, especially in the alkaline media whose pH value is above pK_a of phenol (pK_a = 9.99) and then the phenolate ion is more reactive than protonated phenol molecule [30,31]. In this study, significant discrepancies for phenol degradation among different pH conditions are observed and lower pH favors the enhancement of phenol degradation by integrated Mn(VII)/AC process, which contradicts with the trend of oxidative coupling. The molecular species of phenol are dominating in the tested pH range (4.0–9.0). Therefore, it could be speculated that oxidative coupling is not responsible for the discrepancies of enhanced degradation rate induced by pH differences. Due to the reducing property of AC, significant amount of manganese dioxide will form when permanganate is in contact with AC. Manganese dioxide shows more pronounced catalytic effect on permanganate oxidation for lower pH values than higher pH values, which results in the enhanced phenol degradation for lower pH values.

3.2.2. Effect of AC dosage

Abatement of phenol by integrated Mn(VII)/AC process was studied in the presence of different initial concentrations of AC in order to better understand the role of AC in the system of permanganate oxidation (Fig. 3). Compared with single permanganate oxidation, phenol degradation is significantly accelerated by the presence of AC. With the increase of initial AC concentrations, the removal efficiency is greatly improved, indicating the increased formation of manganese dioxide, which could catalyze permanganate oxidation [32].

3.2.3. Role of carbon materials

Previous research has reported the adsorption of phenols and anilines by carbon materials including AC and CNT [33-35]. The degradation of phenol by permanganate was examined in the presence of AC, MWCNTs, and single-walled carbon nanotubes (SWCNTs), respectively (Fig. 4(a)). In terms of AC, the removal efficiencies of phenol for three different processes (oxidation with permanganate, adsorption on carbon, and oxidation with permanganate in the presence of carbon) are 10%, 40%, and 90%, respectively. In contrast, more than 60% of phenol are degraded by permanganate in the presence of SWCNTs while the adsorption of phenol is 29%. The reactivity of MWCNTs is the lowest compared with AC and SWCNTs. As illustrated in Fig. 4(b), the pseudo-first-order rate (k_1) constants for phenol degradation by permanganate in the presence of AC, SWCNTs, and MWCNTs are 0.120, 0.078, and 0.012 min⁻¹, respectively. This discrepancy can be correlated



Fig. 3. Effect of AC dosage on phenol abatement by AC adsorption (a) and integrated Mn(VII)/AC process (b). Experimental conditions: (a) [phenol] = 5 μ M, pH = 6.0, Temperature = 23°C ± 1°C, (b) [phenol] = 5 μ M, [Mn(VII)] = 50 μ M, pH = 6.0, Temperature = 23°C ± 1°C.



Fig. 4. Effect of various carbon materials on phenol abatement by integrated permanganate/carbon material process. (a) Removal efficiency of phenol, (b) pseudo-first-order rate constant of phenol abatement in integrated permanganate/carbon material process, and (c) pseudo-first-order rate constant of permanganate decay for the reaction of permanganate and carbon materials. Experimental conditions: [carbon materials] = 20 mg/L, [phenol] = 5 μ M, [Mn(VII)] = 50 μ M, pH 6.0, Temperature = 23°C ± 1°C.

to the reactivity of permanganate and carbon materials with the pseudo-first-order rate constant in the order of AC > SWCNTs > MWCNTs (Fig. 4(c)). AC shows best performance on promoting permanganate oxidation to degrade phenol.

3.3. Role of quinones and phenolic acids on phenol degradation by permanganate

Due to the presence of the surface functional groups on AC surface, quinones or phenolic acids were selected as the model oxygen-containing groups to study their effect on phenol abatement by permanganate. Fig. 5 shows phenol degradation by permanganate in the presence of various model quinones or phenolic acids. Phenol degradation is enhanced by permanganate in the presence of quinones including BQ, 2-NQ, *p*-HQ, and *o*-HQ, whereas no significant enhancement or inhibition is observed for AQ in the studied concentrations. The enhancement of phenol degradation follows the order of HQ > BQ > 2-NQ > AQ, which may be related to the redox potential of these quinones. The presence of phenolic acids including TA, GA, and FA also



Fig. 5. Removal efficiency of phenol degradation by permanganate in the presence of quinones/phenolic acids. Experimental conditions: [phenol] = 5 μ M, [Mn(VII)] = 50 μ M, [quinones]/[phenolic acids] = 3 μ M, pH 6.0, Temperature = 23°C ± 1°C.

promotes the degradation of phenol. In the experimental process, it could be obviously observed that the solution became brown quickly because the presence of HQ, BQ, and NQ accelerates the formation of manganese dioxide significantly, which can catalyze the permanganate oxidation process [36].

In order to further understand the role of guinones and phenolic acids, the degradation kinetics of phenol by permanganate was studied as a function of pH in the presence of various quinones and phenolic acids. The apparent second-order rate constants (k_2) of phenol degradation by permanganate in the presence of 3 µM quinones and phenolic acids as a function of pH are shown in Fig. 6. In the pH range of 4.0–9.0, k_2 for phenol degradation exhibits parabola-like shapes in the absence and presence of quinones or phenolic acids. In the lower pH range of 4.0-6.0, facilitation of phenol degradation by quinones and phenolic acids is more pronounced with the decrease of pH. Especially, in terms of pH 4.0, k_2 value in the presence of BQ and FA increases from 9.3 to 22 and 17 M⁻¹s⁻¹, respectively. However, quinones inhibit the reaction at higher pH (6.0-9.0) with the increase of pH. This phenomenon can be attributed to the newly formed manganese dioxide during the reaction process. Manganese dioxide can achieve the rapid destruction of phenol in acid environment and catalyze permanganate oxidation. However, in the basic environment, quinones still react with permanganate to form MnO₂, which competes with phenol to consume permanganate and leads to the reduction of phenol degradation. With respect to the discrepancy among various model quinones, the reactivity between permanganate and quinones may be responsible.

Regarding the formation of manganese dioxide, changes of UV-vis spectra in the reaction process are recorded, which reflect the transformation of manganese species, mainly involving Mn(VII) and manganese dioxide. Fig. 7 presents UV-vis spectra recorded during the reaction process. By comparison with the quinone-free experiment, the absorbance (<500), attributable to colloidal manganese dioxide, is significantly enhanced in the presence of quinone. As shown in Fig. 7, by comparison with quinone-free reference, not only is the decay of permanganate identifiable but also the formation of manganese dioxide is significant. The exception is the presence of AQ. Obviously, permanganate decay and manganese dioxide formation in the presence of AQ are negligible, confirming that AQ shows no enhancement or inhibition for



Fig. 6. Apparent second-order rate constants of phenol degradation by permanganate in the presence of quinones (a) and phenolic acids (b). Experimental conditions: [phenol] = 5 μ M, [Mn(VII)] = 50 μ M, [quinones]/[phenolic acids] = 3 μ M, Temperature = 23°C ± 1°C.



Fig. 7. The changes of UV-vis spectra for oxidation of phenol by permanganate in the presence of quinones. Experimental conditions: [phenol] = $5 \mu M$, [Mn(VII)] = $50 \mu M$, [quinones] = $3 \mu M$, pH 6.0, Temperature = $23^{\circ}C \pm 1^{\circ}C$.

phenol degradation by permanganate in the above section. Consequently, we conclude that quinones or phenolic acids, as a kind of reducing species, induce the formation of manganese dioxide, thus facilitating the phenol abatement by permanganate. The newly formed manganese dioxide would accelerate phenol decay by permanganate in acid solution. However, this acceleration gradually decreases with the increase of pH. That is because the efficacy of manganese dioxide for enhancing permanganate to oxidize phenol is negligible in basic solution.

4. Conclusions

This study investigated the degradation of various phenols by integrated Mn(VII)/AC process. This integrated process significantly enhances the abatement of phenols compared with single permanganate oxidation or AC adsorption. The pH values of water bodies will exert great influence on the degradation rate of pollutants by integrated Mn(VII)/AC process. Dechlorination experiments clearly demonstrate that integrated Mn(VII)/AC process can lead to a significant release of chloride ions from chlorophenols and thus a reduction of toxicity of halogenated phenols. The reduction of permanganate by AC results in the formation of great amounts of manganese dioxide, promoting phenol degradation by permanganate. The influence of solution pH on phenol degradation confirms that manganese dioxide formed in situ induced by the reaction between AC and permanganate contributes to the enhancement of phenol abatement.

With respect to the presence of quinones or phenolic acids on the AC surface, the influence of quinones and phenolic acids on phenol decay was studied. Effect of quinones on phenol degradation depends on solution pH. The in situ formed manganese dioxide induced by reduction contributes to the acceleration of phenol decay. As a consequence, permanganate is transformed to colloidal manganese dioxide with high reactivity in acid environment, thus enhancing phenol oxidation. Surface oxygen-containing functional groups on AC, such as quinones and phenolic acids, will react with permanganate to form manganese dioxide. Regarding the synergistic effect of permanganate and AC, integrated Mn(VII)/AC process is a promising water treatment technology for removing a broad spectrum of phenols.

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