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Optimization of salting-out crystallization for an efficient *in situ* separation of synthetic anthraquinone- and azo-type reactive dyes

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ABSTRACT

A solute can be deposited from solution by the addition of another soluble substance which effectively reduces the solubility of original solute. The process is referred to as 'salting-out' and it is one of the proper methods for effective separation of synthetic reactive dyes in industry. To develop an efficient salting-out process for recovering representative anthraquinone- and azo-type reactive dyes, Reactive Blue 49 and Reactive Black 8 in high yields, various factors such as the kind and amount of inorganic salts, concentration of dye solution, operating temperature, stirring speed, complete time of crystallization were investigated. Reactive Blue 49 could be recovered from 15 wt% of dye solution in approximately 70% yield under the optimized conditions (15 wt% of NaCl, 25 °C, 100 rpm, 12 h) and Reactive Black 8 was obtained from 20 wt% of dye solution in over 90% yield by using 10 wt% of NH_4Cl at room temperature and 100 rpm within 1 h.

1. Introduction

Crystallization is a widely utilized separation process in a variety of industrial applications. This technique allows a desired compound to be isolated selectively from crude mixtures in specialty chemicals and pharmaceuticals manufacture. According to the driving force to form a crystal, crystallization is classified with several methods: reaction crystallization, cooling crystallization, salting-out crystallization, evaporation crystallization, drowning-out crystallization, melting crystallization [1]. Among them, a salting-out crystallization is highly energy efficient and advantageous for the processing of heat-sensitive substances because it is generally operated at an ambient temperature without additional cooling/heating. The salting-out is based on the principle that a solute can be deposited from solution by the addition of another soluble substance which can effectively reduce the solubility of original solute. The salting-out method is not only used for the production of pure inorganic salts from aqueous solution [2–4] but it is also applied to the purification of biological molecules such as protein [5,6] and DNA [7], the isolation of cell [8], and the separation of organic compounds [9–11].

Reactive dyes are common chemicals for colorizing cellulosic textiles and anthraquinone- and azo-type reactive dyes are among most general synthetic dye members [12–14]. They are synthesized via multi-step chemical reactions and their chemical structures bear the functional groups to covalently couple with hydroxy group of cellulose [15,16]. In particular, the final products are often purified via a simple salting-out process because the crude prior to purification contains several components such as unreacted reactants, an excess of reagents, side products, *etc*. For this, a suitable inorganic salt is directly added to the reaction mixture when all the reactions are complete and then the precipitate is collected to afford a desired dye product. Whereas, this long-historic procedure is still dependent on a rule of thumb by accumulated experiences and there is a lack of documentation for salting-out crystallization of reactive dyes.

With this regard, in order to optimize the salting-out crystallization of synthetic reactive dyes, we report the influence of various factors including the kind and the addition amount of inorganic salts, the concentration of dye solution, temperature, stirring speed, and complete crystallization in terms of a recovery yield and energy efficiency. For this study, Reactive Blue 49 (R-Blue 49) and Reactive Black 8 (R-Black 8) were recruited as a representative anthraquinone- and azo-type reactive dye. R-Blue 49 is synthesized from anthraquinone derivative **1** by three step reactions and R-Black 8 is synthesized from 2-amino-4-nitrophenol by five step reactions (Fig. 1 and 2, see Section 2 for detail procedures of synthesis).

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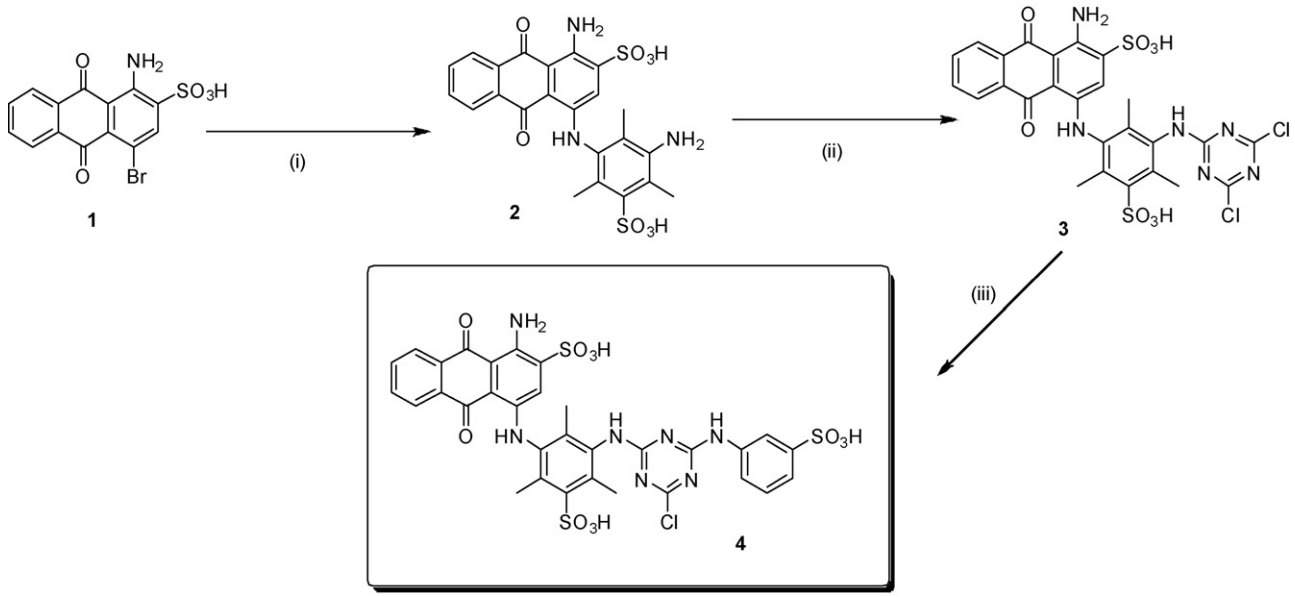

Fig. 1. Synthetic procedure of R-Blue 49: (i) CuCl, 2,4-diamino-1,3,5-trimethylbenzenesulfonic acid, 70 °C, pH > 9; (ii) 2,4,6-trichloro-1,3,5-triazine, 5 °C, pH 6; (iii) 3-aminobenzenesulfonic acid, 35 °C, pH 7.

2. Experimental

2.1. Synthesis of dyes

2.1.1. Reactive Blue 49

Na_2CO_3 (32.5 g, 0.3 mol) was dissolved in water (200 mL) and the solution was stirred at room temperature. Into the solution slowly added 2,4-diamino-1,3,5-trimethylbenzenesulfonic acid (25.8 g, 112 mmol) and the mixture was heated to 40 °C. Then anthraquinone derivative **1** (28.8 g, 75 mmol) was added and the mixture was adjusted to 50 °C. Afterward CuCl (0.9 g, 9 mmol) was added and the temperature was elevated to 70 °C. Additional CuCl (0.4 g, 4 mmol) was put and the mixture was stirred for 20 h. The reaction mixture was diluted to 600–650 mL with water and the temperature was adjusted to approximately 60 °C. Into the reaction mixture put Celite (8 g) and the suspension was filtered. The filtrate was collected and the pH was dropped to 2.5–3.0 with *conc*. HCl (40–50 mL) to precipitate unreacted 2,4-diamino-1,3,5-trimethylbenzenesulfonic acid. After filtering it off, *conc*. HCl (60–65 mL) was added to the filtrate to give **3**. The filtered **2** was

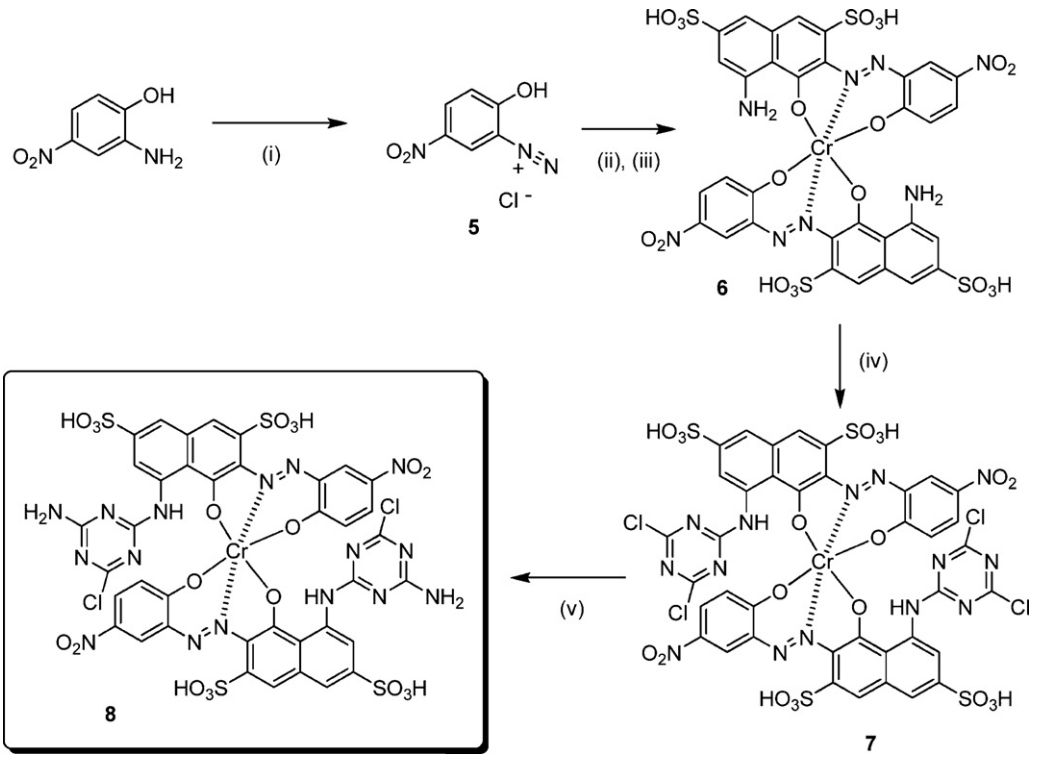

Fig. 2. Synthetic procedure of R-Black 8: (i) $NaNO_2$, HCl, H_2O; (ii) 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid, NaOH, NH_4OH; (iii) $Cr_2(SO_4)_3$; (iv) 2,4,6-trichloro-1,3,5-triazine, 5 °C, pH 5.0–5.5; (v) NH_4OH, 50 °C, pH 9.0.