## SUPPORTING INFORMATION

## Continuous-flow diazotization of Red base KD

## hydrochloride suspensions in a microreaction system

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#### 1. Synthesis and purification of azo dyes by batch process

(1) Preparation of diazonium salt solution:

Red base KD (0.015 mol) was dissolved in deionized water (100 mL) in a 250 mL three-necked flask and concentrated hydrochloric acid (0.044 mol) was added into the flask with stirring to form a slurry solution for 1 hour. Next, the slurry solution was cooled to 3 °C in ice-water bath and the aqueous sodium nitrite solution (0.0155 mol) with a mass fraction of 30% was added dropwise until the slurry was completely dissolved. When the addition was completed, the reaction mixture was further stirred for 30 min at 3 °C. Then, the reaction mixture was tested by the potassium starch iodide paper. When the potassium iodide test paper turned blue, it illustrated that the Red base KD reacted completely. Finally, the diazonium salt solution was transferred to a beaker and stored at low temperature for next step.

(2) Synthesis of azo dyes by batch process:

Sodium 6-hydroxynaphthalene-2-sulfonate (0.016 mol) (coupling component) was dissolved in deionized water (100 mL) in a 500 mL three-necked flask. Then, the flask was submerged in an ice batch and sodium hydroxide was added to the solution to adjust the pH varied between 9 and 10. When the temperature of the solution dropped to 5 °C, the diazonium salt solution was added into the coupling component solution continuously. The azo-coupling reaction temperature was

controlled at 5-8 °C and the pH needed to be maintained at about 9 during the reaction using sodium hydroxide solution. After reacting for 30 min, H acid was used to detect the presence of diazonium salts to determine the endpoint of the reaction. Finally, the mixture solution was filtered by air pump filtration, the filter cake was washed by ethanol, and dried.

(3) Purification of azo dyes:

Crude azo dyes were put in a 100 mL beaker and they were dissolved by deionized water. After the solution was filtered to remove impurities, potassium acetate was added into the filtrate, which is a salting out process. After half an hour, the mixture solution was filtered and the filter cake was obtained. The dissolution and salting out process mentioned above were repeated three times. The last filter cake was washed by cold ethanol until no white precipitate was generated when the filtrate was detected by silver nitrate solution (0.1 mol/L). Finally, the filter cake was dried and the azo dye standards were obtained. (4) Characterization of azo dye standards

1) High performance liquid chromatography of the azo dye standards

As shown in Fig. S1, the purity of the azo dye standard is about 98.5%, as measured by high performance liquid chromatography.



Fig. S1 The high performance liquid chromatography of the azo dye standards

2) Mass spectrometry of the azo dye standards

As shown in Fig. S2, the relative molecular mass of the product was measured to be 476.09 according to the results of mass spectrometry, which was similar to the value of 476.51 from theoretical calculation.



Fig. S2 The Mass spectrometry of the azo dye standards

### 2. The standard working curve of the azo dye standard

(1) Azo dye standards (0.0667g) were weighed by a balance with 0.0001 accuracy and they were diluted in a 250 ml volumetric flask. Then, fixed volume (0.25 mL, 0.5 mL, 1.25 mL, 2.5 mL, 7.5 mL, 12.5 mL, 15mL, 17mL) of solution was removed from 250 ml volumetric flask and they were diluted in a 100 ml volumetric flask. Finally, the absorbance of the solution was measured by UV-visible spectrophotometer at a wavelength of 491 nm. The standard working curve of the azo dye standard was shown in Fig. S3.



Fig. S3 The standard working curve of the azo dye standard

(2) Precision experiments:

Azo dyes (10.9 mg) were dissolved in a 250 mL volumetric flask with deionized water, and the maximum absorbance of the prepared solution was tested five times. Then, the concentration of the solution was obtained by standard working curve. Finally, the relative standard deviation of the concentration of the azo dyes was calculated. The results of concentration measurement of azo dyes were shown in Table S1.

Number	Absorbance (A)	Concentration (mg/L	RSD%
		)	
1	1.287	43.14	0.12
2	1.287	43.14	

Table S1 Precision test results of concentration measurement of azo dye

3	1.289	43.21
4	1.286	43.11
5	1.285	43.07

(3) Reproducible experiments:

Five parts of the same quality azo dyes (10.9 mg) were all diluted in 250 mL volumetric flasks with deionized water. Then, the maximum absorbance of the prepared solution was tested and the concentration of the solution was obtained by standard working curve. Finally, the relative standard deviation of the concentration of the azo dyes was calculated. The results of concentration measurement of azo dyes were shown in Table S2.

Table S2 Reproducible test results of concentration measurement of azo dye

Number	Absorbance (A)	Concentration (mg/L	RSD%
		)	
1	1.286	43.11	0.69
2	1.286	43.11	
3	1.279	42.87	
4	1.302	43.65	

# 3. The scalability of preparation processes of the Red base KD hydrochloride suspensions

The Red base KD hydrochloride suspensions has been prepared in a large reactor for verifying the scalability of the preparation processes. Adding all the excess hydrochloric acid solution at one time could still cause agglomerated particles in the suspension (as shown in Fig. S4(a)). When the hydrochloric acid solution was added in batches to carry out the slurrying reaction of the Red base KD, no agglomerated particles were produced and the crystallization was needle-shaped (as shown in Fig. S4(b)). Therefore, the preparation method of Red base KD hydrochloride suspensions mentioned in our article had a certain degree of scalability.



(a)



(b)

Fig. S4 The micrographs of the Red base KD hydrochloride: (a) Adding all the excess hydrochloric acid solution at one time; (b) Adding hydrochloric acid solution in batches.