

Reuse of Sodium Sulfate Recovered from Farm Drainage Salt as Dyeing Builder of Levelling Dyes

- 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 the dyeing of levelling dyes. In nylon fabrics, the salt samples had little color difference in the dyeing with C.I. Acid Yellow 23 and C.I. Acid Blue 158. All salt samples' gray scale was 5 grade. In wool fabrics, the salt samples had little color difference in dyeing with C.I. Acid Yellow 23 and C.I. Acid Blue 158. All salt samples' gray scale was 5 grade. Generally, the dyeing of levelling dyes using recovered salts from farm drainage had little color difference than the dyeing of levelling dyes using commercial sodium sulfate.

Key words : drainage, levelling dyes, nylon, sodium sulfate, wool.

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, California¹⁻³). 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 waste⁴⁻⁵). As a result of extensive

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¹ R. Lal and B. A. Stewart, Ed. Soil process and water quality, (MI: Lewis Publishers, Ann Arbor, 1994).

² Water quality; Agriculture's role, Task force report, (Council for Agricultural Science and Technology, 1992), 120.

³ Technical Report. Agricultural drainage water treatment, reuse, and disposal in the San Joaquin Valley(1998).

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,⁶⁻⁹⁾ in which sodium and sulfate ions account for 80-96% of total composition. In another words, 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^{10, 11)}.

Among the dyestuffs, the acid dyes have a good affinity for protein and nylon fibers. Levelling dyes that have small molecular structures among the acid dyes are able to diffuse into the fibers easily. Therefore, if much salts is added in dyeing, levelling improves because dye absorption decreases¹²⁾.

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 a almost constant solubility at a wide temperature range¹³⁾. 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, as analyzing color difference in the dyeing of levelling dyes.

II. Experimental Methods

1. Materials

Nylon and wool fabrics(Testfabrics Co.) were 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±2°C and a RH of 65±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).

Analytical grade anhydrous sodium sulfate (Aldrich Chemical Co., Milwaukee, WI) was used without further purification. The five sodium sulfates employed were:

- (1) Na₂SO₄ I (control): anhydrous sodium sulfate commercially available(Aldrich Chemical Co.).
- (2) Na₂SO₄ II: sodium sulfate recovered from a salt mixture obtained from Mendota,

⁴ Water quality, *op. cit.*

⁵ Technical Report, *op. cit.*

⁶ B. Jenkins, Research report on utilization of drainage salt, salt utilization technical committee of San Joaquin Valley(September 1997).

⁷ Water quality, *op. cit.*

⁸ K. K. Tanji, C. G. Ong, R. A. Dalgren, and M. J. Herbel, "Salt deposits in evaporation ponds: an environmental hazard?", *California Agriculture*, Vol. 46, No. 6(1992), pp.18-21.

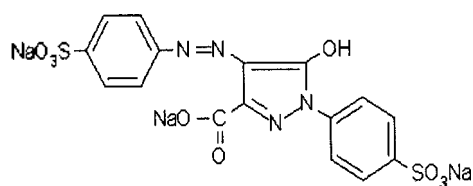
⁹ Technical Report, *op. cit.*

¹⁰ B. Jenkins, *op. cit.*

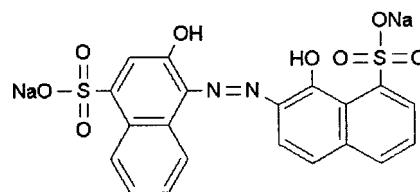
¹¹ D. E. Westcott, J. E. Chilcott, and G. Smith, Pond water, sediment and crystal chemistry. Management of irrigation and drainage systems; Integrated Perspectives, Proceedings of the 1993 National Conference on Irrigation and Drainage Engineering, (Park City, UT, July 1993).

¹² K. R. Cho, *Dyeing theory and practice*, (Hyungsul Publishers, 1991).

¹³ The Merck Index, Twelfth edition, (Merck & Co., Inc., 1996).



C. I. Acid Yellow 23



C. I. Acid Blue 158

〈Fig. 1〉 The Structure of Dyes.

California(U.S.A.).

- (3) Na₂SO₄ III: sodium sulfate resulted from purification of the sample Na₂SO₄ II.
- (4) Na₂SO₄ IV: sodium sulfate recovered from a salt mixture obtained from Red Rock Ranch, California(U.S.A.).
- (5) Na₂SO₄ V: sodium sulfate purified again from Na₂SO₄ IV.

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 Procedure¹⁴. The pH values of dye solutions were measured by using a Corning pH/ion meter 450 (Corning Co., NY, USA).

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

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 500ml of distilled water at 40°C for 30 min.. The mixture was then filtered to remove all insoluble solids. The filtrate solution in a beaker was concentrated to about 250ml 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 dehydrates) 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 (SO₄²⁻), and 4500-NO₃-F (NO₃⁻).

5. Dyeing

Dyeing of nylon fabrics was carried out in a shaker bath with a ratio of the dye solution to fabric (liquor ratio), maintained at pH 3, 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 levelling dyes and different sodium sulfate samples dissolved in distilled water at room temperature. Sodium sulfate

¹⁴ Technical Manual of American Association of Textile Chemists and Colorists, (2000), p. 364-365.

was added according to dye concentrations, 5, 10, 20% (o.w.f.). Nylon fabrics were immersed in the dye bath and temperature of dye bath were increased from 20°C to 95°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.

Dyeing of wool fabrics was carried out in a shaker bath with a ratio of the dye solution to fabric (liquor ratio) maintained at pH 3, 50:1 (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 levelling dyes and different sodium sulfate samples dissolved in distilled water at room temperature. Sodium sulfate was added according to dye concentrations, 10, 15, 20% (o.w.f.). Wool fabrics were immersed in the dye bath and temperature of dye bath were increased from 40°C to 95°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. Clarks and Lubs buffer solution was used by pH of dye bath.

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/ml 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. Actually, large size solar evaporation facilities were equipped in California area. With this study's result, large size solar evaporation facilities is using efficiently to recovery of sodium sulfates from farm drainage (Table 1).

〈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.

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 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%, 99.90%, 67.15% and 76.67%, 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

〈Table 2〉 Elemental Analysis of Recovered Sodium Sulfate Samples

Area	Mendota		Red Rock Ranch	
	Sample II Recovered	Sample III Purified	Sample IV Recovered	Sample V Purified
Elemental Composition %				
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.

¹⁵ B. Jenkins, *op. cit.*

contained almost over 98% of sodium sulfate, which is consistent with the results obtained by other researchers¹⁵⁾. 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%. Table 1 demonstrated that agricultural drainage salts harvested from the solar evaporators located in different areas were significantly different. 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 85.86% and 99.90% 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).

3. Effect of the Salts on the Dyeing with Levelling Dyes

Levelling is increased by sodium sulfate does distribution of dyes between fiber and dye bath profitable to dye bath. In the dyeing with levelling dyes, sodium sulfate of 5 kinds as dyeing builders effect on color difference as following be;

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 the dyeing with levelling dyes, dye concentrations were varied systematically in the dyeing from 1% to 3% and to 5% on weight of fabric (o.w.f.).

(Table 3 and 4) show results of nylon fabrics dyed with two different levelling dyes. Color difference of nylon fabrics dyed with C.I. Acid Yellow 23 were shown (Table 3). Color difference value of all dye concentrations to Na₂SO₄ I was trace in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. Gray scale values of

all dye concentrations to Na₂SO₄ I were 5 grade in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V (Table 3).

Color difference of nylon fabrics dyed with C.I. Acid Blue 158 were shown (Table 4). Color difference value of all dye concentrations to Na₂SO₄ I was trace in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. Gray scale values of all dye concentrations to Na₂SO₄ I were 5 grade in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. In result of above, the purity of sodium sulfate had little color difference in nylon dyeing with levelling dyes (Table 4).

(Tables 5 and 6) show results of wool fabrics dyed with two different levelling dyes. Color difference of wool fabrics dyed with C.I. Acid Yellow 23 were shown (Table 5). Color difference value of all dye concentrations to Na₂SO₄ I was trace in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. Gray scale values of all dye concentrations to Na₂SO₄ I were 5 grade in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V (Table 5).

Color difference of wool fabrics dyed with C.I. Acid Blue 158 were shown (Table 6). Color difference value of all dye concentrations to Na₂SO₄ I was trace in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. Gray scale values of all dye concentrations to Na₂SO₄ I were 5 grade in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. In result of above, the purity of sodium sulfate had little color difference in wool dyeing with levelling dyes (Table 6).

IV. Conclusions

The composition of recovered sodium sulfates from drainage salt in San Joaquin Valley, California and their effect on dyeing of levelling dyes were 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.

In the dyeing with selected levelling dyes,

〈Table 3〉 Color Difference of Nylon Fabrics Dyed with C.I. Acid Yellow 23

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	0.31	5	0.09	5	-0.10	5
Na ₂ SO ₄ III	0.15	5	0.00	5	-0.04	5
Na ₂ SO ₄ IV	0.35	5	-0.27	5	-0.39	5
Na ₂ SO ₄ V	0.25	5	-0.15	5	-0.24	5

〈Table 4〉 Color Difference of Nylon Fabrics Dyed with C.I. Acid Blue 158

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	0.00	5	0.25	5	-0.26	5
Na ₂ SO ₄ III	0.00	5	0.07	5	-0.04	5
Na ₂ SO ₄ IV	0.35	5	0.33	5	-0.21	5
Na ₂ SO ₄ V	0.16	5	0.14	5	-0.09	5

〈Table 5〉 Color Difference of Wool Fabrics Dyed with C.I. Acid Yellow 23

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	0.33	5	0.26	5	-0.13	5
Na ₂ SO ₄ III	0.20	5	0.17	5	-0.02	5
Na ₂ SO ₄ IV	0.40	5	0.35	5	-0.04	5
Na ₂ SO ₄ V	0.19	5	0.19	5	-0.02	5

color difference values of all dye concentrations to Na₂SO₄ I were similar in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. The recovered sodium sulfates from all areas in the valley could be employed in dyeing with levelling dyes. Na₂SO₄ IV had a lot of insoluble precipitate, but effect that a lot of insoluble precipitate gets to color difference was less. Gray scale of all dye concentrations to Na₂SO₄

I were 5 grade in Na₂SO₄ II, Na₂SO₄ III, Na₂SO₄ IV and Na₂SO₄ V. Reason that we consider recrystallization of 2 times in this study is that economic performance drops when compare expense of commercial sodium sulfate with expense by additional recrystallization. Therefore, in this study, we used sodium sulfates that recrystallize until 2 times. Also, We could get conclusion from result of this study that recryst-

〈Table 6〉 Color Difference of Wool Fabrics Dyed with C.I. Acid Blue 158

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	0.31	5	0.27	5	0.18	5
Na ₂ SO ₄ III	0.16	5	0.05	5	0.13	5
Na ₂ SO ₄ IV	0.37	5	0.37	5	-0.14	5
Na ₂ SO ₄ V	0.22	5	0.12	5	-0.10	5

tallization of 2 times is enough as dyeing builder of levelling dyes.

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