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

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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 recrystalization 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 directive dyeing of cotton fabrics. Direct Yellow 27 and direct Blue 1 had similar exhaustions among Na_2SO_4 *I,* Na_2SO_4 *II ,* Na_2SO_4 *III and* Na_2SO_4 *V which had similar ratios of sodium sulfate and sodium chloride in recovered salts.* Na_2SO_4 *IV had high exhaustion despite low ratios of sodium sulfate and sodium chloride. In direct Red 80, exhaustion depends more on the ratios of sodium sulfate and sodium chloride than sodium chloride.* Na_2SO_4 *IV and* Na_2SO_4 *V with high ratios of sodium chloride had more exhaustion than* Na_2SO_4 *II and* Na_2SO_4 *III with low ratios of sodium chloride. Generally, directive dyeing using recovered salts from farm drainage has similar or more excellent exhaustion than directive dyeing using commercial sodium sulfate.*

Key words: sodium sulfate, drainage, cotton dyeing, direct dye.

Ⅰ. Introduction

Agricultural drainage salt, resulting from a mixture of soluble minerals present in repeatedly used irrigation water, is a major kind of environmental waste in San Joaquin Valley, California[1~3]. 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[2,3]. As a result of extensive research, it was found that the salt resulting in San Joaquin Valley mainly contains sodium, calcium, magnesium, potassium, and other trace metal salts of sulfate, chloride, and carbonate[2,5], in which sodium and sulfate ions account for 80~96% of total composition. In other words, the salt contains 80~96% sodium sulfate, together with 3~19% sodium chloride and trace amount of other elements as the rest compositions in the salt[4,6].

The United States supplies of sodium sulfate

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are over 1.5 million tons per year. The sources of sodium sulfate are mining(22%), chemical manufacturing(26%), and import(52%). Sodium sulfate is used in soap and detergent(40%), pulp and paper(25%), textiles(19%), glass making (5%) and in other uses(11%). The last U.S. Geological Survey[7)] predicts the use of sodium sulfate in the textile industry will increase since the industry has begun to use sodium sulfate to replace other corrosive salts.

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[8,9)]. When cellulosics are immersed in water they develop a substantial negative charge which electrostatically repels the negatively charged dye stuff anions. The sodium cations of the salt associate with the negatively charged cellulose substract 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[10)]. Sodium sulfate is added in the dyeing process of direct dyes in amount of as much as 10~40% of textiles weight[8)].

Sodium sulfate has higher solubility in water at elevated temperature (35℃) and lower solubility at temperature below 15℃. Sodium chloride, another major component in the salt, has an almost constant solubility at a wide temperature range[11)]. In the Center Valley of California, the summer temperature changes from about 10℃ in the early morning to above 30℃ 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 recrystalization 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.

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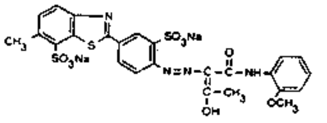
Ⅱ. Experimental Methods

1. Materials

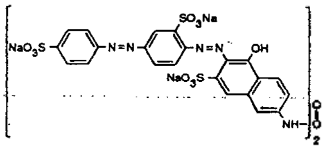
Pure cotton fabrics (# 400, Testfabrics) were pretreated in a solution of 2g/l AATCC standard detergent 124 at 80℃ for 30 min. with a liquor ratio of 100:1. The fabrics were then washed completely in distilled water, dried and kept in conditioning room at 21±2℃ and a RH of 65±10%.

All dyes were purchased from Aldrich Chemical Co. (Milwauke, 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 directive dyeing.

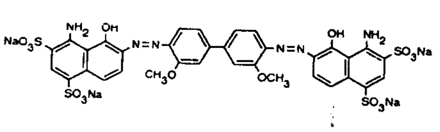
Analytical grade anhydrous sodium sulfate (Aldrich Chemical Co., Milwaukee, KI) was used without further purification. The five sodium sulfates employed were: (1) commerciallyavailable anhydrous sodium sulfate (Na_2SO_4 I); (2) sodium sulfate recovered from a salt mixture obtained from Mendota, California (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).



CI Direct Yellow 27



CI Direct Red 80



CI Direct Blue 1

<Fig. 1> Chemical Structures of the Direct Dyes.

2. Instrumental Measurements

The visible absorbance of dye solutions was recorded on a Hitachi-2000 double-beam UV/Vis photospectrometer (Hitachi Instruments Inc., Japan) at room temperature. The pH values of dye solutions were measured by using a Corning pH/ion meter 450 (Corning Co., NY, USA).

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 500ml of distilled water at 40℃ for 30 min and then filtered to remove all insoluble solids. 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℃ 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℃, and then recrystallizing, following the same procedure. The sodium sulfate samples, after having been grinded to powder forms, were further dried by vacuum and stored in a conditioning room until constant weights were reached. At this moment, the sodium sulfate changes to its anhydrous form completely.

4. Salt Analysis

0.5 grams of the salt sample were dissolved in 100ml of distilled water, and the solution was analyzed 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-NO3-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 from 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 the temperature of dye bath was increased from 20℃ to 98℃. The temperatures were held constant during the entire dyeing process. The dyeing process was continued for another 60 minutes.

6. Determination of Dyeability

For quantitative determination of dye concentration in the dye bath, the degree of exhaustion (E) was measured using the uv/vis spectrophotometer. All of tests were carried out at least in three parallel measurements. Means of exhaustions were analyzed by using one way ANOVA and Duncan's Post Hoc Multiple Comparisons from a SPSS computer statistic package. Percentage exhaustion was calculated using Equation 1:

$$E = [(Ao - Ad)/ Ao] \times 100 \qquad (1)$$

where Ao = the absorbances(at λ max) of dye originally in the dyebath

Ad = the absorbances(at λ max) of residual dye in the dyebath

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 recrystalization method. Solubility of sodium sulfate in water is higher (about 50g/100ml at 40℃) at elevated temperatures (>35℃) than that is at low temperatures (about 10g/100ml at 100℃). Sodium chloride, another major component in the drainage salt, has an almost constant solubility at a wide range of temperatures (10~80℃). Therefore, varying temperatures of the concentrated salt solutions can precipitate certain amount of sodium sulfate due to solubility changes. Repeated precipitation or recrystalization 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 required a 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

<Table 1> Recovery of Sodium Sulfate from Drainage Salt

Water (ml)	Drainage salt (g)	Recovered Na_2SO_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.

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℃. The overall recovery rates of sodium sulfate from the solutions were not very high, ranging from 11.94% wt to 14.16% wt 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

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 the sulfate ion (SO_4^{2-}) was the highest among all of ions detected in the salt, and followed by sodium and chloride ions. 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 Jenkins B. (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 reduced dramatically.

<**Table 2**> Elemental Analysis of Recovered Sodium Sulfate Samples

	Mendota		Red Rock Ranch	
Elemental composition %	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_2SO_4	98.83	99.90	67.15	76.67
NaCl+ Na_2SO_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.

3. Effect of the Salts on Directive Dyeing

In directive 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 suppress solubility of the dyes in the solutions. Thus, the purity of sodium sulfate will definitely interfere dyeing behavior of the dyes and affectthe properties of dyed fabrics such as colors and colorfastness. In order to investigate the influence and significance of the salt purity on directive 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).

<Table 3>~<Table 5> show the results of cotton fabrics dyed with the three different direct dyes.

The effect of sodium sulfates on cotton dyeing with Direct Yellow 27 are shown in Table 3. Recovered salts from the RRR area (Na_2SO_4 Ⅳ, Na_2SO_4 Ⅴ) had low ratios of sodium sulfate than those from the Mendota area (Na_2SO_4 Ⅱ, Na_2SO_4 Ⅲ) but contained high ratios of sodium chloride. The ratios of sodium sulfate and sodium chloride was almost similar and high among Na_2SO_4 Ⅱ, Na_2SO_4 Ⅲ and Na_2SO_4 Ⅴ. Na_2SO_4 Ⅳ had the lowest ratios of sodium sulfate and sodium chloride.

Na_2SO_4 I(commercial sodium sulfate), Na_2SO_4 Ⅱ, Na_2SO_4 Ⅲ, and Na_2SO_4 Ⅴ had similar exhaustion but had lower exhaustion than Na_2SO_4 Ⅳ with low ratios of sodium sulfate and sodium chloride. Exhaustions were not significantly different among various Na_2SO_4 except Na_2SO_4 Ⅳ by duncan's multiple range test ($p<.05$). This implies that not only sodium sulfate and sodium chloride in recovered salts but other materials affect exhaustion. Some of these materials were insoluble and Na_2SO_4 Ⅳ group with higher ratios of these insoluble materials had some uneven dyeing.

<**Table 3**> Dye Exhaustion(%) of CI Direct Yellow 27

Dye concentration / Sodium sulfate	1%	3%	5%
Na_2SO_4 I(Control)	$67.44^{b1)}$	68.03^{b}	64.26^{b}
Na_2SO_4 Ⅱ	68.37^{b}	70.49^{b}	64.86^{b}
Na_2SO_4 Ⅲ	66.50^{b}	68.89^{b}	63.94^{b}
Na_2SO_4 Ⅳ	70.51^{a}	78.00^{a}	73.06^{a}
Na_2SO_4 Ⅴ	68.01^{b}	69.37^{b}	64.81^{b}

1) Means with different superscript within columns are significantly different at $P<0.001$ by Duncan's multiple range test (n=3).

<**Table 4**> Dye Exhaustion(%) of CI Direct Red 80

Dye concentration / Sodium sulfate	1%	3%	5%
Na_2SO_4 I(Control)	$79.26^{b1)}$	77.88^{b}	68.62^{b}
Na_2SO_4 Ⅱ	80.97^{b}	79.08^{b}	70.51^{b}
Na_2SO_4 Ⅲ	80.14^{b}	78.91^{b}	69.33^{b}
Na_2SO_4 Ⅳ	89.96^{a}	85.12^{b}	77.50^{a}
Na_2SO_4 Ⅴ	88.84^{a}	84.45^{a}	76.82^{a}

1) Means with different superscript within columns are significantly different at $P<0.001$ by Duncan's multiple range test (n=3).

The effect of sodium sulfates on cotton dyeing with Direct Red 80 are shown in <Table 4>. In direct red 80, salts with a similar ratio of sodium chloride had similar exhaustion. That is, the exhaustion was similar between Na_2SO_4 Ⅳ and Na_2SO_4 Ⅴ group with higher sodium chloride ratios and between Na_2SO_4 Ⅱ and Na_2SO_4 Ⅲ with lower sodium chloride ratios. Exhaustions of all dye concentrations to Na_2SO_4 Ⅳ and Ⅴ were highest and were not significant between Na_2SO_4 Ⅰ, Na_2SO_4 Ⅱ and Na_2SO_4 Ⅲ and between Na_2SO_4 Ⅳ and Na_2SO_4 Ⅴ by duncan's multiple range test ($p>.001$). Direct Red 80 was less affected by other materials except sodium sulfate and sodium chloride than direct Yellow 27 and direct Blue 1. Despite a lot of insoluble precipitate, Na_2SO_4 Ⅳ had little uneven dyeing.

The effect of sodium sulfates on cotton dyeing with Direct Blue 1. Like direct Yellow 27, direct Blue 1 had similar exhaustions between salts with high ratios of sodium sulfate and sodium chloride (Na_2SO_4 I, Na_2SO_4 Ⅱ, Na_2SO_4 Ⅲ, and Na_2SO_4 Ⅴ) and salts with low ratios of sodium sulfate and sodium chloride (Na_2SO_4 Ⅳ). Exhaustions of all dye concentrations to Na_2SO_4 Ⅳ were highest and were not significantly different among various Na_2SO_4 except Na_2SO_4 Ⅳ by duncan's multiple range test ($p<.05$). That means the exhaustion of direct Blue 1 is affected by other materials, sodium sulfate and sodium chloride of recovered salts.

<Table 5> Dye Exhaustion(%) of CI Direct Blue 1

Sodium sulfate \ Dye concentration	1%	3%	5%
Na_2SO_4 I (Control)	71.88^{b}1)	85.20^{b}	83.23^{b}
Na_2SO_4 II	73.41^{b}	86.64^{b}	83.45^{b}
Na_2SO_4 III	73.13^{b}	85.53^{b}	83.29^{b}
Na_2SO_4 IV	78.98^{a}	89.58^{a}	86.00^{a}
Na_2SO_4 V	73.43^{b}	86.89^{b}	84.26^{b}

1) Means with different superscript within columns are significantly different at $P<0.05$ by Duncan's multiple range test ($n=3$).

Some of other materials are insoluble and Na_2SO_4 IV group with high insoluble materials had some uneven dyeing.

IV. Conclusions

The composition of recovered sodium sulfates from drainage salt in San Joaquin Valley, California and their effect on directive 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 Na_2SO_4 II, III, IV and V were 98.83%, 99.90%, 67.15% and 76.67%, respectively. In all dyes, Na_2SO_4 IV had a lot of insoluble precipitates in all dye baths. The amount of insoluble precipitate was slight in Na_2SO_4 II and Na_2SO_4 V.

Direct Yellow 27 and direct Blue 1 had similar exhaustions among Na_2SO_4 I, Na_2SO_4 II, Na_2SO_4 III and Na_2SO_4 V which had similar ratios of sodium sulfate and sodium chloride in recovered salts. Na_2SO_4 IV had high exhaustion despite low ratios of sodium sulfate and sodium chloride. It seems to be influenced by other materials in recovered salts. The content of these materials is thought to have a corelation with uneven dyeing.

In direct Red 80, exhaustion depends more on the ratios of sodium sulfate and sodium chloride than sodium chloride. Na_2SO_4 IV and Na_2SO_4 V with high ratios of sodium chloride had more exhaustion than Na_2SO_4 II and Na_2SO_4 III with low ratios of sodium chloride. Na_2SO_4 IV had a lot of insoluble precipitate in dye bath but little uneven dyeing.

Generally, directive dyeing using recovered salts from farm drainage has similar or more excellent exhaustion than directive dyeing using commercial sodium sulfate. Because Na_2SO_4 IV group had a lot of insoluble precipitate, it needs caution against uneven dyeing.

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