Nanoscale Fe/Ag particles activated persulfate: optimization using response surface methodology

Jefferson E. Silveira, Marcio Barreto-Rodrigues, Tais O. Cardoso, Gema Pliego, Macarena Munoz, Juan A. Zazo and José A. Casas

ABSTRACT

This work studied the bimetallic nanoparticles Fe-Ag (nZVI-Ag) activated persulfate (PS) in aqueous solution using response surface methodology. The Box–Behnken design (BBD) was employed to optimize three parameters (nZVI-Ag dose, reaction temperature, and PS concentration) using 4-chlorophenol (4-CP) as the target pollutant. The synthesis of nZVI-Ag particles was carried out through a reduction of FeCl₂ with NaBH₄ followed by reductive deposition of Ag. The catalyst was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) surface area. The BBD was considered a satisfactory model to optimize the process. Confirmatory tests were carried out using predicted and experimental values under the optimal conditions (50 mg L⁻¹ nZVI-Ag, 21 mM PS at 57°C) and the complete removal of 4-CP achieved experimentally was successfully predicted by the model, whereas the mineralization degree predicted (90%) was slightly overestimated against the measured data (83%).

Key words | Box–Behnken design, nZVI-Ag, optimization, persulfate

INTRODUCTION

Advanced oxidation processes (AOPs) based on in situ hydroxyl radical (HO·) generation involving the use of hydrogen peroxide (H₂O₂) as an oxidant have been reported using photochemical, chemical, sono-chemical, and electro-chemical methods as a feasible way to mineralize organic pollutants (Babuponnusami & Muthukumar 2014; Pliego et al. 2015).

Activated persulfate (PS)-based AOPs constitute an alternative to the aforementioned procedures. Furthermore, PS can be induced by thermal and chemical activation using multivalent metals to generate a stronger sulfate radical (SO₄²⁻) (Matzek & Carter 2016). Homolysis of PS, by thermal activation, at temperatures from 30 to 99°C, gives rise to two sulfate radicals (Waldemer et al. 2007; Johnson et al. 2008; Xu et al. 2016) whereas using metals lead to the formation of just one sulfate radical (Al-Shamsi et al. 2013; Stoyanova et al. 2014).

The application of nanomaterials such as nano zero-valent iron (nZVI) particles has received increasing attention lately as a reliable procedure to treat industrial wastewater (Su et al. 2012; Taha & Ibrahim 2014; Barreto-Rodrigues et al. 2016). Recent studies (Li et al. 2014) have focused on the use of nZVI particles as an activator of the PS anion for a novel heterogeneous Fenton-like process. The Fe⁡²⁺ released from nZVI (Equation (1)) promotes the homolytic cleavage of the peroxo bond in PS, generating SO₄²⁻ (E⁰ = 2.5 – 3.1 V) (Equation (2)) and HO· (E⁰ = 2.8 V), as shown in Equation (3) (Li et al. 2014; Yan et al. 2015; Ghanbari & Moradi 2017). The system nZVI/PS has been proved to effectively oxidize a variety of organic pollutants such as trichloroethylene, naphthalene, and chlorobenzene (Al-Shamsi & Thomson 2013).

SO₄²⁻ + Fe⁡²⁺ → 2SO₄²⁻ + Fe²⁺ (1)

S₂O₈²⁻ + Fe⁡²⁺ → SO₄²⁻ + SO₄²⁻ + Fe³⁺ (2)

SO₄²⁻ + H₂O → HO· + H⁺ + SO₄²⁻ (3)

However, due to its extremely high reactivity, the Fe⁡⁰ core is quickly passivated by the formation of iron oxides and hydroxides. Also, the nanoparticles tend to spontaneously aggregate due to magnetic attraction, decreasing...
significantly their reactivity (Markova et al. 2015; Liu et al. 2015). The passivation layers can be minimized and the reactivity of nZVI preserved by the deposition of a second metal, such as Pd, Pt, Ni, Ag, or Cu (Liou et al. 2005; Yan et al. 2010; Smuleac et al. 2011). Among the transition metals, Ag is one of the most suitable for industrial applications due to its low cost, easy preparation, and bactericidal property (Xu & Zhang 2000; Xie et al. 2010). Under the metal ion Ag⁺, the PS anion can also be converted into SO₄²⁻ (Equation (4)) (Ayoub & Ghauch 2014). For these reasons, Ag is an interesting option for deposition on nZVI nanoparticles:

\[ \text{Ag}^+ + \text{S}_2\text{O}_8^{2-} \rightarrow \text{Ag}^{2+} + \text{SO}_4^{2-} + \text{SO}_4^{2-} \]  

(4)

This work focuses on the use of bimetallic nZVI-Ag to activate PS, analyzing the synergistic effect of temperature. Several studies have reported the influence of temperature and Fe²⁺ on PS activation (Adewuyi & Sakyi 2013). However, studies focused on the combined effect of both nZVI-Ag and heat activated were not found in the literature.

In this work, bimetallic nZVI-Ag has been synthesized by reduction of ferric chloride with borohydride and reductive deposition of Ag on the freshly prepared nZVI. The obtained nanocatalyst has been characterized to determine its Brunauer–Emmett–Teller (BET)-specific surface area, morphology (scanning electron microscopy, SEM), crystallinity (X-ray diffraction, XRD), and composition (energy dispersive X-ray, EDX). The nZVI-Ag was applied as an activator of PS (X-ray diffraction, XRD), and composition (energy dispersive X-ray, EDX). The nZVI-Ag was applied as an activator of PS (X-ray diffraction, XRD), and composition (energy dispersive X-ray, EDX). The nZVI-Ag was applied as an activator of PS (X-ray diffraction, XRD), and composition (energy dispersive X-ray, EDX). The nZVI-Ag was applied as an activator of PS (X-ray diffraction, XRD), and composition (energy dispersive X-ray, EDX). The nZVI-Ag was applied as an activator of PS (X-ray diffraction, XRD), and composition (energy dispersive X-ray, EDX).

Characterization of nZVI-Ag nanoparticles

A multivariate statistical technique based on response surface methodology (RSM) coupled with Box–Behnken design (BBD) independent quadratic experimental design was applied to optimize and evaluate the experimental parameters nZVI-Ag concentration, PS dose, and reaction temperature effects on 4-CP mineralization. RSM is effective in optimizing processing conditions, reducing the number of tests and hence reducing the costs associated with the experiments (Silveira et al. 2014).

MATERIALS AND METHODS

Materials

Ferrous chloride tetrahydrate (98%), sodium borohydride (98%), silver sulfate (99.5%), 4-chlorophenol (99%), calcium chloride (93%), potassium iodide (99%), sodium carbonate (99.8%), sodium bicarbonate (98%), acetonitrile (99.9%), acetic acid (99%), hydrochloric acid (37%), acetone (99.9%), and ethanol (99%) were purchased from Sigma-Aldrich and used as received without further purification. Sodium PS (98%) was obtained from Panreac. 4-CP solution for the oxidation experiments was prepared in deionized water (Millipore Milli-Q system) and further deoxygenated by purging with N₂ for 3 hours.

Synthesis of nZVI-Ag nanoparticles

The synthesis of nZVI was performed through a reduction of ferrous chloride with sodium borohydride following the method described by Singh et al. (2011). A ferrous chloride solution was prepared by dissolving 5.02 g of FeCl₂·4H₂O salt in 250 mL of distilled water (purged with N₂). A solution of reducing agent was prepared by dissolving 2.82 g of sodium borohydride (NaBH₄) in 250 mL of distilled water (0.3 mol L⁻¹). The reducing agent solution was then added to the Fe solution (via peristaltic pump) at a controlled rate, maintaining proper mixing by stirring. Ferrous iron was reduced to zero-valent species according to Equation (5) (Chang et al. 2011):

\[ \text{Fe}^{2+} + 2\text{BH}_4^- + 6\text{H}_2\text{O} \rightarrow \text{Fe}^0 + 2\text{B(OH)}_3^- + 7\text{H}_2 \uparrow \]  

(5)

The impregnation of nZVI by Ag was then performed by reductive deposition of 0.024 g of the Ag₂SO₄ (equivalent to 2% (w/w) of the iron) into nanoparticles under stirring conditions. After the reaction, approximately 1.2 g of bimetallic nanoparticles were then generated according to Equation (6) (Singh et al. 2011):

\[ \text{Ag}_2\text{SO}_4 + \text{Fe}^0 \rightarrow 2\text{Ag} \downarrow + \text{FeSO}_4 \]  

(6)

The resulting nZVI-Ag nanoparticles were washed at least three times with absolute ethanol, separated by filtration and dried under inert atmosphere (N₂) in a glove-bag.
the nanoparticles was determined by the EDX method using UTW model (USA).

**Typical reaction procedure**

The oxidation runs were performed in 100 mL stirred glass bottles placed in an orbital shaker (200 rpm) with temperature control. All reactants were added simultaneously and submitted to vigorous mixing using a vortex mixer at the beginning of the trials. The reaction volume was set at 50 mL, the initial 4-CP concentration at 25 mg L\(^{-1}\) and the pH of the reaction medium at 3 (concentrated HNO\(_3\)). The yield of 4-CP and total organic carbon (TOC) removal \((D)\) were calculated considering the concentration of 4-CP or TOC at time \(t\) (\(C_t\)) and the initial concentration (\(C_0\)), as described in Equation (7):

\[
D(\%) = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  

(7)

The aliquots from the reaction were withdrawn at regular time intervals and filtered with 0.45 μm PTFE filters before analysis. 4-CP was quantified by high-performance liquid chromatography (HPLC) (Varian Pro-Start 325), equipped with a UV detector and a Microsorb C18 5 mm column (MV 100, 15 cm length, 4.6 mm diameter) as the stationary phase. This analysis was performed at 270 nm using a 70/30% v/v mixture of acetonitrile/acetic acid aqueous solution (75 mM) as the mobile phase. The mineralization degree was determined measuring the TOC by TOC-V (CSH, Shimadzu, Japan). The concentration of PS was determined by a colorimetric method (Liang et al. 2008) and the iron leached to the reaction medium was measured by the o-phenanthroline method.

**Experimental design**

The RSM was applied to evaluate the individual and the interactive effects of the independent variables nZVI-Ag and PS concentration and reaction temperature on the 4-CP or TOC removal. The performance of the process was optimized by BBD, using a second-order polynomial model (Equation (8)). The theoretical optimized values were compared with experimental data:

\[
R = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \epsilon
\]  

(8)

where \(R\) is the predicted response for 4-CP or TOC removal, \(\beta_0\) is the intercept parameter, \(\beta_i\), \(\beta_{ii}\), and \(\beta_{ij}\) are parameters for linear, quadratic, and interaction factor effects, \(x_i\) and \(x_j\) are independent variables and \(\epsilon\) is the error.

The experimental levels for each variable were selected taking into account preliminary results. The levels of the variables (low, center, and high) are denoted as −1, 0, and 1, respectively, as shown in Table 1.

The full experimental design was accomplished using 15 experiments with three replicates at the center. Table 2 summarizes BBD statistical combinations used in calculation and the experimental results obtained at the set conditions for 4-CP and TOC removal.

The fit between the model and the experimental data was evaluated by ANOVA (analysis of variance). The F-test was applied to verify whether the model could predict a significant variation in the experimental data. The probability \(p\)-value was used to estimate whether F is large enough to indicate statistical significance (Kumar et al. 2008). The model was developed using the software Design Expert v.8.0.7.1.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental range and levels of independent variables</th>
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<tbody>
<tr>
<td>Independent variable</td>
<td>Factor</td>
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<tr>
<td>nZVI-Ag (mg L(^{-1}))</td>
<td>A</td>
</tr>
<tr>
<td>PS (mM)</td>
<td>B</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>C</td>
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<tr>
<th>Table 2</th>
<th>The BBD design matrix and experimental results</th>
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<tbody>
<tr>
<td>Route</td>
<td>A: nZVI-Ag (mg L(^{-1}))</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
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<tr>
<td>15</td>
<td>275</td>
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</table>
RESULTS AND DISCUSSION

Characterization of nZVI-Ag nanoparticles

Figure 1 shows the SEM image of the nZVI-Ag nanoparticles. As observed, the nanocatalyst presents a roughly spherical shape and some aggregation due to the magnetic properties of iron species, which is common for this kind of nanoparticles (Babuonnusami & Muthukumar 2014). The nanoparticles show a broad size distribution from 40 to 120 nm. This value is consistent with those previously reported in the literature for nZVI-Ag synthesized using sodium borohydride (Carroll et al. 2013). On the other hand, the specific surface area (SBET) and total pore volume of the bimetallic nZVI-Ag were found to be 21.6 m² g⁻¹ and 0.12 cm³ g⁻¹, respectively, which are also quite close to the previous work reported by Markova et al. (2013).

The XRD pattern of the nanoparticles in the 2θ range of 20–70° is depicted in Figure 2. The characteristic peak of nZVI can be clearly seen at 44.7°, confirming the presence of iron species (Sohrabi et al. 2014), whereas only traces of iron oxide (Fe₃O₄) were found (62.5°).

The presence of Ag in the nanoparticles was not appreciated by the XRD pattern, which seems to be related to the low Ag content compared to nZVI (2% wt.). In the same way, Wang et al. (2013) did not observe any peaks for Pd working with bimetallic nZVI/Pd (0.75 wt %). The use of higher amounts of Ag on iron nanoparticles is not advisable as it might hinder the formation of H₂ by Fe⁰ corrosion, which has been demonstrated for Ag concentrations above 3 wt.% (Luo et al. 2010). In order to confirm the presence of Ag in the prepared nanoparticles, EDX analyses were implemented. The results are shown in Table 3. The main element in the nanoparticles was iron and the content of Ag was around the expected 2%. The relatively low amounts of oxygen and chloride present in the nanoparticles can be attributed to minimal surface oxidation and residual deposits from the iron precursor solution (FeCl₂), respectively.

<table>
<thead>
<tr>
<th>Element</th>
<th>%</th>
</tr>
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<tbody>
<tr>
<td>Iron (Fe)</td>
<td>90.60</td>
</tr>
<tr>
<td>Silver (Ag)</td>
<td>2.23</td>
</tr>
<tr>
<td>Chlorine (Cl)</td>
<td>0.52</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>6.65</td>
</tr>
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</table>

Box–Behnken analysis

The model in the form of ANOVA is shown in Table 4. The model F-value of 8.85 and a probability value (0.0132) implied that it is significant. This fact was confirmed at the level of probability > F ratio less than 0.05. Also A, B, B², and C² are significant model terms for 4-CP removal. Furthermore, the correlation coefficient (R² = 0.94) indicates that a 94% variability can be explained by the empirical model. The adequate precision is a measure of the range in predicted response relative to its associated error, a signal-to-noise ratio greater than 4.0 being desirable (Prakash Maran et al. 2013). The ratio found value of 8.76 is adequate for the model. The TOC removal was evaluated and considered statistically significant as well (Supplementary material, Table S1, available with the online version of this paper).

Based on the RSM model, the relationship between the 4-CP removal and TOC removal on the operating parameters (nZVI-Ag, PS, and reaction temperature) was...
fitted using polynomial equations, in terms of coded factors as shown in Equations (9) and (10).

\[
4\text{- CP removal}(\%) = 95.83 - 13.79A + 20.44B \\
+ 6.05C + 12.98AB + 3.40AC - 0.50BC + 11.05A^2 \\
- 38.25B^2 - 21.08C^2 \\
(9)
\]

\[
\text{TOC removal}(\%) = 79 - 12.94A + 21.25B + 8.39C \\
+ 1.5AB - 8.38AC + 5.5BC + 0.19A^2 - 28.69B^2 - 23.81C^2 \\
(10)
\]

where A is the nZVI – Ag (mg L\(^{-1}\)), B is the PS dose (mM), and C is the temperature (°C).

The response surface and corresponding contour plots allow evaluation of the main interaction effects of experimental variables and their contribution in predicting the response. Figure 3 shows the 3D response surface, showing the relationships of nZVI-Ag and PS (Figure 3(a)), nZVI-Ag and temperature (Figure 3(b)), and PS and temperature (Figure 3(c)) on 4-CP removal efficiency.

The performance of the process was optimized by BBD, considering minimizing operating costs on maximum 4-CP removal. The resulting optimum operating conditions were 50 mg L\(^{-1}\) of nZVI-Ag, 21 mM of PS and 57 °C. On the other hand, in addition to the optimum conditions, the model can provide possible solutions when targeting to specific response values (Xynos et al. 2014).

Model evaluation

Parity plots were used to estimate the accuracy of the regression model. The experimental 4-CP and TOC removal (%) and the predicted values are shown in Figure 4. As observed, the model allowed successful prediction of the experimental values, with correlation coefficients (R\(^2\)) around 0.98.

The comparison of predicted and experimental values was also performed under the optimum conditions to verify the accuracy of the optimized parameter. The complete removal of 4-CP achieved experimentally was successfully predicted by the model, whereas TOC removal was slightly overestimated (X\(_\text{TOC}_{\text{model}}\) = 0.90 vs X\(_\text{TOC}_{\text{exp}}\) = 0.83).

Oxidative degradation of 4-CP in optimum conditions

Figure 5(a) shows 4-CP and TOC removal using PS activated by bimetallic nZVI-Ag under the aforementioned optimal conditions (nZVI-Ag dose of 50 mg L\(^{-1}\), PS concentration of 21 mM and 57 °C). It also depicts the results obtained using only nZVI-Ag in the absence of PS as well as those achieved using only PS. The application of nZVI-Ag alone led to a partial removal of 4-CP (20%) after 1 hour reaction time. On the other hand, the application of PS in the absence of catalyst led to a similar conversion of 4-CP, but in this case due to the oxidation by sulfate radicals upon thermal activation (consuming 9 mM of PS). Also, the presence of SO\(_4^2-\) in aqueous solution can result in radical interconversion reactions to produce the hydroxyl radical, which can also oxidize 4-CP (Ahmad et al. 2013). In any case, those blank experiments did not lead to satisfactory results as 4-CP conversion was, in both cases, below 20%.

The synergistic effects of temperature (57 °C) and nZVI-Ag (50 mg L\(^{-1}\)) activated PS (21 mM) has proved to be an interesting alternative for 4-CP treatment. The complete removal of 4-CP and a high mineralization degree (around 85%) were achieved (Figure 5(a)) with a PS decomposition around 85% after 60 minutes’ reaction time. Pseudo first order rate constants (k\(_{\text{obs}}\)) were obtained by fitting the experimental 4-CP and TOC removal. The k\(_{\text{obs}}\) were 0.111 and 0.032 min\(^{-1}\), respectively. These values improved those previously reported in the literature dealing with the use of ZVI for organochlorinated pollutants’ degradation. Previous studies (Zhao et al. 2010) have reported a first-rate constant of 0.036 min\(^{-1}\) with 200 mg L\(^{-1}\) of ZVI microparticles using 0.156 mM 4-CP initial concentration by activated 0.78 mM PS. After 60 minutes’ reaction, 88% of 4-CP was removed. Li et al. (2014) reported a pseudo first order k\(_{\text{obs}}\) rate of 0.071 min\(^{-1}\) for the removal of 2,4-dichlorophenol within ZVI (2.0 g L\(^{-1}\), Na\(_2\)S\(_2\)O\(_8\) (12.5 mM), and initial contaminant concentration of 30 mg L\(^{-1}\) at 50 °C. Under those conditions, 2,4-dichlorophenol was almost totally removed, although the chemical
oxygen demand was reduced to as low as 40% after 180 min treatment. The bimetallic nZVI-Ag (1% w/w) activated PS for trichloroethylene (TCE) was also investigated by Al-Shamsi et al. They used a TCE/PS/nZVI-Ag molar ratio of 1/20/20 working at 20°C. After 30 minutes' reaction, 50% removal of TCE was achieved.

Figure 5(b) shows the TOC removal achieved using different initial PS concentrations (5–26 mM) and 50 mg L⁻¹ of nZVI-Ag at 57°C. Preliminary experiments were carried out in the absence of PS and catalyst, respectively. In both cases, TOC conversion was lower than 10%, suggesting that adsorption on ZVI-Ag particles and thermal-activation at 57°C can be considered neglected on 4-CP mineralization upon the previous experimental conditions.
The TOC removal yields were 13%, 37%, 43%, 67%, and 86%, respectively, for the relation nZVI-Ag/PS (mg L\(^{-1}\)) of 1/2, 1/10, 1/20, 1/50, and 1/100. The higher the amount of PS, the higher the mineralization efficiency, due to a steady increase in the Fe\(^{2+}\) in solution. The amount of iron ion leached from nanoparticles after the catalytic reaction at different PS concentrations was less than 5 mg L\(^{-1}\) (Figure 5(b)). However, an increase of the PS dosage beyond the optimized condition reduced approximately 16% of the TOC removal efficiency. This was possibly due to scavenging of SO\(_4^{2-}\) by undesirable competitive reactions, as shown in Equation (11) (Ghauch et al. 2013):

SO\(_4^{2-}\) + SO\(_4^{2-}\) → S\(_2\)O\(_5^{2-}\)  
(11)

According to them, the increase in catalyst concentration would lead to a higher degradation yield. Nevertheless, the efficiency decreases with nZVI-Ag concentration beyond 50 mg L\(^{-1}\) because of an excessive amount of released Fe\(^{2+}\), which reduces the amount of PS anion due to the scavenging of sulfate radicals (Equation (12)). In addition, according to Equation (13), an iron sulfate complex on the surface of the nZVI-Ag can also be formed on the surface of the nZVI-Ag (Al-Shamsi & Thomson 2013). Figure 6 summarizes the overall 4-CP oxidation process by nZVI-Ag/PS.

SO\(_4^{2-}\) + Fe\(^{3+}\) → SO\(_2^{2-}\) + Fe\(^{2+}\)  
(12)

Fe\(^{0}\) + SO\(_4^{2-}\) + 2H\(_2\)O → FeSO\(_4\) + H\(_2\) + 2OH\(^{−}\)  
(13)
As can be observed in Figure 6, the values of the TOC kinetic constants obey the Arrhenius equation, which allows the apparent activation energy ($E_A$) to be obtained. An $E_A$ value of 10 kJ mol$^{-1}$ was obtained for nZVI-Ag activated PS, which is in agreement with those reported in the literature. Activated PS using iron and thermal activation required an activation energy of 62 kJ mol$^{-1}$ (Romero et al. 2010) and values between 60 and 250 kJ mol$^{-1}$ (Xu & Li 2010), respectively. Shih et al. (2011) reported activation energy of around 16.6 kJ mol$^{-1}$ for the system based on nZVI activated PS when the temperature increased from 5 to 45 °C for the oxidation of hexachlorobenzene.

**CONCLUSION**

The synthesized nZVI-Ag was found to be effective in activating PS. BBD was proven suitable to determine the effects of the operative variables of nZVI-Ag dosage, reaction temperature, and PS concentration on 4-CP degradation. The results obtained were fitted with a quadratic model, indicating that the proposed regression allows a successful simulation of the experimental results. Under the optimal conditions (50 mg L$^{-1}$ nZVI-Ag, 21 mM PS at 57 °C) complete degradation of 4-CP and a high mineralization degree (83%) were achieved.

Following the results of this study, further research will be addressed to elucidate the mechanisms of degradation of other pollutants of environmental relevance and to confirm the stability of the catalyst, a crucial issue regarding potential application.

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