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Short Communication

Preparation of Ni loaded TiO₂ photocatalyst for photodegradation of phenanthrene in water and soil

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This research focused on the impregnation, characterization, and application of TiO₂ and Ni-loaded TiO₂ photocatalysts for the treatment of phenanthrene (PHEN), a polycyclic aromatic hydrocarbon (PAH) chemical and pollutant found in water and soil sources. The synthesis and integration of wellcrystallized Ni nanoparticles in the TiO₂ matrix are indicated by XRD and FE-SEM studies. The optical analysis revealed that trace embedding of Ni in the TiO₂ matrix resulted in a reduced energy absorption edge, with Eg values of 3.19 and 3.04 eV for TiO₂ and Ni-loaded TiO₂, respectively. When compared to TiO₂, electrochemical tests revealed that Ni-loaded TiO₂ had a lower electrochemical impedance to charge transport and a lower rate of charge recombination. The photocatalytic performance of TiO₂ and Ni-loaded TiO₂ for the degradation of 100 ml of 1 mg/l PHEN solution showed that after 55 and 40 minutes of simulated sunlight illumination, respectively, the Ni-loaded TiO₂ had 100% removal efficiency, demonstrating that the Ni-loaded TiO₂ presented a higher photocatalytic efficiency than various reported photocatalysts in the literature for the treatment of PHEN due to the creation of intermediate states in the semiconductor's energy band-gap and efficient separation of electron-hole pairs. The ability of Ni-loaded TiO₂ to treat PHEN in prepared genuine samples of soil and industrial wastewater was investigated, and the results demonstrated the efficacy of the proposed photocatalyst in the treatment of PHEN in both industrial wastewater and soil.

Keywords: Ni-loaded TiO₂; Photocatalyst; Impregnation method; Polycyclic aromatic hydrocarbons; Phenanthrene; Electrochemical impedance spectroscopy; Photodegradation

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a vast collection of varied chemical compounds made up of numerous aromatic rings and containing just carbon and hydrogen [1, 2]. PAHs are ubiquitous environmental pollutants generated primarily during the incomplete combustion of organic

materials and that occur naturally in coal, crude oil, and gasoline [3-5]. These chemical compounds are widespread across the globe mainly due to long-term anthropogenic sources of pollution [6, 7].

In general, PAHs have low acute toxicity in humans. Meanwhile, cancer is the most important endpoint of PAH toxicity, and studies have linked elevated rates of lung, skin, and bladder malignancies to occupational exposure to PAHs [8, 9]. Furthermore, investigations have shown that a variety of PAHs can cause cancer in laboratory animals when they are exposed to them through their food, contaminated air, or when they are applied to their skin [10-12]. Pregnant mice exposed to high doses of a PAH (benzo(a)pyrene) had reproductive problems. Furthermore, the progeny of the pregnant mice had birth abnormalities and a reduction in body weight. Damage to the skin, body fluids, and immune system, which help the body fight sickness, are among the other side effects [13-15].

Phenanthrene (PHEN), also known as phenanthren, phenanthrin, and phenanthracene, is a polycyclic aromatic hydrocarbon (PAH) made up of three fused benzene rings [16-18]. Dyes, plastics, insecticides, explosives, and pharmaceuticals like morphine, codeine, heroin, hydromorphone, and oxycodone are all made with PHEN [19-22]. Bile acids, cholesterol, and steroids have all been made with it. PHEN is detected in high amounts in PAH-contaminated surface soils, sediments, and waste sites. Crustaceans, fish, mussels, gastropods, and marine diatoms have all been found to be poisonous to it.

As a result, treatment systems for removing PAHs from PAH-contaminated surface soils, sediments, waste sites, and effluents before disposal must be developed [23]. As a result, many investigations based on biological, physical, and chemical degradation strategies have concentrated on adsorption, volatilization, photolysis, and chemical oxidation, as well as microbial degradation and photocatalysis [24-29]. Photocatalysis, as an affordable and environmentally friendly treatment technology for PAH-contaminated sources, may be an appropriate solution for the degradation of many types of PAH molecules [25-28, 30]. As a conclusion, the current research focused on the impregnation, characterization, and application of TiO2 and Ni-loaded TiO2 for photocatalytic treatment of PHEN as a pollutant in water and soil sources under simulated sounlight illumination.

2. EXPERIMENT

2.1. Preparation of photocatalysts

The photocatalyst of Ni-loaded TiO₂ was prepared using an impregnation approach [31]. 2g of TiO2 (99%, Degussa-P25) was ultrasonically mixed with 100 mL of 5 mM Ni(NO)3•6H2O solution (> 98%, Acros brand). After 30 minutes of ultrasonication, the mixture was transformed in an oven and evaporated in a vacuum at 180 °C, followed by drying under a vacuum at room temperature for 12 hours. Then, the resultant powder was calcined in the air at 500 °C for 4 hours.

2.2. Preparation the soil and wastewater samples

The soil sample (top 10 cm) was provided by Dazhen village, Nanhai district, China. The soil was naturally dried before the trials, then put through a 200 mesh filter to remove stones and big particles, before being autoclaved at 115 °C for 40 minutes. Table 1 summarizes the basic features of soil. In preparation for use, 100 g of soil sample and 0.5 g of catalyst were distributed in 100 ml of deionized water in the dark and stored. A real sample of industrial wastewater was obtained from Dazhen village in Nanhai district, China, for repair. Before use, a 100 mL sample of wastewater was mixed with the same catalyst and stored in a dark place. The prepared samples were applied to provide the 1 mg/l solution of PHEN and were used for photodegradation reaction.

Table 1. The basic properties of soil.

Properties	Value	
Moisture (%)	6.05	
Organic carbon content	4.22	
(%)		
Sand (%)	42.11	
Silt (%)	35.07	
Clay (%)	12.55	
Conductivity (S/cm)	66.11	

2.3. Photodegradation experiment

The photocatalytic performance of TiO₂ and Ni-loaded TiO₂ was investigated using photodegradation of 100 ml of PHEN solution under simulated sunshine illumination in a laboratory equipped with a xenon lamp (420 nm, 500 W, Philips, Japan). The sample distance from the light source was 10 cm. The mixture of 0.5 g of catalyst in 100 ml of prepared PHEN solution with deionized water, as well as a prepared real sample of soil and wastewater, were magnetically stirred for 40 minutes in darkness to create an adsorption/desorption equilibrium between PHEN molecules and the photocatalyst prior to photodegradation reactions. For photodegradation reactions, the light source was irradiated on samples for a certain time interval, and irradiated samples were filtered through a 0.22 µm membrane (MF-MilliporeTM, Merck, Germany) and collected. The concentration of PHEN of the supernatants was determined using UV-vis absorbance (spectrophotometer, Jasco V650, Japan) at $\lambda_{max} = 252$ nm [32]. The PHEN concentration corresponded to the absorbance intensity which was used for the calculation of the removal efficiency by the following equation [33, 34]: Removal efficiency (%) = $\frac{I_0-I_t}{I_0} \times 100 = \frac{C_0-C_t}{C_0} \times 100$ (1)

Where I_o and I_t are the absorbance intensities of initial and illuminated PHEN solutions, respectively, and C_o and C_t are the corresponding PHEN concentrations in initial and illuminated PHEN solutions, respectively.

2.4. Characterizations

The crystal-line phases of the photocatalysts were investigated using a Rigaku RINT-2100 Xray diffractometer (XRD) with Cu K radiation (λ = 1.5406). The photocatalysts' morphology was investigated using a field emission scanning electron microscope (FE-SEM; Zeiss SUPRA 55 VP, Germany). Absorption spectra were measured using a UV-vis spectrophotometer (Jasco V650, Japan). EIelectrochemical impedance spectroscopy (EIS) experiments were carried out under visible light illumination, to compare electron transfer rates in photocatalysts at a frequency range from 10⁻¹ to10⁶ Hz and an AC voltage of 10 mV in 0.5 M Na₂SO₄ (\geq 99%, Sigma-Aldrich) solution using a CHI Potentiostat/Galvanostat model 660D (CH Instruments, USA) in a classical three-electrochemical system consisting of saturated Ag/AgCl electrode and a Pt wire as reference and counter electrode, respectively. Working electrodes were Ni-loaded TiO₂ and Ni-loaded TiO₂ modified glassy carbon electrodes (GCE). The EIS data was fitted using equivalent circuits with ZView software.

3. RESULTS AND DISCUSSION

3.1. XRD and FE-SEM analyses

Figure 1 shows the XRD diffractogram patterns of TiO₂ and Ni-loaded TiO₂. The diffraction peaks at 25.43°, 38.01°, 48.15°, 53.98°, 55.33°, and 62.69° are attributed to the (101), (404), (200), (105), (211), and (204) planes anatase crystalline phases of TiO₂, as indicated by diffractogram patterns of TiO₂ and Ni-loaded TiO₂ (JCPDS card no. 04-002-2678) [35-37]. Additional peaks in the XRD pattern of Ni-loaded TiO₂ at 24.26°, 33.23°, 35.65°, 49.65°, and 64.31° are attributed to (012), (104), (110), (024), and (300) reflections of the rhombohedral phase of nickel titanate (NiTiO3) (JCPDS card no. 04-012-0745) [38-40], implying the introduction of well-crystallized Ni nanoparticles to the TiO₂ anatase structure.



Figure 1. The XRD diffractogram patterns of TiO₂ and Ni-loaded TiO₂.



Figure 2. FE-SEM micrographs of (a) TiO₂ and (b) Ni-loaded TiO₂

Figure 2 shows TiO_2 and Ni-loaded TiO_2 FE-SEM micrographs. Both samples show agglomerates of nanosized spherical nanoparticles, as can be seen. These photos show that adding Ni to TiO_2 had no effect on the morphology, which is due to the smaller amount of Ni²⁺ ions integrated into the TiO_2 matrix. However, a comparison of the two micrographs shows that the degree of agglomeration of pure TiO_2 nanoparticles decreased when Ni was added to Ni-loaded TiO_2 nanoparticles, resulting in the formation of a large number of pores. TiO_2 and Ni-loaded TiO_2 nanoparticles had typical diameters of 65 and 80 nm, respectively.

3.2. UV-vis optical absorption spectra



Figure 3. (a) UV-vis optical absorption spectra and (b) Tauc plots of TiO₂ and Ni-loaded TiO₂.

A photocatalyst's photocatalytic activity is mostly determined by its optical features, particularly its electronic band structure and band gap energy (Eg) [41-43]. Due to the wide bandgap (3.2 eV), which is related to the energy level of the O_{2p} orbital, which is located at about +3 eV versus the standard hydrogen electrode, the photocatalytic activity of TiO₂ is limited to ultraviolet (UV) light (<387 nm). The band gap energy between the Ti 3d electronic orbital and O2p-levels is therefore too wide to absorb visible light [14, 44], which represents just a small fraction (3–5%) of the solar photons [45-47]. Thus, the introduction of metal species such as Ni should result in intra-band gap states and a

reduction in TiO₂ Eg [48]. Figure 3a shows the UV–vis optical absorption spectra of TiO₂ and Niloaded TiO₂ which demonstrated the better absorption intensity of Ni-loaded TiO₂ in the UV-light region with different absorption tails extending up to 700 nm. Therefore, the absorption spectra of Niloaded TiO₂ shows that the trace embedment of Ni results the shift the absorption edge to a lower energy and the creation of isolated defect energy levels such as concomitant oxygen vacancies (Vo) and Ti⁴⁺, Ti³⁺ and Ni species located at positions accessible to the surface Vo sites at the bottom of the TiO₂ conduction band [49, 50]. The red shift may be because Ni species are active and effective in the electric structure of Ni-O-Ti heteroatomic clusters on the surface of TiO₂ [51-53]. The isolated levels created by the metal ions work as visible light sensitive photocatalysts, and the electrons in the upper valence band can be directly transferred to the created isolated defect states by absorbing visible-light and can move to the conduction band [54-56]. The Eg of the samples can be determined from the corresponding Tauc plots using the following equation [57, 58]:

$$(\alpha h\nu)^{1/2} = A(h\nu - Eg) \qquad (2)$$

Where α and hv are absorption coefficients and photon energy, respectively, and A is constant. The intersection of the extrapolated linear component of the plot with the hv axis yields Eg values of 3.19 and 3.04 eV for TiO₂ and Ni-loaded TiO₂, respectively (Figure 3b). As can be observed, Eg falls as Ni is added into the TiO₂ matrix, demonstrating that Ni has a significant impact on light absorption qualities. The charge transfer transition between the d-electrons of the dopant and the TiO₂ conduction band reduces the Eg value, which is attributable to the coexistence of Ti³⁺ and Ni²⁺ and Ni³⁺ species in NiOx [59, 60], and substitution of Ni at Ti sites in TiO₂ is responsible for narrowing the Eg. Moreover, Ti⁴⁺ and Vo contribute to the transfer of photo-generated electron-hole pairs, and increase separation of charge carriers due to the formation of the surface barriers and the space charge region and large electric field experienced by the charge carriers [61, 62]. Because of the lower Fermi level of NiO, the photo-generated electrons can immediately move toward the valence band of NiO and become trapped with the metal, thereby leaving back holes leading to the effective separation of electrons and holes [63]. Studies suggest that Ti-Vo can actively and synergistically affect the photocatalytic reaction with the mononuclear Ti-O-Ni heteroatomic clusters in Ni-doped TiO₂ [51, 64].

3.3. Electrochemical analyses

Figures 4a and 4b show the Nyquist and Bode plots of TiO₂ and Ni-loaded TiO₂, respectively, while Table1 lists the parameters obtained by fitting the EIS spectra with the equivalent circuit shown in Figure 4a, including R_{ct1} and R_{ct2} as the charge transfer resistances at the working and counter electrodes, respectively, Rs as the series resistance, and C₁ and C₂ as the constant phase elements corresponding to the working and counter electrodes. It is observed that Nyquist plots contain two semicircles, the first semicircle is attributed to charge transfer resistance at the counter electrode/electrolyte interface at high frequencies (Rct₁) [65]. Meanwhile, the second semicircle at mid and low frequency ranges is ascribed to the charge-transfer resistance at the semiconductor/electrolyte interface (Rct₂) [66-68]. As seen, Ni-loaded TiO₂ shows a lower electrochemical impedance to charge

transport compared to TiO₂. Bode plots in Figure 4b also demonstrate that the characteristic low frequency peaks (f_{max}) are located around 26 KHz and 15 KHz for TiO₂ and Ni-loaded TiO₂, respectively. Since f_{max} is inversely related to the electron life time ($\tau_n = 1/(2\pi f_{max})$), the decrease in f_{max} implies to decreases rate for the charge-recombination process for Ni-loaded TiO₂ [69-71]. Ni-loaded TiO₂ shows a higher chemical capacitance (Cµ) value than that TiO₂ which is associated with higher electron density and effective surface area of Ni-loaded TiO₂ [72-74]. These results indicate lower charge resistance, an efficient injection of electrons to Ni-loaded TiO₂ and a decrease in the rate of electron recombination which provide the rapid electron transport and higher photodegradation efficiency.



Figures 4. (a) The Nyquist and (b) Bode plots of TiO₂ and Ni-loaded TiO₂.

Table1. The parameters obtained by fitting the EIS spectra

Sample	Rs (Ω.cm ⁻²)	C _μ (μF.m ⁻¹)	Rct ₁ (Ω .cm ⁻²)	Rct ₂ (Ω .cm ⁻²)
TiO ₂	4.82	1366	2.5	25.2
Ni-loaded TiO ₂	4.51	1545	2.1	21.1

3.4. Study the photocatalytic performance

Figure 5 shows the findings of a study of the photocatalytic performance of TiO₂ and Ni-loaded TiO₂ for the degradation of 100 ml of 1 mg/l PHEN solution in darkness (first 40 minutes) and under simulated sunlight illumination. In darkness, the removal efficiency for all samples was found to be negligible (0.9%). Meanwhile, the significant removal is observed under simulated sunlight illumination in the first minutes, such that the removal efficiency is obtained at 20.1% and 25.6% using TiO₂ and Ni-loaded TiO₂ after 5 minutes of simulated sunlight illumination, respectively. Furthermore, the removal efficiency in the PHEN solution without photocatalyst (blank) is \leq 2% after 2 hours of illumination of simulated sunlight. These findings indicate the noteworthy roles of light and photocatalysts in the removal of PHEN solution. Figure 5 also shows that TiO₂ and Ni-loaded TiO₂

have 100% removal efficiency under 55 and 40 minutes of simulated sunlight illumination, respectively. Thus, Ni-loaded TiO₂ exhibits a faster rate of PHEN treatment, implying a larger active site area available for photocatalytic processes [75-77]. Light irradiation demonstrated more efficient photo-generated electron-hole separation and quick charge transfer than TiO₂, which could explain the improved photocatalytic elimination of PHEN on Ni-loaded TiO₂. The pores on the TiO₂ surface can operate as a strong oxidizing agent, interacting with water molecules or hydroxyl groups to start the treatment process [78, 79]. Moreover, the photo-generated electrons can also react with molecular oxygen to produce superoxide radicals (O^{-2}), which subsequently react with protons to produce more hydroxyl radicals (OH·) through an oxidative process [80, 81].



Figure 5. The photocatalytic performance of TiO₂ and Ni-loaded TiO₂ for treatment of 100 ml of 1 mg/l PHEN solution in darkness and under simulated sunlight illumination



Figure 6. The effect of initial PHEN concentrations (0.2, 0.5, 1, 5, 10 and 50 mg/l) on the removal efficiency of Ni-loaded TiO₂

The addition of Ni in the TiO_2 matrix narrows the band gap and creates impurity states just below the conduction band of TiO_2 which acts as a trapping center of electrons, which leads to an increase in the lifetime of the photo-generated charges [82, 83], implying enhanced photocatalytic activity. These findings are in good accordance with FE-SEM, EIS and optical analyses.

The Ni-loaded TiO₂ is not only more photoactive, but can also facilitate more efficient transfer of the photo-generated charge carriers due to the mixed-interface. Equations 3-14 display the mechanism of the photocatalytic mechanism of PHEN degradation. The photo-generated charge carriers due to the mixed-interface (Equations 6 and 7). The electrons and surface trapped electrons (Equation 8) can react with other acceptors, such as oxygen and water, to form superoxide radicals and hydroxyl radicals (Equations 9-12). In addition, the holes can directly attack/oxidize PHEN and/or H₂O molecules (Equations 13 and 14) [25, 28]:

$TiO_2/SiO_2 + hv \rightarrow TiO_2 (e_{Ti^-} - h_{Ti+})$		(3)
$Ti(O-H)^{-}$ (surface) + $h_{Ti} \rightarrow Ti(O-H)$. (surface)	(surface trapping)	(4)
$h_{Ti^+} + O^2 O^{\bullet}$	(surface trapping)	(5)
Ti^{4+} (surface) + $e_{Ti} \rightarrow Ti^{3+}$ (surface)	(surface trapping)	(6)
$e_{\text{Ti}-(\text{rutile})} \rightarrow e_{\text{Ti}~(\text{anatase})}$	(electron transfer)	(7)
$O_2 + e^- \rightarrow \bullet O_2^-$		(8)
$H_2O + h^+ \rightarrow \bullet OH + H^+$		(9)
•O ₂ ⁻ + e ⁻ +2H ⁺ \rightarrow H ₂ O ₂		(10)
Ti^{3+} (surface) + $H_2O_2 \rightarrow Ti^{4+}$ (surface) + $OH^- + \bullet OH$		(11)
$H_2O_2 + \bullet O_2 \xrightarrow{-} OH^- + \bullet OH + O_2$		(12)
PHEN + h $^+$ \rightarrow intermediates \rightarrow products + CO ₂		(13)
PHEN + reactive oxygen species \rightarrow intermediates \rightarrow products + CO ₂		(14)

Table 2. Comparison the photocatalytic activity of photocatalyst in this study with that of various reported photocatalysts in the literature for the treatment of PHEN

Photocatalyst	PHEN content	Light source	Degradatio n time	Removal efficienc	Ref.
	(mg/l)		(minute)	y (%)	
Ni-loaded TiO ₂	0.2	Simulate	25	100	This
	0.5	d sunlight	30	100	work
	1		40	100	
	5		55	100	
	10		110	100	
	50		150	100	
Cobalt-doped TiO ₂ NTs	0.2	Solar	720	100	[26]
Cu(II) on TiO ₂ /Ti NTs	0.2	UV	120	95	[25]
TiO ₂ /SiO ₂	0.5	Visible	420	100	[28]
Activated charcoal supported TiO ₂	0.5	UV	150	100	[84]
NTs					
TiO ₂	1	UV	30	92	[27]

NTs: Nanotubes

The influence of starting PHEN concentrations (0.2, 0.5, 1, 5, 10, and 50 mg/l) on the Niloaded TiO₂ removal efficiency was studied. Figure 6 demonstrates that the removal effectiveness reduces dramatically as the starting PHEN concentration rises, with complete treatment of 0.2, 0.5, 1, 5, 10, and 50 mg/l of PHEN taking 25, 30, 40, 55, 110, and 150 minutes, respectively, of simulated sunshine illumination. Table 2 compares the photocatalytic activity of the photocatalyst in this study to that of various published photocatalysts for the treatment of PHEN, demonstrating that Ni-loaded TiO₂ has a high photocatalytic efficiency due to the creation of intermediate states in the semiconductor's energy band-gap and efficient separation of electron–hole pairs.

The ability of Ni-loaded TiO₂ to remediate PHEN in real-world soil (SS) and industrial wastewater (SIW) samples was investigated. Figures 7 and 8 show the removal efficacy of 100 ml of 1 mg/l PHEN solutions made from genuine samples and a control sample made from deionized water under simulated sunshine illumination. As can be seen, complete PHEN treatment takes 40, 50, and 80 minutes in the control sample, samples prepared from industrial wastewater, and samples prepared from soil mixture, respectively, implying that complete PHEN treatment takes longer (10 minutes) in samples prepared from industrial wastewater due to the presence of organic and inorganic pollutants in industrial wastewater. Because of the presence of solid and colloidal particles in the mixture, which scatter and absorb light and prevent light from reaching the catalyst particles in the photodagaradtion process, the treatment of PHEN in prepared real samples of soil takes more than 80 minutes. However, the results illustrate the efficacy of the suggested photocatalyst in the treatment of PHEN in industrial wastewater and soil.



Figure 7. Removal efficiency of 100 ml of 1 mg/l PHEN solutions in control sample and samples prepared from industrial wastewater (SIW) and soil (SS) using Ni-loaded TiO₂ under simulated sunlight illumination.

4. CONCLUSION

In conclusion, this study described the synthesis and characterization of TiO_2 and Ni-loaded TiO_2 photocatalysts, as well as their application to the photocatalytic treatment of PHEN, a PAHs

component and pollutant found in water and soil sources. The photocatalyst of Ni-loaded TiO2 was prepared using an impregnation process. According to structural analysis, the manufacture and integration of well-crystallized Ni nanoparticles in the TiO₂ matrix were presented. Study of the optical absorption spectra showed that the trace embedment of Ni in the TiO₂ matrix resulted in the shift of the absorption edge to a lower energy, and the creation of isolated defect energy levels which work as a visible light sensitive photocatalyst. The electrons in the upper valence band can be directly transferred to the created isolated defect states by absorbing visible-light and can move to the conduction band. Eg values were obtained at 3.19 and 3.04 eV for TiO₂ and Ni-loaded TiO₂, respectively, indicating Eg decreased with Ni incorporated into the TiO₂ matrix which indicates that Ni has a remarkable effect on the light absorption properties. Results of electrochemical analyses showed Ni-loaded TiO₂ had a lower electrochemical impedance to charge transport and lower rate for the charge-recombination process compared to TiO₂. Studying the photocatalytic performance for degradation of 100 ml of 1 mg/l PHEN solution showed that TiO₂ and Ni-loaded TiO₂ had 100% removal efficiency after 55 and 40 minutes of simulated sunlight, respectively. Because of the creation of intermediate states in t, the effect of initial PHEN concentrations on the removal efficiency of Ni-loaded TiO₂ revealed that complete treatment of 0.2, 0.5, 1, 5, 10, and 50 mg/l of PHEN is achieved after 25, 30, 40, 55, 110, and 150 minutes of simulated sunlight illumination, respectively, demonstrating that Ni-loaded TiO₂ presented a higher photocatalytic efficiency than various reported photocatalysts in the literature for the treatment of PHEN. The potential of the Ni-loaded TiO₂ for the treatment of PHEN in prepared real samples of soil and industrial wastewater was examined and results illustrated the efficacy of the suggested photocatalyst in treatment of PHEN in industrial wastewater and soil.

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