

Recovery of Sodium Sulfate from Farm Drainage Salt and Using It in Direct Dyeing of Cotton

– Analysis of Color Difference –

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Abstract

Agricultural drainage salt generated during irrigation of crops in San Joaquin Valley, California, exceeds 600,000 tons annually and cumulates in the field in a rapid rate. As a result, the waste is taking out more farmlands for salt storage and disposal, imposing serious concerns to environment and local agricultural industry. In searching for a potential solution to reduce or eliminate the waste, this research explored feasibility of producing a value-added product, sodium sulfate, from the waste and utilizing the product in textile dyeing. The results indicated that sodium sulfate could be produced from the salt and could be purified by a recrystallization method in a temperature range within the highest and lowest daily temperatures in summer in the valley. The recovered sodium sulfate samples, with purities ranging from 67% to 99.91, were compared with commercially available sodium sulfate in direct dyeing of cotton fabrics. The salt samples recovered from Mendota, California (>98.8% sodium sulfate) cause little color difference in the dyeing with selected direct dyes, and the purified salt (III) (99.91% sodium sulfate) is more applicable for direct dyeing of cotton fabrics if it has no other toxic effect. The recovered sodium sulfate from certain areas in the valley could not be employed in direct dyeing due to the high level of impurities in it.

Key words: Sodium Sulfate, Drainage, Cotton Dyeing, direct Dye

I. Introduction

Agricultural drainage salt, resulted from a mixture of soluble minerals present in repeatedly used irrigation water, is a major environmental waste in San Joaquin Valley, California (Lal, 1994; Water quality, 1992; Technical report, 1988). Studies on how to solve the agricultural drainage salt problem in California have been conducted for years with many valuable and effective technologies on treatment of the waste (A status report, Feb. 1998; Water quality, 1992; Technical report, 1988). As a result of extensive

research, it was found that the salt resulted in San Joaquin Valley mainly contains sodium, calcium, magnesium, potassium, and other trace metal salts of sulfate, chloride, and carbonate (A status report, Feb. 1998; Jenkins, 1997; Water quality, 1992; Tanji et al., 1992; Technical report, 1988), in which sodium and sulfate ions account for 80~96% of total composition. In another word, the salt contains 80~96% of sodium sulfate, together with 3~19% of sodium chloride and trace amount of other elements as the rest compositions in the salt (Jenkins, 1997; Westcot, July 1993).

Direct dyes are one of the most important

and widely used colorants for cotton fabrics in the world. The effect of salt such as sodium sulfate on the take-up exhaustion of direct dyes is of great practical importance (Kulkarni S. V. et al., 1986; Cockett S. R. et al., 1961). When cellulose is immersed in water they develop a substantial negative charge which electrostatically repels the negatively charged dye anions. The sodium cations of the salt associate with the negatively charged cellulose substrate and shield the dyestuff from these repulsion forces. This allows the dye molecule to approach the substrate closely enough to hydrogen bond. Since the anionic groups of the dye are the sulfonic acid group (or sulfonates) themselves, the more of these group present, the more pronounced the effect of salt addition (Shenai, 1973). Sodium sulfate is added in the dyeing process of direct dyes in amount of as much as 10–40 % of textiles weight (Kulkarni S. V. et al., 1986).

Sodium sulfate has higher solubility in water at elevated temperature (35°C) and lower solubility at temperature below 15°C. Sodium chloride, another major component in the salt, has an almost constant solubility at a wide temperature range (the Merck Index, 1996). In the Center Valley of California, the summer temperature changes from about 10°C in the early morning to above 30°C in the afternoon, which is the range in which the solubility of sodium sulfate varies significantly. Therefore, varying temperature of concentrated salt solution will possibly precipitate 50% of sodium sulfate out of the liquid. Repeated precipitation or recrystallization of the solid can obtain very pure sodium sulfate.

Our study evaluated the possibility of using sodium sulfates, which were recovered from drainage water, in cotton dyeing with direct dyes.

II. Experimental Methods

1. Materials

Pure cotton fabrics (# 400, Testfabrics) were

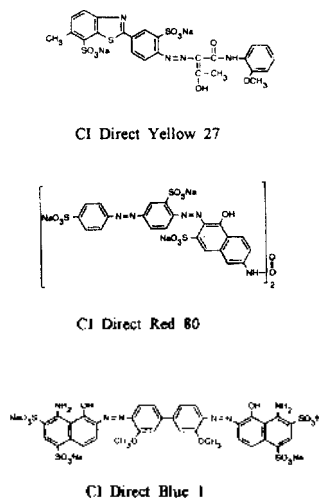


Fig. 1. Chemical Structures of the Direct Dyes.

pretreated in a solution of 2g/l AATCC standard detergent 124 at 80°C for 30 min. with a liquor ratio of 100:1. The fabrics were then washed completely in distilled water, dried and kept in conditioning room at $21 \pm 2^\circ\text{C}$ and a RH of $65 \pm 10\%$.

All dyes were purchased from Aldrich Chemical Co. (Milwaukee, WI) and used without purification. The structures of the dyes are given in Fig. 1. These dyes were selected to assess the effectiveness of sodium sulfate, which was recovered from drainage salt in San Joaquin Valley of California, in direct dyeing.

Analytical grade anhydrous sodium sulfate (Aldrich Chemical Co., Milwaukee, WI) was used without further purification. The five sodium sulfates employed were: (1) commercially available anhydrous sodium sulfate (Na_2SO_4 I); (2) sodium sulfate recovered from a salt mixture obtained from Mendota, California (Na_2SO_4 II); (3) sodium sulfate resulted from purification of the sample Na_2SO_4 II (Na_2SO_4 III); (4) sodium sulfate recovered from a salt mixture obtained from Red Rock Ranch, California (Na_2SO_4 IV); and (5) Na_2SO_4 purified again from Na_2SO_4 IV (Na_2SO_4 V).

2. Instrumental Measurements

The values of light reflectance of the fabrics were measured with a Minolta Colorimeter CM-2002 (Minolta Camera Co., LTD, Japan), and color difference (ΔE) was calculated according to Equation 1, following American Association of Textile Chemists and Colorists (AATCC) Evaluation Procedure I (Technical Manual of AATCC, 2000). The pH values of dye solutions were measured by using a Corning pH/ion meter 450 (Corning Co., NY, USA).

$$\Delta E = [(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2]^{1/2} \quad (1)$$

3. Purification Methods

Extraction of sodium sulfate from the agricultural drainage salt was conducted in such a way that 300g of the salt (directly collected from solar evaporators) were mixed with 500 ml of distilled water at 40°C for 30 min and then filtered to remove all insoluble solid. The filtrate solution in a beaker was concentrated to about 250 ml by evaporating excess water at an elevated temperature, and then the concentrated solution was cooled to about 10°C to precipitate sodium sulfate. The recovered sodium sulfate (Sodium sulfate decahydrates) was filtered and then vacuum-dried.

The purified sodium sulfate was prepared by re-dissolving the recovered sodium sulfate in distilled water at 40°C, and then recrystallized following the same procedure. The sodium sulfate samples, after been grinded to powder forms, were further dried under vacuum and stored in a conditioning room until constant weights are reached. At this moment, the sodium sulfate changes to its anhydrous form completely.

4. Salt Analysis

0.5 gram of the salt sample was dissolved in 100ml of distilled water, and the solution was analyzed by using a Perkin Elmer Elan-6000 ICP/MS spectrometer according to US EPA Methods 200.7 (ICP) and 200.8 (ICP/MS). Anionic ions in the salt were analyzed by following EPA Methods 325.2 (Cl^-), 375.2 (SO_4^{2-}), and 4500- NO_3-F (NO_3^-).

5. Dyeing of Cotton Fabrics

Dyeing of cotton fabrics was carried out in a shaker bath with a ratio of the dye solution to fabric (liquor ratio) maintained at 30:1 (w/w) and the dye concentrations in the dye baths varied in 1, 3 and 5 % on weight of fabric (o.w.f.), respectively. Dye baths were prepared with proper amounts of direct dyes and different sodium sulfate samples dissolved in distilled water at room temperature. Cotton fabrics were immersed in the dye bath and temperature of dye bath were increased from 20°C to 98°C. The temperatures were held constant during the entire dyeing process. The dyeing process was continued for another 60 minutes, then the dyed fabrics were rinsed and air-dried for the following color measurements.

III. Results and Discussion

1. Recovery of Sodium Sulfate

Two agricultural drainage salt samples were employed in the study, with one coming from solar evaporators in Mendota, Fresno, California, and the other from the evaporators in Red Rock Ranch, California. Both samples contain a major portion of soil due to structure characteristics of the solar evaporators in the Valley. Thus, the insoluble soil must be removed from the salt before conducting the purification of the salt, which serves as the recovery of sodium sulfate. The purification of sodium sulfate can be achieved by using a simple recrystallization method. Solubility of sodium sulfate in water is higher (about 50g/100ml at 40°C) at elevated temperatures (>35°C) than that is at low temperatures (about 10g/100ml at 10°C). Sodium chloride, another major component in the drainage salt, has an almost constant solubility at a wide range of temperatures (10~80°C). Therefore, varying temperatures of the concentrated salt solutions can precipitate certain amount of sodium sulfate due to solubility changes. Repeated precipitation or recrystallization of the solid should result in very pure sodium sulfate.

Due to the existence of a large quantity of insoluble residues in the salt mixtures, the extraction of soluble salts from the drainage salt mixture consumed large volume of water. Thus, the filtrate solution (warm solution) should be concentrated to a smaller volume at a higher temperature, and then the concentrated solution should be cooled to a lower temperature (cold solution), resulting in a reduced solubility of sodium sulfate in an over saturated solution. Obviously, the recovery rate of sodium sulfate crystals (sodium sulfate decahydrate) from the salt solution depends on its solubility difference of the salt solution at the two different temperatures and the concentration of sodium sulfate in the warm solutions.

However, based on economic preference on using solar energy as the major energy resource and the difference of the daily maximum and minimum temperatures in summer in the central Valley, we restricted the temperature range within 10~40°C. The overall recovery rates of sodium sulfate from the solutions were not very high, ranging from 11.94% wt to 14.16% wt from using a method, in which the filtration solutions were first concentrated by evaporation at a higher temperature before precipitating sodium sulfate, and 3.38% wt to 10.43% wt from using the filtration solutions that were not concentrated by the evaporation.

2. Compositions of Recovered Sodium Sulfate

<Table 1> Recovery of Sodium Sulfate from Drainage Salt

Water (ml)	Drainage salt (gram)	Recovered Na ₂ SO ₄ (%)	
		Method I	Method II
700	300	12.98	3.38
500	300	14.16	6.14
400	300	11.94	8.25
300	300	12.61	10.43

Method I : solution was concentrated to precipitate sodium sulfate

Method II : without concentration

The main compositions of recovered and purified sodium sulfates are shown in <Table 2> listed as percentages of ions and salts based on the detected compositions. The proportion of sulfate ion (SO₄²⁻) was predominately high among all of ions detected in the salt, and followed by sodium and chloride ions in order. The percentage compositions of sodium sulfate found in samples I, II, III, IV and V were 99.9, 98.83, 99.91, 67.14 and 76.66%, respectively, calculated by adding percentages of sodium and sulfate ions together. The results in <Table 1> demonstrated that agricultural drainage salts harvested from the solar evaporators located in different areas were significantly different in their chemical compositions.

The samples resulted from the Mendota evaporators contained almost over 98% of sodium sulfate, which is consistent with the results obtained by other researchers (Jenkins, 1997). But samples from Red Rock Ranch (RRR) involved relatively high ratios of chloride and nitrate, as well as calcium and magnesium minerals. After the following purification step, the resulted sodium sulfate (sample III) was in the same purity as the commercially available sample, while the purity of sodium sulfate produced from the RRR mixture was only increased from 67.14% to 76.66%. However, if chloride ion is also included as the other component in the products, the total contents of sodium, sulfate, and chloride could make up to 85.85% and 99.89% compositions in the recovered and purified RRR samples, respectively. During the purification step, the amounts of calcium, magnesium, and boron ions in the products of the Mendota reduced more than those of RRR mixture.

3. Effect of the Salts on Direct Dyeing

In direct dyeing of cotton fabrics, sodium sulfate is a very necessary chemical in assisting dye adsorption and facilitating reactions between cellulose and the direct dyes. The dissociated sodium sulfate ions in aqueous solution can also help penetration of the dyes into cellulose and

<Table 2> Elemental Analysis of Recovered Sodium Sulfate Samples

Elemental composition %	Mendota		Red Rock Ranch	
	Sample II Recovered	Sample III Purified	Sample IV Recovered	Sample V Purified
B	0.0085	0.00176	0.147	0.002
Ca	0.31	0.02	9.02	0.025
Mg	0.088	0.0067	1.47	0.01
Na	31.59	31.22	23.82	35.56
Cl	0.75	0.063	18.71	23.23
SO ₄	67.24	68.68	43.33	41.11
NO ₃	0.00036	0.0002	3.49	0.068
Na ₂ SO ₄	98.83	99.90	67.15	76.67
NaCl + Na ₂ SO ₄	99.58	99.96	85.86	99.90
Color	White	White	Light yellow	White
pH*	7.0~7.2	6.8~7.0	7.8~8.0	7.0~7.4

* Salt solution of 1g in 100ml of distilled water

suppress solubility of the dyes in the solutions. Thus, the purity of sodium sulfate will definitely interfere dyeing behavior of the dyes and affect the properties of dyed fabrics such as colors and colorfastness. In order to investigate the influence and significance of the salt purity on direct dyeing, dye concentrations were varied systematically in dyeing the same fabric from 1% to 3% and to 5% on weight of fabric (o.w.f).

<Tables 3~5> show results of cotton fabrics dyed with three different direct dyes. Low purity of sodium sulfate can affect dye solubility in water and consequently reduce its adsorption by cellulosic fibers, particularly in existence of some metal ions that can form precipitates with the dye molecules. Reactivity of cellulose to direct dyes could be inhibited by calcium ions because of their interactions with ionized cellulose

(Kulkarni, 1986).

Color difference of sodium sulfates on cotton dyeing with Direct Yellow 27 are shown in <Table 3> Color difference value of all dye concentrations to Na₂SO₄ I was slight or trace in Na₂SO₄ II, III and V, much in Na₂SO₄ IV. Color difference values of all dye concentrations to Na₂SO₄ I were lowest in Na₂SO₄ III, and then Na₂SO₄ V, Na₂SO₄ II and Na₂SO₄ IV in order. Na₂SO₄ IV is considered to be inadequate to cotton dyeing with Direct Yellow 27, because Na₂SO₄ IV has more color difference compared with Na₂SO₄ I, III and V and also has uneven dyeing.

Color difference of sodium sulfates on cotton dyeing with Direct Red 80 are shown in <Table 4> Color difference values of all dye concentrations to Na₂SO₄ I were trace or slight among

<Table 3> Color Difference of CI Direct Yellow 27 Dyed Fabrics

Dye Conc. (% o.w.f)	1%		3%		5%	
	ΔE	Gray scale	ΔE	Gray scale	ΔE	Gray scale
Sodium Sulfate Na ₂ SO ₄ I (control)	-	-	-	-	-	-
Na ₂ SO ₄ II	-0.97	4~5	-2.30	3~4	-1.71	4
Na ₂ SO ₄ III	-0.04	5	-0.33	5	0.34	5
Na ₂ SO ₄ IV	-4.03	3	-8.34	1~2	-18.83	1
Na ₂ SO ₄ V	-0.24	5	0.35	5	1.81	4

<Table 4> Color Difference of CI Direct Red 80 Dyed Fabrics

Dye Conc.(% o.w.f)	1%		3%		5%	
	ΔE	Gray scale	ΔE	Gray scale	ΔE	Gray scale
Sodium Sulfate Na ₂ SO ₄ I(control)	-	-	-	-	-	-
Na ₂ SO ₄ II	0.21	5	0.39	5	0.54	4~5
Na ₂ SO ₄ III	0.19	5	-0.13	5	-0.28	5
Na ₂ SO ₄ IV	1.65	4	0.53	4~5	-0.69	4~5
Na ₂ SO ₄ V	0.44	4~5	-0.25	5	-0.37	5

<Table 5> Color Difference of CI Direct Blue 1 Dyed Fabrics

Dye Conc. (% o.w.f)	1%		3%		5%	
	ΔE	Gray scale	ΔE	Gray scale	ΔE	Gray scale
Sodium Sulfate Na ₂ SO ₄ I (control)	-	-	-	-	-	-
Na ₂ SO ₄ II	2.50	3~4	2.47	3	2.21	3~4
Na ₂ SO ₄ III	2.37	3~4	2.27	3	2.10	3~4
Na ₂ SO ₄ IV	5.48	2~3	4.35	2~3	3.09	3
Na ₂ SO ₄ V	2.89	3~4	2.64	3	2.25	3~4

various sodium sulfates. Color difference values of all dye concentrations to Na₂SO₄ I were lowest in Na₂SO₄ III, and then Na₂SO₄ II, Na₂SO₄ V and Na₂SO₄ IV in order. In Na₂SO₄ IV, direct Red 80 has less color difference by the recovered areas and the number of purification than direct Yellow 27. All the recovered sodium sulfates are considered to be adequate to cotton dyeing with direct Red 80.

Color difference of sodium sulfates on cotton dyeing with Direct Blue 1 are shown in <Table 5> Color difference values of all dye concentrations to Na₂SO₄ I were appreciable or noticeable among various sodium sulfates. Color difference values of all dye concentrations to Na₂SO₄ I were lowest in Na₂SO₄ III, and then Na₂SO₄ II, Na₂SO₄ V and Na₂SO₄ IV in order. Direct Blue 1 has more color difference by the recovered areas and the number of purification than direct Yellow 27 and direct red 80. Na₂SO₄ IV showed heavy uneven dyeing. Therefore all the recovered sodium sulfates are expected of better dyeing effect with one more purification step.

IV. Conclusions

The composition of recovered sodium sulfates from drainage salt in San Joaquin Valley, California and their effect on direct dyeing were also examined. Sulfate showed the highest proportion in the composition of recovered sodium sulfates, then sodium and chloride in order, and various minerals were also contained. The purities of Na₂SO₄ II, III, IV and V were 98.83%, 99.90%, 67.15% and 76.67%, respectively. The amount of insoluble precipitate was slight in Na₂SO₄ II and IV. The salt samples recovered from Mendota, California (>98.8% Na₂SO₄) cause little difference in the dyeing with selected direct dyes, and the purified salt (III) (99.91% Na₂SO₄) is more applicable for direct dyeing of cotton fabrics if it has no other toxic effect. Color difference values of all dye concentrations to Na₂SO₄ I were lowest in Na₂SO₄ III, and then Na₂SO₄ II, Na₂SO₄ V and Na₂SO₄ IV in order. The level of color difference, insoluble precipitate and uneven dyeing were different according to dyes. Na₂SO₄ IV was not useful as an additive of direct dyeing due to a lot of insoluble precipitate and uneven

-dyeing in direct Yellow 27 and direct Blue 1 dye baths but useful in direct Red 80 dye baths.

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