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The influence of sol gel drying temperature to surface aggregate structure of CTAB on magnetite silica as phenol adsorbent

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Abstract. The Magnetite silica-CTAB (MS-CTAB) as phenol adsorbent was made with sol gel process. Magnetite silica was functionalized with cetyltrimethylammonium bromide to increase the tendency as phenol adsorbent. The aim of this paper was to investigate, the role of drying temperature parameter in sol-gel routes that influence CTAB micelles formation on magnetite silica. CTAB varied upper the CMC (1 mM, 5 mM, 10 mM) in two varied temperatures (80 and 350°C). The deconvolution of FTIR spectra showed that the heating at relative high temperatures (350°C) accelerate condensation phase, remove the water and lead the formation of covalent Si-O-Si bonds and reduce Si-OH bonds compared with 80°C. The aggregate structure of CTAB seem dependent on the amount of silanol. The adsorption diagram at pH 11 showed that the silanol bond influenced the CTAB formation on magnetite silica surfaces, end up in reducing the phenol adsorption capacity, with a reverse with low heating temperature.

Keywords: CTAB, drying temperature, magnetite silica, phenol, sol-gel

1. Introduction

This work was focus on synthesis adsorbent using magnetite silica to deal with hazardous contaminants such as phenols in water. Phenol was very dangerous because its high toxicity level i.e. 1 µg/L. Phenol was widely found in waters because intensively used in industry and agriculture [1]. The phenol degradation technology from water needed to be done to maintain water quality that supports the survival of aquatic life and human health.

Magnetite was known as black iron oxide or ferrous ferrite had the most powerful magnetic properties [2] that nowadays considers as a valuable adsorbents to deal with large volume of wastewater that had a fast separation efficiency using an external magnetic field [3]. Unfortunately, magnetite was easy to be leaching under acidic conditions and get autoxidation. Therefore, it was needed to protect the surface of bare magnetite. Silica coating was an ideal candidate to protect magnetite because it could improve the chemical and thermal stability of magnetite. The silanol terminated on silica surface also played important role because it provided an easy modification that increased effectivity, capacity and selectivity of the adsorbent as needed [4-7].

Modification of the magnetite silica surface could be carried out with surfactants because surfactants were adsorbed on the surface of silica by forming aggregates such as micelles/admicelles if the concentration was above critical micellization concentration (CMC) [8]. This admicelles could interact with solubilized ions/non ions in micelles through a mechanism called adsolubilization [9] including



organic substances [10]. Adsolubilization used to be applied to remove organic pollutants from waste water by increasing the surface concentration of pollutants in adsorbed in surfactant aggregates [11].

Sol-gel process widely adopted for preparation of silica-coated magnetic compared with the other methods because it was done in relatively mild reaction condition and low cost [6]. The process involved hydrolysis and condensation reaction of precursors such as tetraethylorthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) or sodium silicate (Na_2SiO_3) in the presence of mineral acid (e.g., HCl) or base. The hydrolysis of precursor formed silanol groups. The condensation between the silanol groups created siloxane bridges (Si-O-Si) that formed entire silica structure, but silanol was expected to still present because it provided a side to modification. The silanol (-SiOH) expected to interact electrostatically with positively charged of cationic surfactant head-group to form monolayer then formed an aggregate called micelles with the CTAB concentrations near or higher than the CMC [12].

The process of sol gel was influenced by some parameters such as precursor, pH, catalyst and drying temperature [11]. Drying helped to increase the crystallinity of silica because the structure, pore texture and the morphology of the aerogels were found to be dependent on the drying procedure [13]. Milea *et al.* [14] said the drying temperature will be produced a good porosity at 350°C [14] but this temperature also triggers the oxidation reaction of magnetite into hematite that will change the nature of magnetite magnetism as a core of the adsorbent [15]. This reason made the transition of silica structure in this critical temperature was important in order to reach the optimal surfactant modification as phenol adsorbent. The aims of this research was to find the influence of drying temperature to structure of aggregate CTAB on magnetite silica as phenol adsorbent.

2. Experimental

2.1. Reagents

All reagents were analytical grade and used as received. Sodium silicate, sodium hydroxide $\geq 99\%$, hydrochloric acid 36%, cetyltrimethylammonium bromide $\geq 98\%$, hydroxylamine hydrochloride $\geq 99\%$, phenol $\geq 99\%$, sodium nitroprusside dihydrate 99% and sodium dihydrogen phosphate dihydrate $\geq 99\%$ were using Merck Damstat Germany reagents and dissolution was done with distilled water.

2.2. Synthesis of Magnetite Silica-CTAB

Magnetite silica were synthesized according to previous reported method as performed by Zhao *et al.* [4] with a minor modification in precursor composition as follows:

Magnetite taken from the iron sand separated by a permanent magnet diameter 15 cm and thickness 4 cm. Size reduction of magnetite was done by Retsch PM400 Ball mill, dried using Memmert oven in 80°C for 4 hours then sieved with a mesh sieve. The mass ratio of magnetite to Na_2SiO_3 10% was 1:20. Sodium silicate was added dropwise into magnetite (pass 45 μm mesh sieve) and the pH value of the mixture was adjusted to 7.0 by adding HCl 3 M. The mixture was had to maintained at 80°C until the water content reduced. Finally, the formed magnetite silica gel were then thoroughly washed with deionized water until free of chloride ion and neutral [4]. The product then was dried at a temperature of 80°C with oven for 24 h (MSA_0) and at temperature 350°C (MSB_0) for 3 h. Preparation to functionalize magnetite silica was done by weighing 10 g of each varied MS were put into a 500 mL conical flask containing 250 mL of different concentration of CTAB (1, 5 and 10 mmol/L). Then, the mixture was stirred on magnetic stirrer for 24 h. The solid then was washed with distilled water repeated until no Br^- was detected by AgNO_3 solution and dried at 50°C for 24 h in an oven [16]. The magnetite silica with 1, 5 and 10 mmol/L of CTAB solutions were named as MSA_1 , MSA_2 and MSA_3 (drying temp. 80°C) and MSB_1 , MSB_2 and MSB_3 (drying temp. 350°C).

2.3. Characterization of MS-CTAB

Functional group binding tested with Fourier transform infrared (FTIR) spectrometer (FTIR 8201, Shimadzu) collected in the 400-4000 cm^{-1} wave number range. The curve fitting analysis was performed using Origin Pro 8 software involved Gaussian curve fitting. Base line correction was done on minimum

intensity. The surface characteristic was done with Brunner-Emmet-Teller (BET) N₂ physisorption using GSA Quantachrome Instrument. The concentration of phenol uptake by adsorption in aqueous solutions was determined by UV-Vis spectrophotometer (Genesys 10 Thermoscientific).

2.4. Phenol adsorption capacity

In the test tube was added 15 mL phenol 10 mg/L. The initial acidity of the phenol solution was set to 11 using 0.1 M NaOH and 100 mg of CTAB magnetite silica were added to the solution. The reaction tube was placed into a shaker and rotated at 200 rpm at room temperature with variants 0, 1, 2, 3, 4, 5, 6 minutes. Periodically, samples were collected and suspended solids are separated using magnets for 10 minutes. The solution was filtered with fine filter paper and analysed to determine the remaining phenol concentration using UV-Vis spectrophotometer [1]. The separation process determined by the amount of adsorbent q_t (mg/g) with the formula: $q_t = (C_0 - C_t) \cdot V / m$ with q_t =adsorption capacity (mg/g), C_0 =initial concentration, C_t =concentration at t time, V =volume adsorbate, m =adsorbent mass.

3. Results and Discussion

3.1. Surface area of the MS-CTAB

The amount of CTAB effected the surface area of magnetite silica shown on in table 1. It was shown that the magnetite coated with silica for two variant drying temperature had a similar result. The magnetite silica without CTAB adding (MSA_0 and MSB_0) gave the highest BET surface area at 328-337 m²/g, while the modified magnetic silica with the amounts of CTAB reduced significantly. The addition of CTAB above the silica magnetite changed the character of the surface by the presence of wide narrowing of surface area. It could be explained that CTAB added above the silica filled the deep pores and filled the pore magnetite silica so that there was a decrease in the surface area of silica to 84-87 m²/g and pore size 1.8 nm. This was consistent with research which stated that the more CTAB added would decrease the surface area of silica [17, 18].

Table 1. Surface properties of MS-CTAB in all variant.

Drying temperature	Amount of CTAB (mM)	symbols	S_{BET} (m ² /gr) ^a	V_p (cm ³ /gr) ^b	d_p (nm) ^c
80°C	0	MSA_0	337.44	0.76	8.74
	1	MSA_1	84.22	0.14	1.80
	5	MSA_2	83.08	0.13	1.78
	10	MSA_3	87.17	0.15	1.54
350°C	0	MSB_0	328.38	0.87	10.39
	1	MSB_1	82.33	0.13	1.76
	5	MSB_2	86.92	0.14	1.58
	10	MSB_3	81.48	0.14	1.83

^a Surface area, ^b Pore Volume, ^c Pores Diameter (BJH method)

Based on the plot data of the BJH on MSA_1 and MSB_1 , two types of pore distributions appeared to show the type of bimodal distribution (Fig. 1A) around 1.8 and 3.7 Å. This order pores distribution supported the indication of CTAB micellization above silica with a concentration of 1 mM in accordance with the CMC [19]. The Distribution for MSA_3 and MSB_3 have a broadening pore distribution to 5 to 8 Å (Fig. 1B) but with a slightly changes in average pores diameter as shown in table 1 probably because the micelle density of CTAB increases as the concentration had risen up to form the bilayer micelles [20].

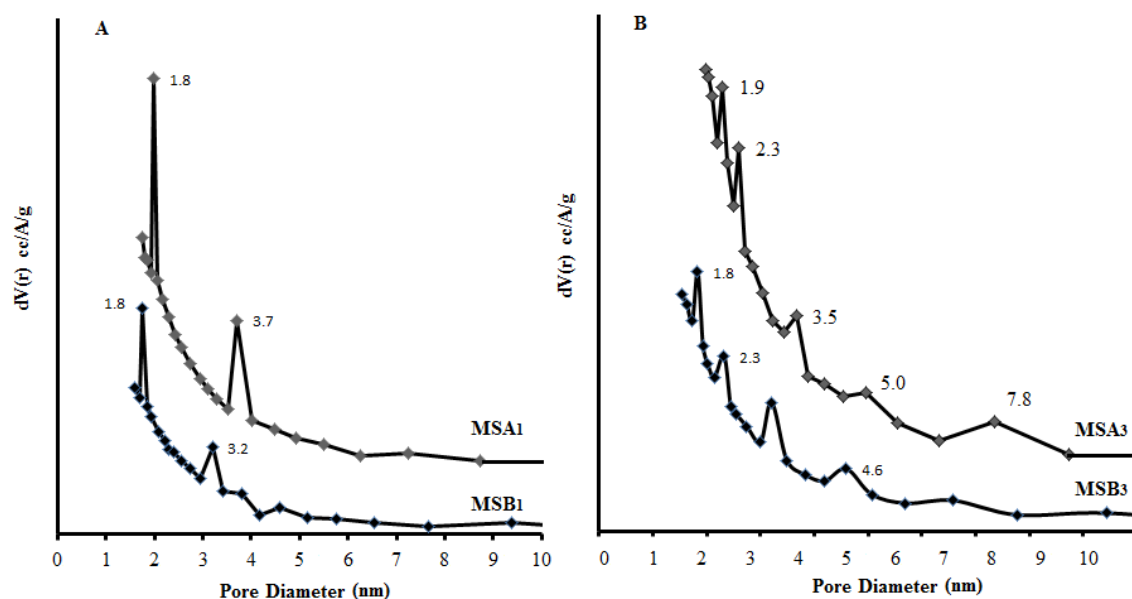


Figure 1. (A) Bimodal pores distribution for MSA₁ and MSB₁, (B) Broadened pores distribution of MSA₃ and MSB₃.

3.2. FTIR spectra of the MS-CTABs

Spectra for all variant of Magnetite silica CTAB characterized by Fourier Transform Infra-Red (FTIR) as shown in Fig. 2.

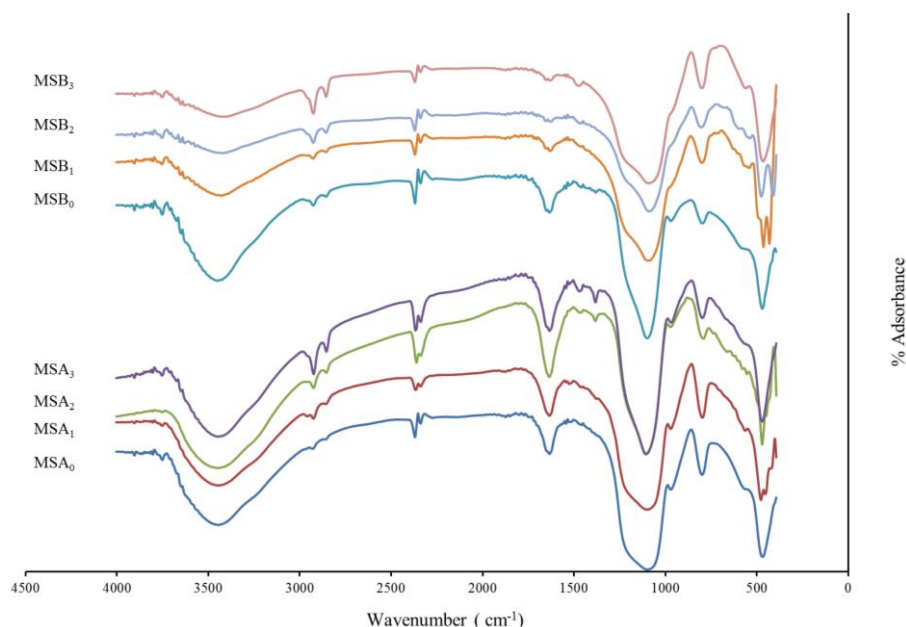


Figure 2. FT-IR spectra of all variant of MS-CTAB.

The presence of silica on magnetite was indicated by the appearance of strong SiO₂, including symmetric stretching of Si-O-Si at 795 cm⁻¹, stretching vibration of Si-O-H at 964 cm⁻¹, and asymmetric stretching of Si-O-Si at 1096 and 1233 cm⁻¹. Also, the broad peak of OH groups in silanol and adsorbed water in the range 3200-3750 cm⁻¹ and 1628 cm⁻¹ [21]. The presence of magnetite appeared in peak Fe-O at a wavelength of 471 cm⁻¹ [22]. Functionalization of magnetite silica with CTAB had asymmetric

and symmetric stretching vibration of C-CH₂ from the methylene chain around 2924 and 2855 cm⁻¹, respectively. Several weak bands in the region of 2940 to 2963 cm⁻¹ arose from C-CH₃ asymmetric stretching and N-CH₃ symmetric stretching vibrations of CTAB spectrum. The band at 1483 cm⁻¹ were the asymmetric CH₃-N⁺ deformation modes ($\delta_{as}CH_3-N^+$) of the CTAB head group and these bands were sensitive to the packing density [23]. The appearance of these peaks showed the presence of CTAB above the silica magnetite.

The effect of drying temperature on the characteristics of silica magnetite during sol gel process was done by calculating the ratio of silanol and siloxane peak adsorption groups at two drying temperatures. Deconvolution for both peaks found three peaks at 963 cm⁻¹, 1099 and 1200 cm⁻¹ wavelength which were the peak of Si-O-H and asymmetric vibrations of Si-O-Si as seen in Fig. 3. The peak ratio of the two clusters calculated to determine the difference in silanol and siloxane peak intensities. It found that ratio of 963/(1099+1200) for MSA₀ was 0.024 while MSB₀ had a ratio of 0.021 was shown in table 2. It can be concluded that MSB₀ which used a higher drying temperature at 350°C increased the speed of the process of evaporation of residual water and increased the formation of Si-O-Si bonds which causes a reduction in Si-O-H groups [14].

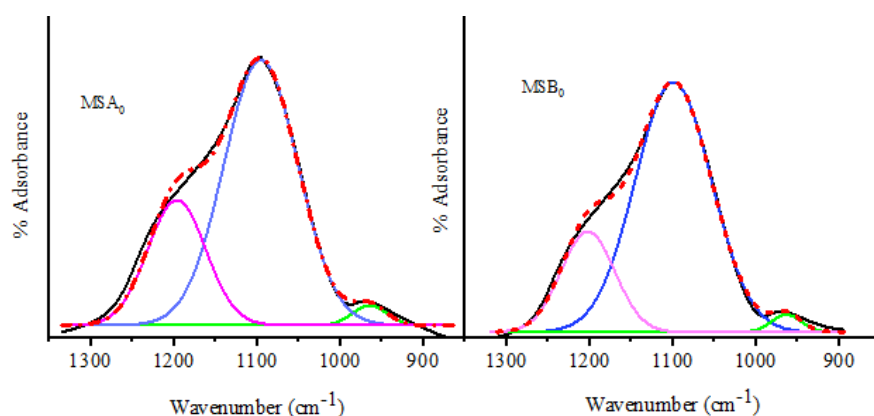


Figure 3. FTIR spectrum (black line) and peak deconvolution of the bottom phase for MSA₀ and MSB₀ spectral subtraction. The dotted lines are summation (red) of the fitted peaks with an R² value ≥ 0.994 .

Table 2. The result of peak area deconvolution.

Wavenumber (cm ⁻¹)	vibration	Area of MSA ₀	Area of MSB ₀
963	ν Si-O-H	6.25	1.96
1099	ν -as Si-O-Si	187.30	71.96
1202	ν -as Si-O-Si	68.98	20.28
Si-OH/Si-O-Si ratio		0.024	0.021

Further study of FTIR spectra in Fig. 2 showed that the CTAB binding on magnetite silica for all variants were generally seen that the increase amount of CTAB added gave the increase of the methylene tail peak (2850 and 2940 cm⁻¹) and CTAB head peak (1380 cm⁻¹) intensity. But there was a tendency that this binding reduced silanol peaks (972 cm⁻¹) and at the same time increased siloxane peaks (1100 cm⁻¹), which indicates the presence of cationic head side interactions with the silanol side which was more hydrophilic [24] as expected.

3.3. Phenol Adsorption using MS-CTAB

The adsorption of phenol by MS-CTAB was expected to occur in accordance with the acid-base reaction mechanism. The reaction scheme between phenol and CTAB occurred as follows where R is the

methylene tail of CTAB (Fig. 4). The acidity of phenol was set at pH 11. It was known that the level of ionization of phenol was very dependent on the pH of the solution. When the pH of the solution was more than the price of pKa phenol (+9.92), this compound was dissociating into phenolate ion ($\text{C}_6\text{H}_5\text{O}^-$). These ions expected to be easily attracted to the surface of the MS-CTAB which was had a cationic surfactant on it.

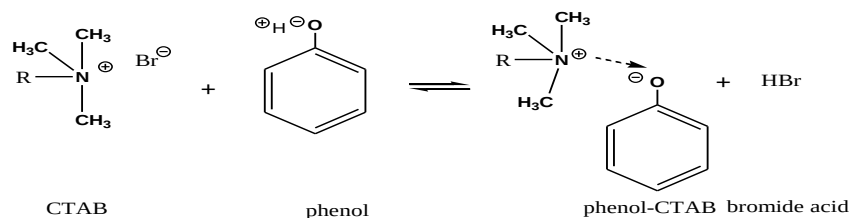


Figure 4. Reaction scheme between CTAB and phenol.

The scheme explained that the micelles structure of CTAB on magnetite silica surface will influence the electrostatic interaction between phenolate and adsorbent. These phenolate ions was easily be attracted to the surface of the adsorbent which tended.

The phenol adsorption using MS-CTAB at pH 11 showed in Fig. 5. The adsorption capacity increased with the amount of CTAB added. MSA in all variant CTAB added gave a higher adsorption capacity to phenol up to 0.63 mg phenol/g adsorbent even in initial minutes compared to MSB which was only about 0.13 mg/g. The MSA₃ gave the optimum condition with a capacity 0.93 mg/g.

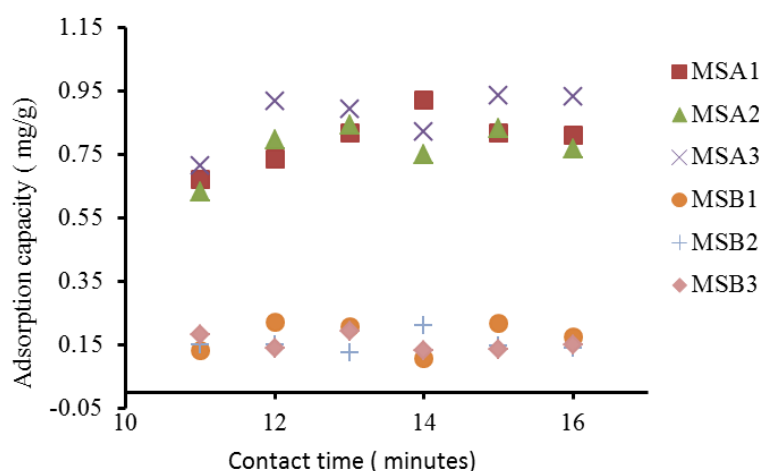


Figure 5. The adsorption capacity phenol at MS-CTAB.

3.4. Surface aggregate structure of CTAB on MS

The amount of CTAB on the surface of the silica influenced the amount of silanol which was ruled by the drying temperature. It had proved by the deconvolution results in table 1 and FTIR spectra that found that silanol groups at MSB₀ were less than at MSA₀ gave a less CTAB binding energy to MSB₀ compared to MSA₀. Although both of it had similar surface properties as explained in BET and BJH data.

The drying temperature in 80°C made MSA which was richer of silanol make it interacted with CTAB to form bilayer micelles tended to be positively charged because the presence of the CTAB head side above the silica magnetite. Conversely, The MSB which dried in 350°C poorer of silanol less interacted with head of CTAB formed the reverse micelles on magnetite silica actually gave electrostatic repulsion to phenolate ions which will reduce the phenol adsorption capacity above the magnetite silica [20]. The scheme of CTAB aggregation on magnetite silica illustrated on Fig. 6. So it could be concluded

that the drying temperature had affected the amount of silanol groups which influence the amount of CTAB binding above silica. This was consistent with the results of Parida *et al.* [25] research that the surface characteristics of magnetite silica with the addition of CTAB are influenced by the number of silanol groups [25].

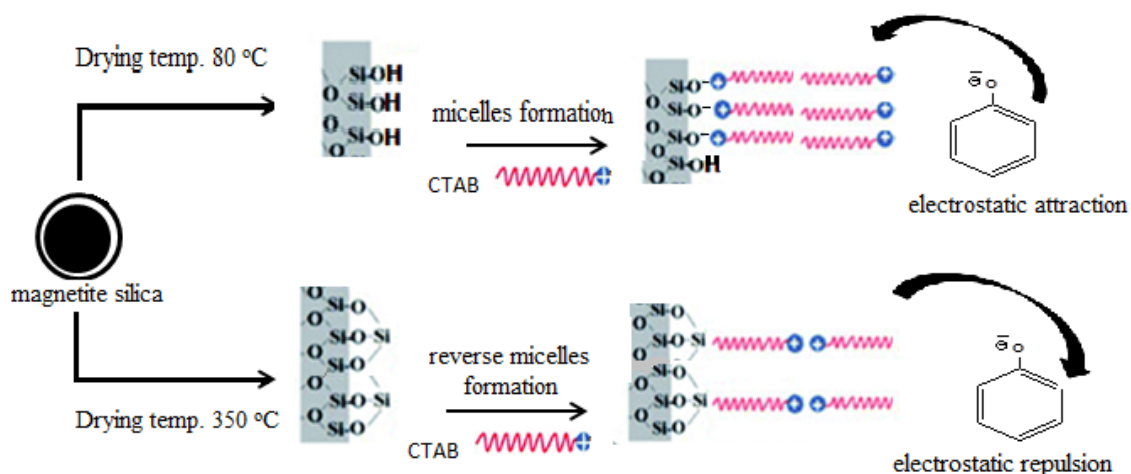


Figure 6. Scheme aggregation of CTAB on magnetite silica.

4. Conclusion

Magnetite silica had been synthesized using CTAB as surface modification agent. The drying temperature changed the structure aggregate of CTAB on magnetite silica. The drying temperature of sol-gel process at higher temperature increased the speed of the process of evaporation of residual water and increased the formation of Si-O-Si groups which causes a reduction in Si-O-H groups. The silanol was an important side to make electrostatic interaction to head group of CTAB. The surface aggregate of CTAB on magnetite silica impacted the adsorption capacity toward phenol.

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