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Dyes and Pigments 64 (2005) 251–257

DYES and PIGMENTS

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Selective extraction and separation of textile anionic dyes from aqueous solution by tetrabutyl ammonium bromide

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Received 7 February 2004; received in revised form 11 March 2004; accepted 31 May 2004

Abstract

Tetrabutyl ammonium bromide (TBAB) has been demonstrated to be a very effective reagent for selective extraction of anionic dyes from aqueous solution. The solution of TBAB in methylene chloride is able to extract 98% of 50 mg L^{-1} concentration of dye solution. The distribution ratio is reasonably high ($D = 49.0$) even in the presence of excess chloride and sulphate ions. Extracted dye in the organic phase can be back extracted with excess of salicylic acid and sodium carbonate solution. After salicylic acid–sodium carbonate stripping and water washing, the organic layer of TBAB becomes regenerated and it can be recycled for further extraction. The stripped solution on acidification precipitated salicylic acid and the dye is recovered.

Keywords: Separation; Anionic dyes; TBAB; Recovery; Solvent reuse

1. Introduction

Large quantities of dyes are manufactured annually worldwide and are used in a variety of applications such as textiles, paper, foodstuffs and cosmetics. Textile dyes are of environmental interest because of their widespread use, their potential for formation of toxic aromatic amines and their low removal rate during waste treatment [1]. The growth in industry and the changes in manufacturing processes have resulted in an increase in the volume and complexity of wastewater discharges to the environment [2].

Other than solvent extraction, various techniques have been found to remove dyes from effluent. The adsorption of basic violet 10 and acid red on sulphonated coal and Ganoderma Lucidum were investigated [3]. Several classes of dye stuffs [DSs] have been removed by adsorption on activated carbon. Ozoh [4] investigated the adsorption of cotton fabric DSs wastewater on Nigeria agricultural semi-activated carbon. In this case, disposal of spent activated carbon is a problem. Removal of basic dyes from aqueous solution using bagasse ash is reported by Vinod et al. [5]. Removal and recovery of DSs using ion exchange method is proposed by Mona and Yeha [6]. Recovery of acid dyes from water using anion exchange compounds was investigated by Farag et al. [7]. Similarly, membrane separation process is destined to play an increasing role in the reduction and/or recovery of DSs [8]. Fouling of membrane is a problem in this case.

The electrochemical oxidation of DSs wastewater was studied by various researchers [9,10]. Zinha [11] studied the composition of textile dyeing wastewater and treatment practices especially with ozonation treatment. Photocatalysis [12,13] and Fentons method [14] were also reported for degradation of textile dyes.

A novel method of using colloidal gas aphrons (CGA) was proposed by Roy et al. [15] for the removal

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doi:10.1016/j.dyepig.2004.05.014

of organic dyes from wastewater. Removal of dyes using polyethylene glycol based aqueous biphasic system was proposed by Rogers et al. [16]. Removal of anionic and cationic organic dyes from water by liquid–liquid extraction using reverse micelles was proposed by Pandit and Basu [17]. Removal of methyl orange and methylene blue dyes from water using CGA was reported by Basu and Malpani [18]. Roy et al. [15] studied the separation of organic dyes such as methyl orange, methylene blue, cibacrome-4G, and cibacrome-6B from wastewater using CGA .They used hexadecyl trimethyl ammonium bromide (HTAB) and sodiumdodecyl benzene sulfonate (SDBS) as surfactants for generation of CGA.

Solvent extraction method is used for the purification, enrichment, separation and analysis of various compounds in mixtures. These are based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents. Therefore, the selection of both a diluent and an extractant determines the equilibrium for a given system and efficiency of the extraction process depends on its mass transfer rate [19]. The advantage of solvent extraction includes high through put, ease of automatic operation and of scale up, and high purification [20].

In the present study, solvent extraction of anionic dyes namely Golden yellow (G.Y), Cibacron LSG-HC (Ciba LSG), Brown ERN (Br.ERN), Levafix Red CA (Le.Red) and Levafix Scarlet CA (Le.Scar) using TBAB prepared in methylene chloride as carrier was studied. The dye extraction and stripping of extracted dyes were investigated and the conditions optimised. Further recovery of dye and stripping reagent were studied.

2. Experimental procedures

2.1. Materials

All the chemicals used were of analytical grade reagents. They were used as supplied TBAB, Potassium hydrogen phathalate, salicylic acid (Merck, India), methylene chloride (CDH, India). Textile anionic dyes (Golden yellow, Brown ERN, Levafix Red CA, Levafix Scarlet CA) were supplied by Dy star (India) and the dye Cibacron was supplied by Ciba specialty chemicals (Switzerland).

UV–visible spectrophotometer (Spekol 1200 Analytical Jena, Germany) was used to measure the absorbance of dyes to establish its λ_{max} and its concentration. To find out the nature of dyes (anionic or cationic), electrophoresis apparatus (submarine Gel system, India) was used. pH of the aqueous solution was measured by pH meter (WTW, Germany). For agitation of solutions, a shaker was used. (IKA-KS 501).

TBAB was used as the extractant and dissolved in CH_2Cl_2. The dye solution was prepared in distilled water. Sulphuric acid and NaOH were used for pH adjustment

2.2. Liquid–liquid extraction of dyes

The organic solvent (V_o ml) used for extraction was added to the prepared dye aqueous solution (V_a ml) in a glass stoppered bottle and the glass stoppered bottle was shaken for known time in a shaker at 100 rpm. The solution was then transferred into a separating funnel. The aqueous phase at the top of the separating funnel was drawn out with pipette for absorbance measurement. The distribution ratio (D) and the percentage of extraction (E) were calculated as per the following equation

$$D = [\text{dye}]_{org}/[\text{dye}]_{aq}$$

$$E = 100C_{aq}0 - C_{aq}t/C_{aq}$$

In the stripping, the loaded extractant (V_o' ml) and the strippant (V_a' ml) were added together into glass stoppered bottle and shaken at 100 rpm, then transferred into a separating funnel. The aqueous strippant was taken for measurements. All experiments were run in duplicate and analytical parameters were performed in triplicate for each run. Confidence limit of 95% was taken for reliable results.

3. Results and discussion

3.1. Spectral characteristics

The λ_{max} for the dyes are presented in Table 1. The λ_{max} for Golden yellow was at 385 nm, Cibacron LSG-HC at 621 nm, Brown ERN at 446 nm, Levafix Red CA at 518 nm and Levafix Scarlet CA was at 509 nm.

In the preliminary experiments, it was found that all the dyes are anionic in nature, and TBAB has the desired ability to extract the anionic dyes with CH_2Cl_2 solvent.

In the next step, the experimental variables such as pH of the aqueous phase, concentration of stripping solution, concentration of TBAB in organic phase, equilibration time, concentration of dye, and effect of

Table 1
Spectral characteristic of textile dyes

S. No.	Name of dyes	λ_{max} (nm)	Charge
1	Golden yellow	385	anionic
2	Cibacron LSG-HC	621	anionic
3	Brown ERN	446	anionic
4	Levafix Red CA	518	anionic
5	Levafix Scarlet CA	509	anionic

salt were studied in order to achieve maximum efficiency in the removal of dye.

3.2. *Effect of pH of source phase*

The effect of pH of the source phase on the efficiency of dye transport is shown in Fig. 1. Aqueous solutions were maintained in the pH range 1–9 to study dye extraction efficiency. The results revealed that the maximum extraction of dye had occurred in the pH range 3–7.5. At a pH > 7.5 and pH below 3 extraction efficiency decreased. For further studies, it was decided to maintain the extraction pH at 7 ± 0.1.

3.3. *Effect of nature of solvent on extraction of dye*

The extraction of dye from aqueous solution was studied using 3.1×10^{-5} M TBAB in various solvents and the results are furnished in Table 2. Several solvents were tried for the extraction of dyes from aqueous solution. The extraction was maximum (98%) with dichloromethane. Very minimal extraction was found with solvents like carbon tetra chloride, chloroform, benzene, toluene, xylene and hexane. Due to the high extraction efficiency of dye observed when CH_2Cl_2 was used as a solvent, subsequent studies were carried out using CH_2Cl_2 as a solvent.

Table 2
Effect of nature of solvent

Solvent	*D* value				
	G.Y	Br.ERN	Le.Scar	Le.Red	Ciba LSG
CCl_4	0.03	0.02	0.03	0.02	0.03
$CHCl_3$	0.02	0.03	0.02	0.03	0.03
CH_2Cl_2	49	49	48.4	48.5	49.1
Toluene	0.03	0.02	0.03	0.02	0.03
Benzene	0.03	0.03	0.02	0.02	0.02
Xylene	0.04	0.02	0.03	0.03	0.03
Hexane	0.02	0.04	0.04	0.03	0.04

Experimental conditions: dye concentration—50 mg/L pH at 7 ± 0.1, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration—3.1×10^{-5} M, equilibration time—15 min.

3.4. *Effect of TBAB concentration on the extraction of dye*

The effect of TBAB concentration on the distribution ratio (*D*) of the dyes was next investigated in the range 4.8×10^{-7} to 6.2×10^{-4} M concentration. Increasing the TBAB concentration, the efficiency of dye extraction increased. The distribution ratio (*D*) of dye was calculated at different molar concentrations of TBAB .The plot of log *D* versus log [TBAB] gave a straight line with a slope of 0.97–0.99 indicating that dye to carrier ratio was 1:1 and forms 1:1 complex. Further excess of TBAB for a given concentration of dye has no considerable effect on the extraction efficiency. It is interesting to note that, in the absence of TBAB, no extraction of dye occurred in the organic phase. This confirms that positively charged tetrabutyl ammonium cation is necessary to extract the anionic dyes. Thus, it can be assumed that 1 mole of TBAB extracts 1 mole of dye. Further studies were carried out using 3.1×10^{-5} M TBAB in CH_2Cl_2.

3.5. *Effect of equilibration time*

The concentration of dyes extracted into organic phase at different times was studied. Fig. 2 shows a rapid rise in the dye concentration in organic phase as well as a sharp decrease in dye concentration in aqueous phase (feed phase) during the first 5 min. After 5 min, 95% of the dyes are transported to the organic phase and about 5% of dye remained in the aqueous phase. After 15 min almost all dye ions are transported (98%) to the organic phase and hence an equilibration period of 15 min is recommended.

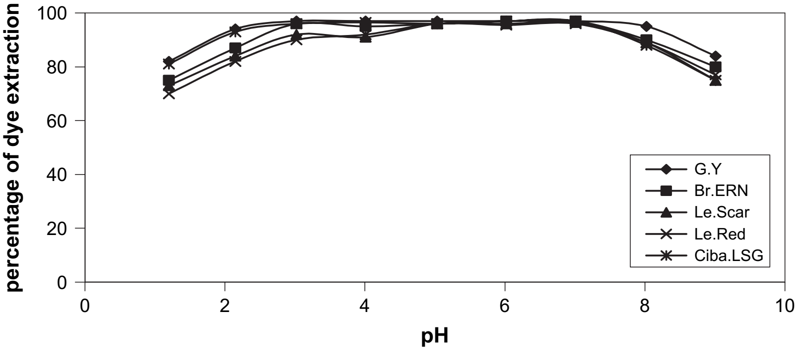


Fig. 1. Effect of pH (experimental conditions: dye concentration—50 mg/L, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration 3.1×10^{-5} M, equilibration time—15 min).

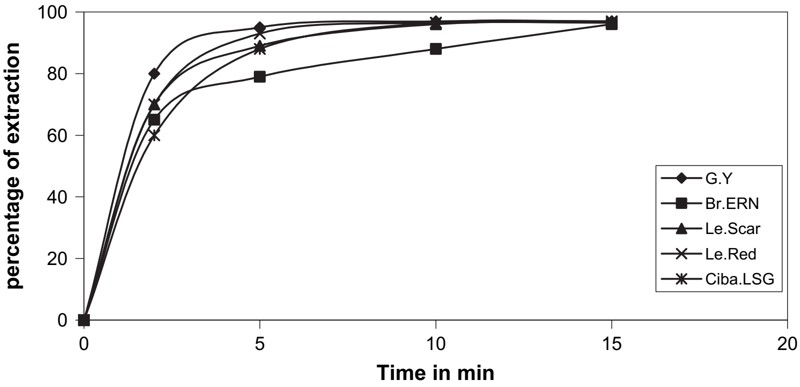


Fig. 2. Effect of equilibration time (experimental conditions: dye concentration—50 mg/L pH at 7 ± 0.1, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration 3.1×10^{-5} M).

3.6. *Effect of dye concentration*

The effect of initial dye concentration on the extraction process was investigated at 3.1×10^{-5} M TBAB in methylene chloride. It can be seen from Table 3 that the percentage removal of dye decreases with increase in dye concentrations. It is observed that at the dye concentration of 50 mg/L, 98% extraction was observed. With further increase in dye concentration, the percentage of extraction of dye decreased. However, the absolute amount of dye extracted, increased with increase of dye concentration.

3.7. *Effect of salt concentration*

In the actual textile dye bath effluent, the dye will present along with salts like NaCl and Na_2SO_4. To understand the influence of sulphate and chloride concentration on dyes extraction, dye solution with different concentration of sodium chloride and sodium sulphate were prepared and tested at neutral pH. Table 4 shows the effect of NaCl and Na_2SO_4 on the percentage removal of dyes from aqueous solution in the presence of TBAB as a carrier at neutral pH. It can be seen that the percentage removal of dye is not affected with the increase in NaCl and Na_2SO_4 up to 5000 ppm

Table 3
Effect of dye concentration

Initial dye concentration (G.Y) (mg/L)	Extracted dye (mg/L)	% of extraction
10.0	9.8	98.0
50.0	49.0	98.0
100.0	97.5	97.5
200.0	193.1	96.5
400.0	350.4	87.6

Experimental conditions: pH at 7 ± 0.1, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration—3.1×10^{-5} M, equilibration time—15 min.

3.8. *Effect of A/O*

Treat volume ratio, i.e. aqueous to solvent volume in the following range 1:1, 5:1.10:1, 15:1 were varied to study the effect of treat ratio on the extraction with 50 mg/L dye. The results are presented in Table 5. From the table, it is evident that the highest ratio of 15:1 maximum percentage of removal was 85%. When ratio was reduced to 5:1, the maximum removal of efficiency was 95%. Further reduction ratio to 1:1, percentage removal was 98%. The lower ratio 1:1 yields high percent removal dyes due to better interaction of dye with organic phase.

3.9. *Loading of dye in TBAB*

TBAB (3.1×10^{-5} M) in 25 ml of CH_2Cl_2 solvent was repeatedly extracted at ambient temperature for 15 min with equal volume of aqueous phase containing 200 mg L^{-1} of dye .The aqueous phase was analyzed for dye after each stage of extraction and the cumulative dye content transferred into organic phase was calculated.

Table 4
Effect of salt concentration

Concentration anions (mg/L)	% of extraction				
	G.Y	Ciba LSG	Br.ERN	Le.Red	Le.Scar
Chloride					
1000	98.0	97.5	96.0	96.5	98.1
2000	98.0	98.0	96.0	96.5	98.0
3000	98.0	97.4	97.0	96.0	98.1
5000	98.0	98.0	97.0	96.0	98.0
Sulphate					
1000	98.0	98.0	96.0	95.0	96.5
2000	98.0	97.0	96.0	96.0	97.0
3000	98.0	97.0	96.0	97.0	97.0
5000	98.0	97.0	96.0	97.0	97.0

Experimental conditions: dye concentration—50 mg/L pH at 7 ± 0.1, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration—3.1×10^{-5} M, equilibration time—15 min.

Table 5
Effect of aqueous to solvent ratio

Ratio	Concentration of dyes after extraction (mg/L)	% of extraction
1:1	49.0	98.0
5:1	47.5	95.0
7:1	47.0	94.0
10:1	46.0	92.0
15:1	42.0	85.0

Experimental conditions: dye concentration—50 mg/L pH at 7 ± 0.1, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration—3.1×10^{-5} M, equilibration time—15 min.

The plot of cumulative dye per 3.1×10^{-5} M TBAB versus equilibration number is presented in Fig. 3. After four stages of extraction, emulsion formation was observed. It is clear from the figure that the loading capacity of TBAB in CH_2Cl_2 for extraction of dye from aqueous solution is 8.9–9.2 mg dye per 3.1×10^{-5} M of the extractant.

3.10. Effect of stripping reagents

In any extraction process, it becomes imperative to back extract the extracted species from organic phase and allow recycling of the organic phase without loss of efficiency. Various inorganic and organic anions were investigated for the dyes recovery. Inorganic anions like Cl^-, SO_4^{2-}, OH^-, CO_3^{2-} were ineffective in stripping the dyes as revealed by stripping with 10% solution of sodium hydroxide, sodium carbonate, calcium hydroxide, hydrochloric acid, and sulphuric acid. Stripping experiments of extracted dyes were carried out using organic chemicals capable of furnishing anionic species and the results are tabulated in Table 6. Organic anions like citrate, tartarate, sterate were also not effective. About 50% of dye was stripped using benzoic acid in potassium dihydrogen phosphate, but emulsion was formed in organic phase. Instead of potassium dihydrogen phosphate, disodium hydrogen phosphate–benzoic acid combination was tried. Even though stripping was slightly improved, emulsion was formed in both the phases (organic and aqueous) so this combination was dropped out. Potassium hydrogen phthalate (KHP) was useful in stripping the extracted dyes from the organic layer. But, KHP is water soluble and it is difficult to separate the dye from KHP. Further studies were carried out using water insoluble salicylic acid which was dissolved in NaOH, Na_2CO_3 or $NaHCO_3$ solution. Among this salicylic acid with Na_2CO_3 stripped the dye better than others. Concentration of salicylic acid and Na_2CO_3 was varied in the range of 1 M–2 M. The results are also presented in Table 6. Dye stripping was maximum (98%) with 1:1 M ratio. Hence, salicylic acid in Na_2CO_3 (1:1 M) was chosen for stripping purpose. After completion of stripping the dye, the recovery was tried by adding one molar sulfuric acid solution to precipitate salicylic acid. The salicylic acid precipitated out from the aqueous solution leaving the dye in aqueous solution. The precipitated salicylic acid was dissolved with Na_2CO_3 solution for further recovery processes.

3.11. Reusability of solvent

When the stripped solvent was reused for dye extraction under the optimized condition, it was found that 97% of dye was extracted to the solvent. The extraction efficiency was not decreased with increasing number of times of extraction. From the dye loaded solvent 96% of the extracted dye was stripped with 1:1 M salicylic acid in sodium carbonate .The extraction and stripping were carried out five times and found no loss in efficiency.

3.12. Extraction and stripping reaction

The investigations carried out so far showed that anionic dyes are extracted into tetrabutyl ammonium bromide–methylene dichloride under neutral condition

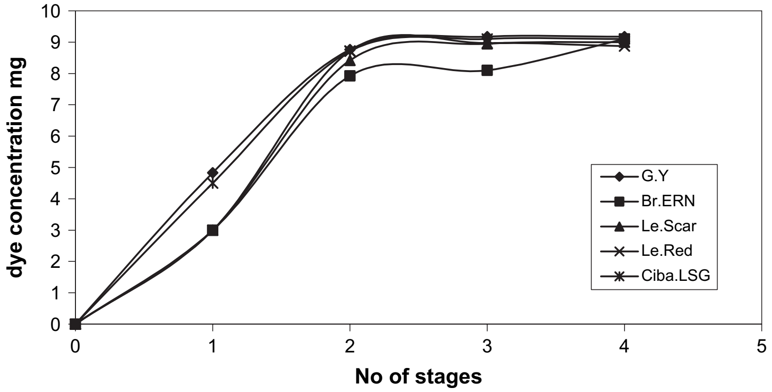


Fig. 3. Effect of loading capacity (experimental conditions: dye concentration—20 mg pH at 7 ± 0.1, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration 3.1×10^{-5} M, equilibration time—15 min).

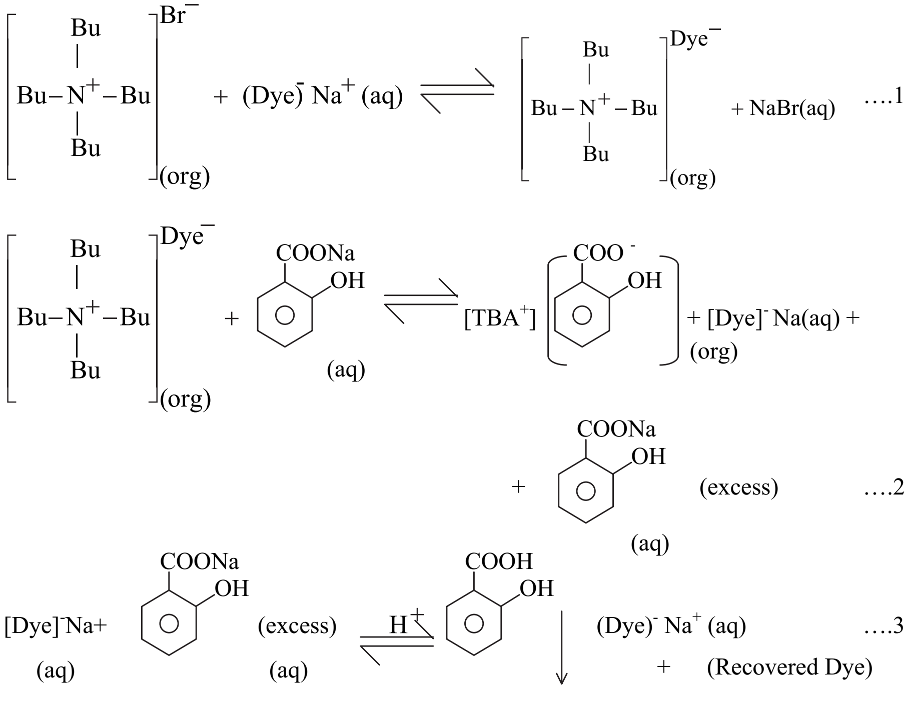
Table 6
Effect of stripping agents

Stripping agent	pH	% of dyes extraction	Remarks
10% Sod.Citrate	5	dye was not stripped	nil
10% Sod.Pot.Tartarate	6	dye was not stripped	nil
10% KHP	4	97% stripped	nil
C_6H_5COOH + NaOH (1:1 M)	12	dye was not stripped	nil
C_6H_5COOH + $NaHCO_3$ (1:1 M)	10	dye was not stripped	nil
C_6H_5COOH + NaH_2PO_4	10	dye was not stripped	nil
C_6H_5COOH + Tri.sod.citrate 2 hydrate	9.5	dye was not stripped	nil
Na_2HPO_4 + NaH_2PO_4	10	dye was not stripped	nil
C_6H_5COOH + K_2HPO_4	10	50% stripped	emulsion was formed (organic)
C_6H_5COOH + Na_2HPO_4	12	55% stripped	emulsion was formed (organic and aqueous)
Salicylic acid + Na_2HPO_4	12	65% stripped	no emulsion
Salicylic acid + K_2HPO_4	12	65% stripped	no emulsion
Salicylic acid + NaOH	14	65% stripped	no emulsion
Salicylic acid + Na_2CO_3 (1:1 M)	11	97% stripped	no emulsion
Salicylic acid + Na_2CO_3 (2:1 M)	11	95% stripped	no emulsion
Salicylic acid + $NaHCO_3$ (1:1 M)	7.5	90% stripped	no emulsion
Salicylic acid + $NaHCO_3$ (2:1 M)	7.5	87% stripped	no emulsion

Experimental conditions: dye concentration—50 mg/L pH at 7 ± 0.1, volume of aqueous—25 ml, volume of organic—25 ml, carrier concentration—3.1×10^{-5} M, equilibration time—15 min, various stripping agent—25 ml.

and the extracted dye is stripped into 1:1 M salicylic acid in sodium carbonate solution. One $(Dye)^-$ molecule combines with one tetrabutyl ammonium cation to form an ion-pair as evident from 1:1 stoichiometry of the extracted complex. The reaction for extracting and stripping of the dye is

In the second recycling to find out whether salicylate anion is associated with TBA cation or not, the aqueous layer after extraction of dye was collected and tested for violet colour by adding $FeCl_3$. The formation of violet colour in the aqueous layer confirmed that the salicylate anion is exchanged for dye.



4. Conclusions

The method presented seems to be promising and offers a simple approach for selective extraction of anionic dyes for recovery

- TBAB is able to extract more than 98% of dye ions from aqueous solution in a short time of 15 min.
- The extraction efficiency of dyes was not affected in the presence of salts like NaCl and Na_2SO_4.
- Extraction efficiency of dye reduced, when solvent to aqueous ratio increased.
- TBAB can be regenerated by salicylic acid and Na_2CO_3 solution and it can be recycled along with the methylene chloride solvent.
- Having these advantages, the present methods seem to be promising and might be of interest to use in textile industries.

Acknowledgements

Authors wish to thank M/s. Dy star Ltd for providing necessary dyes during the time of research work.

Appendix A

D = Distribution ratio
E = Percentage of extraction
C = Concentration of dyes
org = Organic
aqu = Aqueous
0 = Initial concentration of dye at zero time
t = Dye concentration at the time.

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