

MATHEMATICAL KINETIC MODELLING AND REPRESENTING DESIGN EQUATION FOR A PACKED PHOTOREACTOR WITH IMMOBILISED TiO₂-P25 NANOPARTICLES ON GLASS BEADS IN THE REMOVAL OF C.I. ACID ORANGE 7

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In this work, a design equation was presented for a batch-recirculated photoreactor composed of a packed bed reactor (PBR) with immobilised TiO₂-P25 nanoparticle thin films on glass beads, and a continuous-flow stirred tank (CFST). The photoreactor was studied in order to remove C.I. Acid Orange 7 (AO7), a monoazo anionic dye from textile industry, by means of UV/TiO₂ process. The effect of different operational parameters such as the initial concentration of contaminant, the volume of solution in CFST, the volumetric flow rate of liquid, and the power of light source in the removal efficiency were examined. A rate equation for the removal of AO7 is obtained by mathematical kinetic modelling. The results of reaction kinetic analysis indicate the conformity of removal kinetics with Langmuir-Hinshelwood model ($k_{L-H} = 0.74 \text{ mg L}^{-1} \text{ min}^{-1}$, $K_{ads} = 0.081 \text{ mg}^{-1} \text{ L}$). The represented design equation obtained from mathematical kinetic modelling can properly predict the removal rate constant of the contaminant under different operational conditions ($R^2 = 0.963$). Thus the calculated and experimental results are in good agreement with each other.

Keywords: heterogeneous photocatalysis, batch-recirculated photoreactor, design equation, mathematical kinetic modelling, TiO₂-P25 nanoparticles, C.I. Acid Orange 7

1. INTRODUCTION

Coloured wastewater generated by textile industries is an important source of environmental contaminations (Behnajady and Modirshahla, 2006; Daneshvar et al., 2007; Gupta et al., 2011; Sauer et al., 2002). It is estimated that about 1-20% of the total world production of dyes is lost during the dyeing process and is released into wastewater (Akpan and Hameed, 2009; Konstantinou and Albanis, 2004). Colour removal from wastewater is often more important than its removal from other colourless organic substances (Grzechulska and Morawski, 2002). Heterogeneous photocatalysis seems to be an interesting treatment method for the removal of toxic pollutants from industrial wastewaters due to its ability to convert them into innocuous end products such as CO₂, H₂O and mineral acids (Damodar and Swaminathan, 2008). A variety of semiconductors such as TiO₂, ZnO, CdS, and WO₃ have been studied as photocatalysts (Gupta et al., 2007; Gupta et al., 2012; Ismail et al., 2011; Lin et al., 2005; Liu et al., 1998). TiO₂ is the most extensively used effective photocatalyst, owing to its high efficiency, photochemical stability, non-toxic nature, and low cost (Ismail et al., 2011). In most cases, TiO₂ is applied in the form of suspension or slurry (Behnajady et al., 2007a). From a practical point of view, using slurry systems involves several major problems such as: (a) separation of the catalyst from the slurry is difficult, (b) suspended particles especially in high concentrations tend to aggregate, (c) using the suspensions in systems with continuous flow is difficult, and (d) due to the high absorption by TiO₂

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and dissolved organic samples, particularly in the case of colours, the penetration depth of UV light is limited (Arabatzis et al., 2002; Behnajady et al., 2007b; Khataee et al., 2011; Zhou and Ray, 2003). In order to solve these problems, the catalyst was immobilised onto solid substrates such as glass beads, activated carbon fiber, cotton material, cement surface, sand, polymer films and Rasching rings (Behnajady et al., 2007a; Behnajady et al., 2008; Daneshvar et al., 2005; Fernandez et al., 2004; Khataee, 2009). The aim of this paper is kinetic modelling and representing of design equation for a batch-recirculated photoreactor. To the authors' knowledge, there is no report about kinetic modelling and representing of design equation for a batch-recirculated photoreactor. The reactor is a combination of a photoreactor packed with TiO₂-P25 nanoparticle thin films on glass beads and a continuous stirred tank for the removal of a model contaminant from textile industry.

2. MATERIALS AND METHODS

2.1. Materials

C.I. Acid Orange 7 (AO7), a monoazo anionic dye, was obtained from Fluka (Switzerland) as a model contaminant from monoazo textile dyes. Titanium dioxide (TiO₂) was Degussa P-25, and it constitutes approximately 80% of anatase and 20% of rutile. TiO₂-P25 had a BET surface area of 50±10 m² g⁻¹ and an average particle diameter of 21 nm, containing 99.5% TiO₂.

2.2. Immobilization of TiO₂-P25 on glass beads

The immobilised TiO₂ on glass beads was prepared by heat attachment method (Behnajady et al., 2007a; Sakthivel et al., 2002). In this procedure, a suspension containing TiO₂-P25 (2.5 g) in 250 mL of double distilled water was prepared, and the pH was adjusted to about 1.5 by HNO₃ (1 M). The prepared suspension was sonicated in an ultrasonic bath (Elma T460/H, Windaus, Germany) under the frequency of 35 kHz for 60 min in order to improve the dispersion of TiO₂-P25 in water. Glass beads were treated with a dilute HF solution for 24 h and then washed with double distilled water. At this stage, the sonicated suspension was poured on glass beads and stirred with rotary (Heidolph, Germany) for 30 min, then it was left intact in a fixed place for 30 min. The suspension was removed from the glass beads, and the glass beads with thin films of TiO₂-P25 were placed in an oven at 150°C for 150 min. After drying, the glass beads were fired at 400°C for 120 min and washed with double distilled water for the removal of weakly attached TiO₂-P25 nanoparticles. This process was repeated two times.

2.3. Photoreactor

All experiments were carried out in a batch-recirculated photoreactor. Figure 1 shows that the photoreactor comprises an annular photoreactor packed with a catalyst supported on glass beads with 130 mL volume and 5.48 g catalyst loading as well as a continuous-flow stirred tank (CFST). The radiation source at the packed bed photoreactor was UV-C lamp emitting at 254 nm.

For photocatalytic degradation of AO7, a solution containing a known concentration of AO7 was prepared and then a known value of the prepared solution was transferred into CFST and agitated with a magnetic stirrer during experiments. The solution was recirculated with a peristaltic pump (Heidolph, PD 5001, Germany) with a known flow rate into the reactor, and regularly, the AO7 concentration was analysed at the outlet with a UV-vis spectrophotometer (Ultrospec 2000, Biotech pharmacia, England) at 485 nm. Experiments were carried out with variations in AO7 concentration, the volume of solution in CFST, the volumetric flow rate, and the power of light source.

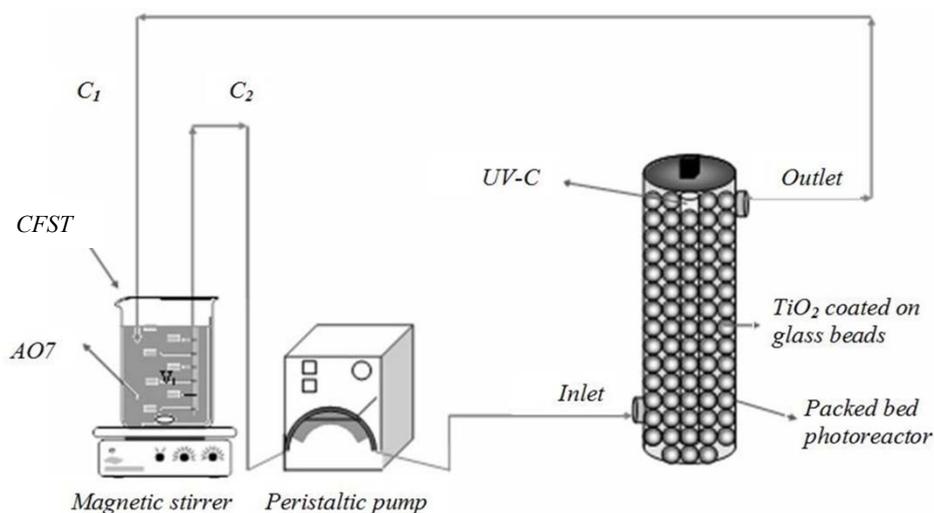


Fig. 1. Scheme of batch-recirculated photoreactor

3. RESULTS AND DISCUSSION

3.1. SEM analysis

SEM images of thin films from TiO₂-P25 nanoparticles immobilised on glass beads at two different magnifications are shown in Fig.2. A significant density of the prepared substrate and particularly, a suitable distribution of particle size are the benefits of the established technique. SEM images show that the nanoparticle size on the substrate is about 50 nm that is due to agglomeration of nanoparticles during calcination.

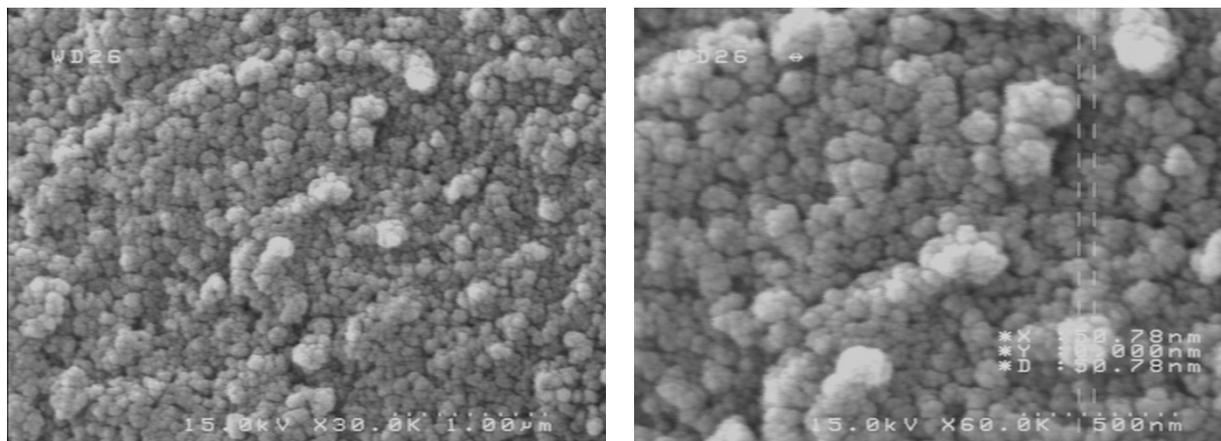


Fig. 2. SEM images of immobilised TiO₂-P25 nanoparticle thin films on glass beads

3.2. Kinetic modelling

Langmuir-Hinshelwood kinetic model is one of the most common kinetic models that have been used for studying the kinetics of heterogeneous systems such as heterogeneous photocatalysis. The general formula of this kinetic model is as follows (Turchi and Ollis, 1990).

$$R = -\frac{d[AO7]}{dt} = \frac{k_{L-H}K_{ads}[AO7]}{1 + K_{ads}[AO7]} \quad (1)$$

Many researchers have shown that competitive adsorption by intermediates should be within the equation rate (Al-Ekabi and Serpone, 1988; Chan et al., 2001). Under this condition, the Eq. (1) can be written as follows:

$$R = -\frac{d[AO7]}{dt} = \frac{k_{L-H}K_{ads}[AO7]}{1 + K_{ads}[AO7] + \sum K_i C_i} \quad (2)$$

Beltran-Heredia et al. made the following assumption (Beltran-Heredia et al., 2001).

$$K_{ads}[AO7] + \sum K_i C_i = K_{ads}[AO7]_0 \quad (3)$$

In this equation, $[AO7]_0$ is the initial concentration of AO7. By substituting Eq. (3) for Eq. (2), we will have:

$$R = -\frac{d[AO7]}{dt} = \frac{k_{L-H}K_{ads}[AO7]}{1 + K_{ads}[AO7]_0} = k_{ap}[AO7] \quad (4)$$

where

$$k_{ap} = \frac{k_{L-H}K_{ads}}{1 + K_{ads}[AO7]_0} \quad (5)$$

Equation (4) shows a pseudo-first-order reaction that the reaction rate constant in accordance with Eq. (5) is linked to the initial concentration of the pollutant. In Fig.3 the semi-logarithmic graphs of AO7 concentration versus irradiation time in different initial concentrations of AO7, the volume of solution in CFST, the volumetric flow rate, and the power of light source have been reported. In all cases, yield straight lines confirm pseudo-first-order kinetics for this process. The pseudo-first-order reaction rate constant (k_{ap}) for the photocatalytic removal of AO7 was obtained from the slope of semi-logarithmic graphs. The constants k_{L-H} and K_{ads} in L-H model using the software Polymath (Version 6.0) with trial and error nonlinear regression fitting k_{ap} to $[AO7]_0$ were obtained as $0.74 \text{ mg L}^{-1} \text{ min}^{-1}$ and $0.081 \text{ mg}^{-1} \text{ L}$, respectively. The results indicate that k_{ap} decreases with increasing the initial concentration of AO7 and increasing the volume of solution in CFST. On the other hand, k_{ap} increases with increasing volumetric flow rate and power of light source. A decrease of k_{ap} with an increase of the initial concentration of AO7 can be ascribed to the reduction of the number of active sites on the $\text{TiO}_2\text{-P25}$ surface due to the covering of the surface with AO7 molecules and generated intermediates. Moreover, AO7 molecules at high concentrations absorb more light than the catalyst surface, and therefore catalyst activity will be decreased (Behnajady and Modirshahla, 2006; Khataee, 2009). Furthermore, our results indicate that k_{ap} increases with increasing power of light source. With the increase in the power of light source, the catalyst absorbs more photons, which generates more electron-hole pairs, and therefore a larger number of hydroxyl radicals which eventually leads to higher catalyst activity (Behnajady and Modirshahla, 2006; Khataee, 2009).

A decrease of k_{ap} with the increasing of volume of solution can be related to the higher rotatable volume of solution for a given irradiation time. More wastewater volume needs longer time for treatment (Hao et al., 2009). The liquid flow rate influences the residence time of liquid and the mass transfer in the packed bed photoreactor. The enhancement of k_{ap} with increasing volumetric flow rate of liquid can be related to the higher amount of liquid passing through the packed bed photoreactor and an increase in the mass transfer rate (Hao et al., 2009).

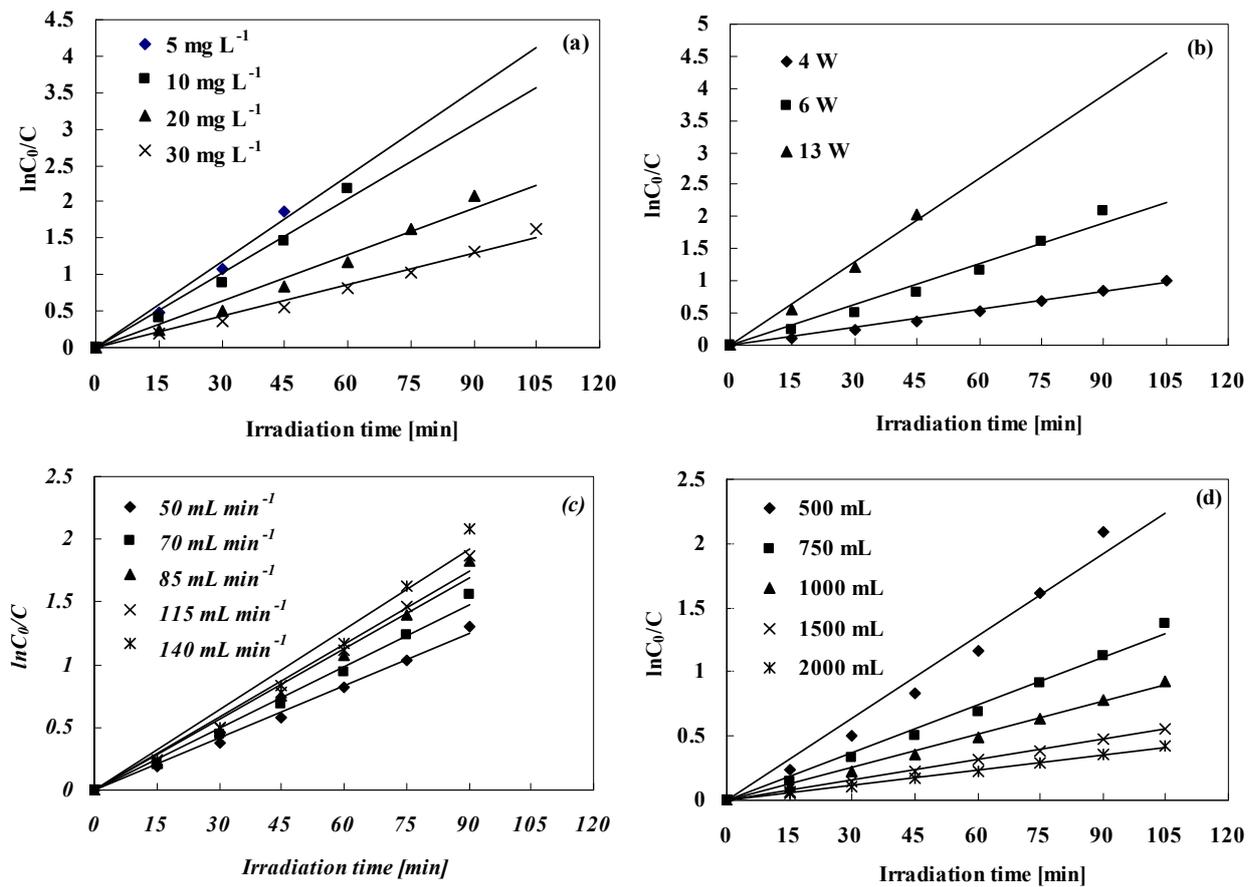


Fig. 3. Semi-logarithmic plot of AO7 concentration versus irradiation time (a) in different initial concentrations of AO7, (b) powers of light source, (c) volumetric flow rates and (d) volumes of solution in CFST

3.3. Design equation and mathematical kinetic modeling

The design equation for a packed bed reactor can be written as follows:

$$-v_0 \frac{dC}{dW} = -r'_A \quad (6)$$

After integration of Eq. (6), we obtain:

$$\int_{C_2}^{C_1} \frac{dC}{-r'_A} = -\int_0^W \frac{dW}{v_0} \quad (7)$$

The rate equation was assumed to be first-order:

$$-r'_A = k_2 C \quad (8)$$

With substituting Eq. (8) in Eq. (7), we will have:

$$C_1 = C_2 e^{\frac{wk_2}{v_0}} \quad (9)$$

This equation correlates the outlet concentration for packed bed photoreactor (C_1) to the inlet concentration (C_2).

The CFST operates under unsteady state conditions. The mass balance of substrate for the CFST with V_1 volume is represented by the following equation:

$$v_0 C_1 - v_0 C_2 = V_1 \frac{dC_2}{dt} \quad (10)$$

By substituting Eq. (9) for Eq. (10), the following equation will be obtained:

$$v_0 C_2 e^{-\frac{Wk_2}{v_0}} - v_0 C_2 = V_1 \frac{dC_2}{dt} \quad (11)$$

or

$$-\frac{dC_2}{dt} = \frac{v_0}{V_1} \left[1 - e^{-\frac{Wk_2}{v_0}} \right] C_2 \quad (12)$$

By comparing Eq. (12) with the first-order reaction rate, k_1 can be written as follows:

$$k_1 = \frac{v_0}{V_1} \left[1 - e^{-\frac{Wk_2}{v_0}} \right] \quad (13)$$

The effective factors in the removal of the pollutant in the photoreactor are the initial concentration of AO7 ($[AO7]_0$), the volume of solution in CFST (V), the volumetric flow rate (v_0) and the power of light source (P). While k_2 may be empirically related to the effective parameters with nonlinear regression analysis, model parameters are calculated as follows:

$$k_2 = -0.11[AO7]_0 + 4.589, \quad R^2 = 0.9858 \quad (14)$$

$$k_2 = 0.251 P^{1.13}, \quad R^2 = 0.9836 \quad (15)$$

$$k_2 = 0.289 v_0^{0.41}, \quad R^2 = 0.994 \quad (16)$$

$$k_2 = 5.61 \times 10^{-7} V_1^2 - 0.0018 V_1 + 2.948, \quad R^2 = 0.9865 \quad (17)$$

Eq.(18) can be obtained with the combination of Eqs.(14), (15), (16) and (17) as follows:

$$k_2 = k'_0 P^{1.13} v_0^{0.41} (5.61 \times 10^{-7} V_1^2 - 0.0018 V_1 + 2.948) (-0.11[AO7]_0 + 4.589) \quad (18)$$

The value of k'_0 was obtained from substituting of experimental data to Equation (18). By substituting Eq. (18) into Eq. (13), the final equation will be obtained as follows:

$$k_1 = \frac{v_0}{V_1} \left[1 - e^{-\frac{W}{v_0} [0.0069 P^{1.13} v_0^{0.41} (5.61 \times 10^{-7} V_1^2 - 0.0018 V_1 + 2.948) (-0.11[AO7]_0 + 4.589)]} \right] \quad (19)$$

In order to evaluate Eq. (19) in predicting k_1 at different conditions, a comparison between experimental and calculated k_1 for the removal of AO7 is shown in Fig. 4.

The plot shows that the results obtained from the model are in good agreement with the experimental data for the removal of AO7 in the photoreactor at different operational conditions. Although the rate expression is semi-empirical in nature, it provides information about the effect of operational parameters on the reaction rate which is favourable for design purposes.

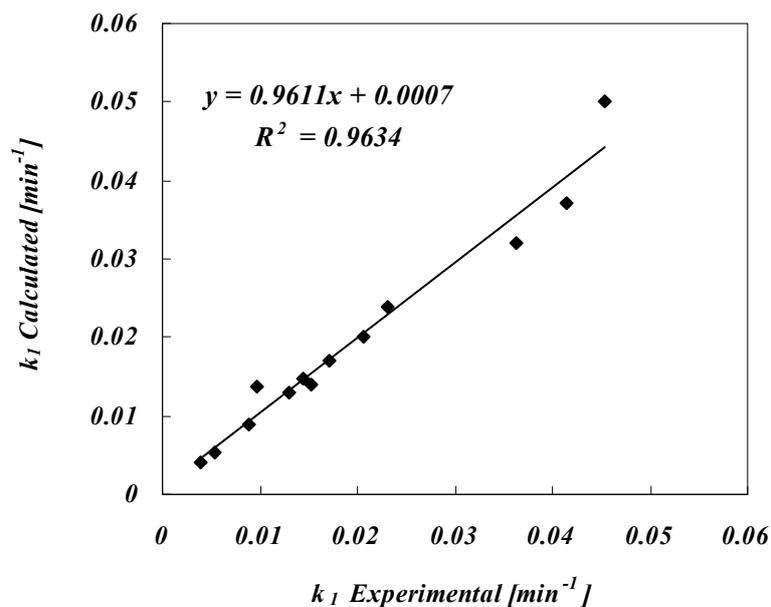


Fig. 4. Comparison between experimental and calculated k_1 for removal of AO7 in batch-recirculated photoreactor

4. CONCLUSIONS

The results show that a batch-recirculated photoreactor can be used efficiently in the removal of AO7 with UV/TiO₂ process. The represented design equation which is obtained by combining the equations of mass balance and kinetics mathematical modelling can properly predict the removal rate constant of a contaminant in the photoreactor under different operational conditions. Therefore, based on our experiments, the calculated results and experimental findings are compatible, and there is good consistency between them.

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SYMBOLS

[AO7]	concentration of AO7, mg L^{-1}
[AO7] ₀	initial concentration of AO7, mg L^{-1}
C	concentration of contaminant, mg L^{-1}
C_i	concentration for intermediates, mg L^{-1}
C_1	outlet concentration, mg L^{-1}
C_2	inlet concentration, mg L^{-1}
k_2	rate constant in PBR, $\text{mL min}^{-1} \text{gcat}^{-1}$
k_1	rate constant in CFST, min^{-1}
k_{ap}	pseudo-first-order reaction rate constant, min^{-1}
R	reaction rate, $\text{mg L}^{-1} \text{min}^{-1}$
k_{L-H}	reaction rate constant, $\text{mg L}^{-1} \text{min}^{-1}$
K_{ads}	adsorption coefficient of AO7 on the immobilised titanium dioxide nanoparticles on glass beads, $\text{mg}^{-1} \text{L}$
K_i	adsorption equilibrium constant for intermediates, $\text{mg}^{-1} \text{L}$

P	power of light source, W
r'_A	reaction rate in PBR, mol gcat ⁻¹ min ⁻¹
R	reaction rate, mg L ⁻¹ min ⁻¹
V	volume of solution in CFST, mL
W	weight of catalyst, g
v_0	volumetric flow rate of liquid, mL min ⁻¹

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