Hybrid System of Flocculation—Photocatalysis for the Decolorization of Crystal Violet, Reactive Red X-3B, and Acid Orange II Dye

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ABSTRACT: A hybrid system of flocculation—photocatalysis (HSFP) was applied to evaluate the color removal from simulative dye wastewater. The decolorization performance of HSFP was investigated considering four key factors: flocculant dosage, pH, turbidity, and ionic strength. Compared with flocculation alone, HSFP showed better decolorization effectiveness for simulative Crystal Violet—Reactive Red X-3B dye wastewater (CV-RR) and simulative Crystal Violet—Acid Orange II dye wastewater (CV-AO). The dosage of flocculant was determined by the molecular structure of target dyes. A higher dosage was required for the color removal of dyes with a lower molecular weight and less sulfonic acid groups. The dominant decolorization mechanism was different with different initial pH values of simulative dye wastewater, which influenced the decolorization efficiency of flocculation and photocatalysis. For dyes with a lower molecular weight and less sulfonic acid groups, better decolorization performance was achieved under neutral conditions, mainly depending on strong charge neutralization and adsorption bridging capacity. For dyes with a higher molecular weight and more sulfonic acid groups, decolorization efficiency was improved with an increase in pH, due to stronger deprotonation. An increase of turbidity reduced the dye removal efficiency of flocculation alone and HSFP. The presence of NaCl, CuCl₂, and CrCl₃ led to a different decrease in the flocculation efficiency and photodegradation efficiency.

1. INTRODUCTION
Removing dyes from industrial wastewater is an important and urgent environmental issue. Many industries, such as printing and dyeing, textile, plastic, pulp, and paper, produce dye wastewater. The existence of various and complex dyes not only represents esthetic influence and reduces the transmittance of the water body but also causes health threat. The biochemical oxygen demand/chemical oxygen demand ratio of dye wastewater is usually lower than 0.30. Low biodegradability of dye wastewater is one of the major challenges in removal of dyestuff because of the azo group and aromatic ring exhibiting stable and resistant characteristics. In addition, aromatic amines, such as aniline, toluidine, benzidine, and naphthalene, are possibly produced during the biological degradation process. Therefore, an effective chemical degradation method is significant and imperative for the purpose of discharge or water reuse.

To remove contaminants from dye wastewater, there are many chemical methods to choose, such as flocculation, oxidation, adsorption, photocatalysis, electrochemical methods, and the membrane process. However, complete elimination of dyes from water cannot be achieved by one single method. Flocculation technology is one of the most popular choices for the removal of dye. However, whether inorganic or organic compounds are used as a flocculant, a large amount of refractory degradable sludge will be generated, which requires expensive disposal. Many scholars focus on the synthesis of new materials for the treatment of dye wastewater, such as papermaking sludge-based flocculant and self-floating adsorbent. However, it will take some time for these new agents to be widely used in sewage treatment plants because of the complicated synthesis or expensive production cost. Under the premise of using a traditional coagulant, it is necessary to combine it with other processes to improve the color removal efficiency and reduce the dosage of agents. The photocatalytic method is effective to decolor dye wastewater and degrades complex dyes into nontoxic and harmless byproducts such as carbon dioxide and water. However, photocatalysis has a fatal disadvantage, that is, it is only suitable for the effective treatment of low-concentration dye wastewater. By combining the advantages of these two methods, a hybrid system...
composed of flocculation and photocatalysis is favorable to effectively treat dye wastewater. Low sludge production and high decolorization efficiency are expected. Recent reports indicate that the hybrid system is capable of removing dissolved organic matter and humic substances from river water. The combination of flocculation and photocatalysis is also employed for the treatment of household graywater and dairy industrial wastewater. A few studies investigated the decolorization performance of flocculation combined with photocatalysis.

Considering that colored effluents usually consist of more than one type of dye, simulative dye wastewater solutions were prepared, each solution including two types of dyes. The main objectives of the present study are to (1) investigate the decolorization performance of flocculation alone and in conjunction with photocatalysis; (2) explore the enhancement of the decolorization efficiency using the photocatalytic process as a post-treatment; and (3) analyze the effect of flocculant dosage, pH, turbidity, and ionic strength on flocculation and photocatalysis.

2. RESULTS AND DISCUSSION

2.1. Evaluation of Flocculation Performance for Dye Removal. 2.1.1. Effect of Flocculant Dosage on Dye Removal Efficiency. The decolorization treatment of simulative dye wastewater was initially performed using polyaluminum chloride (PAC) as a flocculant with different dosages. Variations of dye removal efficiency ($R_d$) versus flocculation dosage are presented in Figure 1. The test range of dosage where the highest removal efficiency was obtained. At 240 mg/L dosage, dye removal efficiency was only 26.04% for CV-AO, far less than that for CV-RR. Therefore, a much higher dosage of PAC was added for the treatment of CV-AO. When 1000 mg/L PAC was dosed, the maximum dye removal efficiency (75.61%) was achieved. The results indicated that CV-AO was more difficult to decolor at a low dosage of PAC. This can be explained to be due to different molecular structures of dyes used in this study. It is well known that the decolorization mechanism of PAC mainly includes charge neutralization and adsorption bridging, which are influenced by the molecular structure of the studied dye. Both Acid Orange II dye and Reactive Red X-3B dye were water-soluble, while the former had one sulfonic acid group (−SO$_3$H), less than the latter. The charge neutralization capacity of −SO$_3$H of the Reactive Red X-3B dye and the positively charged polyhydroxy complex in PAC was thereby much stronger than that of Acid Orange II dye. In addition, better adsorption bridging performance was observed in treating the Reactive Red X-3B dye, due to its higher molecular weight. Consequently, CV-RR was removed more easily than CV-AO at a low dosage of PAC. In other words, the dosage cost of CV-RR was lower than that of CV-AO.

2.1.2. Effect of pH on Dye Removal Efficiency. Flocculation performance of PAC was often affected by pH for the treatment of various industrial wastewater samples, including textile dyeing wastewater and dairy wastewater. In this study, the effect of pH on dye removal efficiency was investigated in treating simulative dye wastewater under acidic, neutral, and alkaline conditions. The dye removal efficiency ($R_d$) of PAC as a function of pH is illustrated in Figure 2. To evaluate the influence of different pH values on dye removal efficiency, the following experiments were carried out under the condition of the respective optimum dosage. There was a significant variation in dye removal efficiency for the removal of CV-RR and CV-AO. Within a pH range of 3–13, dye removal efficiency remained almost constant for the treatment of CV-RR. Until pH was higher than 10, the decolorization efficiency for CV-RR increased slightly with the increase of pH. In contrast, less dye was removed from CV-AO within the test range of pH. When pH was lower than 7, decolorization efficiency for CV-AO increased rapidly as pH increased. When pH was between 7 and 10, dye removal from CV-AO decreased marginally and then declined sharply after pH was higher than 10. In conclusion, the optimum initial pH values were 7 and 12 for the flocculation of CV-AO and CV-RR, respectively. Accordingly, the maximum dye removal efficiency
reached 77.27 and 90.78% for CV-AO and CV-RR, respectively. 

As indicated in Figure 2, the dye removal efficiency for CV-RR was always higher than that for CV-AO; nevertheless, their changing trends were similar within a pH range of 6–9. It should be pointed out that the initial pH of CV-AO exhibited an important influence on the dye removal efficiency of PAC, especially under acidic and alkaline conditions. PAC showed relatively stable decolorization performance for CV-RR under acidic, neutral, and alkaline conditions. The pH of the hydrolyzate of PAC was closely related to the initial pH of dye wastewater; therefore, the decolorization capacity of PAC fluctuated with pH. The dominant decolorization mechanism was variable in different situations. With pH lower than 5, charge neutralization was dominant for dye removal, which occurred mainly between positively charged hydrolyzates (Al₅(OH)(3n−m)SO₃−) and −SO₃−. The Reactive Red X-3B dye with two sulfonic acid groups was easier to absorb and destabilize, leading to the formation and growth of flocs. With a pH range of 6–9, primary hydrolyzates included positively charged polymer and Al(OH)₃ precipitation, which showed strong charge neutralization and adsorption bridging capacity due to their large adsorption area and low solubility. With a pH higher than 10, positively charged hydrolyzates were converted to negatively charged dissolved substance Al(OH)₃. At this time, dye removal principally depended on adsorption bridging of PAC. The Reactive Red X-3B dye with a higher molecular weight was easier to absorb and destabilize. In comparison with CV-AO, PAC demonstrated better decolorization performance for CV-RR with a wide range of pH.

2.1.3. Effect of Turbidity on Dye Removal Efficiency. A high concentration of suspended solids (SSs) was one of the typical characteristics of textile dye effluents. In this research, the content of SSs in simulated dye wastewater was characterized by turbidity. To investigate the effect of turbidity on decolorization efficiency, different concentrations of humic acid were applied to adjust the turbidity of simulative dye wastewater. Flocculation experiments were carried out at the optimum pH of each simulative dye wastewater. The variations of dye removal efficiency (Rₜ) with the percentage increase in turbidity for CV-RR and CV-AO are illustrated in Figure 3.

By increasing the initial turbidity of test water, dye removal efficiency reduced significantly. The increase of initial turbidity led to a dramatic increase in the number of colloidal particles, and thus active adsorption sites on the surface of colloidal particles increased. With the addition of a cationic flocculant, negatively charged colloidal particles immediately bonded to positively charged particles through adsorptive charge neutralization. Consequently, these stable particles were connected together to form compact flocs by adsorption bridging. Finally, the removal of contaminants was achieved by floc settling. During the flocculation process, a part of the positive charge on the surface of the cationic flocculant was occupied by initial turbidity. High turbidity removal was reported using coagulants to treat industrial dye wastewater. Therefore, the amount of positive charge for adsorbing dye molecules decreased greatly. Due to the competition effect of initial turbidity, dye removal efficiency decreased with the increase of initial turbidity. The higher the initial turbidity, the more significant the reduction. The results suggested that the turbidity of CV-RR and CV-AO played an important role in the decolorization performance of PAC.

2.1.4. Effect of Ionic Strength on Dye Removal Efficiency. High salinity was another typical characteristic of textile dye effluents. NaCl, CuCl₂, and CrCl₃ were chosen to adjust the ionic strength of simulative dye wastewater at the optimum pH and flocculant dosage. The effect of ionic strength on the flocculation efficiency of PAC is presented in Figure 4. It was observed that dye removal efficiency varied marginally as the NaCl concentration increased from 0 to 1100 mg/L, for both CV-RR and CV-AO. The presence of NaCl had an influence on the decolorization performance of PAC. When CuCl₂ was chosen as the interfering salt, different experimental results were obtained. Dye removal efficiency decreased progressively as the ionic concentration increased. Especially for CV-AO, dye removal efficiency reduced from 77.18 to 43.9%, with CuCl₂ concentration increasing to 300 mg/L. When CrCl₃ was used, there were more obvious inhibitory effects on decolorization efficiency. The reduction of dye removal efficiency was observed in the following order: CrCl₃ > CuCl₂ > NaCl. The existence of highly positively charged ions was harmful to the decolorization of dye wastewater by flocculation. Similar experimental phenomena occurred in the presence of CuCl₂ and CrCl₃ for the color removal of an anionic dye. At the same molar concentration, the number of anions in CuCl₂ and CrCl₃ was higher, thus the interaction with the cationic flocculant was stronger, which formed a competitive relationship with the anionic dye. The charge neutralization between test dyes and PAC was weakened due to the presence of CuCl₂ and CrCl₃. At this moment, nonelectrostatic interactions between flocculant and dye molecules were dominant, including van der Waals forces and hydrogen bonds. The possible reason was that the anions in salts neutralized the positive sites of PAC.

Contrary to the results observed for Acid Orange 7, NaCl did not compete with CV-RR and CV-AO for active sites of the flocculant. Therefore, decolorization efficiency was not reduced but slightly improved. It is possible that Na⁺ had a positive contribution to adsorption bridging and sweeping abilities of PAC, thereby forming more dense flocs. On the other hand, the presence of Na⁺ and Cl⁻ suppressed dye ionization, leading to the transformation from the dissolved state (−SO₃− sulfonic acid group) to a colloidal state. Colloidal particles maintain a stable dispersion state in water. After the addition of PAC, colloidal particles were strongly adsorbed by the polymer with a linear structure. Moreover, polymers could adsorb colloidal particles from both ends, consequently forming large flocs. Finally, flocs were removed from water by precipitation. The results
indicated that the ionic strength of simulative dye wastewater showed different influences on the decolorization efficiency of PAC, depending on the nature of interfering salts.

2.2. Evaluation of Flocculation–Photocatalysis Performance for Dye Removal. All dye components in CV-RR and CV-AO were not completely eliminated by flocculation alone, and merely partial decolorization was achieved. For example, the dye removal efficiency of CV-AO was 77.27% at the optimum pH and flocculant dosage. Taking into account the initial concentration of the simulative dye wastewater and decolorization rate, the residual dye concentration was calculated to be 114 mg/L. It is necessary to apply a secondary wastewater treatment for decolorization. Photocatalysis was performed after the primary treatment of flocculation with the optimum dosage of PAC. The following study focused on how much increase in decolorization effectiveness could be achieved by the hybrid system of flocculation–photocatalysis.

2.2.1. Effect of pH on Dye Removal Efficiency. Photocatalytic degradation of the flocculation supernatant was conducted with different pH values ranging from 3 to 13. Variations of dye removal efficiency ($R_d$) versus illumination time are presented in Figure 5, and the effect of pH on photocatalytic degradation efficiency was analyzed. It is obvious that dye removal efficiency gradually increased with an increase in illumination time. For the photocatalytic degradation of CV-RR, the increase of pH resulted in the improvement in dye removal efficiency. Especially, at a pH of 13, 85.47% of dye removal efficiency was achieved after 20 min of photocatalysis. With illumination time up to 120 min, dye removal efficiency was further improved to 97.25%. The changing trends were similar to the effect of pH on flocculation (Figure 2). Decolorization performance was greatly improved under the condition of high alkalinity. With regard to CV-AO, a neutral environment was not only suitable for flocculation decolorization but also promoting photocatalytic degradation. Under highly acidic or alkaline conditions, dye removal efficiency was enhanced insignificantly even with prolonged illumination time. When pH was 7, 45.38 and 61.74% of dye removal efficiencies were obtained after 20 and 120 min of photocatalysis, respectively.

The results indicated that pH had a conspicuous impact on the photocatalytic degradation of different dyes. One of the possible reasons was that the surface charge of dye molecules changed as a consequence of pH variation.30 The deprotonated state of dye molecules was dominant when pH was higher. Based on the composition amount of simulative dye wastewater, it is calculated that the molar ratio of $\text{−SO}_3^−$ in CV-RR was higher, resulting in much stronger deprotonation at higher pH. The solubility of dye molecules in CV-RR increased accordingly. Dye degradation was related to the generation of $\cdot\text{OH}$ and $\cdot\text{O}_2^−$ radicals, which was dependent on the absorption of UV light by TiO$_2$.31 Through the oxidation reaction with radicals, chromogenic groups (such as $\text{−NSN−}$ and $\text{−CHSCH−}$) in dyes were broken, resulting in higher color...
removal efficiency for CV-RR. It is confirmed that the molecular structure is related to the photocatalytic degradation of dye.\textsuperscript{32} The molar ratio of $\text{SO}_3^-$ to aromatic rings in the dye was larger, and photocatalytic degradation efficiency was higher. For this reason, better decolorization performance was achieved for photocatalytic degradation of CV-RR, under the same conditions as for CV-AO. In brief, the effect of pH on decolorization performance was consistent in both flocculation and photocatalytic processes.

According to eq 3, the highest dye removal efficiency ($R$) of the hybrid system was 99.31% for CV-RR, which was obtained at 240 mg/L PAC, pH 13, and 120 min of irradiation. For the treatment of CV-AO, the maximum dye removal efficiency ($R$) calculated was 90.67%, and the operational parameters of the hybrid system were 1000 mg/L PAC, pH 7, and 120 min of irradiation. Above 90% of dye was eliminated owing to the coupling interaction between flocculation and photocatalysis, and almost total elimination was achieved for CV-RR.
2.2.2. Effect of Turbidity on Dye Removal Efficiency. To explore the influence of turbidity on decolorization performance of the photocatalytic process, dye removal efficiency (R2) at varied turbidity (calculated by a percentage increase in turbidity), keeping pH and PAC dosage fixed, is shown in Figure 6. Photocatalytic degradation efficiency decreased dramatically as turbidity increased. When the turbidity of CV-RR increased by 200%, the reduction percentage of dye removal efficiency was 41.17% after 120 min of photocatalysis. As for CV-AO, turbidity had similarly negative effects on photocatalytic degradation. The dye removal efficiency of CV-AO sharply decreased by 43.92% after 120 min of photocatalysis, while turbidity was doubled. Moreover, when the turbidity increase rate was more than 250%, photocatalytic degradation efficiency did not rise but fell for the treatment of CV-RR, where R2 turned negative. The results demonstrated that the photocatalytic process was not suitable for the decolorization of high-turbidity wastewater. Maintaining transparency was conducive to photocatalytic degradation of dye wastewater. In general, the presence of inorganic, organic, and colloidal substances leads to an increase in turbidity of wastewater. These impurities absorbed a large part of UV radiation, which inhibited the optically induced reaction of TiO2. Furthermore, competition may occur between dye molecules and interferents for the photocatalytic sites of TiO2. As a result, turbidity exhibited an evident harmful impact on photocatalytic degradation of CV-RR and CV-AO.

2.2.3. Effect of Ionic Strength on Dye Removal Efficiency. The adsorption and degradation of dyes by photocatalysis not only depend on pH and turbidity but also on ion strength.33 By adding different concentrations of NaCl, CuCl2, and CrCl3, the impact of ionic strength on photocatalytic degradation was assessed, as indicated in Figures 7–9. The flocculation process, followed by photocatalysis, was carried out at respective optimum values of pH and PAC dosage.

Apparent declines were observed in dye removal efficiency (R2) for the treatment of simulative dye wastewater, particularly for CV-RR. With a progressive increase in NaCl concentration, photocatalytic degradation performance deteriorated. After 120 min of irradiation, the dye removal efficiency of CV-RR reduced by 9.11, 23.01, 25.56, 31.25, 34.45, and 34.92% at NaCl concentrations of 100, 300, 500, 700, 900, and 1100 mg/L, respectively. With regard to CV-AO, ionic strength revealed similarly negative effects on photocatalytic degradation. The maximum reduction (33.93%) took place when CV-AO was exposed to UV light for 120 min at a NaCl concentration of 1100 mg/L. These results indicated that photocatalytic efficiency decreased continuously with an increase in the NaCl concentration of solutions. Although dye removal efficiency was slightly improved, the increased amplitude was greatly reduced. Similar results were observed when CuCl2 and CrCl3 were added. Moreover, dye removal efficiency (R2) decreased more significantly. For the treatment of CV-RR, the presence of CrCl3 led to R2 becoming negative. After photocatalytic degradation, decolorization efficiency was not improved, but offset a part of flocculation efficiency, resulting in a decrease in the decolorization efficiency of HSFP. The negative effect of salts on dye removal efficiency varied in the following sequence: NaCl < CuCl2 < CrCl3.

Based on the generation of highly active electrons (e−) and holes (h+), *H and *OH radicals were induced, and dye molecules were oxidized during the photocatalytic process. Supposing that one of the reactions was disturbed, the ultimate oxidation of free radicals would be limited greatly. The presence of interfering ions may result in the inactivity of electron–hole pairs, thus reducing the formation of free radicals. On the other hand, adsorption competition on the surface of TiO2 perhaps occurred between inorganic ions and dyes.34 Another possible reason was that the viscosity of simulative dye wastewater increased with increasing salt concentration. Therefore, the mass transfer rate of dyes to the TiO2 surface slowed down, which also led to a decrease in photocatalytic degradation efficiency.

3. CONCLUSIONS
HSFP with a designed bubbling fluidized bed photocatalytic reactor (BFBPR) was applied to remove the dye, considering four key factors: flocculant dosage, pH, turbidity, and ionic strength. The main conclusions were as follows.

The dye molecular structure was an important factor influencing the flocculant dosage. The optimum flocculant dosage was much lower for the treatment of CV-RR because the target dye molecule has higher molecular weight and more sulfonic acid groups. The effect of pH on decolorization performance was also closely related to the structure of dye molecules. The highly alkaline condition was conducive to improve flocculation and photodegradation efficiency for the decolorization of dye with higher molecular weight and more sulfonic acid groups. Better decolorization performance was attributed to stronger charge neutralization and adsorption.
bridging interactions between the flocculant and dye. As for CV-AO with lower molecular weight and less sulfonic acid groups, a neutral environment was favorable for decolorization due to high photodegradation efficiency. Therefore, it is necessary to adjust the initial pH of raw water according to the target dye. Flocculation combined with photocatalysis was effective to further reduce dye concentration. However, the negative effect of turbidity was significant in treating CV-RR and CV-AO by flocculation or HSFP. The presence of interfering ions was detrimental to dye removal. Therefore, it is important to rationally control the turbidity and ionic strength of target wastewater by HSFP.

4. MATERIALS AND METHODS

4.1. Test Water. Azo and triarylmethane dyes are two types of dyes widely used in the printing and dyeing industry. To investigate the relationship between the molecular structure and decolorization performance, Crystal Violet dye containing aromatic rings and chromogenic groups was chosen as a representative of the triarylmethane dye in this research. Reactive Red X-3B and Acid Orange II dyes were selected as representatives of azo dye in this study, with different molecular weights and different amounts of sulfonic acid groups. All of the dyes were purchased from Nanjing Duly Biotechnology Company (Jiangsu, China), and the corresponding chemical structural formula is presented in Figure 10. Simulative Crystal Violet–Reactive Red X-3B dye wastewater (CV-RR) was prepared by dissolving 0.25 g of Crystal Violet dye and 0.25 g of Reactive Red X-3B dye in 1 L of tap water. Simulative Crystal Violet–Acid Orange II dye wastewater (CV-AO) was prepared by dissolving 0.25 g of Crystal Violet dye and 0.25 g of Acid Orange II dye in 1 L tap water. The maximum absorption wavelength ($\lambda_{\text{max}}$) was determined using a T9-UV spectrophotometer (Beijing Persee General Instrument Co., Ltd., China). Relevant parameters of test water are shown in Table 1.

4.2. Hybrid System of Flocculation–Photocatalysis (HSFP). The hybrid system consisted of flocculation and photocatalysis for the color removal of test dye wastewater. The flocculation process was carried out with an HJ-6 stirrer (Jiangsu Kexi Instrument Co., Ltd., China). The flocculant was provided by Shandong Zhongke Tianze Water Purification Material Co., Ltd., China and prepared with a solution of 10% (w/w) polyaluminum chloride (PAC). The effective aluminum content of PAC was 28% (measured by Al2O3), with 75% of basicity. With the addition of PAC, flocculation experiments were performed through a jar test that was composed of three procedures. First, a rapid mixing was conducted for 0.5 min at 150 rpm, followed by a slow mixing for 15 min at 50 rpm. The final settling process was maintained for 30 min. The absorbance value of the supernatant after flocculation was denoted $A_i$.

After the pretreatment of flocculation, the supernatant of simulative dye wastewater was transferred to a designed bubbling fluidized bed photocatalytic reactor (BFBPR). Photocatalytic experiments were carried out using TiO2 as a photocatalyst, lasting for 2 h in UV light. TiO2 with a purity of 99.80%, band gap value of 3.2 eV, surface area of 50 m2/g, and particle size of 21 nm was purchased from Shanghai Macklin Biochemical Co., Ltd., China. During the photocatalytic process, samples were taken to determine the absorbance of the supernatant after photocatalysis was denoted $A_0$.

To monitor the degradation progress, UV-visible spectrophotometry (T6, Beijing Persee General Instrument Co., Ltd., China) was used to determine the absorbance of the supernatant at 5 minutes intervals to get the relationship between absorbance and concentration of dye wastewater. Simulative dye wastewater was adjusted to pH 2.0 by 0.10 M HCl and 0.10 M NaOH and then analyzed by a pH meter. The turbidity of simulative dye wastewater was adjusted by adding humic acid and quantified with a turbidity meter (WGZ-200/2000, Shanghai INESA Physico-Optical Instrument Co., Ltd., China). The ionic strength of simulative dye wastewater was expressed in terms of NaCl concentration.

Dye removal efficiency $R_1$ (%) of flocculation was calculated by eq 1 as follows

$$R_1 = \frac{A_0 - A_i}{A_0} \times 100 \quad (1)$$

Dye removal efficiency $R_2$ (%) of photocatalysis was calculated by eq 2 as follows

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Notes
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