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Removal of sodium salts and chemical oxygen demand from real reactive dye wastewater by the integrated process of chemical precipitation and extraction

Yun Liu[a,*], Dao-lin Xu[a,b,c], Ping Wang[c], Yuan-hua Dong[a,*]

[a]*State Key Laboratory of Soil and Sustainable Agriculture, Chinese Academy of Sciences, Institute of Soil Science, Nanjing 210008, China, Tel. +86 25 86881370; Fax: +86 25 86881000; emails: yliu@issas.ac.cn (Y. Liu), 573744930@qq.com (D.-l. Xu), yhdong@issas.ac.cn (Y.-h. Dong)*
[b]*Shandong Ming Ren Fu Rui Da Pharmaceutical Limited Co., Jinan 250104, China*
[c]*School of Chemical & Biological Engineering, Lanzhou Jiao Tong University, Lanzhou 730070, China, email: 4938238@163.com*

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ABSTRACT

Real reactive brilliant red K-2BP (C. I. Reactive Red 24) dye wastewater is characterized by its very high chemical oxygen demand (COD), high concentration of sodium salt, and low biodegradability. A combined process of precipitation, complex extraction, and stripping was proposed as a method for treating such wastewater. Fluosilicic acid was selected as a precipitator for the recovery of sodium ions, trialkylamine (N235) as the extractant, and sodium hydroxide (NaOH) as a back-extractant. Our results indicated that desalination had the greatest influence on extraction rates while the phase ratio and the N235 concentration also influenced the reaction. Acid, which was an important factor affecting COD extraction, was produced during desalination process. We also noted a number of points of interest: that the extraction reaction could reach equilibrium in 20 min; that the COD removal rates tended to increase under certain conditions, with an increase in acidity of wastewater resulting in increased desalination rates, and an increased N235 concentration and phase ratio (O/A). Under optimum conditions the COD removal rates can reach 92%, the extractant could be regenerated by stripping with NaOH, and the stripping rate could reach an efficiency of 100%.

Keywords: Desalination; Liquid–liquid extraction; Stripping; K-2BP; Water treatment

1. Introduction

More than 0.7 million tons of synthetic dyes are produced annually, worldwide, [1] and about 15% of the total dyes are lost in industrial effluents [2]. Colored industrial effluents have a negative impact on public health and the environment and also produce visual pollution. Many studies on decolorization methods have been carried out with the main focus being on physical and chemical treatment methods, such as adsorption [3–5], coagulation/flocculation [6,7], ozonation [8,9], Fenton or photo-Fenton processes [10,11], UV/NaOCl methodologies [12], electrochemical degradation [13–15], ultrasonic irradiation [16,17], and UV/H_2O_2 methodologies [18–20]. Reactive dyes are the most commonly used dyes, worldwide, due to their high level of fixation in the fibers and their chemical stability. This category of dye is the most problematic [21] and comprises 20–30% of the total dyes in the

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*Corresponding authors.

market [22,23]. Reactive azo dyes constitute the largest and most important class of reactive dyes, which is of special environmental concern, due to the toxicity of their precursors and their degradation products, such as the aromatic amines that are considered to be highly carcinogenic [24]. Reactive brilliant red K-2BP (C.I. Reactive Red 24) is one of the important azo reactive dyes, mainly used for dyeing cotton ramie, viscose fiber, and some fabrics. K-2BP is usually prepared from H-acid and cyanuric chloride. In China these dyes are usually obtained via the salting-out process. The wastewater is thus, characterized by high COD, high-sodium salt content, and low biodegradability.

In recent years the separation and recovery of reactive dyes from wastewater has given rise to a number of alternative methods [25,26]. Potential advantages are associated with liquid–liquid extraction methods, which include two types of operation: selective extraction or co-extraction and selective stripping [27,28]. Liquid–liquid extraction is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents, and the extraction process depends on its mass transfer rate [27,28]. Such methods are simple and have the capacity to deal with a large number of samples in a short time. Reactive dye wastewater, such as K-2BP wastewater, is known to contain a large amount of salt (NaCl or Na_2SO_4) [29]. Highly concentrated sodium salt in wastewater represents a form of pollution that is difficult to treat. Combining strategies of wastewater reuse and desalination technology makes it possible to convert wastewater into water of a suitable quality that can meet the standards required for various industrial applications [25,26,30]. Reverse osmosis and evaporation techniques, such as multi-stage flash, multi-effect evaporator, and reverse osmosis methods, are popular techniques used to desalinate contaminated waters [30,31]. The high cost of desalination may be ameliorated by the use of certain pollutants, such as fluorine—produced in fertilizer plant wastewater and hydrometallurgical wastewater—for water treatment processes. The fluoride ions are usually present in the form of fluosilicic acid. For fluoride recovery as a by-product, sodium or potassium ion is usually used as a precipitator to precipitate Na_2SiF_6 by adding sodium salt or potassium salt [32]. Sodium silicofluoride can be used in the manufacture of vitreous enamels, opalescent glass, coagulants for latex, insecticides, and as a water fluoridation agent in drinking water [33,34]. The fluorine, therefore, has a potential for use as precipitator to precipitate sodium ions from dye wastewater. This could lead to the development of a treatment method involving the simultaneous recovery of sodium and fluoride, as by-products of the desalination of high-concentration sodium wastewater, using fluorine that had been sourced from the two kinds of wastewater. This would represent a new means of treating reactive dye wastewaters that contain high concentrations of sodium ions.

The main objectives of this study were to demonstrate the process of simultaneous recovery of dye and sodium ions from reactive dye wastewater. In addition, the factors influencing extraction and stripping efficiency were investigated.

2. Experimental sections

2.1. Materials

Reactive brilliant red K-2BP wastewater was collected from the salting-out process in a Jiangsu plant manufacturing reactive dye, whose production of such wastewater was about 25 m^3/d. If not used immediately, the wastewater sample was stored at 4℃. Sufficient wastewater was stored for the study. Table 1 presents the results of the ingredient analysis of the wastewater. With the exception of N235 and sulfonated kerosene (which are industrial products), the reagents used were of analytical grade. The potassium dichromate method and the dilution method were, respectively, used to determine the COD and chroma value of the aqueous phase. The acidity of the aqueous phase was determined via titration with aqueous NaOH, using an automatic potentiometric titrator (ZDJ-5, Shanghai Jingke, China). The concentration of Na^+ was measured using a flame photometer (AP 1302, Shanghai). The concentration of H_2SiF_6 was determined via titration with aqueous NaOH. An ion chromatography (Dionex ICS-1100) was used to measure the concentrations of chloride and sulfate ions. A spectrophotometer (UV8100, LabTech, Beijing) was used to measure the UV-vis spectra of the recovered dyes and reactive brilliant red K-2BP industrial products.

2.2. Desalination

The precipitation of sodium ion as Na_2SiF_6 resulted from the addition of 43.22% H_2SiF_6 solution to the wastewater. Desalination experiments were carried out in 1 L beakers with magnetic stirring. Then 346.4 g H_2SiF_6 (43.22%wt) was added to 500 mL wastewater at 0℃ and filtered after stirring for 5 min. The main ingredients of the filtrate were detected.

Table 1
The ingredients of real wastewater

pH	COD (mg/L)	Chroma, color	Cl^- (mg/L)	Na^+ (mol/L)	SO_4^{2-} (mol/L)
7.56	2.21×10^4	8×10^5	1.39×10^5	4.15	0.02

2.3. Liquid–liquid extraction of dye

2.3.1. Effect of extraction time

The stirring time, necessary to attain the equilibrium distribution of dye between the organic phase and wastewater, was investigated by employing a phase ratio (O/A) of 1:1. The organic phase was prepared by mixing N235 and diluent sulfonated kerosene together. The concentration of N235 in the organic phase (V_{N235}/V_{Org}) was 40% and a sodium ions removal rate, by H_2SiF_6, of 100% was attained. The wastewater phase and organic phase were mixed in a conical flask and shaken at a frequency of 150 rpm for a certain time at 25℃. After the two phases had settled, the COD in the aqueous solution was determined.

2.3.2. Optimization of the extraction parameters

An orthogonal array ($L_9(3^4)$) was employed to optimize the extraction conditions. Three factors were involved: (A) N235 concentration; (B) phase ratio (O/A); and (C) desalination ratios. The experimental conditions are listed in Table 2.

Table 2
Experimental conditions of the orthogonal array

Factor tests	N235 concentration (A) (%)	Phase ratio (B) (O/A)	Desalting rate (C) (%)
1	20	1:4	1
2	20	1:3	2
3	20	3:7	80
4	20	7:13	100
5	25	1:4	2
6	25	1:3	1
7	25	3:7	100
8	25	7:13	80
9	30	1:4	80
10	30	1:3	100
11	30	3:7	1
12	30	7:13	2
13	35	1(1:4)	100
14	35	2(1:3)	80
15	35	3:7	2
16	35	7:13	1

2.3.3. Effect of acidity

A series of 2 mL acid chloride solutions containing different concentrations of HCl were placed into 18 mL of wastewater in order to setup a series of wastewater samples at different acidity levels, at concentrations ranging from 0.05 to 0.70 mol/L. The concentration of N235 in the organic phase (V_{N235}/V_{Org}) was 40% and the phase ratio (O/A) was 1:1. Experiments were carried out at 25℃. Wastewater and the organic phase were mixed in a conical flask and shaken at a frequency of 150 rpm for 40 min. After the two phases settled, the COD of the wastewater was determined.

2.3.4. Effect of desalination

A series of different volumes of H_2SiF_6 were added to the 500 mL wastewater samples, in order to setup a series of samples with different desalination ratios. The concentration of N235 in the organic phase (V_{N235}/V_{Org}) was 35% and the phase ratio (O/A) was 1:1. The wastewater and organic phase were mixed in a conical flask and shaken at a frequency of 150 rpm for 40 min at 25℃. After the two phases had settled, the COD in the aqueous solution was determined.

2.3.5. Effect of N235 concentration

A series of organic phase samples were prepared with different concentrations of N235 (V_{N235}/V_{Org}), ranging from 20 to 70%. The phase ratio (O/A) was 1:1. The sodium ion removal rate, by H_2SiF_6, was 100%. Wastewater and organic phase were mixed in a conical flask and shaken at a frequency of 150 rpm for 40 min at 25℃. After the two phases had settled, the COD in the aqueous solution was determined.

2.3.6. Effect of phase ratio (O/A)

The concentration of N235 in the organic phase (V_{N235}/V_{Org}) was 40% and the sodium ion removal rate, by H_2SiF_6, was 100%. Wastewater and organic phases were mixed in a conical flask and shaken at a frequency of 150 rpm for 40 min for each different phase ratio (O/A). After the two phases had settled, the COD in the aqueous solution was determined.

2.4. Stripping of loaded organic phase

The NaOH was used as a back-extractant. The effects of NaOH concentration and the stripping phase ratio (O/A) in the regeneration experiment of extraction by $L_4(2^3)$ orthogonal test were investigated. After 20 min contact, the phase was allowed to disengage (as enough time had been allowed to reach equilibrium during the preliminary experiment). The aqueous phases were separated and analyzed.

3. Theory

In this paper, H_2SiF_6 was used as a precipitator to precipitate sodium ions, after which the precipitate was separated from the aqueous phase. The following reaction occurred:

$$H_2SiF_6 + NaCl = Na_2SiF_6 \downarrow + HCl \tag{1}$$

The liquid–liquid complex extraction, also referred to as solvent extraction or partitioning, is a kind of ion-associated extraction system, in which cations and anions are associated with each other in the organic phase, from aqueous phase [35,36]. The sulfonic group $–SO_3Na$ of K-2BP in aqueous solutions of organic compounds is in the state of $–SO_3^-$. When $pH < 7$ there is a strong anion association action between the trialkylamine extractant and the organic compounds [35]. The extraction mechanism of trialkylamine in kerosene is mainly based on the ion exchange [35]. The extraction reactions can be described as follows:

$$R_3N(o) + HCl \rightarrow R_3[NH^+]Cl^-(o) \tag{2}$$

$$[NH^+]Cl(o) + R' - SO_3^- \rightarrow R_3NH^+SO_3 - R'(o) + Cl^- \tag{3}$$

The total extraction reaction can be shown as follows:

$$R_3N(o) + R' - SO_3 - HCl \rightarrow R_3NH + SO_3 - R'(o) \tag{4}$$

An excessive amount of HCl can also be extracted by the trialkylamine extractant, as follows:

$$R_3N(o) + HCl \rightarrow R_3[NH^+]Cl^-(o) \tag{5}$$

When $pH > 7$, the amine salt is soluble in alkali and stripped by the NaOH solution, as described in the following reactions:

$$R_3NH^+SO_3 - R'(o) + NaOH \rightarrow R' - SO_3Na^+R_3N(o) + H_2O \tag{6}$$

$$R_3[NH^+]Cl^-(o) + NaOH \rightarrow R_3N(o) + NaCl \tag{7}$$

Thus, the organic compounds were generated and reused.

4. Result and discussion

4.1. Wastewater ingredients after desalination

The wastewater ingredients after desalination are shown in Table 3, which shows an almost complete precipitation of sodium ions was obtained. The sodium ion can be precipitated by fluosilicic acid. In COD, chroma and the concentration of ions (Cl^- and SO_4^{2-}) decreased slightly. This was due to the dilution of wastewater by the addition of fluosilicic acid.

4.2. Effect of extraction time on COD removal

During the extraction process, it is important to mix the wastewater thoroughly with the solvent and to allow sufficient contact time for the transfer of pollutants between the two phases. Using an A/O ratio of 1:1, the optimum contact time was determined. Fig. 1 shows the effect of mixing time on COD removal, which was found to increase with an increase in the phase mixing time. After 5 min of mixing time most dyes have been extracted into the organic phase, and the chroma removal rates can reach 99.5%. A further increase in mixing time results in a very slow improvement of extraction efficiency. The COD removal rates were around 92% after 20 min contact time. Prolonged contact time did not result in much improvement in COD and chroma removal rates.

4.3. Optimization of the extraction parameters

An orthogonal experiment was employed to optimize extraction conditions. Three factors were involved: (A) N235 concentration, (B) phase ratio (O/A), and (C) desalination ratio. The experimental factors, corresponding levels, and orthogonal designs $L_9(4^3)$ were presented. The COD removal was used as a criterion for the selection of the optimal extraction conditions. Independent variables at four variation levels—in terms of extractant N235 concentration (A), phase ratio (O/A) (B), and desalination ratios (C) are listed in Table 4. The largest range of the three factors

Table 3
Wastewater ingredient after desalination

Acidity (mol/L)	COD (mg/L)	Chroma	Cl$^-$ (mg/L)	Na$^+$ (mol/L)	SO$_4^{2-}$ (mol/L)
3.30	1.60×10^4	4×10^5	1.08×10^5	–	0.015

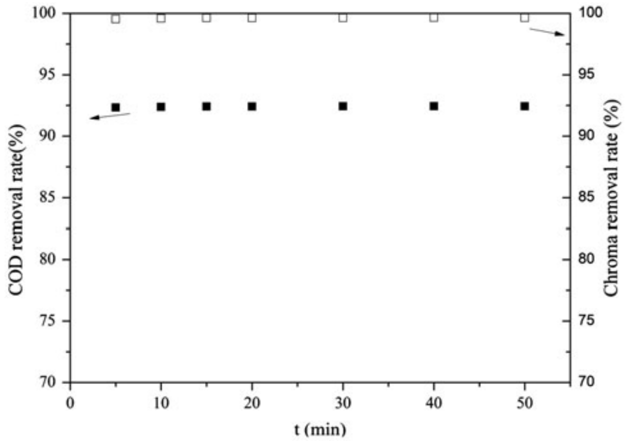

Fig. 1. Effect of mixing time on COD removal.

was 12.39% (of factor C), while the smallest was 5.97% (of factor A). This means that factor C is the primary factor affecting the extraction conditions of wastewater. COD removal rate was influenced by the following factors, in descending order: desalination ratio > phase ratio > N235 concentration. The third level of factor C had the highest average value, compared to the other two levels. This means that the third level is the best condition in terms of factor C. Analogously, the second level of factor B and the third level of factor C were the best conditions. The optimum extraction conditions are as follows: 100% of desalting rate, 30% of N235 concentration, and a 3:7 phase ratio (O/A). Chroma of the treated wastewater can reach 2,000 times and COD can reach a level in the range of 1,500–1,800 mg L^{-1} under the proper experimental conditions.

4.4. Effect of acidity on the COD removal

A volume of 2 mL of different concentrations of hydrochloric acid was added to 18 mL of wastewater, in order to adjust the acidity of wastewater to a level within the range of 0.05–0.70 mol/L. The effect of wastewater acidity on COD and chroma removal is shown in Fig. 2, which indicates that COD and chroma removal increased with an increase in the acidity of the aqueous phase, and reached maximum COD and chroma removal rates at 0.1–0.2 mol/L of acidity. Nevertheless, the COD removal rates decreased slightly at acidity levels of >0.2 mol/L. When the acidity was <0.1 mol/L, the low COD and chroma removal rates could be accounted for by the fact that this ion-association extraction only occurs in acidic conditions (see Eqs. (1) and (2)) and the higher the [H$^+$], the more efficient the extraction. When acidity >0.2 mol/L, for trialkylamine, it is also possible to extract HCl (see Eq. (2)), which leads to less free trialkylamine extractant (for K-2BP), resulting in very low COD removal rates.

Table 4
Orthogonal experiment of extraction and analysis results

No.	(A) N235 concentration (%)	(B) Phase ratio (O/A)	(C) Effluents desalting rate (%)	COD removal (%)
1	20	1:4	1	59.92
2	20	1:3	2	85.69
3	20	3:7	80	88.62
4	20	7:13	100	89.88
5	25	1:4	2	84.55
6	25	1:3	1	60.51
7	25	3:7	100	89.89
8	25	7:13	80	91.11
9	30	1:4	80	87.94
10	30	1:3	100	89.78
11	30	3:7	1	62.72
12	30	7:13	2	89.49
13	35	1:4	100	89.28
14	35	1:3	80	90.75
15	35	3:7	2	86.72
16	35	7:13	1	63.33
K1	324.11%	321.70%	246.48%	
K2	326.06%	326.73%	346.45%	
K3	329.93%	327.95%	358.41%	
K4	330.08%	333.80%	358.84%	
R	5.97%	12.11%	12.39%	
K´1	6.33	6.36	0	
K´2	6.22	6.24	0	
K´3	6.34	6.34	10.41	
K´4	6.26	6.21	14.73	
R´	0.07	0.14	10.41	

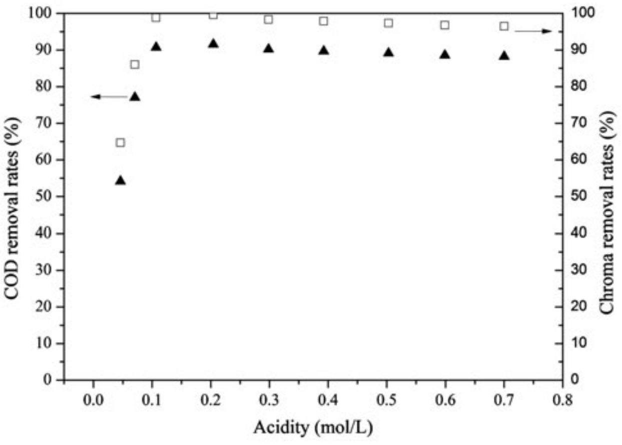

Fig. 2. Effect of wastewater acidity to COD removal.

4.5. Effect of desalting rate on COD removal

A series of different quality fluosilicic acids (at 43.22%wt) were added to a given volume of wastewater. Results indicated that various desalination ratios were attained, ranging from 1 to 100%. The effect of desalination ratios on the dyes extraction ratio is shown in Fig. 3. The results indicated that the dyes extraction rate increased with an increase in desalination ratios. COD removal rate and the acidity of wastewater were shown to reach levels of 87.2% and 0.90 mol/L, respectively, at a desalination ratio of 2%, and only a slight increase in the removal of COD was noted when the desalination ratio was more than 2%. It was, however, noted that the COD removal rate decreased slightly when the desalination ratio reached 100%. We had previously noted that fluosilicic acid can react with sodium ions, and gained sodium fluosilicate and HCl, therefore the acidity of wastewater increased with the removal of sodium ions (Fig. 3). Results shown in Fig. 3 also indicated that the acidity of the solution is proportional to the desalination rate. Previous research has indicated that the acidity of wastewater has a significant effect on COD removal, so desalination can be regarded as an indication of changed acidity of wastewater.

4.6. Effect of concentration of N235

The concentration of N235 in mixed organic solvent is in the range of 20–70%. As shown in Fig. 4, the COD and chroma removal rates increased with an increase in N235 concentration, but were not directly proportional to N235 concentration. When the N235 concentration reached 30%, the COD removal rates had already reached 92% and the chroma removal rates could reach a level of 99.3%. The COD and chroma removal rates also increased very slowly with a rapid increase in the concentration of N235. Since N235 is expensive, increasing the concentration of N235 cannot be regarded as an economical choice. For this reason, we recommend an optimal N235 concentration range of 30–40%.

4.7. Effect of phase ratio (O/A)

The effect of phase ratio (O/A) on the dyes extraction ratio is shown in Fig. 5. These results indicate that COD and chroma removal rates increased as the phase ratio (O/A) increased, but the COD and chroma removal rates slowed down when the phase ratio (O/A) reached levels greater than 0.54 (7/13). At a phase ratio of 0.54 (7/13) the COD removal rates and the chroma removal rates can reach levels of 92 and

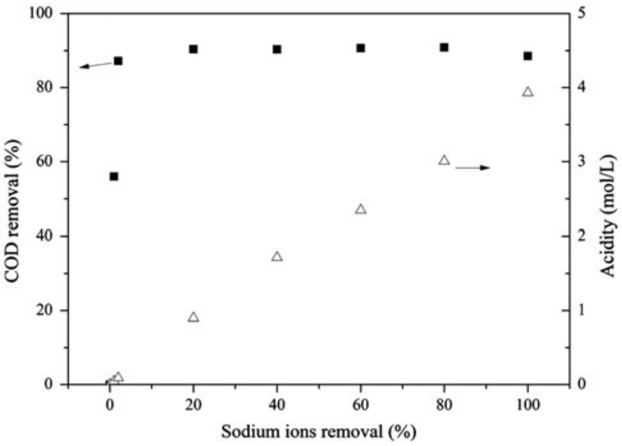

Fig. 3. The effect of desalting rate.

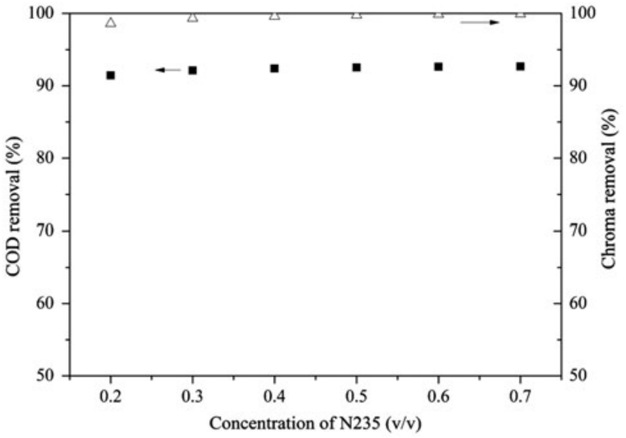

Fig. 4. Effect of N235 concentration.

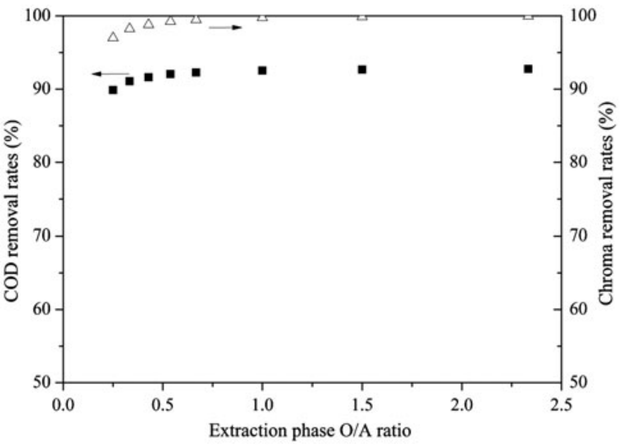

Fig. 5. The effect of phase ratio (O/A) on COD and Chroma removal.

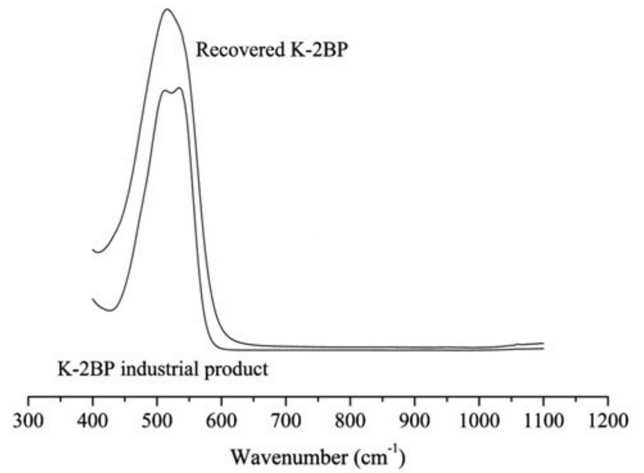

Fig. 6. UV-vis spectra of the recovered dyes and industrial products.

Table 5
Orthogonal regeneration experiment of extraction and analysis results

No.	(A) Concentration of sodium hydroxide (%)	(B) stripping phase ratio (O/A)	Organic phase regeneration (%)
1	1 (15%)	1 (4:1)	99.97
2	1 (15%)	2 (5:1)	99.70
3	1 (15%)	3 (6:1)	99.07
4	2 (20%)	1 (4:1)	100.00
5	2 (20%)	2 (5:1)	99.99
6	2 (20%)	3 (6:1)	99.99
7	3 (25%)	1 (4:1)	100.00
8	3 (25%)	2 (5:1)	99.99
9	3 (25%)	3 (6:1)	99.99
K1	298.74	299.97	
K2	299.98	299.68	
K3	299.98	299.05	
R	1.24	0.92	

99.7%, respectively. The maximum COD removal rate is only 92.8%. If the extraction ability of one volume organic phase is taken into consideration, the extraction efficiency reduces with an increase in the phase ratio. A relatively low phase ratio (O/A) can, therefore, be regarded as the most economical option.

4.8. Optimization of stripping

NaOH solution is a back-extractant in the regeneration experiment of the extraction process and the regeneration experiment is similar to the extraction experiment. NaOH concentration and stripping phase ratio (O/A) were selected as influencing factors. The experimental factors, corresponding levels, and orthogonal designs $L_4(2^3)$ are presented in Table 5. The results show that the stripping ratio was influenced by the following factors, in descending order: concentration of N235 > phase ratio (O/A). The regeneration effect has little effect on the NaOH solution concentration at levels 2 and 3. After the treatment, the COD of the regenerated concentrated solution was 1.89×10^5–2.06×10^5 mg L^{-1}. The solvent could be used repeatedly after regeneration, without affecting the efficiency of the extraction.

After the stripping experiment, the dyes in the organic solvent were transformed into NaOH solution. Fig. 6 represents the UV-vis spectra of the recovered dyes and the reactive brilliant red K-2BP industrial products. Fig. 6 shows that the UV-vis spectra of the two dye solutions were very similar, which suggests that the recovered dyes could be used as low-grade products.

5. Conclusions

Our experiments demonstrated that the chemical precipitation–extraction–stripping method has a high potential in terms of sodium salt and reactive dye recovery from wastewater. The extraction rates were influenced by the following factors, in descending order: desalination ratios > phase ratio (O/A) > N235 concentration. It was also noted that the stripping ratio was influenced by the following factors, in descending order: concentration of N235 > phase ratio (O/A). We also demonstrated that the extraction reaction could reach equilibrium in 20 min. The COD removal rates increased with an increase in the acidity of wastewater and desalination rates, and reached high removal rates during the following experimental conditions: acidities ≥0.1 mol/L; desalination rates ≥2%; N235 concentration ≥30%; and at a phase ratio (O/A) ≥1.0. The optimum experimental conditions for regeneration are as follows: NaOH solution concentration: 20%; phase ratio (O/A): 4:1; and the regeneration rate approached 100%, which indicates that the solvent could be used repeatedly after regeneration.

Compared to other methods, the precipitation–extraction–stripping method is considered to be much more efficient and feasible. It also has the advantage of making use of an extractant that can be regenerated, thus reducing operation costs. The recovered dyes can also be used as low-grade products, and sodium ions can be recovered as a by-product, which meets the requirement of zero discharge and no sludge. It should also be noted that wastewater containing fluoride may be useful as a means of precipitating sodium ions.

Acknowledgments

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