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Removal of Liquid Crystal in Discarded Liquid Crystal Display by Sodium Dodecyl Sulfate Cleaning Method

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Abstract

LCD (Liquid Crystal Display) is the important parts of TV, computer, mobile phones, and other electronic products. The liquid crystal in LCD belongs to the high molecular organic compounds. SDS (Sodium Dodecyl Sulfate) as surfactants was used to clean liquid crystal from waste LCD and removal rate of liquid crystal reached 99.6% under the conditions of 1.0 g/L of SDS dosage, 30 min of cleaning time, 500°C of temperature. BaCl₂ was used to precipitate the liquid crystal from the cleaning solution and removal rate of TOC reached 97.0% under the conditions of 1.33 g/L of concentrations of BaCl₂. This result indicates that almost all of the liquid crystal was precipitated.

1. Introduction

Since the beginning of the 21st century, liquid crystal displays (LCDs) [1-3] have rapidly replaced cathode ray tube displays as their mainstream products because of their imaging efficiency and low energy consumption. They are mainly used in liquid crystal computers, televisions and mobile phones. By the end of 2008, LCD TV sales have surpassed the traditional cathode ray tube monitor television. According to statistics [4], in 2013, sales of LCD computers, TVs and mobile phones in China were 230 million, 120 million and 1.2 billion respectively. LCD screen retirement age is about 4 to 6 years, of which cell phone replacement more frequently. Liquid crystal and other materials contained in LCDs have certain physiological toxicity. After a number of years, massively discarded LCDs will endanger the environment. Therefore, proper and effective disposal of discarded LCDs has become an important issue nowadays [5].

Due to the late study of liquid crystal imaging technology than in Japan [6], Germany and Taiwan, China, there is no reason why LCD screens are scrapped. In recent years, scholars in related fields have studied the removal of liquid crystal in liquid crystal displays [7], and have made some progress.

The molecular structure of the liquid crystal can be represented by the following general formula for [8]:

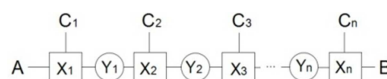


Figure 1. The molecular structure of the liquid crystal.

In the formula, A and B as terminal groups, containing cyano group (CN), (R), alkyl alkoxy (RO), F, NCS, Br, Cl, OCHF₂, OCF₃; X ring system, including benzene, pyridine, pyrimidine ring, two ring, six oxygen cyclohexane ring etc.; Y is a linking group containing olefinic bonds (C=C), acetylene bond (C≡C), sub ethoxy (CH₂O), ethyl ester (CH₂CH₂), (COO); C is the lateral group, its structure and end groups similar to cyano group (CN), (R), alkyl alkyl oxygen radicals (RO) etc.

The liquid crystal belongs to the high organic matter recycling method about LCD in liquid crystal in the literature is the use of organic solvents (e.g. acetone) dissolved in liquid crystal attached to the glass substrate, but the use of most of the organic solvent is toxic and volatile [9-11], have adverse effects on the environment and health. Twelve sodium alkyl sulfate (Sodium Dodecyl Sulfate, SDS) is a common surface active agent [12-13], which can effectively dissolve and remove high grade organic matter. In view of this, this paper uses twelve alkyl sodium sulfate solution to clean the liquid crystal in the liquid crystal glass substrate. The concentration of sodium dodecyl sulfate and washing twelve respectively when asked to rate the influence of temperature on the removal and cleaning liquid crystal, liquid crystal projection by BaCl₂: addition crystallization of the cleaning solution, the total organic carbon of the cleaning solution (Total Organic Carbon, TOC) represents the value content of the cleaning fluid in a liquid crystal.

2. Experimental

2.1. Materials

The selection of raw materials used Samsung 14-inch LCD monitor, the LCD dismantling, remove the LCD glass, conductive film, and other components. Remove the polarizer on the upper and lower surfaces of the liquid crystal glass substrate, in order not to affect the test, do not use organic solvents. The glass substrate with the polarizer removed was washed with distilled water and a glass knife was used to cut open the upper and lower glass substrates.

2.2. Experimental Procedure

A liquid crystal glass substrate as a unit, including the upper and lower glass substrate, each unit by adding different concentrations of SDS cleaning agent 1000 mL, control the cleaning time and temperature, shaken cleaning in the shaker, TOC value in the washing liquid LCD said the removal rate. After cleaning, take a certain amount of cleaning solution in a clean test tube, adding different concentrations of barium chloride solution, shock 3 min after filtration, the residue was 50°C low temperature drying, the filtrate standby. The thermal analysis of the liquid crystal glass substrate before and after cleaning was performed by the Shimadzu TA-50 thermal analyzer. The nitrogen atmosphere was used. The nitrogen flow rate was 25 mL / min and the heating rate was 5°C / min. The total organic carbon Analyzer multi N / C 2100 determination

of TOC in the cleaning solution; the surface structure of the precipitate (liquid crystal - barium lauryl sulfate) was analyzed using a Leica microscope DM4000 M from the United States.

3. Results and Discussion

3.1. SDS Cleaning Test Results

3.1.1. Cleaning Liquid Crystal Content and TOC Values

The liquid crystal material in the liquid crystal glass substrate was extracted by acetone extraction method, and several liquid crystal display glass substrates were placed in acetone solution, and the liquid crystal glass substrate was taken out after soaking for 4 hours. The soaking solution is filtered and placed in a water bath, using a 60 ° C water bath to evaporate the acetone in the soaking solution. Acetone evaporated completely after the liquid crystal placed in the evaporating dish sheltered sheltered from the shade.

Configured 1.0 g·L⁻¹ SDS detergent and measured the TOC value, recorded as TOC1, were taken 0.1 g, 0.5 g, 1.0 g, 1.5 g and 2.0 g of the prepared liquid was dissolved in SDS cleaning agent, shock After 10 min, the TOC in the filtrate was filtered and measured, which was recorded as TOC2. The TOC values produced by different liquid crystal concentrations are the difference between TOC2 and TOC1, which is recorded as TOC. The relationship between the liquid crystal content and the TOC value in the cleaning solution is shown in Figure 2.

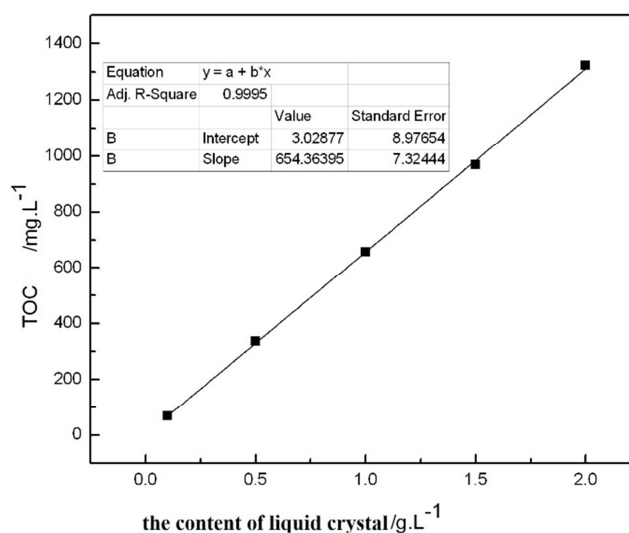


Figure 2. The relationship between the content of liquid crystal and the TOC value in the cleaning solution.

As shown in Figure 2, the cleaning liquid crystal concentration and TOC values are basically proportional relationship, the correlation coefficient of 0.9995. Therefore, the size of the TOC value in the cleaning agent can indicate the level of the liquid crystal. That is, the larger the TOC value in the cleaning agent, the more the liquid crystal is cleaned from the liquid crystal glass substrate and the higher the liquid crystal removal rate

3.1.2. SDS Concentration Effect

Separately prepare 0.1, 0.5, 1.0 and 2.0 g·L⁻¹ of SDS cleaning agent, the upper and lower glass substrate is placed in the cleaning agent. Shake in the shaker clean, shaker speed

120 r / min. The effect of the concentration of the SDS cleaning agent on the cleaning effect of the liquid crystal at a cleaning time of 20 min and a temperature of 40°C is shown in Table 1.

Table 1. The effect of SDS dosage on cleaning rate of liquid crystal.

SDS dosage /g·L ⁻¹	group	TOC value before cleaning /mg·L ⁻¹	TOC value after cleaning /mg·L ⁻¹	difference /mg·L ⁻¹	average value /mg·L ⁻¹	liquid crystal removal rate /%
0	1 #	3.93	6.81	2.88	2.86	0.25
	2 #	3.91	6.76	2.85		
	3 #	4.01	6.84	2.83		
0.1	1 #	244.1	520.4	276.3	276.5	24.5
	2 #	239.8	517.1	277.3		
	3 #	242.4	518.3	275.9		
0.5	1 #	480.2	1023.4	543.2	542.4	48.1
	2 #	483.7	1024.9	541.2		
	3 #	479.5	1022.1	542.6		
1.0	1 #	900.7	2016.7	1116	1114.8	98.9
	2 #	900.5	2014.8	1114.3		
	3 #	902.8	2016.9	1114.1		
2.0	1 #	1705.5	2314.4	608.9	610.36	54.1
	2 #	1706.3	2316.8	610.5		
	3 #	1708.5	2320.1	611.6		

It can be seen from Table 1 that when the SDS concentration in the cleaning agent is within the range of 0 to 1.0 g·L⁻¹, the TOC value in the cleaning solution increases continuously, indicating that the amount of liquid crystal is gradually increased. When the SDS concentration is 1.0 g·L⁻¹, the TOC value of the cleaning solution reached the maximum, and the liquid crystal removal rate was 98.9%. When the concentration of SDS was continuously increased, the TOC value decreased as the concentration of SDS increased to a certain extent,, The formation of "micelles", leading to weakening of the cleaning agent, the LCD cleaning ability to remove. LCD removal rate R is calculated as shown in formula (1) (the same below).

$$R = \frac{\text{TOC average}}{\text{TOC maximum}} \times 100\% \quad (1)$$

Where: TOC maximum value under the best conditions that the cleaning fluid TOC value, 1127.3 mg·L⁻¹

3.1.3. The Impact of Cleaning Time

Preparation of 1.0 mg·L⁻¹ SDS detergent, the upper and lower glass substrate was placed at a temperature of 40°C cleaning agent shaker in the shaker cleaning, shaker speed 120 r/min respectively, at different times measured TOC cleaning solution, cleaning time Impact on the LCD cleaning effect as shown in Table 2.

Table 2. The effect of cleaning time on cleaning rate of liquid crystal.

cleaning time /min	group	TOC value before cleaning /mg·L ⁻¹	TOC value after cleaning /mg·L ⁻¹	difference /mg·L ⁻¹	average value /mg·L ⁻¹	liquid crystal removal rate /%
5	1 #	900.4	1537.5	637.1	634.7	56.3
	2 #	900.9	1539.4	638.5		
	3 #	901.7	1530.3	628.6		
10	1 #	900.9	1744.6	843.7	845.8	75.1
	2 #	898.4	1739.8	841.4		
	3 #	897.1	1749.5	852.4		
20	1 #	901.2	2015.1	1113.9	1114.6	98.9
	2 #	902.3	2017.2	1114.9		
	3 #	900.8	2015.9	1115.1		
30	1 #	899.7	2019.8	1120.1	1119.9	99.3
	2 #	901.4	2019.4	1118		
	3 #	902.9	2024.6	1121.7		
40	1 #	900.5	1816.6	916.1	918.7	81.4
	2 #	898.3	1815.3	917		
	3 #	897.9	1820.9	923		
50	1 #	899.8	1607.4	707.6	708.0	62.8
	2 #	900.6	1614.8	714.2		
	3 #	903.1	1605.4	702.3		
60	1 #	901.8	1605.1	703.3	704.4	62.5
	2 #	897.9	1603.9	706		
	3 #	896.7	1600.7	704		

It can be seen from Table 2 that the TOC of the cleaning solution increases continuously within 5 min to 30 min, reaches the maximum value at 30 min, and the liquid crystal removal rate is 99.3%. When the cleaning time continues to increase, the liquid crystal removal rate decreases because the liquid crystal The VOCs contained will have a part of volatile, so the cleaning time should not be too long.

3.1.4. Cleaning Temperature Effects

Preparation of $1.0 \text{ g} \cdot \text{L}^{-1}$ SDS cleaning agent, the upper and

lower glass substrate was placed in a cleaning agent on the shaker washes, speed 120 r / min, cleaning time was 30 min. TOC values were measured at different temperatures in the cleaning solution, cleaning temperature on the LCD cleaning effect as shown in Table 3. As can be seen from Table 3, the TOC value increases continuously at a temperature in the range of 20°C to 60°C. When the temperature reaches 60°C, the TOC value reaches the maximum, and the liquid crystal removal rate is 99.9%.

Table 3. The effect of cleaning temperature on cleaning rate of liquid crystal.

cleaning temperature /°C	group	TOC value before cleaning /mg·L ⁻¹	TOC value after cleaning /mg·L ⁻¹	difference /mg·L ⁻¹	average value /mg·L ⁻¹	liquid crystal removal rate /%
20	1 #	901.4	1493.2	591.8	597.5	53.0
	2 #	897.4	1501.2	603.8		
	3 #	899.5	1496.4	596.9		
30	1 #	898.9	1659.3	760.4	759.8	67.4
	2 #	900.1	1658.1	758		
	3 #	901.6	1662.7	761.1		
40	1 #	899.7	1896.5	996.8	999.6	88.7
	2 #	900.8	1899.3	998.5		
	3 #	897.6	1901.2	1003.6		
50	1 #	902.1	2025.7	1123.6	1122.5	99.6
	2 #	903.1	2024.3	1121.2		
	3 #	901.7	2024.6	1122.9		
60	1 #	899.8	2027.1	1127.3	1126.5	99.9
	2 #	900.8	2025.9	1125.1		
	3 #	897.9	2025.1	1127.1		
70	1 #	900.6	2004.4	1103.8	1106.4	98.1
	2 #	898.6	2001.9	1103.3		
	3 #	897.4	2009.5	1112.1		

It can be seen from Table 3 that the TOC value increases continuously when the temperature is in the range of 20°C to 60°C. When the temperature reaches 60°C, the TOC value reaches the maximum, and the liquid crystal removal rate is 99.9%.

3.1.5. Before and After Cleaning Liquid Crystal Glass TG Curve

The thermal gravimetric analysis of the liquid crystal glass powder before and after cleaning under the condition of the concentration of SDS cleaning agent $1.0 \text{ g} \cdot \text{L}^{-1}$, the cleaning time 30 min and the cleaning temperature 60°C, the thermogravimetric curves of the liquid crystal glass before and after cleaning are shown in Figures 3 and 4.

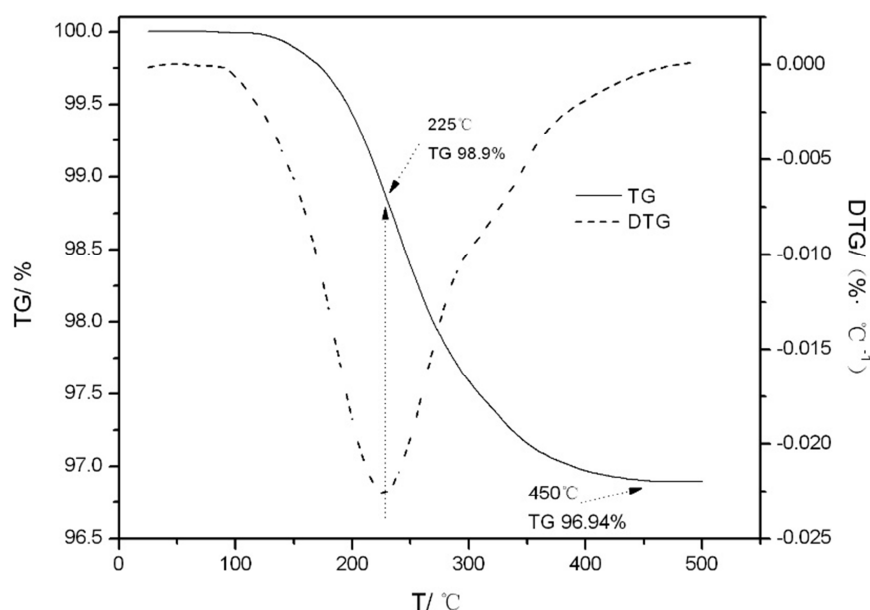


Figure 3. The TG curves of liquid crystal glass powder before cleaning.

As can be seen from Figure 3, the weight of the liquid crystal glass before washing started to lose weight at about 150°C, that is, the liquid crystal attached to the liquid crystal glass powder began to decompose; the peak of DTG curve appeared at 225°C, indicating that the decomposition was most rapid; when the temperature reached 450°C, Weight loss rate was 96.94%.

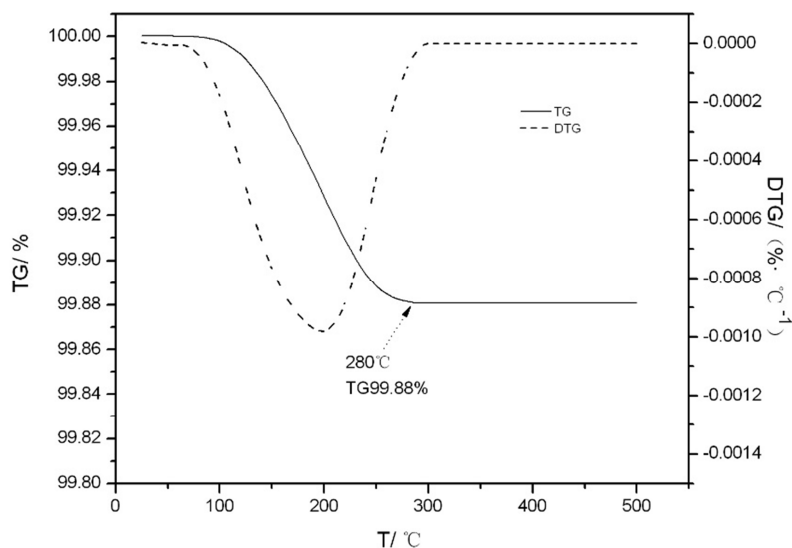
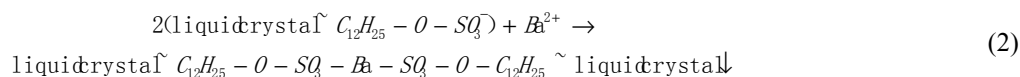


Figure 4. The TG curves of liquid crystal glass powder after cleaning.

As can be seen from Figure 4, the weight of the liquid crystal glass powder after cleaning started to appear weight loss at about 150°C; when the temperature reached 280°C, the weight loss rate was 99.88%; the weight loss of the sample was not obvious; thereafter, Indicates that the liquid crystal has been completely decomposed. Therefore, SDS cleaning liquid crystal cleaning removal effect is obvious, LCD cleaning removed almost completely.

3.2. SDS Washing Liquid Crystal Precipitation Test Results

The combination of liquid crystal and SDS in the cleaning solution, and the proper amount of BaCl₂ added to the cleaning solution will precipitate the crystal of SDS, accompanied by the precipitation of the liquid crystal. Precipitation mechanism as shown in formula (2):



The sulfonic acid group in SDS can combine with barium ion, while the alkyl group can combine with liquid crystal to form crystal precipitation finally, so as to achieve the purpose of liquid crystal removal in the cleaning liquid. The TOC value of the cleaning solution before dosing was 1126.5 mg·L⁻¹. After adding appropriate amount of BaCl₂ to the

cleaning solution under the best conditions, the solution was shaken for 3 minutes, and the filtrate was filtered to obtain the filtrate. The effect of different BaCl₂ concentrations on the liquid crystal precipitation in the SDS cleaning solution is shown in Table 4.

Table 4. The effect of concentrations of BaCl₂ on liquid crystal precipitation form SDS cleaning solution.

concentrations of BaCl ₂ /g·L ⁻¹	groups	TOC value of the filtrate after dosing/mg·L ⁻¹	TOC filtrate average/mg·L ⁻¹	TOC removal rate /%
0.33	1 #	169.6	168.3	85.1
	2 #	166.5		
	3 #	168.9		
0.67	1 #	40.1	41.4	96.3
	2 #	42.3		
	3 #	41.7		
1.33	1 #	33.4	33.3	97.0
	2 #	34.5		
	3 #	32.1		
2.0	1 #	32.8	32.9	97.1
	2 #	32.3		
	3 #	33.6		
2.67	1 #	32.3	31.6	97.2
	2 #	31.9		
	3 #	30.6		

As can be seen from Table 4, when the concentration of BaCl_2 varies from $0.33 \text{ g} \cdot \text{L}^{-1}$ to $1.33 \text{ g} \cdot \text{L}^{-1}$, the concentration of TOC in the filtrate decreases with the increase of BaCl_2 concentration. When the concentration of BaCl_2 is $1.33 \text{ g} \cdot \text{L}^{-1}$, the TOC is removed. When the concentration of BaCl_2 was higher than $1.33 \text{ g} \cdot \text{L}^{-1}$, the TOC removal rate did not change significantly with the increase of BaCl_2 concentration.

Two sets of $1.0 \text{ g} \cdot \text{L}^{-1}$ SDS detergent were set up, one of which was placed on the liquid crystal glass substrate and the other one was untreated in the control group. The solution was shaken for 30 min on a shaker and controlled at a temperature of 60°C . After cleaning, add appropriate amount of BaCl_2 to each of the two cleaning solutions for 3 min, filter to obtain residue, and filter residue to dry at a low temperature of 50°C . Observed and analyzed the surface structure of the two pieces of the residue by microscope under magnification of 200 times. The results are shown in Figures 5 and 6.

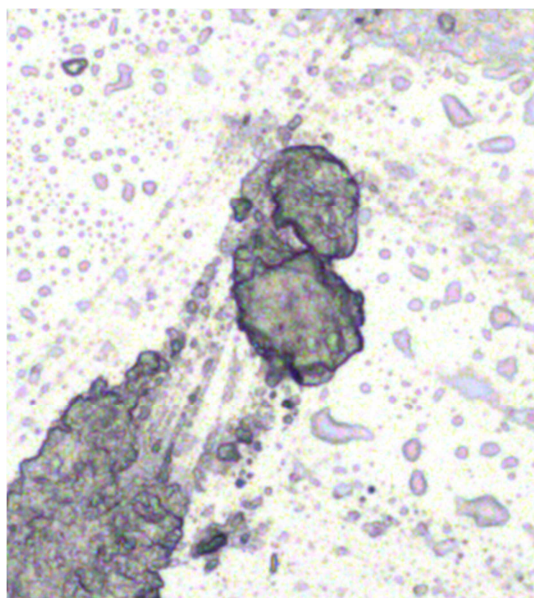


Figure 5. The drawing of crystallization of the blank cleaning liquid.

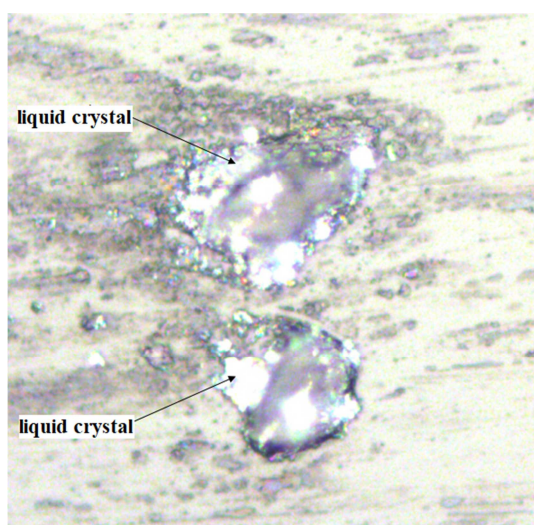


Figure 6. The drawing of crystallization of the cleaning liquid of LCD.

Can be seen from Figure 5, untreated control group cleaning fluid residue powder (Sodium Dodecyl Sulfate) surface dimming. As shown in Figure 6, the surface of the cleaning liquid residue (liquid crystal-barium lauryl sulfate) after washing the liquid crystal glass substrate is bright, indicating that the liquid crystal is attached with the reflective material, and the precipitation effect of BaCl_2 on the liquid crystal is obvious.

4. Conclusion

The liquid crystal in the liquid crystal glass substrate was cleaned with SDS cleaning agent. The liquid crystal cleaning removal rate on the glass substrate was 99.6 at a SDS concentration of $1.0 \text{ g} \cdot \text{L}^{-1}$, a cleaning time of 30 min and a cleaning temperature of 50°C . The liquid crystal in the cleaning solution was precipitated by BaCl_2 doping method. Under BaCl_2 concentration of $1.33 \text{ g} \cdot \text{L}^{-1}$, the liquid crystal was precipitated with barium lauryl sulfate. The removal rate of TOC in the cleaning solution was 97.0% Completely precipitated.

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