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Catalytic effect of soil colloids on the reaction between Cr^{VI} and *p*-methoxyphenol

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"Capsule": Adsorption of Cr^{VI} and p-methoxyphenol on soil colloids was affected by pH.

Abstract

Adsorption of Cr^{VI} and *p*-methoxyphenol (PMP) on soil colloids at different pH media was studied. The resulting k_1 and *n* of 1.89×10^2 and 0.53 ($r^2 = 0.99$) and k_2 and *b* of 0.13 and 1.25×10^3 ($r^2 = 0.96$) were obtained from Freundlich ($Q = k_1 C_{aq}^n$) and Langmuir [$Q = k_2 b C_{aq}/(1 + k_2 C_{aq})$] simulation equations, respectively, for Cr^{VI} adsorption on soil colloids (pH 4.20). The adsorption of PMP on soil colloids in pH 5.72 media was simulated by five different equations and the results indicated that the Fritz-Schluender one ($r^2 = 1.00$) was the most suitable among them. Adsorption quantity of Cr^{VI} and PMP on colloids increased with increasing acidity in the pH range of 3.5-9.0. Study of Cr^{VI} adsorption kinetics indicated that the adsorption equilibrium of Cr^{VI} was reached rapidly within 2 h. In pure aqueous solution, Cr^{VI} reduction by PMP was observed only when the media's pH was lower than 4.0. Oxidation and reduction reaction between Cr^{VI} and *p*-methoxyphenol obviously occurred when soil colloids were involved in this system, even at pH ≥ 7.0 , which strongly suggested that minerals in soil colloids acted as catalysts to speed the reaction of Cr^{VI} and PMP. The oxidized product of PMP by Cr^{VI} , extracted by chloroform in acid media and analyzed by gas chromatography–mass spectrometry, was identified as benzoquinone. The reaction included two steps of one electron process. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: CrVI; p-methoxyphenol; Catalytic reaction; Soil colloids; Pollution

1. Introduction

More and more organic pollutants and heavy metals exist in the environment as a result of anthropogenic activity. Usually, these pollutants appear not singly but as co-contamination. Compared with individual pollutants, combinations in the forms of organic–organic, organic– inorganic and inorganic–inorganic contaminants are very complex and usually produce more serious pollution. Therefore, the study of combined pollutants rather than single ones is more important for improved understanding of the behavior of pollutants in real systems (Balsberg, 1989).

Most phenolic compounds were listed as priority organic pollutants by the US Environmental Protection Agency because of their large amounts, diverse forms and high toxicity. These pollutants, once in environment, will undoubtedly interact with their surroundings

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via adsorption/desorption between soil (or sediment) and water, hydrolysis, photolysis and volatilization. Furthermore, they will react chemically with other species or be degraded by microorganisms (Kawaguchi and Inagaki, 1994; Gonzalez and Ukrainezyk, 1996; Senesi et al., 1997). So, the migration and conversion of phenolic compounds will be influenced by other coexisting species.

As a heavy metal, Cr^{VI} is toxic to humans and other living organisms when it is discharged into the environment. In acid medium, Cr^{VI} is unstable, and it will be easily reduced to less toxic Cr^{III} by some metal ions or organic pollutants. Since the 1970s, migration and conversion of Cr^{VI} in minerals and soil has attracted great attention (Bartlett and Kimble, 1976; James and Bartlett, 1983; Cifuentes, et al., 1996). Interaction of Cr^{VI} and concrete particles indicated that the reduction of Cr^{VI} was mainly caused by Fe^{II} ions (Wang et al., 1996), and organic ligands and pH played very important roles in the reaction of Cr^{VI} and Fe^{II} in aqueous media (Buerge and Hug, 1998).

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However, the above research concerned Cr^{VI} behavior in the form of a single pollutant. Recently, interactions of Cr^{VI} and organic pollutants, such as phenol and its derivatives, were studied in aqueous media (Elovitz and Fish, 1994, 1995) and on metal oxides such as aluminum oxide, goethite and titanium oxides (Deng and Stone, 1996a,b). It was found that the reaction of Cr^{VI} and phenolic compounds in pure aqueous solution occurred only in acid media, and metal oxides could act as efficient catalytic reaction centers for the reaction even when pH > 7.0. Soil, especially "red soil" of China containing large amounts of Fe and Al oxides, can be imagined to act as the catalyst for Cr^{VI} and organic compounds.

Here, the adsorption behavior of Cr^{VI} and *p*-methoxyphenol (PMP) on soil colloids was studied. Meanwhile, the interaction of Cr^{VI} and PMP was examined in the presence of soil colloids over a wide pH range. The product was analyzed by gas chromatography-mass spectrometry (GC-MS), and the reaction mechanism was proposed according to our research results.

2. Materials and methods

2.1. Reagents and materials

All reagents were of analytical grade, and deionized water was used here in all experiments. Chloroform was distilled prior to use, and the middle fraction (60° C) was collected.

Air-dried soil (red soil, Udic Ferrisol), sampled from Jingxian, Jianxi province, China, was sieved through a 20-mesh screen ($\phi = 0.84$ mm), then, a portion of soil was weighed and soaked in deionized water and sonicated to disperse. Soil colloids with $\phi < 0.002$ mm were separated and collected from the solution of soil colloids according to Stokes' equation, and the soil colloids were washed with saturated CaCl₂ solution and then with deionized water to diminish chloride ions. So, the subsamples were Ca-saturated and reserved to use after being dried under an infrared lamp. The total contents of Fe, Al and Si oxides in the soil colloids were analyzed using DCP (Direct Couple Plasma) -atomic absorption spectroscopy (AAS) with fused Li₂CO₃-H₃BO₃ (Sheng et al., 1983). Cation exchange capacity (CEC) of colloids was determined with BaCl₂-H₂SO₄ method (Institute of Soil Science, Chinese Academy of Sciences, 1978). The characteristics of soil colloids are shown as Table 1.

2.2. Experimental procedure

Stock solutions of Cr^{VI} and PMP were prepared before each experiment, and 0.100 ± 0.002 g of soil colloids were weighed and placed into 50ml PVF plastic tube. Then, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0, 10.0, 15.0, 25.0 mg/l Cr^{VI} and 13.0, 26.0, 46.0, 72.0, 96.0 mg/l PMP were

Table 1 Characteristics of soil colloids^a

OM	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	TiO ₂	CEC
(g/kg)	(%)	(%)	(%)	(%)	(mmol/kg)
12.60	11.18	40.86	29.08	1.14	25.67

^a OM, organic matter; CEC, cation exchange capacity.

added into these tubes to perform the batch equilibrium experiments besides the corresponding blank ones. The pH of samples was adjusted by adding different content of 10^{-3} mol/l HCl or NaOH and equilibrated prior to the addition of Cr^{VI} and PMP. The total volume was 10 ml, and all media contained 0.01 mol/l NaNO₃. Samples were shaken horizontally and continuously, then centrifuged for 10 minutes at $1211 \times g$ to examine the change of Cr^{VI} and PMP content in solution. The centrifugates were used to analyze the contents of Cr^{VI} and PMP. Meanwhile, accurate pH values were measured by glass pH electrode in the centrifugates. Experimental temperature was controlled at $22\pm0.5^{\circ}$ C in a constant temperature room. The experimental results were the average values of two replications.

2.3. Chemical analysis

Cr^{VI} analysis was performed by the colorimetric method with diphenylcarbazide using a 721 visible-spectrometry (Shanghai Instrumental Factory, China) at detection wavelength of 540 nm. Samples, used for the analysis of PMP, were obtained by extracting the above solution in acid media using 5.0 ml chloroform three times (PMP cannot be ionized in acid media, which resulted in a high extraction efficiency). Then, phenol was added as an internal standard, and the resultant samples were condensed to 2.0 ml and filtered through a 0.3-µm microporous cellulose ether filtration film (Hailin Medical Instrumental factory, Zhejian Province, China). The analysis of PMP samples was carried out in a Finnigan-SSQ710 MS connected to a Varian GC with a 60 m×0.32 mm i.d. DB-5 fused silica capillary column. The temperatures of the procedure were 50°C (1 min)-150°C (10°C/ min)-250°C (20°C/min)-250°C (5 min). MS operated in the electron impact mode at 70 ev. Significant total-ion chromatographic peaks were identified by mass spectral interpretation, and the mass ion distributions were compared with a data system library (Elovitz and Fish, 1995).

3. Results and discussion

3.1. Adsorption of Cr^{VI} on soil colloids

Soil colloids used here included a high content of Fe and Al oxides, and its pH, determined with colloids to water ratio of 1:100 under our experimental condition, was 6.52. The content of oxides, CEC and organic matter content are listed in Table 1. Meanwhile, these soil colloids, as variable charged ones, showed a high buffer capacity to acid or base addition.

Fig. 1(a) shows the adsorption isotherm of Cr^{VI} on soil colloids as well as the influence of pH [Fig. 1(b)]. Cr^{VI} adsorption increased with the increasing initial concentration and finally reached its equilibrium. Adsorption isotherm of Fig. 1(a) was simulated using the Freundlich equation $(Q = k_1 C^{1/n})$ and Langmuir equation $(Q = k_1 C^{1/n})$ $k_2bC/[1+k_2C]$ (b is the maximum adsorption quantity) with the resulting k_1 and *n* of 1.89×10^2 and 0.53 ($r^2 = 0.99$) and k_2 and b of 0.13 and 1.25×10^3 ($r^2 = 0.96$), respectively. Therefore, it suggested that both of these two simulation equations could be used to describe Cr^{VI} adsorption on the soil colloids very well with high correlation coefficient. Moreover, Cr^{VI}, as an anion, showed a strong adsorption on these colloids, which can be ascribed to large amounts of Al and Fe oxides included in these colloids (Aide and Cummings, 1997).

 CrO_4^{2-} adsorption is a surface complexation reaction, possibly accompanied by protonation of the ligand at the surface (Ainsworth et al., 1989; Mesuere and Fish,

1992). The pH influence on Cr^{VI} adsorption showed that the adsorption quantity of Cr^{VI} would increase with increasing acidity, as shown in Fig. 1(b), which could be due to the $-OH_2^+$ groups formed on the surface of colloids resulting in a strong adsorption to the anionic Cr^{VI} (Aide and Cummings, 1997). Meanwhile, $HCrO_4^-$, dominated at pH <4.6, is the major adsorption ions among Cr^{VI} forms in aqueous solution (Deng and Stone, 1996a). The change of Cr^{VI} adsorption is significant with pH, and no Cr^{VI} adsorption occurred when pH exceeds 9.0.

3.2. Adsorption isotherm of PMP on soil colloids

Fig. 2 shows the adsorption isotherm of PMP on soil colloids and the influence of pH on this adsorption process. Usually, organic chemicals are mainly adsorbed on the organic matter of soil; also, it can be linked to the surface of soil or mineral by hydrogen bonds or other chemical bonds (Sawhney and Brown, 1989; Xing and Pignatello, 1998). So, organic matter contained in soil colloid would contribute to the major portion for the adsorption of PMP; meanwhile, mineral surface of the soil colloids can also contribute to the adsorption of PMP,



Fig. 1. (a) Adsorption isotherm of Cr^{VI} on soil colloids (pH 4.20); (b) represents the influence of pH on the adsorption of 10.0 mg/l Cr^{VI}.



Fig. 2. (a) Adsorption isotherm of PMP on soil colloids (pH = 5.72); (b) represented the influence of pH on the adsorption 96.0 mg/l PMP.

especially in weakly acid media due to the easy formation of hydrogen bonds.

PMP (p K_a 10.21) can be ionized and its two forms, ions and molecules, exist depending on pH. According to the results from adsorption/desorption of phenolic compounds on granular activation carbon (Mollah and Robinson, 1996), we use five adsorption equations, including Langmuir [$q = kbC_{aq}/(1 + kC_{aq})$]; Freundlich ($q = kC_{aq}^n$); Radke-Prausnitz [$q = aC_{aq}^n/(1 + bC_{aq}^{n-1})$]; Mathews-Weber [$q = aC_{aq}^n/(1 + bC_{aq}^n)$) and Fritz-Schluender ($q = aC_{aq}^{n1}/(1 - bC_{aq}^{n2})$], to simulate the experimental data and compared the results correspondingly here. The results are shown in Table 2. The total errors are smaller from the modified simulation equations, which usually give the best description of equilibrium adsorption of phenol derivatives (Radke and Prausnitz, 1972), rather than that from the simple ones.

Adsorption quantity of PMP would increase gradually with the decreasing pH along with the decrease of ionized PMP. This result is consistent with that from the adsorption of pentachlorophenol on six natural soils and three synthetic soils with pH (Lagas, 1988). $K_{oc'}$ values (equilibrium constant) for phenolate are about 15–30 times lower than that from undissociated mole-

 Table 2

 The simulation results with adsorption equations

Equation	Simulation parameters	The relative errors (%) ^a
Freundlich	$k = 1.87 \times 10^2$, $n = 0.54$, $r^2 = 0.08$	7.59
Langmuir	$k = 0.03, b = 2.78 \times 10^3,$ $k^2 = 1.00$	100
Radke-Prausnitz	r = 1.00 $a = 7.62 \times 10^3, n = -0.22,$ $h = 1.21 \times 10^2, n^2 = 1.00$	1.35
Mathews-Weber	$b = 1.21 \times 10^2, r^2 = 1.00$ a = 53.34, b = 0.02, $n = 1.13, r^2 = 1.00$	3.29
Fritz-Schluender	a = 71.96, b = -0.01, $n1 = 0.93, n2 = 1.27, r^2 = 1.00$	0.66

^a One-hundred percent is described as the error of [(Obs–Pred)²] for Langmuir equation, and others were compared with the errors of Langmuir's.

cules. In addition, the ionization density of soil colloids would be changed with pH simultaneously. In acid medium, PMP was adsorbed on the soil colloids easily because of the strong adsorption of molecular PMP on colloids and the easy formation of hydrogen bond between PMP and the ionized soil colloid surface.

3.3. Adsorption and reaction kinetics of Cr^{VI} with and without PMP

In pure aqueous systems, it was observed that the chemical reaction of Cr^{VI} and PMP was relatively fast in low pH media, but it would be significantly slowed down with the increase of pH, and no reaction occurred at pH > 4.7 (Deng and Stone, 1996a). However, Cr^{VI} reduction by phenolic compounds was observed in the presence of metal oxides, and the pH of reaction medium can be greatly extended to a higher value.

Fig. 3(I) shows the adsorption kinetics of Cr^{VI} on the soil colloids in different pH media. In near neutral media (pH 6.5), the change of Cr^{VI} in solution decreased rapidly in the first 2 h, then reached its adsorption equilibrium. Meanwhile, lower pH, as discussed above, would result in higher Cr^{VI} adsorption on soil colloids. When pH was 4.20, Cr^{VI} adsorption equilibrium was shown in Fig. 3(I)(c), and Cr^{VI} concentration in solution decreased continuously with time, possibly due to the slow reaction of Cr^{VI} and organic matter or other reduced species of soil colloids (Wittbrodt and Palmer, 1996). Of course, this part is very small because of the low content of organic matter and other reduced species included in the soil colloids (12.60 g/kg).

However, when PMP was added in this system, the changes of Cr^{VI} content in solution with time were significantly different from that obtained in the absence of PMP, as shown in Fig. 3(II). In the first 2 h, no difference for Cr^{VI} content in pH 6.50 medium was observed in the absence and presence of PMP, which indicated that no obvious interaction occurred between Cr^{VI} and PMP in this time window. Meanwhile, the presence of PMP did not influence Cr^{VI} adsorption. However, with a low pH media or an extended time, an obvious decrease



Fig. 3. Change of Cr^{VI} ($C_0 = 10.0mg/L$) in aqueous solution with time in (I): (a) pH 6.50; (b) pH 5.20 and (c) pH 4.20; and (II) (I) + 100.0 mg/l PMP.

of Cr^{VI} in solution was observed even with pH exceeding 6.50. It cannot be due to the influence of PMP on Cr^{VI} adsorption with time (Mesuere and Fish, 1992); on the contrary, it strongly suggested that some reactions between Cr^{VI} and PMP occurred. The decrease of Cr^{VI} in solution may be ascribed to the reduction of Cr^{VI} by PMP along with the catalytic effect of the soil colloids. The catalytic reaction is mainly due to metal oxides like Fe₂O₃ and Al₂O₃ included in the soil colloids.

When Cr^{VI} was recovered from both the soil colloids (using 0.1 M KH₂PO₄ to extract Cr^{VI} (James et. al., 1995) and aqueous solution, almost no decrease of Cr^{VI} was found after its adsorption on soil colloids without PMP, or with PMP in aqueous media in the pH range from 4.0 to 7.0, which suggested that almost no Cr^{VI} chemical reaction occurred in these two systems (Fig. 4). However, recovery of Cr^{VI} decreased very much in the presence of PMP and soil colloids simultaneously, obviously indicating a catalytic reaction occurred on the surface of the soil colloids.

Fig.5(a) shows the adsorption isotherms of Cr^{VI} with and without PMP. The experimental data was determined after equilibrium of 50 hours. It can be observed from Fig. 5(a) that the apparent adsorption of Cr^{VI} in the presence of PMP was greater than that obtained in the absence of PMP. So, it also supports the conclusion that the presence of soil colloids extended the reaction of Cr^{VI} and PMP to a wide pH range. Using the Freundlich equation ($Q = kC^n$) to simulate isotherm (*a*), the resulting simulation parameters were 1.01×10^2 and 0.61 for *k* and *n*, respectively ($r^2 = 0.99$). As for isotherm (*b*), the apparent adsorption should include two parts: Cr^{VI} adsorption and Cr^{VI} reduction, so, it could be assumed as follows:

$$Q_{\text{app}} = Q_{\text{ads}} + Q_{\text{reac}} = k_1 C^{n1} + k_2 C^{n2}$$
$$= 1.01 \times 10^2 C^{0.61} + k_2 C^{n2}$$



Fig. 4. Recovery of Cr^{VI} from colloids in different pH with (a) 10.0 mg/l Cr^{VI+} soil coloids; (b) 10.0 mg/l $Cr^{VI+}96.0$ mg/l PMP and (c) 10.0 mg/l $Cr^{VI+}96.0$ mg/l PMP+soil colloids.

 $Q_{\rm app}$ refers to the total apparent adsorption of Cr^{VI}; $Q_{\rm ads}$ and $Q_{\rm reac}$ represent the quantity of Cr^{VI} adsorption and of chemical reaction, respectively.

When this equation was used for the simulation of Fig. 5(b), a very good result was obtained with k_2 of 1.95×10^2 and n_2 of 0.30 ($r^2 = 1.00$). So, the decrease of Cr^{VI} in solution was quantitatively described as $Q_{app} = 1.01 \times 10^2$ $C^{0.61} + 1.95 \times 10^2 C^{0.3}$. The ratio of Cr^{VI} adsorbed and reduced was written as $Q_{ad}/Q_{reac} = 0.52 C^{0.31}$.

Plot of $\ln(Cr^{VI})_{aq}$ (mol/l) versus time (hours) [data from Fig. 3(II)] gives linear curves with good correlation coefficient shown as Fig. 6. So, the reaction can be described as $-d(Cr^{VI})_{aq}/dt = k_{obs}(Cr^{VI})_{aq}$. According to this equation, the k_{obs} values were 0.24×10^{-2} h⁻¹, 0.51×10^{-2} h⁻¹ and 0.83×10^{-2} h⁻¹ in the media with pH 6.50, 5.20 and 4.20, respectively. In comparison with the k_{obs} of $9.78 \pm 1.28 \times 10^{-2}$ h⁻¹ resulted from pure minerals (Deng and Stone, 1996a), the reaction kinetic constant of Cr^{VI} and PMP was smaller in soil colloids.

According to the reaction process (Deng and Stone, 1996a,b), four reactions in parallel contribute to overall



Fig. 5. Apparent adsorption isotherms of Cr^{VI} on soil colloids without (a) and with (b) 96.0 mg/l PMP (pH = 5.72).



Fig. 6. $ln(Cr_{aq}^{VI})$ as a function of time in pH (a) 4.20; (b) 5.20 and (c) 6.50. $Cr^{VI} = 10.0 mg/L$, PMP = 100.0 mg/l.

PMP oxidation, yielding the four terms in the differential equation listed below:

$$\begin{split} d[PMP]_{T}/dt &= k_{1}[Cr^{VI}]_{aq}[PMP]_{aq} \\ &+ k_{2}[Cr^{VI}]_{aq}[PMP]_{ads} \\ &+ k_{3}[Cr^{VI}]_{ads}[PMP]_{aq} \\ &+ k_{4}[Cr^{VI}]_{ads}[PMP]_{ads} \end{split}$$

where the subscripts of aq and ads refer to dissolved and adsorbed species concentration, and the subscript T stands for total of PMP oxidation. The first part can be ignored because no reaction of Cr^{VI} and PMP occurred in aqueous solution in near neutral medium. Reaction of Cr^{VI} and PMP is a surface-catalyzed one, and catalysis arises from the adsorption of Cr^{VI} (Deng and Stone, 1996a). So, the second part in the above equation could also be neglected. Meanwhile, the adsorption of PMP can be described using Fritz-Schluender as shown above $[q = ac_{aq}^{n1}/(1 - bc_{aq}^{n2})]$. So, the above equation can be rewritten as below,

$$d[PMP]_{T}/dt = k_{3}[Cr^{VI}]_{ads}[PMP]_{aq}$$
$$+ k_{4}[Cr^{VI}]_{ads}[PMP]_{ads}$$
$$d[PMP] = k_{3}[Cr^{VI}]_{ads}[PMP]_{aq}$$

+
$$k_4$$
[Cr^{VI}]_{ads} × a [PMP]ⁿ¹_{aq}/(1 – b[PMP]ⁿ²_{aq})

$$d[PMP]_T/dt = k_5[Cr^{VI}]_{aq}^{n3}([PMP]_{aq} + k_6[PMP]_{aq}^{n1}/(1 - b[PMP]_{aq}^{n2}))$$

From the above equations, it can be found that decrease of PMP is related with the contents of Cr^{VI} and PMP in aqueous solution.

3.4. Analysis of PMP oxidation product and the possible reaction mechanism

The preparation and analysis of PMP samples by GC–MS were described in the experimental section. The

GC–MS chromatogram of standard sample indicated that the retention time of internal standard (phenol) and PMP were 6'26" min and 10'17", respectively. However, there was an additional new peak appeared at 5'20" from the experimental sample after PMP reacted with Cr^{VI} in the presence of soil colloids. This new peak should be due to a new chemical formed by the reaction of Cr^{VI} and PMP on the surface of soil colloids. Further study exhibited that its molecular mass to charge ratio was 108. As shown in Fig. 7, the resulting mass chromatogram and the standard mass chromatogram of benzoquinone are entirely the same. So, it can be concluded that the main reaction product of PMP by Cr^{VI} is benzoquinone.

The reaction of Cr^{VI} and phenolic compounds in aqueous media was studied and the reaction mechanism was proposed (Elotivz and Fish, 1995). The major products were benzoquinone and its derivatives. According to the reaction product obtained here, the mechanism of



Fig.7. The resulting mass chromatogram of sample obtained by the interaction of Cr^{VI} and PMP on the surface of soil surface (a) and the standard mass chromatogram of benzoquinone (b).



Fig. 8. Proposed reaction mechanism of CrVI and PMP in the presence of soil colloids.

a surface catalytic reaction for Cr^{VI} and PMP was similarly proposed in Fig. 8.

4. Conclusions

Adsorption of Cr^{VI} and PMP on soil colloids as well as pH influence were studied, and the results exhibited that these adsorption processes could be quantitatively described with general simulation equations very well. In addition, the adsorption quantities increased with increasing acidity for both Cr^{VI} and PMP.

Cr^{VI} adsorption was very fast and it reached equilibrium within 2 h in neutral media. Meanwhile, the reaction of Cr^{VI} and organic matter or other reduced species of soil colloids occurred mainly in acid media.

Soil colloids could act as the catalytic reaction center for Cr^{VI} and PMP over a wide pH range, and the reaction was described quantitatively using the related equations. The product of interaction of Cr^{VI} and PMP was analyzed by GC–MS here and the result showed that the major product of PMP was benzoquinone. The reaction of Cr^{VI} and PMP in the presence of soil colloids included two steps of one electron process.

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