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Effect of dosing method on color removal performance and flocculation dynamics of polyferric-organic polymer dual-coagulant in synthetic dyeing solution

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ABSTRACT

Three inorganic–organic dual-coagulants were comparatively evaluated in terms of color removal, zeta potential and flocculation dynamics in treating simulative reactive and disperse dyeing wastewater. The flocculation kinetics, including floc growth rate, floc size and floc size difference in the steady-state phase, was investigated using photometric dispersion analyzer (PDA). The first dual-coagulant PFC–PDADMAC was prepared by premixing polyferric chloride (PFC) and polydimethyldiallylammonium chloride (PDAD-MAC) before dosing. The other two were achieved by dosing PFC and PDADMAC in different order. Results indicated that PFC–PDADMAC gave higher color removal efficiency, stronger entrapment and bridging ability, higher floc growth rate, larger floc size and wider range of floc size distribution in treating Reactive Yellow K-4G. 60.2% color removal was obtained by PFC–PDADMAC at a dosage of 30 mg/L. For the removal of Disperse Yellow RGFL, three dual-coagulants gave similar color removal rate, coagulation–flocculation mechanism, floc growth rate, floc size and floc size distribution. The maximal color removal (95.5%) was obtained by PFC–PDADMAC at a dosage of 30 mg/L.

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1. Introduction

Dyeing water is characterized by high color, large amount of suspended solids and high chemical oxygen demand (COD), and thus the release of dyeing wastewater from industries of textile dyeing and printing has caused severe water pollution problems. In addition, the synthetic dye compounds usually have very complex structure and poor biodegradability, and thus they are difficult to decolorize by conventional biological treatments [1].

Coagulation–flocculation is widely employed in dyeing wastewater treatment process [2], and it has been proved effective in removing dye compounds, especially dissolvable dyes in wastewater [3]. In coagulation–flocculation process, the coagulants applied play an important role in the removal of target pollutants. Conventional aluminum and ferric-based salts, such as polyaluminum chloride (PAC) and polyferric chloride (PFC), are widely used in practice. However, high dosages are required and large volume of sludge is usually produced when coagulating with metal coagulants in dyeing wastewater treatment. The high cost of sludge disposal is a main drawback of conventional metal coagulants. Synthetic polymers, such as polydimethyldiallylammonium chloride (PDADMAC), have long been used as primary coagulants or flocculant aids in wastewater treatment. Compared with metal coagulants, the superior performance of PDADMAC is manifested in their wider working pH range and the lower dosage required when the equivalent treatment efficiency is obtained. It has been reported that PDADMAC achieved super color removal performance in treating disperse and reactive dye solution [4]. However, the high cost limited its application in wastewater treatment. In order to achieve better coagulation-flocculation performance and better floc characteristics in terms of size, strength, settleability and filterability, the metal coagulants were usually used in combination with organic coagulant [5,6]. In principle, composing cationic inorganic flocculants with cationic organic flocculants should be more effective in dealing with negatively charged contamination, such as clay, dye and humic acid [7]. In addition, considerable savings on coagulant dose of conventional metal coagulants can also be achieved by inorganic-organic dual-coagulants for the same removal performance [8].

The removal of reactive and disperse dyes by regular coagulation–flocculation has been studied by some researchers [9–13]. In general, organic polymers are used as coagulant aids after the addition of inorganic coagulants [14]. However, for the specific purpose of comprehensive examining the coagulation–flocculation behavior of the inorganic–organic polymer dual-coagulants in coagulation–flocculation process, few researchers focused on another two dual-coagulants: (1) inorganic and organic coagulants were premixed before dosing; (2) inorganic coagulant was

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dosed after the addition of organic coagulant. In this study, PFC and PDADMAC were selected as inorganic and organic coagulants, respectively. In order to examine the effect of dosing method on color removal, coagulation-flocculation mechanism and flocculation dynamics of the PFC/PDADMAC dual-coagulant, three PFC/PDADMAC dual-coagulants mentioned above were comparatively investigated in treating simulative reactive and disperse dyeing wastewater. The flocculation dynamics monitoring technology, photometric dispersion analyzer (PDA), was adopted to observe the floc aggregation processes in this study. Gregory was the first researcher to introduce PDA in monitoring the state of aggregation of floc [15], and increasing researchers adopted the optical technique to describe the dynamics of flocculation in recent years [16-20]. However, few investigators focused on the effect of dosing method on floc aggregation process of dual-coagulants in dyeing wastewater treatment. Consequently, flocculation dynamics of the three PFC/PDADMAC dual-coagulant were also comparatively investigated in terms of floc growth rate, floc size and floc size difference in this study.

2. Materials and methods

2.1. Dye compounds and test waters

The two most commonly used dyestuffs in textile industry are reactive and dispersed dyes. One dye from each group, Reactive Yellow K-4G (R.Y. K-4G) and Disperse Yellow RGFL (D.Y. RGFL), were chosen to be investigated. It was hoped that the use of pure dye solutions would make it possible to obtain information about the color removal efficiency of coagulants for different types of dyes. The dyes were obtained from Changmai Dye Co. Ltd., Shandong, China. The synthetic dye solution was prepared by dissolving 0.10 g of dye powder and 1.00 g NaCl in 1.0 L deionized water with 3 h of continuous stirring, and the dye concentration in this solution is close to that in actual dyeing wastewater. The characteristic wavelength for each simulated dye water was determined by running a scan of the dye solution on a spectrophotometer (UV-754, Precision Scientific Instrument Co. Ltd., Shanghai, China). The maximum absorbance wavelength (λ_{max}) (after filtering through a 0.45 mm membrane) was used for all absorbance readings. Because the relationship between absorbance value at λ_{max} and dye concentration is linear, constituting a basis of conversion of absorbance value at λ_{max} data to an "equivalent" dye concentration, percentage of color removal was calculated by comparing the absorbance values for the treated wastewater to the absorbance value for the original dye wastewater. Distilled water served as a reference. The name, type, molecular structure and the λ_{max} of the dyes selected for this study and the maximum absorbance of original dye solution are shown in Table 1. It is known that dyeing wastewater are usually characteristically basic, and thus the pH of dye solutions were controlled

Table 1

Dye characteristics.

at around 8.0 by 0.1 mol/L HCl and 0.1 mol/L NaOH solutions for all subsequent experiments.

2.2. Coagulants

PFC was prepared with FeCl₃·6H₂O (A.R.) and Na₂CO₃ (A.R.). Firstly, FeCl₃ solution of 7% (w/w) as Fe was prepared by dissolving FeCl₃·6H₂O (A.R.) in distilled water. Then, Na₂CO₃ powder was gradually added to FeCl₃ solutions by stirring at room temperature to reach the final [OH⁻]/[Fe] ratio to 0.5 (The results obtained in previous jar test has indicated that PFC with B value 0.5 achieved better color removal performance than those with B value 0 (FeCl₃), 1.0 and 1.5 for the removal of both R.Y. K-4G and D.Y. RGFL). The mixture was stirred until foam disappeared. Subsequently, Na₂HPO₄ (A.R.) was added to the PFC solution as a stabilizer ([Na₂HPO₄]/[Fe]=0.08). The concentration of Fe was about 7% (w/w) in the final PFC solution.

The cationic polymer PDADMAC (40%, w/w aqueous solution, 100% charge density, intrinsic viscosity was 1.02 dL/g, provided by manufacturer) was obtained from Bin Zhou Chemical Co., Shandong, China.

The first dual-coagulant was achieved by dosing PFC at the start of rapid mixing period and then followed by PDADMAC. This dualcoagulant was referred as PFC + PDADMAC. For a 2 min rapid mixing, PFC was added first, after 1 min of rapid mixing, PDADMAC was added, and rapid mixing continued for an additional 1 min. The second dual-coagulant, referred as PDADMAC+PFC, began with the addition of PDADMAC. After 1 min of rapid mixing period had passed, the PFC was added, and then rapid mixing continued for the remaining 1 min. The third dual-coagulant, denoted as PFC-PDADMAC, was a novel composite coagulant. It was prepared by injecting a measured amount of PDADMAC into the PFC solution and stirring thoroughly until it was absolutely mixed with the solution. The mass ratio of Fe and PDADMAC is 1:1 in all three dualcoagulants in this investigation, which is based on comprehensive consideration of coagulants cost and coagulation-flocculation performance. The dosages of PFC and all three dual-coagulants were calculated as mg/L of Fe for convenience.

2.3. Jar tests and on-line optical determination of floc aggregation process

Standard jar tests were conducted at room temperature $(20 \pm 1 \circ C)$. 1.5 L beakers, containing 1000 mL of dyeing waster, were placed on a jar test apparatus (ZR4-6, Zhongrun Water Industry Technology Development Co. Ltd., China). During the rapid stir phase (200 rpm), a measured amount of coagulant was pipetted into the water sample (1.0 L) to give a certain Fe or PDAD-MAC concentration. The water samples were stirred rapidly at 200 rpm (G = 102.5 s⁻¹) for 2 min after dosing, and mixed slowly





Fig. 1. Typical ratio curve as a function of coagulation time.

at 40 rpm ($G = 11.8 \text{ s}^{-1}$) for 10 min, and then settled for 15 min. PFC and dual-coagulants dosages ranged from 5 to 30 mg/L as Fe. PDADMAC dosages ranged from 5 to 30 mg/L. Throughout the coagulation–flocculation periods, the suspension was continuously sampled by peristaltic pump (LEAD-1, Baoding Longer Precision Pump Co., Ltd., China) and monitored by a photometric dispersion analyzer (PDA2000; Rank Brothers Ltd.) to obtain data. After settling, the supernatant was pipetted from about 25 mm below the water surface and a filtered supernatant through a 0.45 μ m glass fiber membrane was tested for absorbance and zeta potential. The absorbance of the liquid was measured by UV-754 spectrophotometer. The zeta potential was measured with Zetasizer 3000HSa (Malvern Instruments, UK).

In this study, three pertinent calculations were performed to analyze the data collected by PDA2000 during the coagulation-flocculation process. These theoretical calculations included the slope of the initial growth region, a time-weighted average steady-state ratio value, and a time-weighted relative standard deviation (R.S.D.) of the steady-state ratio value. A brief description is given here of the widely used photometric dispersion analyzer for the determination of floc aggregation process. Details in the theory of PDA and these theoretical calculations have been reported in a few literatures [21-23]. Fig. 1 shows the PDA monitor responses collected at every 1 s. The ratio value was plotted as a function of coagulation-flocculation time. The entire floc aggregation process including three phases: lag phase, floc growth phase and steady-state phase. The slope of the linear initial growth region indicated the rate at which flocs developed. Similar methods have been used to analyze aggregation rates by Ching et al. [22]. A best-fit line was constructed for the approximate linear growth region of the ratio curve (Fig. 1). From the best-fit line, the floc growth rate was determined as

$$floc growth rate = \frac{\Delta ratio}{\Delta time}$$
(1)

In this work, the time-weighted average steady-state ratio value was referred as "Flocculation Index" (FI) for the sake of illustration and discussion, which is strongly correlated with floc size and always increases as flocs grow larger [23]. The FI value was computed as

$$FI = \frac{\sum_{i=1}^{N} (ratio_i \cdot time_i)}{\sum_{i=1}^{N} time_i}$$
(2)

In this research, the time-weighted R.S.D. of the steady-state ratio value was used to provide a measure of floc size differences. The ratio variance was computed using data from the final steadystate portion of the ratio curve in Fig. 1. It was thought that a smaller variance signified a tighter floc size distribution and an indication of a more homogeneous, dense, and less porous floc structure [19]. The time-weighted variance was calculated as

variance =
$$\frac{\sqrt{\frac{\sum_{i=1}^{N} [(ratio_i - \overline{ratio})^2 \cdot time_i]}{\sum_{i=1}^{N} time_i}}}{\frac{1}{\overline{ratio}} \times 100$$
(3)

3. Results and discussion

3.1. Comparison of color removal efficiency and coagulation–flocculation mechanism

The coagulation–flocculation performance and mechanism of PFC, PDADMAC, PFC+PDADMAC, PDADMAC+PFC and PFC–PDADMAC were comparatively investigated in this study. The color removal efficiencies of them in treating R.Y. K-4G and D.Y. RGFL were shown in Figs. 2 and 3, respectively. It can be seen that the color removal rate given by dual-coagulants increased with the increase of coagulant dosage. For R.Y. K-4G, both PFC and



Fig. 2. Removal of R.Y. K-4G as a function of coagulant dose.



Fig. 3. Removal of D.Y. RGFL as a function of coagulant dose.



Fig. 4. Zeta potentials of coagulated material as a function of coagulant dose in the removal of R.Y. K-4G.

PDADMAC gave poor color removal results within the dosage range investigated. In the treatment of D.Y. RGFL, no observable flocs were formed at dosage 10 mg/L and below when PFC was used alone. Similarly, PDADMAC did not work when the dosage was less than 20 mg/L. The zeta potential as a function of coagulant dose for the removal of R.Y. K-4G and D.Y. RGFL were shown in Figs. 4 and 5, respectively. It can be seen that PDADMAC gave much higher zeta potential and thus much stronger charge neutralization than PFC for the removal of R.Y. K-4G and D.Y. RGFL. Compared with PFC. PDADMAC performed better by stronger charge neutralization for the R.Y. K-4G removal. In the treatment of D.Y. RGFL, however, PFC gave higher color removal efficiency although its charge neutralization is very weak. This is because the efficiency of dye removal greatly depends on the solubility and chemical structures of the dyes as well as the characteristic of the coagulant. The R.Y. K-4G contains—SO₃⁻ groups, which are negatively charged when dissolved in water. The electrostatic repulsion between negative charges on different molecules enhances the solubility of dyes. The high positively charged PDADMAC could effectively neutralize the negative charge on R.Y. K-4G molecule and lead to the formation of insoluble complex. Consequently, charge neutralization is the dominant mechanism for the removal of R.Y. K-4G. In contrast, the D.Y. RGFL investigated in this study has many -NH- and aromatic



Fig. 5. Zeta potentials of coagulated material as a function of coagulant dose in the removal of D.Y. RGFL.



Fig. 6. Floc growth rate as a function of coagulant dose in the removal of R.Y. K-4G.

groups, which are prone to be adsorbed by $Fe(OH)_x$ particles [11]. As a result, bridging and entrapment is dominant mechanism of PFC for the removal of D.Y. RGFL.

Compared with PFC and PDADMAC, the color removal efficiency and zeta potential significantly increased when PFC was used in combination with PDADMAC. For the three dual-coagulants investigated, the order of dye removal and zeta potential were different in the treatment of two dyes. In the case of R.Y. K-4G, the color removal efficiency and zeta potential of the dual-coagulants (Figs. 2 and 4) increased gently with the increase of dosage. The order of color removal was PFC-PDADMAC>PDADMAC+PFC>PFC+PDADMAC, but the zeta potential were in the following order: PDAD-MAC + PFC > PFC-PDADMAC > PFC + PDADMAC. As discussed above, charge neutralization is the dominant mechanism for the removal of R.Y. K-4G, while PFC-PDADMAC outperformed the other two dualcoagulants in color removal in this instance but gave lower zeta potential than PDADMAC + PFC. It can be concluded that adsorbing and entrapment also played an important role when coagulating with PFC-PDADMAC. Compared with the R.Y. K-4G removal, the difference of three dual-coagulants in color removal were narrowed in treating D.Y. RGFL. As is shown in Fig. 3, the D.Y. RGFL removal curves associated with different coagulants exhibited similar changing trends with the increase of coagulant dosage: rapid increase within low dosage range, then followed by a gentle increase with dosage, and almost 100% removal was obtained at high dosage. Likewise, similar zeta potential were also obtained by three dual-coagulants in the case of R.Y. K-4G removal. The zeta potential of PFC+PDADMAC was slightly higher than the other two dual-coagulants. It is noted that the zeta potential of PFC + PDADMAC shifted into the positive region when the dose was larger than 20 mg/L, which resulted in the particle restabilization and thus the decrease in color removal. The above phenomenon is attributed to strong charge neutralization of PDADMAC. In addition, it has been discussed that bridging and entrapment is the dominant mechanism of PFC for the removal of D.Y. RGFL. Consequently, D.Y. RGFL was removed by the co-effect of charge neutralization, bridging and entrapment when coagulating with dual-coagulants.

3.2. Comparison of floc growth rate

The floc growth rate of the three dual-coagulants as a function of coagulant dosage in the treatment of R.Y. K-4G and D.Y. RGFL were shown in Figs. 6 and 7, respectively. It can be see that the floc growth rate increased as the increase of dosage for all three dual-coagulants, and the orders of floc growth



Fig. 7. Floc growth rate as a function of coagulant dose in the removal of D.Y. RGFL.

rates were different in the treatment two dyes. For R.Y. K-4G (Fig. 6), the floc growth rates were in the following order: PFC–PDADMAC > PDADMAC + PFC > PFC + PDADMAC, which is consistent with the order of color removal. In the treatment of D.Y. RGFL (Fig. 7), the impact of addition sequence on floc growth rate was very slight. Three dual-coagulants gave similar floc growth rate within the dosage range 5–20 mg/L. PFC + PDADMAC gave a much smaller floc growth rate than other two dual-coagulants at the dosage 20 mg/L and above, which corresponded with the drop in color removal in Fig. 3.

Because PFC and PDADMAC were premixed in the case of PFC-PDADMAC, these two single coagulants reacted with dye molecule nearly at the time after PFC-PDADMAC was dosed. Steric crowding of Fe(III) precipitates and PDADMAC chains on the particle surface tend to favor an extended conformation of PDADMAC chains away from the particle surface. Because only one end or segment of PDADMAC chains attached to the particle surface in the PFC-PD flocs, only a portion of the positive charge on PDADMAC chains can neutralize the negative charge on particles. Although the charge neutralization ability of PDADMAC was weakened, this conformation contributed PDADMAC act as a bridge between particles. Therefore, a combination of charge neutralization and bridge coagulation occurs, which is the possible reason why PFC-PDADMAC gave higher floc growth rate. When PFC and PDADMAC were dosed successively, the initial microflocs formed by the reaction of dye molecule and the first coagulant dosed. The second coagulant dosed was then adsorbed on the surface of the microflocs formed. Compared with PFC-PDADMAC, this conformation did not contribute to the aggregation of microflocs and the floc growth rate was slower. In the treatment of D.Y. RGFL, three dual-coagulants gave similar increase in floc growth rate as coagulant dosage increased, which indicated the impact of addition sequence on floc growth rate was very slight. This is possibly because D.Y. RGFL was less negatively charged than R.Y. K-4G, the adsorption of the polymers on D.Y. RGFL was less favorable, and the reaction between D.Y. RGFL molecule and coagulants was relatively slow at the initial stage of coagulation-flocculation. However, the time interval (1 min) between the additions of the two coagulants was short and negligible. For this reason, different dual-coagulants reacted with the D.Y. RGFL molecule in the similar way and so did the aggregation rate of flocs.

3.3. Comparison of floc size in steady-state phase

The FI value obtained by Eq. (2) represents the state of aggregation obtained over a steady-state time interval. As has been



Fig. 8. FI as a function of coagulant dose in the removal of R.Y. K-4G.

discussed. FI could be used as a reliable indicator of floc size. A larger FI imply larger aggregate sizes and thus better separation by subsequent sedimentation [24]. The changes of FI with the coagulant dosage in the treatment of R.Y. K-4G and D.Y. RGFL are shown in Figs. 8 and 9, respectively. In the case of R.Y. K-4G, the FI values of the dual-coagulants were in the order: PFC-PDADMAC > PDADMAC + PFC > PFC + PDADMAC, which is in good agreement with that of color removal and floc growth rate. In this instance, it is worthwhile to note that the floc size of PFC-PDADMAC was much larger than that of another two dualcoagulants. For PFC-PDADMAC, it has been discussed that the repulsive forces allowed the PDADMAC chains to be extended, which lead to the formation of large open-structure flocs. For PDAD-MAC + PFC and PFC + PDADMAC, the second coagulant dosed would nearly completely adsorb on the microfloc surface, which result in the loss of bridging between microflocs. As a result, the size of flocs formed by PDADMAC+PFC and PFC+PDADMAC was much smaller than those produced by PFC-PDADMAC. In the case of D.Y. RGFL (Fig. 9), all three dual-coagulants gave similar floc size at each dosage except PDADMAC + PFC which gave a sudden drop in FI value at 20 mg/L and above. Consequently, the floc size in steady-state phase was slightly affected by the addition sequence of PFC and PDADMAC which was also attributed to the similar coagulation-flocculation mechanism as discussed above. Corre-



Fig. 9. FI as a function of coagulant dose in the removal of D.Y. RGFL.



Fig. 10. Floc size variance as a function of coagulant dose in the removal of R.Y. K-4G.

sponding with the decrease of color removal at a dosage of 20 mg/L and above, the decrease in FI for PDADMAC + PFC also resulted from the particle restabilization when coagulant was overdosed.

3.4. Comparison of floc size difference in steady-state phase

The steady-state variance values for all three dual-coagulants in treating R.Y. K-4G and D.Y. RGFL were displayed in Figs. 10 and 11, respectively. In general, a larger variance value indicates a wider range of floc size distribution. For R.Y. K-4G, it can be seen that the variance decreased as the increase of coagulant dosage, and then fell to a relatively constant value when the dosage was larger than 15 mg/L. As a result, the flocs obtained at high dosage were more tight and uniform than those obtained at low dosage for D.Y. RGFL removal. It also can be seen in Fig. 10 that the variance values of three dual-coagulants were in the following order: PFC-PDADMAC > PDADMAC + PFC > PFC + PDADMAC, which is consistent with the color removal and FI results. This result suggested that the dual-coagulant which gave higher color removal also gave larger floc and a wider range of floc size distribution in the treatment of R.Y. K-4G. As other researchers have observed [19], large variance may indicate the formation of flocs with porous structure and low fractal dimension value. Moreover, flocs formed under sweep and bridging tend to have open structure and possibly with



Fig. 11. Floc size variance as a function of coagulant dose in the removal of D.Y. RGFL.

a wider distribution of floc sizes. By contrast, charge neutralization creates tighter and more condensed flocs with less variance in the distribution of floc size. In this case, PFC-PDADMAC produced flocs with more porous and open structure depending on its stronger bridging and sweep ability than PFC+PDADMAC and PDADMAC+PFC. In the case of D.Y. RGFL, the variance value of all three dual-coagulants increased gradually with the increase of coagulant dose. As mentioned above, entrapment and bridging of PFC play important role in the coagulation of D.Y. RGFL, which contribute to the formation of flocs with open and irregular structure, especially for the large floc at high dosage. It also can be seen that the difference of the variance of three dual-coagulants was very slight. Consequently, the addition sequence also had little effect on the floc size difference, which further confirmed that all three dual-coagulants gave similar mechanism in the treatment of disperse dye. It is also worth noticing that the variance value given by PFC + PDADMAC decreases as the dosage beyond 20 mg/L, which corresponded with the decrease in color removal rate and floc size within the same dose range. This is likely attributed to over dose of PFC + PDADMAC. Overdosed PDADMAC rapidly saturate the particle surface sites, which give fine and uniform flocs.

4. Conclusions

Three PFC/PDADMAC dual-coagulants with different dosing methods were comparatively investigated in terms of color performance, coagulation-flocculation mechanism and floc aggregation process in the treatment of synthetic dyeing solution. In the coagulation of Reactive Yellow K-4G, charge neutralization is the dominant mechanism for all three dual-coagulants. PFC-PDADMAC, prepared by premixing of PFC and PDADMAC before dosing, gave higher color removal performance depending on its stronger sweep and bridging ability than PFC+PDADMAC and PDADMAC+PFC which were achieved by dosing PFC and PDADMAC in different order. 60.2% color removal was obtained by PFC-PDADMAC at a dosage of 30 mg/L. In addition, higher floc growth rate, larger floc size and wider range of floc size variance were also obtained by PFC-PDADMAC. The synergic effect of PFC and PDADMAC was enhanced by premixing PFC and PDADMAC in the removal of Reactive Yellow K-4G. For the removal of Disperse Yellow RGFL, the color removal, coagulation-flocculation mechanism, floc growth rate, floc size in steady-state phase and floc size variance of three dualcoagulants were slightly influenced by dosing methods. D.Y. RGFL was removed by the co-effect of charge neutralization, bridging and entrapment. The maximal color removal (95.5%) was obtained by PFC-PDADMAC at a dosage of 30 mg/L.

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