Solvent Extraction of Silk Dyes Acid Red 10B and Acid Pink Using Tri-n-butyl Phosphate as Carrier

K. Palanivelu*
Centre for Environmental Studies, Anna University, Chennai 600 025

N. Hajarabeevi and I. Mohammed Bital
B.S.A. Crescent Engineering College, Chennai 600 048

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The extraction behaviour of anionic Acid Red 10 B and Acid Pink, which are commonly used as textile silk dyes, was studied by tri-n-butyl phosphate (TBP) as carrier and hexane as diluent. The effect of parameters such as pH of feed, stripping reagent concentration, ratio of carrier and diluent (TBP & Hexane), equilibrium time, ratio of aqueous to solvent and reusability of solvent, and initial concentration of dyes were examined. The optimum conditions for recovery were pH of the feed 1.0 ± 0.2, 0.5 M sodium hydroxide as stripping phase, 1:1 TBP - Hexane ratio, 1:1 aqueous / solvent ratio and 5 minutes equilibrium time. The maximum extraction and stripping under optimum conditions observed for Acid Red 10 B were 99.0% and 98.5 % and for Acid Pink were 91.3 % and 90.5% , respectively.

The textile industry is one of the oldest and largest industries in the country. The textile dyeing industry produces large quantity of wastewater varying from 50-100 L / kg of the cloth processed. The disposal of wastewater causes significant environmental problems. Indeed, these effluents are toxic and mostly non bio-degradable [1]. Most of the textile dyes are resistant to either aerobic and / or anaerobic biological treatment [2]. Removal of azo dye acid red B by adsorption and catalytic combustion using magnetic $CuFe_2O_4$ powder was reported by Rongecheng Wu et al. [3]. Chemical coagulation is very unsatisfactory as a result of which large amounts of sludge are formed which results in high disposal costs [4]. Degradation of azo dyes Acid Red B on manganese dioxide in the absence and presence of ultrasonic irradiation was reported by Jiantuan Ge et al. [5]. Currently, physico-chemical processes like chemical oxidation, reduction, precipitation, adsorption, etc., [6] and biological methods have been investigated for treatment of dye-effluent. Studies on decolourisation, toxicity and the possibility for recycling of treated water from acid dye effluents using ozone treatment have been referred by Muthukumar et al. [7]. The photo-catalytic decomposition of organic dyes by titanium dioxide was reported by Beata Zieli et al. [8]. In all these methods, valuable dyes are destroyed and they are not recovered.

Solvent extraction process involves extraction and stripping steps, in which the desired pollutants could be recovered. Studies made on solvent extraction of metal ions have been extensive [9-13] but that of organics have been relatively few. Shri Chand and Jain [14] investigated the recovery of acetic acid from dilute wastewater using TBP in kerosene which was effective than tri-octyl-phosphine oxide (TOPO). Urtiaga Ane et al. [15] investigated the extraction of phenol using trialkyl phosphine oxides (cyanex 923) in kerosene. However, little information is available in the literature about the recovery of dyes by solvent extraction. Removal of organic dyes from water by liquid-liquid extraction using reverse micelles was reported by Pandit and Basu [16]. They [17] also reported the treatment of ionic dyes from water by liquid- liquid extraction using reverse micelles. An organic dye removal from water using a predispersed solvent extraction was investigated by Dong Woo Lee et al. [18]. Separation of food colouring dyes, using aqueous biphasic extraction chromatographic resins, was also reported by Huddlestone et al. [19]. Treatment of textile dye effluent using a polyamide-based nanofiltration membrane was studied by Akbari et al. [20]. Recently, recovery of golden yellow dye by tri-n-butyl phosphate [21] and selective extraction and separation of reactive textile anionic dyes by tetra butyl ammonium bromide were studied by Muthuraman and Palanivelu [22].

Extraction and recovery of silk dyes Acid Red 10 B and Acid Pink, anionic dyes by solvent extraction process have not been reported so far, and, hence, it is proposed to study the extraction and stripping of

* Author to whom correspondence should be addressed
E-mail: kpvelu@hotmail.com

Acid Red 10 B and Acid Pink using TBP in hexane. The optimum conditions such as effect of pH, effect of aqueous solvent ratio and effect of stripping reagent concentration, effect of TBP- hexane ratio and effect of equilibration time initial dye concentration variation for the maximum removal of the dyes were studied and applied for the recovery of dye in a real silk dyeing effluent.

Experimental Procedures

Reagents

Tri-n-butyl phosphate, hexane, sodium hydroxide were purchased from Merck, India. Hexane and TBP were used without any purification. Sulphuric acid used was supplied by Excel Chemicals India. All the reagents used were of AR grade. The commercially available silk dyes Acid Pink and Acid Red 10 B anionic dyes were kindly donated by Uma Dyeing works, Kancheepuram, Tamil Nadu.

Apparatus and Measurement

The spectrophotometer used for the measurement of dye concentration in the aqueous phases was a Spectronic 20 Genesys (Germany). The pH measurements were made using WTW pH meter (Germany) with combined electrode. Electro-phoresis apparatus (Submarine Gel System, India) was used to find out the nature of dyes. The λ_{max} value for Acid Red 10 B and for Acid Pink was found to be 566 nm and 519 nm, respectively.

Extraction Procedure

All the experiments were carried out at ambient temperature (27°C). The preparation of dye solutions was as follows. 0.1 g of Acid Red 10 B and Acid Pink (as received) were dissolved in 1000 mL of distilled water to make a dye solution typical of dye bath rinse effluents (100 mg/ L). About 30 mL aqueous solution of dye (adjusted pH to 1.0 ± 0.2) containing 100 mg/ L was taken in a separating funnel along with 30 mL mixture of TBP+hexane (1:1 ratio). The phases were mixed gently for five minutes and allowed to stand for separation of phases. The aqueous layer was analysed for the remaining dye using spectrophotometer at 566 nm for Acid Red 10 B and 519 nm for Acid Pink. The extracted dye was shaken with 0.5 M sodium hydroxide solution for five minutes and allowed to stand for separation of phases. The aqueous layer (sodium hydroxide) was neutralised and analysed for recovered dye using spectrophotometer.

Results and Discussion

Selection of Diluent

In the electrophoresis method, both the silk dyes were found out to be anionic. Preliminary studies indicated that these anionic dyes were extracted from acidic solution. The extraction was carried out in different solvents like carbon tetrachloride, chloroform, hexane, toluene and methyl isobutyl ketone with TBP as carrier (1:1 ratio) from aqueous solution at pH 1.0 ± 0.2. The extraction was less with carbon tetrachloride (30 %), toluene (30 %) and methyl isobutyl ketone (40 %). The maximum extraction was obtained in hexane (99 %) as diluent. Further, extraction studies were carried out using hexane as diluent.

Effect of pH

The effect of pH on the extraction of the dyes Acid Red 10 B and Acid Pink was studied by varying the pH from 1.0 to 7.0 and the results are shown in Fig. 1. The extraction of dyes was maximum at lower pH. The percentage of extraction of dyes was found to decrease with the increase in pH and there was no extraction at pH 7.0. This study reveals that maximum extraction (99.0 % for Acid Red 10 B and 91.3 % for Acid Pink) was achieved at pH 1.0 ± 0.2. This may be due to the fact that at lower pH, H^+ ion concentration is high, and, hence, the anionic dye readily forms an ion-pair complex with cationic TBP. At higher pH, TBP does not form an ion pair with dye because TBP remains neutral and not present in cationic form, thus resulting in poor extraction.

Selection of Stripping Reagent and Effect of Sodium Hydroxide

Higher amount of dye was extracted at acidic pH, and, hence, alkaline reagents for stripping purpose were used. Stripping reagents like aqueous ammonia, sodium hydroxide and calcium hydroxide (0.5 M) were tested for stripping the dye from hexane and

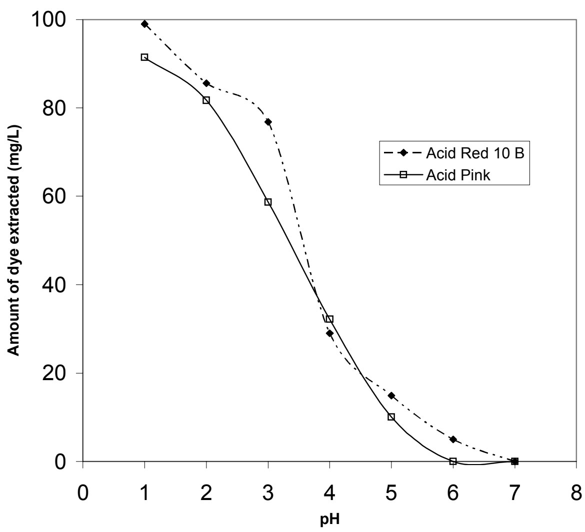

Fig. 1 : Effect of pH on Extraction of Dyes

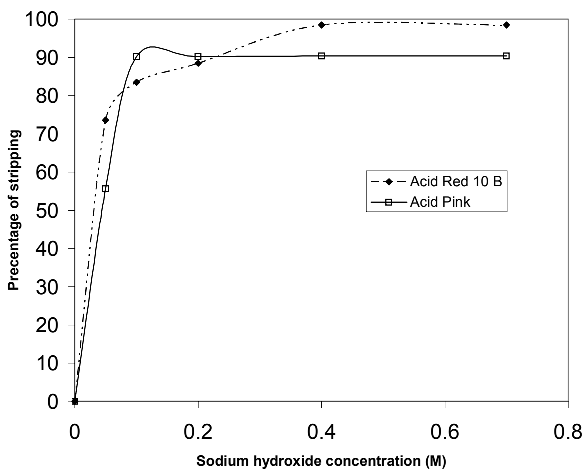

Fig. 2 : Effect of Stripping Concentration

TBP. This study reveals that sodium hydroxide has high stripping efficiency compared to calcium hydroxide and aqueous ammonia, and, hence, further studies were carried out with sodium hydroxide as stripping agent.

The effect of stripping reagent concentration on recovery of Acid Red 10 B and Acid Pink was studied and the results are shown in Fig. 2. It is clear that the recovery of dyes increases by increasing the concentration of sodium hydroxide from 0.05 to 0.7 M. The recovery of Acid Red 10 B dye in 300 seconds was found to be 73.6 mg/L at 0.05 M NaOH and slightly increased to 88.5 mg/L at 0.2 M NaOH. In the range of 0.4 M – 0.7 M NaOH, stripping efficiency is still increased to 98.5 mg/L. In the case of Acid Pink, the recovery was found to be 55.6 mg/L at 0.05 M NaOH and increased to about 90.5 mg/L in the range of 0.1 M to 0.7 M NaOH. This is probably due to an increase in the concentration of hydroxyl ions. Hence, 0.5 M sodium hydroxide solution was selected for further studies.

Effect of Carrier / Diluent Ratio

The solvent extraction was studied at different hexane /TBP ratio, viz 1:1, 1.5: 1, 2:1, 3:1 and 4:1, and the results are furnished in Table 1. The extraction of Acid Red 10 B dye was found to be maximum (99.5%) when the hexane/TBP ratio was 1:1. When the hexane/TBP ratio was further increased to 1.5:1, the extraction was found to decrease (99.3%). The extraction was 92.1% at 2:1, 90.1% at 3:1 and 89.6% at 4:1, respectively. The extraction of Acid Pink also showed the same result. About 91.3% removal was found with a ratio of 1:1, 87.1% for 1.5:1, 75.8% for 2:1, 71.5% for 3:1 and 67.0% for 4:1, respectively. The extraction decreased with the decrease in carrier concentration because with lower carrier (TBP) volume (4:1), the interface

Table 1 : Effect of Hexane-TBP Ratio on Extraction

S.No	Hexane-TBP Ratio	Amount of dye Extracted (mg/L) Acid Red 10 B	Acid Pink
1.	1:1	99.5	91.3
2.	1.5:1	99.3	87.1
3.	2:1	92.1	75.8
4.	3:1	90.1	71.5
5.	4:1	89.6	67.0

Experimental conditions: pH at 1± 0.2, Dye initial concentration 100 mg/lit, Aqueous/ solvent ratio (1:1), equilibration time 5 min .

between the aqueous and the solvent was not saturated by the carrier. Hence, in all subsequent studies, carrier to diluents ratio was fixed as 1:1. A blank experiment was also performed using the solvent alone. Negligible amount of dye in the solvent was found. This has led to the confirmation that the transport of dye ion in solvent was facilitated only by the TBP carrier.

Effect of Equilibration Time

The two immiscible phases of aqueous dye solvent and Hexane-TBP solvent were equilibrated for a period ranging from 30 seconds to 10 minutes and the results are depicted in Fig. 3. It is obvious that an increase in equilibration time increased the percentage of extraction of dyes. The extraction was rapid and quantitative even with 2 minutes time and maximum extraction obtained was 96.0 % for Acid Red 10 B and 90.0 % for Acid Pink. With further increase in equilibration time to 5 minutes, the percentage extraction was increased to 99.0 % for Acid Red 10 B and 91.3 % for Acid Pink. However, to ensure maximum extraction, 5 minutes equilibration

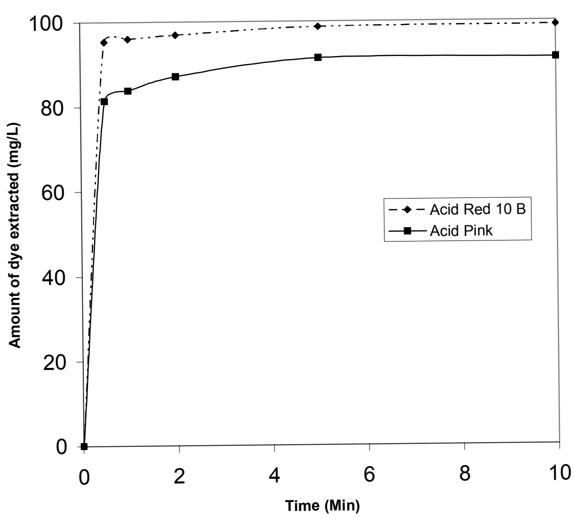

Fig. 3 : Effect of Equilibration Time

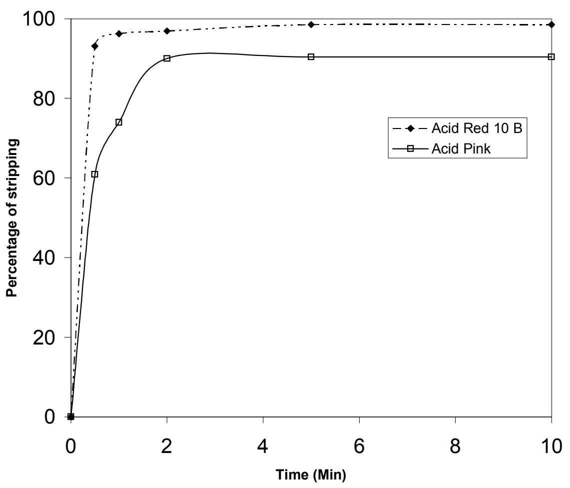

Fig. 4 : Effect of Stripping Time

time was maintained for extraction but longer extraction time showed no adverse effect. Stripping studies were also carried out from 30 seconds to 10 minutes and the results are shown in Fig. 4. The recovery of dye obtained was 98.5 mg/L for Acid Red 10B and 90.5 mg/L for Acid Pink, which again reveals that 5 minutes is adequate for stripping the extracted dye using 0.5 M NaOH solution.

Aqueous to Solvent Ratio

The result of contacting different volume ratio of aqueous to organic phase was studied. Aqueous and organic in different ratios (A/O) and their efficiency are presented in Fig.5. The results indicate that for Acid Red 10 B 98.8%, 96.9%, 94.8%, & 92.4% extraction was achieved at 1:1, 1.5:1, 2:1 and 3:1, respectively. With the decrease in organic volume further (4:1), the extraction was also reduced to 57.4 %. This may be due to the reduced availability of organic carrier for Acid Red 10 B dye interaction. In

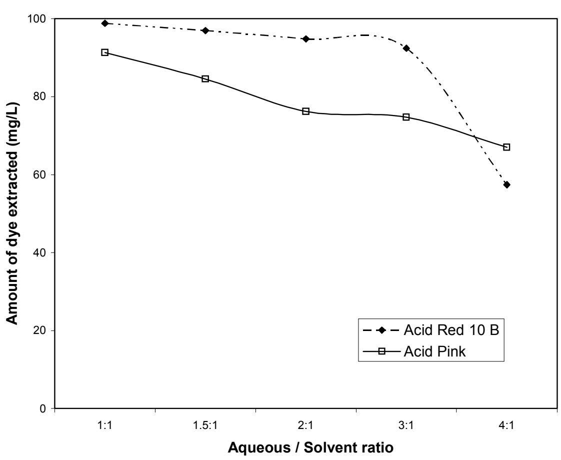

Fig. 5 : Effect of Aqueous / Solvent ratio

Table-2
Effect of Salt Concentration (Sodium Chloride & Sodium Sulphate) on Dyes Recovery.

Concentration of salt (mg/L)	Acid Red 10 B Dye recovery (mg/L) (in NaCl)	Acid Red 10 B Dye recovery (mg/L) (in Na_2SO_4)	Acid Pink Dye recovery (mg/L) (in NaCl)	Acid Pink Dye recovery (mg/L) (in Na_2SO_4)
100	99.0	91.3	99.0	91.3
500	99.0	91.3	99.0	91.2
1000	98.9	91.0	98.5	91.0
2000	97.4	90.4	97.1	90.2
2500	95.8	89.0	95.4	88.5
3000	94.6	88.5	94.2	88.2

(Experimental Conditions: Dye concentration 100 mg/L, pH at 1.0 ± 0.2, TBP- Hexane (1:1) ratio, Aqueous/ solvent ratio (1:1), equilibration time 5 min.

case of Acid Pink, it is gradually decreased from 91.3% (1:1) to 67 % (4:1). This may enable us to draw the conclusion that extraction decreases with the decreased availability of organic carrier for Acid Pink dye interaction.

Effect of Chloride and Sulphate Concentration in the Aqueous Dye Solution

In the real textile effluent, chloride and sulphate may be present along with dyes. Hence, their effect on dyes extraction was studied. The chloride and sulphate concentration in the aqueous dye solution was varied from 100 mg/L to 3000 mg/L. The results are presented in Table 2. There was no appreciable effect on the dye extraction upto 1000 mg/L of salt concentration. However, the extraction efficiency was slightly lowered when the concentration was increased from 1000 mg/L, to 3000 mg/L. The extraction efficiency of Acid Red 10 B was 97.4%, and 97.1 % when the concentration of chloride and sulphate was 2000 mg/L, respectively. The extraction efficiency of Acid Pink was 90.4% and 90.2 % respectively. The extraction efficiency of Acid Red 10 B was lowered to 94.6% and 94.2 % for 3000 mg/L chloride and sulphate concentration, respectively. Similar effect (slight decrease) was observed in the case of Acid Pink also.

Initial Dye Concentration Variation in Aqueous Solution

Various concentration of dye (50-1000 mg/L) in 30 mL of aqueous phase was tried with 30 mL of TBP-Hexane (1:1 ratio) at pH 1.0 ± 0.2. The results are furnished in Table 3. It was observed that for Acid Red 10 B 99.0 % of efficiency was achieved up to 500 mg/L using 1:1 TBP-hexane ratio. Then it was reduced to 92.8 % at 1000 mg/L. The effect was similar for Acid Pink also. When the initial dye

Table 3 : Effect of Hexane-TBP Ratio on Extraction

S.No	Dye initial Concentration (mg/lit)	Acid Red 10 B Dye Recovery (mg/lit)	Acid Pink Dye Recovery (mg/lit)
1.	50	49.7	45.3
2.	100	98.5	90.5
3.	250	246.8	226.2
4.	500	494.2	452.4
5.	800	784.4	715.4
6.	1000	923.4	891.2

Experimental conditions: pH at 1± 0.2, TBP- Hexane (1:1) ratio, Aqueous/ solvent ratio (1:1), receiving phase 0.5 M NaOH, equilibration time 5 min.

concentration is high, more and more dye molecules are expected to be extracted and the availability of organic carrier is reduced for extraction. Hence, by increasing the dye concentration, the extraction efficiency is decreased.

Reuse of the Solvent

When the stripped solvent was reused for dye extraction under the optimized conditions, it was found that 99.0 % of Acid Red 10 B dye was extracted in the solvent. After five extraction cycles, Hexane + TBP mixture showed no loss in efficiency of extraction and retained the same extraction ability. From the dye loaded solvent, 98.5 % of Acid Red 10 B was stripped with 0.5 M NaOH. Similarly, for Acid Pink, 91.3 % of extraction and 90.5 % of stripping was obtained. From these results, it is inferred that the process developed has good economy.

Transport Mechanism

The dye was found to be an anionic by electrophoresis method. In acidic pH, the extractant TBP is protonated form with Dye^-. The extraction is due to the formation of ion-pair.

$$[R_3P\ H^+]_{org} + Dye_{aq}^- \rightleftarrows [R_3P\ H^+Dye]_{org} \quad ... (1)$$

The stripping reaction with OH- is as follows.

$$[R_3P\ H^+Dye]_{org} + OH_{aq}^- \rightleftarrows [R_3P]_{org} + H_2O + Dye_{aq}^- \quad ... (2)$$

Application to Dye Effluent

The untreated dye effluent was collected from silk dyeing works, Kancheepuram to test the applicability of proposed method. The characteristics of the effluent are given in Table 4. Under optimised conditions, the actual dye effluent was tested and 95.7 % of extraction and stripping was obtained for Acid Red 10 B. For Acid Pink, the maximum extraction and stripping was found to be 88%. The very small decrease in efficiency may be due to other impurities present in the effluent.

Table 4 : Characteristics of Silk Dyeing Effluent

S.No.	Parameter	Dye effluent (Acid Red)	(Acid Pink)
1.	pH	8.30	8.65
2.	Conductivity m S/cm	2.47	2.46
3.	Total dissolved solids (mg/L)	2400	2350
4.	Total suspended solids (mg/L)	38.0	39.5
5.	Dye Concentration (mg/L)	550	500
6.	Chloride (mg/L)	925	750
7.	Sulphate (mg/L)	435	365

Conclusions

Acid Red 10 B and Acid Pink anionic type silk dyes used in textile industry were extracted and recovered from the aqueous solution by solvent extraction method using TBP-hexane. Experimental results show that by controlling different parameters such as pH, equilibrium time, aqueous /solvent ratio and stripping reagent (sodium hydroxide) concentration, high efficiency can be achieved. Extraction of dyes is higher at lower pH. The extent of recovery of dyes is maximum in 5 minutes. The decrease in recovery is observed with increase in the initial concentration of dyes. The optimum conditions of transport are feed pH 1± 0.2, equilibration time 5 minutes, aqueous / solvent ratio 1:1, 0.5 M sodium hydroxide as stripping phase. The maximum extraction and stripping under optimum conditions were observed as 99.0 % and 98.5 % respectively. Under the optimum conditions, the real dye effluent was tested and it yields satisfactory results.

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