

# ALTERNATIVE METHOD FOR EXHAUSTED DYE BATH RECYCLING BASED ON REMOVAL OF RESIDUAL DISSOLVED REACTIVE ANIONIC DYES

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**Abstract:** This work presents precipitation and removal of hydrolyzed reactive dyes by action of liquid ion exchangers in co-action of inorganic flocculant. After addition of cationic surfactant and aqueous aluminium chloride the precipitation occurs and practically decolorized aqueous phase is obtained. The treated water was completely decolorized and purified by addition of powdered charcoal.

**Keywords:** reactive dye, ion exchange, ionic liquid, flocculant

## 1 INTRODUCTION

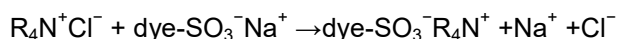
In batch dyeing a certain amount of textile material is loaded into a dyeing machine and brought to equilibrium with a solution containing the dye and the auxiliaries over a period of minutes to hours. In batch dyeing, dye, alkali (sodium hydroxide or sodium carbonate or bicarbonate) and salt are added to the dye bath in one step, at the beginning of the process, or stepwise. Its amount is determined by the reactivity of the system and the desired depth of shade. Salt is added to improve bath exhaustion: the concentration employed depends on the substantivity of the dye and on the intensity of the shade. After dyeing, the liquor is drained off and the material is rinsed and then washed off with the addition of auxiliaries.

Concentrated waste water streams (spent liquors) containing hardly- or non-biodegradable compounds (hydrolyzed reactive dyes, etc.) should be treated at source. For the textile finishing industry, advanced oxidation with a Fenton-like reaction is proposed as a viable pretreatment technique [1]. However, application of strong oxidants causes production of adsorbable organic halogens (AOX) by reaction with NaCl and dissolved organic compounds and moreover oxidation process is not able to remove the dissolved inorganic salts from treated water.

Above mentioned problems could be solved by efficient removal of dissolved dyes from spent dyeing liquors and subsequent re-use of colorless aqueous NaCl solution for next dyeing step. Usually membrane techniques are applied in various ways for the treatment of segregated streams to allow water reclamation and re-use closely integrated with the process. However, membrane separation is very

expensive technique. By our opinion, the more cost-effective method for dye bath recycling is based on removal of dissolved dyes using ion-exchange accompanied by flocculation and subsequent action of low quantities of common adsorbent (active carbon).

Effective removal of acid dyes from spent dyeing liquor is based on ion exchange reaction caused by addition of hydrophobic quarternary ammonium chlorides (ionic liquids,  $R_4N^+Cl^-$  [2]) into the spent liquor.  $R_4N^+Cl^-$  serve as a liquid anion exchanger. We observed that the replacement of chloride anions of  $R_4N^+Cl^-$  by larger anions (anions of the acid dyes) proceeds smoothly even at room temperature [3, 4]:



The interaction of these dyes with suitable  $R_4N^+Cl^-$  salts produces slightly soluble ionic salts which can settle after a long contact time or can be removed more efficiently by the action of common inorganic flocculants [3-5].

The aim of this work is to verify possibilities for simple decolorization of model and subsequently industrial aqueous effluents produced in dyeing process. For this purpose decolorization efficiencies of three commonly used reactive dyes by action of five industrially produced and cheap ionic liquids were tested and the most efficient procedure was subsequently applied for treatment of spent industrial dye baths.

## 2 MATERIALS AND METHODS

### 2.1 Dyes and reagents

The used dyes Remazol Brilliant Blue R (**RBBR**, CAS No. 2580-78-1), Reactive Blue 4 (**RB4**, CAS No. 13324-20-4), Reactive Black 5 (**RB5**, CAS No. 17095-24-8) and quarternary ammonium salts  $R_4N^+Cl^-$  (cetyltrimethylammonium chloride (cetylNMe<sub>3</sub>Cl), benzalkonium chloride 50 wt.% aqueous solution (AlkBzNMe<sub>2</sub>Cl), Aliquat 336, Luviquat™ FC 370 (copolymer of poly[(3-methyl-1-vinylimidazolium chloride)-co-(1-vinylpyrrolidone)] (40 wt.% active ingredients) and 20 wt.% aqueous solution of poly(diallyldimethylammonium chloride) (Table 3) and inorganic coagulant AlCl<sub>3</sub>·6H<sub>2</sub>O were supplied by Sigma-Aldrich Co. Powdered charcoal Silcarbon CW20 was supplied by Silcarbon AktivKohle GmbH (Germany).

Solid reagents cetylNMe<sub>3</sub>Cl and AlCl<sub>3</sub> were used as 0.1 M aqueous stock solutions. Mixed aqueous  $R_4N^+Cl^-$  based reagent AB consisted of 0.1 M Aliquat 336 and 0.4 M benzalkonium chloride was prepared by dissolution of 10.1 g of Aliquat 336 in concentrated aqueous solution of AlkBzNMe<sub>2</sub>Cl (70 g of 50 wt.% aq. AlkBzNMe<sub>2</sub>Cl dissolved in 150 mL of water), the obtained solution was diluted to the exact volume of 250 mL by water. Mixed aqueous  $R_4N^+Cl^-$  reagent AC containing 50 mM Aliquat 336 and 0.1 M cetylNMe<sub>3</sub>Cl was prepared by dissolution of 5.25 g of Aliquat 336 in 0.1 M aqueous solution of cetyltrimethylammonium chloride (8 g of cetylNMe<sub>3</sub>Cl dissolved in 200 mL of water under heating), the obtained solution cooled to the room temperature was diluted to the exact volume of 250 mL with demineralized water.

### 2.2 Exhausted dye baths

Hydrolyzed dye solutions (RB4, RB5 and RBBR) were obtained by addition of sodium carbonate (1 g) to the 250 mL of 10 mM reactive dye aqueous solution and heating at 90°C for 30 minutes (Table 1).

Model exhausted dye bath was prepared by mixing of above mentioned hydrolyzed RB5, RB4 and RBBR aqueous solutions (50 mL of each hydrolyzed dye solution).

Exhausted red dye bath 1 was wastewater after the specific dyeing process obtained from Czech textile Company.

Exhausted red dye bath 2 was wastewater obtained after the same dyeing process using recycled red dye bath 1.

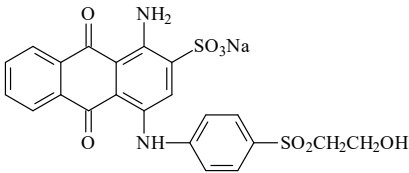
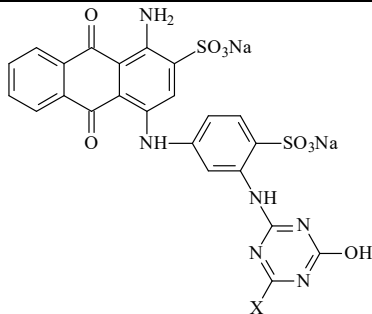
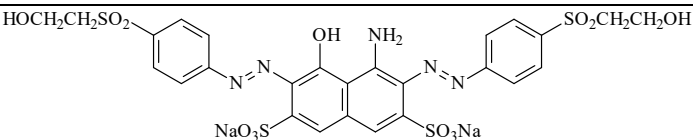
The composition of the (model) exhausted dye baths are given in Table 2.

### 2.3 Instruments

A UV-visible spectrophotometer Libra S22 (Biochrom, Great Britain) was used to measure the absorbance values of the dyes to establish their  $\lambda_{max}$  and concentrations. A magnetic stirrer HeiTEC (Heidolph Instruments GmbH&Co.) was used for stirring of (model) exhausted dyeing baths.

Chemical oxygen demand (COD) measurements were obtained using the HACH-LANGE apparatus (DR2800) according to standard methods given by the producer. The COD analyses were done with the dichromate (VI) LCK 014 and LCK 914 tests.

**Table 1** Description of used dyes

Applied dye ( $\lambda_{max}$ )	Structure and molecular weight of studied hydrolyzed dyes
Hydrolyzed Remazol Brilliant Blue R ( <b>hRBBR</b> ) 592 nm	 $M_r = 524.5 \text{ g/mol}$
Hydrolyzed Reactive Blue 4 (X = Cl or OH) ( <b>hRB4</b> ) 597 nm	 $M_r = 644.5 \text{ g/mol}$
Hydrolyzed Reactive Black 5 ( <b>hRB5</b> ) 596 nm	 $M_r = 787.7 \text{ g/mol}$

**Table 2** Composition of exhausted dye baths

Exhausted dyeing bath composition	pH	NaCl content [g/L]	Dye content [mmol/L]	COD [mg O <sub>2</sub> /L]
Model	11.1	2.8	10	13290
Red 1	11.2	80	approx. 1	8180
Red 2	11.0	76	approx. 0.5	4137

#### 2.4 Colour removal from (model) dye baths

Aqueous R<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> solution (or appropriate amount of ionic liquid R<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup>) was added drop wise to 100 mL of (model) spent dyeing bath under stirring until precipitation of ion pairs occurs (optimal molar ratio R<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup>:dye-SO<sub>3</sub><sup>-</sup> 1:1) and after 15 minutes (or 120 min. in case of Aliquat 336 addition) of vigorous stirring, the sample of obtained mixture was collected, filtered and measurement of absorbance of filtrate was accomplished. To the stirred reaction mixture of produced ion pair dye-SO<sub>3</sub><sup>-</sup>R<sub>4</sub>N<sup>+</sup> in water, 0.1 M aq. AlCl<sub>3</sub> was added drop wise until pH value reached pH=6.0-6.4. After 15 minutes of stirring at the speed of 400 rpm and the temperature of 22±2°C, filtration and subsequent measurement of absorbance of filtrate was accomplished. Alternatively, powdered charcoal was added to the obtained filtrate and suspension was filtered after 30 min. of stirring. Absorbance of obtained filtrate and COD were measured.

The decolorization efficiency (*DE* %) of dyes was determined from absorbance measurements, according to the concentration-absorbance standard curves at the respective maximum adsorption wavelength of the individual dye solutions. Afterwards, *DE* % was calculated from (1):

$$DE (\%) = [1 - (A/A_0) \times 100] \quad (1)$$

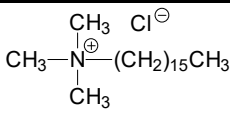
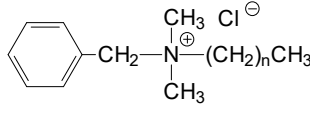
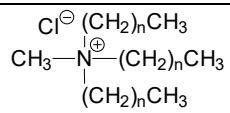
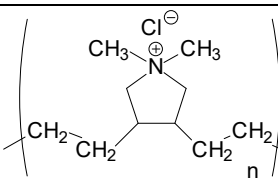
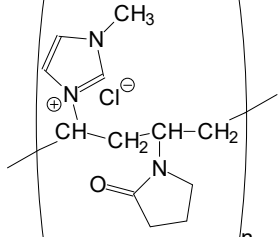
where *A* and *A*<sub>0</sub> denote the absorbance in the solution after and before precipitation, respectively.

Removal efficiency of chemical oxygen demands (*RECOD*) of dye baths, hydrolyzed dye solutions and obtained filtrates were measured using Hach-Lange cuvette tests LCK 1014 and LCK 914 and the *COD* removal efficiency was calculated using (2):

$$RECOD (\%) = [1 - (COD/COD_0) \times 100] \quad (2)$$

where *COD* and *COD*<sub>0</sub> denote the chemical oxygen demand in the solution after and before precipitation, respectively.

**Table 3** Description of used R<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup>

Used R <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	Structure of used R <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>
Cetyltrimethyl-ammonium chloride cetylNMe <sub>3</sub> Cl C <sub>19</sub> H <sub>42</sub> ClN M <sub>r</sub> =320.0 g/mol	
Benzalkonium chloride AlkBzNMe <sub>2</sub> NCl average M <sub>r</sub> =348.4 g/mol	
Aliquat 336 average M <sub>r</sub> =432.0 g/mol	
Poly(diallyldimethyl-ammonium chloride) NdiallylMe <sub>2</sub> Cl monomer unit: C <sub>12</sub> H <sub>26</sub> ClN M <sub>r</sub> =219.8 g/mol	
Luviquat™ FC 370 (copolymer of poly[(3-methyl-1-vinylimidazolium chloride)-co-(1-vinylpyrrolidone)]) MIM-(CH <sub>2</sub> ) <sub>4</sub> NMPCl monomer unit: C <sub>14</sub> H <sub>24</sub> ClN <sub>3</sub> O M <sub>r</sub> =285.8 g/mol	

### 3 RESULTS AND DISCUSSION

Model exhausted dyeing baths were prepared by alkaline hydrolysis of 10 mM reactive dye solutions. In case of vinyl sulfone-type reactive dyes (RBBR and RB5) vinylsulfonyl groups were hydrolyzed to the corresponding inorganic sulphate ( $\text{Na}_2\text{SO}_4$ ) and dye- $\text{SO}_2\text{CH}_2\text{CH}_2\text{OH}$ . In case of chlorotriazine-type reactive dye RB4 chlorotriazine was hydrolyzed to the corresponding hydroxytriazine and  $\text{NaCl}$  (Table 1).

For practical reasons the cheap  $\text{R}_4\text{N}^+\text{Cl}^-$  salts industrially used as cationic surfactants (cetyltrimethylammonium chloride, benzalkonium chloride and Aliquat 336) were tested for the precipitation of hydrolyzed hRBBR, hRB5 and hRB4 in the form of appropriate dye- $\text{SO}_3^-\text{R}_4\text{N}^+$  ion pairs and their *DE* were compared with action of polymeric  $\text{R}_4\text{N}^+\text{Cl}^-$  agents poly(diallyldimethylammonium) chloride and Luviquat<sup>TM</sup> FC 370 (copolymer of poly[(3-methyl-1-vinylimidazolium chloride)-co-(1-vinylpyrrolidone)]) (Table 3).

It was proved that optimal dosage of  $\text{R}_4\text{N}^+\text{Cl}^-$  into the spent dyeing bath is related to molar quantity of  $\text{R-SO}_3^-$  groups found in the treated bath [2-4]. As we described earlier, the precipitation of produced ion pair dye- $\text{SO}_3^-\text{R}_4\text{N}^+$  occurred entirely in case, if ion pair of low polarity (substituent R is long alkyl chain preferably) is formed [3-6].

Using mentioned  $\text{R}_4\text{N}^+\text{Cl}^-$ , the best separation of hydrolyzed dyes was occurred in case of application of water-insoluble Aliquat 336 (ionic liquid composed of 2:1 mixture of methyl trioctyl- and methyl tridecylammonium chloride) [7]. However, the time for effective separation (reactive extraction of dyes into the Aliquat 336 layer) takes hundreds of minutes under vigorous stirring due to the slow

mass transfer of dyes from aqueous phase into the lipophilic ionic liquid Aliquat 336 phase. In case of water-soluble  $\text{R}_4\text{N}^+\text{Cl}^-$ , the precipitation occurred during few minutes of vigorous stirring after addition of appropriate amount of 0.1 M aqueous  $\text{R}_4\text{N}^+\text{Cl}^-$  solution (Table 2). Benzalkonium chloride and cetyltrimethylammonium chloride were tested as the most effective water-soluble  $\text{R}_4\text{N}^+\text{Cl}^-$ . As could be seen, the decolorization efficiency depends more or less on molecular weight of produced ion pair dye- $\text{SO}_3^-\text{R}_4\text{N}^+$ . On the other hand (Table 2), in most applications, the polymeric  $\text{R}_4\text{N}^+\text{Cl}^-$  failed in separation of dyes based on precipitation of produced dye- $\text{SO}_3^-\text{R}_4\text{N}^+$  ion pairs. This is probably caused by high polarity (aqueous solubility) of these polymers and low molecular weight of obtained dye- $\text{SO}_3^-\text{R}_4\text{N}^+$  ion pair (calculated using mol. weight of monomer unit of Luviquat FC370 or poly(diallyldimethylammonium chloride)) in comparison with above mentioned liquid ion exchangers  $\text{R}_4\text{N}^+\text{Cl}^-$  (Table 4).

We observed that even though Aliquat 336 is not water soluble. It is soluble in concentrated aqueous solutions of benzalkonium chloride or cetyltrimethylammonium chloride. To solve the problems with required long reaction time essential for achievement of high *DE* in case of Aliquat 336 application and difficulties with precise dosing of highly viscous Aliquat 336, mixed  $\text{R}_4\text{N}^+\text{Cl}^-$  aqueous solutions of benzalkonium chloride or cetyltrimethylammonium chloride with Aliquat 336 were prepared and tested for the removal of hydrolyzed reactive dyes from exhausted dye baths. These mixtures enable simple and precise dosage of  $\text{R}_4\text{N}^+\text{Cl}^-$  into the treated hydrolyzed dye solution (model) spent dyeing baths and rapid separation of produced insoluble dye- $\text{SO}_3^-\text{R}_4\text{N}^+$  ion pairs from the aqueous mixture (Table 4).

**Table 4** Changes in relative molar mass ( $M_r$ ) of dyes caused by ion exchange of cations and determined *DE* related to aqueous solubility of obtained dye( $\text{SO}_3\text{NR}_4$ )<sub>n</sub> ion pairs

Used anionic dye dye( $\text{SO}_3\text{Na}$ ) <sub>n</sub>	Applied $\text{R}_4\text{N}^+\text{Cl}^-$	Produced ion pair	$M_r$ of ion pair [g/mol]	<i>DE</i> [%]
hRB5	$\text{C}_{16}\text{Me}_3\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NMe}_3\text{C}_{16})_2$	1310.8	79.1
hRB5	$\text{AlkBzMe}_2\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NAlkBzMe}_2)_2$	1463	68.6
hRB5	$\text{MeOct}_3\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NMeOct}_3)_2$	1282.8	86.1
hRB5	Luviquat <sup>TM</sup> FC370 MIM-( $\text{CH}_2$ ) <sub>4</sub> NMPCl	$\text{hRB5}(\text{SO}_3\text{MIM}-(\text{CH}_2)_4\text{NMP})_2$	1136.3	44.6
hRB5	polydiallyldiMeNCl	$\text{hRB5}(\text{SO}_3\text{NdiallylMe}_2)_2$	994.2	36.8
hRB4	$\text{C}_{16}\text{Me}_3\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NMe}_3\text{C}_{16})_2$	1167.6	97.2
hRB4	$\text{AlkBzMe}_2\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NAlkBzMe}_2)_2$	1319.8	99.92
hRB4	$\text{MeOct}_3\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NMeOct}_3)_2$	1335.9	99.95
hRB4	Luviquat <sup>TM</sup> FC370 MIM-( $\text{CH}_2$ ) <sub>4</sub> NMPCl	$\text{hRB5}(\text{SO}_3\text{MIM}-(\text{CH}_2)_4\text{NMP})_2$	993.1	11.5
hRB4	polydiallyldiMeNCl	$\text{hRB5}(\text{SO}_3\text{NdiallylMe}_2)_2$	851	-
hRBBR	$\text{C}_{16}\text{Me}_3\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NMe}_3\text{C}_{16})_2$	786	62.2
hRBBR	$\text{AlkBzMe}_2\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NAlkBzMe}_2)_2$	862.2	76
hRBBR	$\text{MeOct}_3\text{NCl}$	$\text{hRB5}(\text{SO}_3\text{NMeOct}_3)_2$	870.2	97
hRBBR	Luviquat <sup>TM</sup> FC370 MIM-( $\text{CH}_2$ ) <sub>4</sub> NMPCl	$\text{hRB5}(\text{SO}_3\text{MIM}-(\text{CH}_2)_4\text{NMP})_2$	721.8	66.5
hRBBR	polydiallyldiMeNCl	$\text{hRB5}(\text{SO}_3\text{NdiallylMe}_2)_2$	627.7	50.5

**Table 5** Effect of  $R_4N^+Cl^-$  mixtures, addition of  $AlCl_3$  and adsorption on charcoal *DE* and *RECOD*

Exhausted dye bath	Applied $R_4N^+Cl^-$ mixture	DE [%]	Quantity of 0.1M aq. $AlCl_3$ solution	DE [%]	Quantity of added charcoal	DE [%]	RECOD [%]
Model	AB (13 mL/L)	99.7	50 mL/L	99.9	1 g/L	99.99	98.0
Model	AC (40 mL/L)	90.5	50 mL/L	92.3	1 g/L	99.8	97.1
Red 1	AB (5 mL/L)	61.8	10 mL/L	96.7	1 g/L	97.0	41.9
Red 1	AC (5 mL/L)	51.5	10 mL/L	92.5	1 g/L	96.5	36.3
Red 1	-	-	-	-	20 g/L	97.9	31.2
Red 2	AB (2.5 mL/L)	58.8	38 mL/L	94.5	0.5 g/L	96.7	31.6
Red 2	AC (2.5 mL/L)	36.9	42 mL/L	71.3	0.5 g/L	95.9	42.3
Red 2	-	-	-	-	20 g/L	98.4	22.9

Subsequent addition of 0.1 M  $AlCl_3$  in quantity ensuring neutralization of exhausted dye bath treated with  $R_4N^+Cl^-$  mixture was accompanied by coagulation and flocculation of  $Al(OH)_3$ . The produced dye- $SO_3^-R_4N^+$  ion pairs were well removable by adsorption on the rapid sedimented flocs of  $Al(OH)_3$  (Table 5).

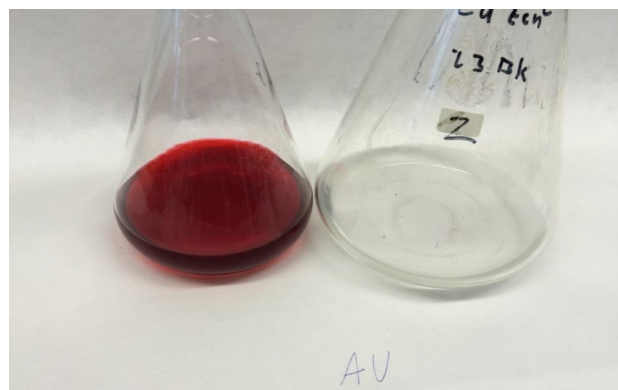
The subsequent short time mixing of obtained filtrates with charcoal enables complete decolorization of filtered treated dye baths in optimal cases (Table 5).

As could be seen in Table 5, the obtained decolorization efficiency (DE) and removal efficiency of chemical oxygen demand (RECOD) using combination of dye- $SO_3^-R_4N^+$  ion pair formation with subsequent neutralization and flocculation using  $AlCl_3$  is higher than in case of simple action of large-quantity powdered charcoal.

#### 4 CONCLUSIONS

In this study, the model (laboratory prepared) and real exhausted reactive dye baths after the industrial reactive dyeing process were decolorized for re-use in the next dyeing step. Due to high salinity, high pH and intense color, it is the most problematic textile wastewater type from an environmental point of view. However, using appropriate mixture of hydrophobic and hydrophilic ionic liquids combined with coagulation/flocculation enables simple separation of precipitated hydrolyzed dyes and subsequent final treating with low quantity (0.5-1.0 g/L) of powdered charcoal results in excellent decolorization of original exhausted dye baths which enables complete re-use of obtained filtrate in next dyeing step (Figure 1).

We verified in this study that especially mixture of cheap and commercially simply available ionic liquids benzalkonium chloride and Aliquat 336 prepared in the form of the easy to handle aqueous mixture with subsequent addition of  $AlCl_3$  as neutralizing and flocculating agent can be more efficient, economically reasonable and cheaper than decolorization using high quantity (20 g/L) of charcoal. In addition, application of aluminium chloride for neutralization of treated exhausted dye baths enables not only additional decolorization but also simple removal of precipitated dye- $SO_3^-R_4N^+$  by flocculation and sedimentation.



**Figure 1** Red dye bath 2 (recycled) before and after treatment

The treated exhausted red dye bath 1 was recycled efficiently in dyeing process and subsequently treated using described combined method based on application of benzalkonium chloride and Aliquat 336 mixture with  $AlCl_3$  and subsequent simple adsorption using low quantity of powdered charcoal (Figure 1).

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