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Research Article

Fixed Bed Adsorption Study on Phosphate Removal Using Nanosized FeOOH-Modified Anion Resin

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Removal of phosphate from solution using nanosized FeOOH-modified anion resin was studied in fixed bed column. Effect of bed height and flow rate on the breakthrough curves were investigated. Longer breakthrough time was obtained by increasing the bed height and decreasing the flow rate. Bed service depth time (BDST) model was applied to recount the relationship between bed service time and bed height. The value of N_0 was calculated to be 21.4 g/L. Yoon-Nelson model, which fitted well with the experimental data, is allowable to estimate the breakthrough curves and characteristic parameters for phosphate adsorption in the column filled with nanosized FeOOH-modified anion resin.

1. Introduction

Phosphorus is an essential nutrient element to agricultural and industrial development. However, the disposal of dissolved phosphate contained in wastewater is a major inducement of water eutrophication all over the world [1]. Several treatment techniques are used in the wastewater treatment industry in large-scale treatment facilities or only in the experimental project. Biological phosphorus removal (BPR) [2], chemical precipitation, and adsorption by functionalized materials [3] are commonly used for phosphorus removal. BPR has been proved to be an economic and efficient technique which is widely applied in wastewater treatment plant [4–6]. Nevertheless, the functional microorganism, which is called phosphorus-accumulating organisms (PAOs), is sensitive to the variation of environmental and operating conditions. Though chemical precipitation is an effective method to remove phosphorus, high cost and generation of metal sludge are major hindrances for its widely application [3]. Adsorption is used widely for phosphorus removal and recovery [7]. The bottleneck for application of adsorption in wastewater treatment is the development of low-cost and efficient adsorbent.

In the previous study, it has been proved that nanosized ferric oxides showed high adsorption performance towards pollutants like chromium, arsenic, plumbum, and phosphate [8–12] due to their large specific surface area [13]. The hybrid adsorbent by loading nanosized ferric oxyhydroxide on anion resin has indicated efficient adsorption performance for phosphorus removal [14–17]. However, little knowledge is obtained about continuous flow fixed bed experiment adsorption which is necessary to investigate the performance of practical operation [18].

The main objective of the present study is to investigate the adsorption of phosphate in fixed bed column filled with nanosized FeOOH-modified anion resin. Effect of several important design parameters such as bed height, flow rate, and initial concentration of phosphate in solution was investigated. In addition, bed depth service time (BDST) and Yoon-Nelson model were applied to fit with the data obtained from fixed bed study.

2. Materials and Methods

2.1. Preparation of Nanosized FeOOH-Modified Anion Resin and Phosphate Solution. The nanosized FeOOH-modified anion resin adsorbent was prepared by loading nanosized ferric oxyhydroxide onto anion resin according to the method reported in previous study in our lab [17].

All chemicals used were analytical grade. Phosphate stock solution (50 mg/L) was prepared by dissolving KH_2PO_4 into distilled water. The stock solution was diluted to obtain phosphate solution of different concentrations.

2.2. Fixed Bed Column Experiments. Bulk removal of phosphate onto nanosized FeOOH-modified anion resin was investigated in a fixed bed column (10 mm in diameter and 300 mm in length). To maintain a constant flow of the fixed bed column, a constant flow variable speed peristaltic pump (Longer-BT100) was equipped. The upflow of solution was introduced at the bottom of the column. Liquid samples were collected at regular time intervals at the exit of the fixed bed column for phosphate concentration analysis.

2.3. Analyses and Calculation. The concentrations of phosphate in the fixed bed adsorption experiments were determined according to standard methods for the examination of water and wastewater [19]. Nanosized FeOOH-modified anion resin samples were analysed by a scanning electron microscope (SEM, Nanosem 430, FEI Inc., USA).

2.4. BDST Model. The BDST model which is based on Bohart-Adams equation was commonly applied to depict the relationship between bed depth and service time at fixed bed adsorption.

The linear form of BDST model can be expressed as follows [20]:

$$t = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_t} - 1\right), \quad (1)$$

where N_0 is the adsorption capacity of fixed bed column (mg/L), Z is the bed height of column (cm), C_0 represents the initial phosphate concentration (mg/L), C_t represents the phosphate concentration at time t (mg/L), v is the linear flow rate of solution through the bed (cm/min), t is the service time of column (min), and K_a is the rate constant (L/mg·min).

2.5. Yoon-Nelson Model. Yoon-Nelson model is a less complicated model which can be used to investigate the adsorption and breakthrough curves in fixed bed column [21]. This model is based on the hypothesis that the probability of adsorption decrease rate of each adsorbate molecule is linearly related to the probability of amount of adsorbate adsorption and breakthrough on the adsorbent [21].

The linear form of Yoon-Nelson model is represented as follows [22]:

$$\ln\left(\frac{C_t}{C_0 - C_t}\right) = k_{\mathrm{YN}} t - \tau k_{\mathrm{YN}}, \quad (2)$$

where k_{YN} is the Yoon-Nelson rate constant (min^{-1}), τ is the breakthrough time required for 50% adsorbate breakthrough (min). The values of k_{YN} and τ can be determined by the linear plot of $\ln(C_t/(C_0 - C_t))$ against t.

3. Results and Discussion

3.1. Characterization of Nanosized FeOOH-Modified Anion Resin. The nanosized FeOOH-modified anion resin was deep brown spherical adsorbent bead, which was quite different from the white spherical bead of anion resin. The SEM images have clearly indicated that after preparation of nanosized FeOOH-modified anion resin, nanosized Fe had been successfully loaded on anion resin (Figure 1). After FeOOH loading, the adsorption capacity of anion resin increased from 38.70 to 51.52 mg/g. by the formation of inner-sphere surface complexes between phosphate and FeOOH [23, 24].

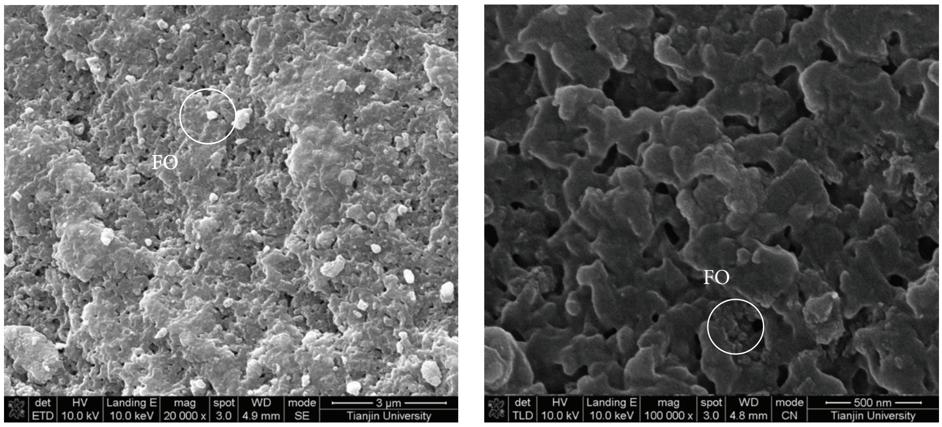
The adsorption performance of nanosized FeOOH-modified anion resin was much better than some other kinds of anion resin (with adsorption capacity of 12.09 [25], 20.9 [26], and 26.5 mg/g [27], resp.).

3.2. Effect of Bed Height. Effect of bed height on the fixed bed adsorption was investigated at a constant initial concentration of 20 mg/L phosphate in solution. The flow rate of influent was set at 10 mL/min. Breakthrough concentration (C_b) is fixed at 10% of the initial concentration (C_0). The breakthrough curves were obtained by varying bed heights from 5 cm to 15 cm (Figure 2.) It was observed that the breakthrough time increased from 300 to 1140 min with the increase of bed height. Besides, the exhaustion time increased from 720 to 2100 min. The increase of breakthrough time and exhaustion time was due to more nanosized FeOOH-modified anion resin filling in column with higher bed height, which provide greater functional sites and broadened mass transfer zone for phosphate adsorption.

The BDST model was applied to predict the phosphate adsorption in column filled with nanosized FeOOH-modified anion resin. According to (1), C_0 and v are assumed to be reasonably constant for fixed bed adsorption. The values of N_0 and K_a are calculated to be 21.4 g/L and 5.43×10^{-3} L/mg·min, respectively.

3.3. Effect of Flow Rate. Fixed bed adsorption experiments were operated at different flow rate in columns filled with nanosized FeOOH-modified anion resin. The breakthrough curves for fixed bed column adsorption at different flow rates were given in Figure 3. The breakthrough of fixed bed column for flow rates 5, 10, and 15 mL/min occurred at 1320, 720, and 420 min, respectively. The breakthrough time decreased with the increase of flow rate, because of more phosphate exchanging with functional group sites in shorter time. The flow rate also influences the shape of breakthrough curve. The steeper breakthrough curve was observed at higher flow rate, indicating a more prominent effect of intraparticle diffusion and shorter service time of fixed bed column.

3.4. Yoon-Nelson Model. The Yoon-Nelson model was applied to predict the adsorption process and breakthrough curves. Calculated according to linearized Yoon-Nelson equation, k_{YN} decreased and τ increased with increase of bed height (Figure 4(a) and Table 1). In contrast, when the flow rate increased from 5 to 15 mL/min, the value of k_{YN}



(a) (b)

Figure 1: SEM micrograph of nanosized FeOOH-modified anion resin.

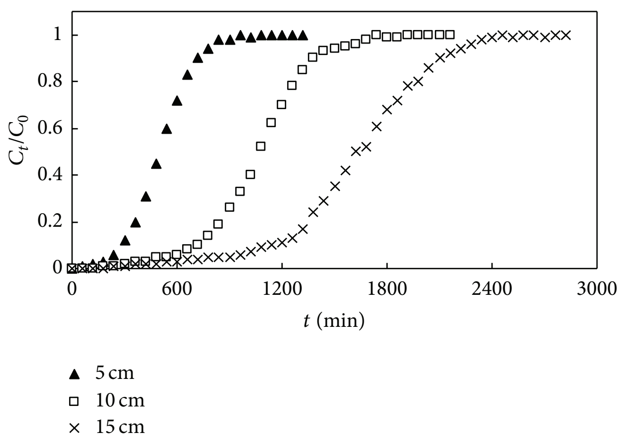


Figure 2: Effect of bed height on phosphate adsorption in column filled with nanosized FeOOH-modified anion resin. (Conditions: initial phosphate concentration 20 mg/L; flow rate 10 mL/min.)

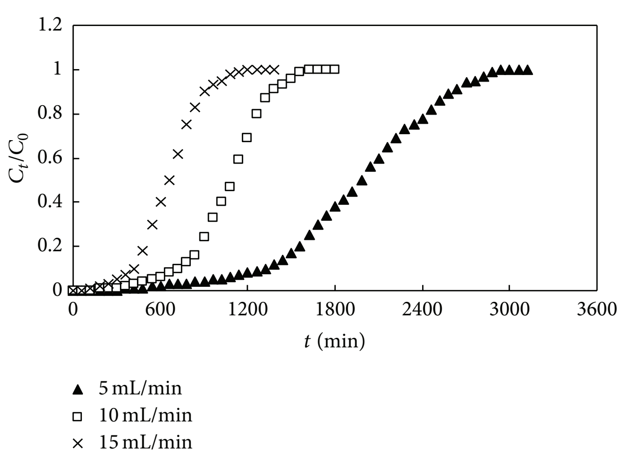


Figure 3: Effect of flow rate on phosphate adsorption in column filled with nanosized FeOOH-modified anion resin. (Conditions: initial phosphate concentration 20 mg/L; beh height 10 cm.)

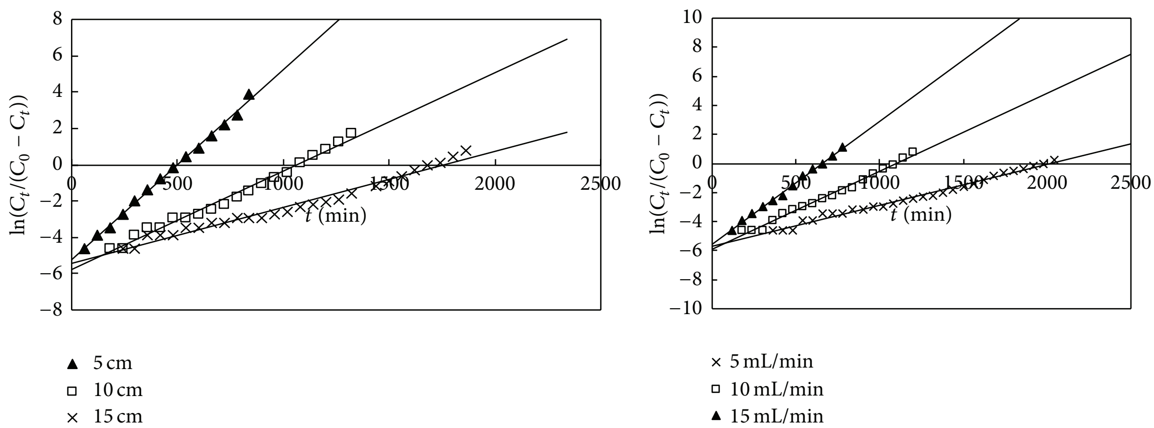
Table 1: Yoon-Nelson model parameters for fixed bed adsorption of phosphate in column filled with nanosized FeOOH-modified anion resin.

Q (mL/min)	Z (Cm)	C_0 (mg/L)	k_{YN} (min^{-1})	τ_{theo} (min)	τ_{exp} (min)	R^2
5	10	20	0.0028	2030.4	1980	0.9883
10	10	20	0.0053	1109.8	1140	0.9899
15	10	20	0.0084	659.7	660	0.9972
10	5	20	0.0105	498.0	540	0.9976
10	10	20	0.0054	1069.8	1080	0.9873
10	15	20	0.0031	1745.8	1680	0.9752

increased from 0.028 to 0.0084 min^{-1} (Figure 4(b) and Table 1). Accordingly, the value of τ decreased from 2030.4 to 659.7 min. The theoretical breakthrough time τ_{theo} required for 50% adsorbate breakthrough was very close to the τ_{exp}, which proved that the Yoon-Nelson model fitted well with the experimental data for phosphate adsorption in column filled with nanosized FeOOH-modified anion resin.

4. Conclusion

Continuous adsorption of phosphate from aqueous solution was experimentally and theoretically studied in fixed bed columns filled with nanosized FeOOH-modified anion resin. Both breakthrough time and exhaustion time increased with increase of bed height. In contrast, the breakthrough time decreased from 1320 to 420 min with increase of the flow rate from 5 to 15 mL/min. According to BDST model, the adsorption capacity N_0 was calculated to be 21.4 g/L. Steeper breakthrough curves were observed at lower bed height. It has been observed that Yoon-Nelson model fitted well with experimental data with high correlation coefficient, which proved that Yoon-Nelson model is allows to estimating the breakthrough curves and characteristic parameters of the column.



(a) (b)

FIGURE 4: Yoon-Nelson model for phosphate adsorption in column filled with nanosized FeOOH-modified anion resin at (a) different bed height, and (b) different flow rate.

Acknowledgments

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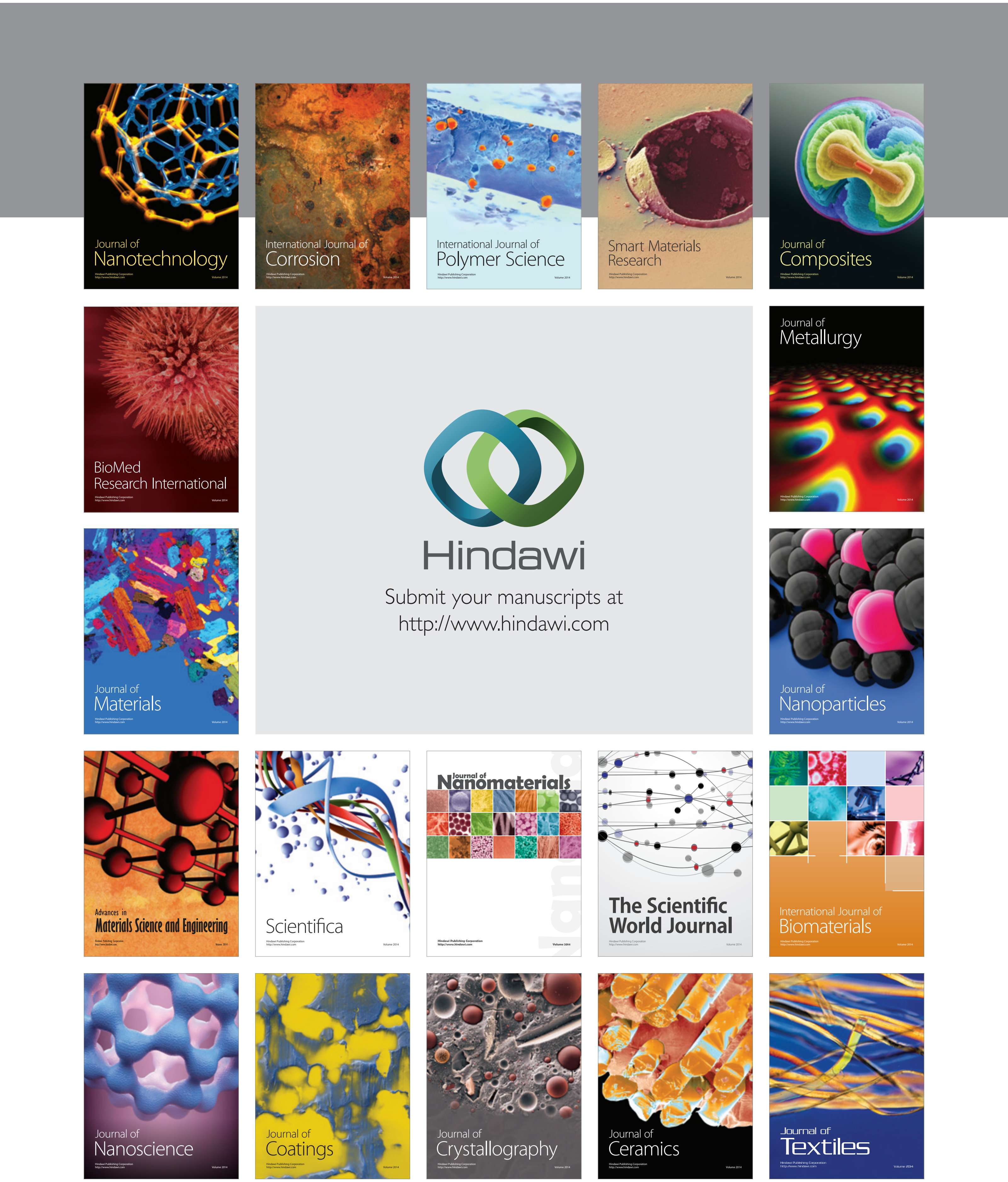
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