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Original Article

Ionic liquid-based hollow fiber-supported liquid-phase microextraction enhanced electrically for the determination of neutral red



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ABSTRACT

A method of ionic liquid-based hollow fiber liquid-phase microextraction enhanced electrically was successfully developed and applied to the extraction and determination of neutral red (NR) dye, which was selected as the model analyte. A room temperature ionic liquid, 1-octyl-3-methylimidazolium hexafluorophosphate ($[\text{C}_8\text{mim}][\text{PF}_6]$), was placed in the pores of a polytetrafluoroethylene hollow fiber, which acts as a liquid membrane and the acceptor solution. The extraction parameters affecting the enrichment factor of NR, such as pH, extraction time, elution time, stirring rate, and the voltage were optimized. In addition, UV–Visible (UV–Vis) or electrochemiluminescence spectra were also determined. The extraction rate and capacity of NR could be improved significantly by cathodic polarization. Under the optimized extraction conditions (organic liquid microextraction phase $[\text{C}_8\text{mim}][\text{PF}_6]$, pH 7, stirring rate 300 rpm, extraction time 20 minutes, ultrasonic-assisted elution time 3 minutes, voltage -70 V), the detection limit of $0.38\ \mu\text{g/L}$ and linear correlation coefficient of $r > 0.99$ were obtained. The established method was successfully applied to the analysis of three soft drink samples, which were spiked with NR standards at the concentrations of 0.1, 1.0, and 5.0 mg/L, and satisfactory results were obtained.

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1. Introduction

Because of the wide application of synthetic chemical dyes there is a high-level risk of contamination to humans and animals [1,2]. Therefore, identifying effective techniques to

remove and determine the amount of dye in food and environmental samples attracts noteworthy attention [3–5]. The conventional methods for dye removal are trickling filter, activated sludge, chemical coagulation, and photo-degradation processes. However, most dyes, including neutral red (NR, a cationic dye), show fairly high solubility in

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the aqueous media, and therefore, conventional methods are ineffective [6–8]. Adsorption and extraction are well-known separation processes and widely used [9–12]. Ionic liquid-based liquid-phase extraction process is strongly favored because of its unique physical and chemical properties, including good dissolving capacity, lower volatility, high thermal stability, simple regeneration, and low pollution [13–16].

Hollow fiber liquid-phase microextraction (HF-LPME) is an effective technology to preconcentrate or separate organic pollutants [17–20]. Ionic liquid was placed in the pores of a hollow fiber, and hollow fiber-supported liquid membrane extraction method has been reported to have better stability and more extraction efficiency. Ionic liquid-based HF-LPME has many advantages over traditional liquid–liquid extraction, such as more safety, being environmentally friendly, and possesses high enrichment factors. HF-LPME can be enhanced by the application of electrical fields across the liquid–liquid interface. The electrical potential is the driving force for the extraction, and the potentials are easily varied and controlled from a power supply. Thus, extraction can easily be adjusted by a simple change of the applied voltage, and the voltage can be used to optimize the rate of extraction. In addition, it is characterized by the compact size of the equipment, simplicity of operation, and low capital and operating costs [21–23].

In this study, we tried to establish a new method of HF-LPME enhanced electrically, with NR as the target dye to investigate the extraction characteristics. A room temperature ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8mim][PF_6]$) was placed in the pores of a polytetrafluoroethylene hollow fiber, acting as a liquid membrane and the acceptor solution. We optimized several parameters affecting the performance of the system, including pH of the sample, extraction time, stirring rate, the electrical field's conditions, etc.

Under the optimized extraction conditions, the analyte was separated and enriched effectively, and this facilitates accurate determination of the extraction characteristics. For general environmental samples, it is not necessary to detect low levels of NR, and in such cases, direct spectrophotometry determination is a commonly used method. However, for some other samples (e.g., food samples), it is necessary to detect even lower concentrations of the dye. It is well-known that food safety problems are issues of serious concern. In recent years, many food safety incidents were reported, for example, melamine milk scandal, red duck egg (the carcinogenic dye Sudan red), yellow croaker (tartrazine dye), dyed steamed buns, lean meat powder. These food scandals have given Chinese shoppers more cause for concern at the supermarket, and such contaminated food products cannot be consumed. Before these food safety events were exposed, lower levels of illegal additives (melamine, Sudan red, etc.) were not an issue of concern [24,25].

Chemiluminescence and electrochemiluminescence (ECL) have been applied in a number of fundamental studies and bio-related applications [26–29]. As a powerful analytical technique, there is an increased attention in applying ECL, because of wide dynamic concentration range, simple optical requirement for instruments, and excellent sensitivity to

obtain lower detection limits (DLs) of dye concentration. The wider application of this method would potentially expand its scope as a routine technique for real-sample analyses. Hence, we also tried to realize the feasible detection at low concentrations of NR using the ECL system.

2. Experimental analysis

2.1. Apparatus and reagents

UV–Visible (UV–Vis) absorption spectra were recorded using a Persee general TU-1901 spectrophotometer (Beijing, China). ECL intensity versus potential was detected using a lab-made system, which consisted of a BPCL ultraweak chemiluminescence analyzer (Institute of Biophysics, Chinese Academy of Sciences, Beijing, China) and a CHI model 1100A electrochemical analyzer (Shanghai Chenghua Instrument Co., Shanghai, China). A conventional three-electrode system was used for the electrolytic system, including a glassy carbon electrode as the working electrode, a platinum wire as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode. A homemade 5-mL cylindrical quartz cell was used as ECL cell, and was placed directly in front of the photomultiplier tube. The ECL spectra of the $Ru(bpy)_3^{2+}/(dibutylamino)etha$ (DBAE) and $Ru(bpy)_3^{2+}/DBAE/NR$ systems from 535 nm to 640 nm were obtained by putting a series of filters between the ECL cell and the photomultiplier tube one by one, and by successively recording the ECL intensity. Results showed that maximum ECL intensity could be obtained at 620 nm. Therefore, all further experiments were tested using the 620-nm filter.

$[C_8mim][PF_6]$, NR, $Ru(bpy)_3^{2+}$, DBAE, HCl, NaOH, Na_2CO_3 , $NaHCO_3$, ethanol, acetone, and polytetrafluoroethylene hollow fiber (250- μ m wall thickness, 800- μ m inner diameter, 0.45- μ m pore size, 75% porosity) were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). A stock solution of NR was prepared by dissolving the powder in double-distilled water and kept at 4°C. The pH of the solution was adjusted by adding 0.01 mol/L HCl or NaOH solutions. All chemicals used were of analytical grade.

2.2. Preparation of ionic liquid-based hollow fiber containing an electrode

A stainless steel wire (70 mm \times 1.0 mm i.d.) was cleaned, dried, and coated with a thin layer of commercially available epoxy adhesive system. The hollow fiber was cut manually into 1-cm length piece; 100 such pieces were then immersed in a mixture solution of 0.3017 g $[C_8mim][PF_6]/5$ mL acetone for 24 hours. By evaporating slowly until complete removal of acetone, the ionic liquid was immobilized in the pores of the hollow fiber. The prepared stainless steel wire was inserted into the hollow fiber, thereby permitting application of a voltage within this unit.

2.3. Extraction of NR on HF-LPME enhanced electrically

The homemade experimental apparatus included an electro-sorption tank, a magnetic stirrer, a power supply, a platinum

wire as the positive electrode, and an ionic liquid-based hollow fiber containing a stainless steel wire electrode as the negative electrode (Fig. 1). In the prepared extraction unit, the HF-LPME device was immersed into 15 mL of 1 mg/L NR solution for 20 minutes and the solution was constantly stirred. In the electric field-enhanced extraction process, the HF-LPME device was immersed at -70 V, and stirred at 300 rpm for a certain period at room temperature. After extraction, the hollow fibers were taken out from the aqueous solution and immersed into the eluant (1 mL of 95% ethanol) in order to wash the dye with ultrasonic assistance. The eluting solution was then collected and mixed together with phosphate-buffered solution ($\text{Na}_2\text{HPO}_4\text{-NaH}_2\text{PO}_4$, pH 7.0, 1 mL). The concentration of NR could then be measured and calculated using a UV–Vis spectrophotometer or ECL apparatus. The determination parameters for UV–Vis spectrophotometry were the following: 1×1 cm cuvette, $\lambda = 530$ nm, differential spectrophotometry. ECL signals were measured using an electrochemical analyzer and an ultraweak chemiluminescence analyzer. Other experimental conditions were as follows: 1.0 mol $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ buffer solution, 0.1 mol/L, pH = 11; $\text{Ru}(\text{bpy})_3^{2+}/\text{DBAE}$ ECL system, $\text{Ru}(\text{bpy})_3^{2+}$ 1.0×10^{-3} mol/L, 10 μL , DBAE 1.0×10^{-2} mol/L, 10 μL ; scan rate, 0.05 V/s.

3. Results and discussion

3.1. Effect of pH

The pH of sample solution plays an important role in the extraction process because it can influence the existing forms of the targets [21,30]. To examine the effect of sample solution pH on extraction efficiency, the concentration of NR was 1 mg/L and the pH was adjusted to 2–12 by adding HCl or NaOH solutions. As shown in Fig. 2, at lower or higher pH, the higher ionization degree of NR molecules would increase their solubility in the water, which can decrease the uptake on the ionic liquids. At pH 6–8, NR exists mainly in molecular state, and pH 7.0 was selected in the following experiments.

3.2. Effect of extraction time

Extraction time is another important factor influencing the extraction efficiency [31,32]. In this study, extraction time was evaluated in the range of 5–60 minutes, and the results are

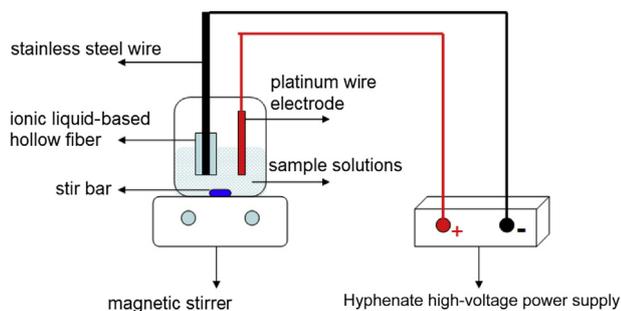


Fig. 1 – Schematic diagram of extraction apparatus for hollow fiber liquid-phase microextraction enhanced electrically.

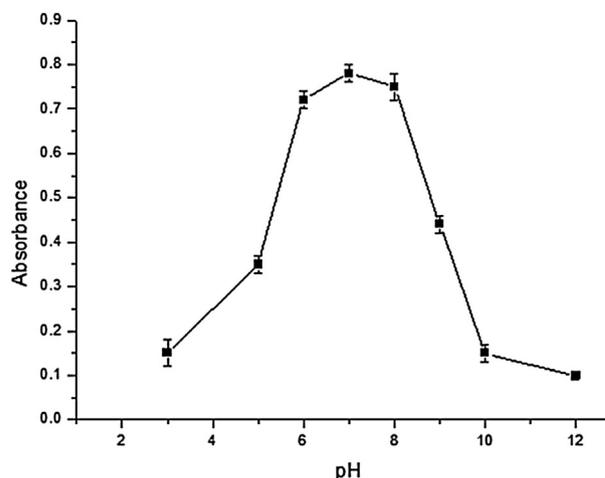


Fig. 2 – Effect of pH. Extraction conditions: neutral red, 5 mg/L; extraction time, 20 minutes; stirring speed, 300 rpm; and electrical voltage -70 V.

shown in Fig. 3. The signal intensity increased with the increase of extraction time and gradually became slower after 20 minutes. In some cases, HF-LPME is performed with extraction time approaching equilibrium to maximize recovery. In some other cases, extraction need not reach equilibrium to minimize ionic liquid loss and guarantee efficient extraction. Considering the appropriate extraction efficiency, enough sensitivity, and shorter extraction time, 20 minutes was selected.

3.3. Effect of stirring rate

In this work, $[\text{C}_8\text{mim}][\text{PF}_6]$ was used as the acceptor solution in the HF-LPME extraction of NR. To accelerate the mass-transfer velocity from the donor through the organic membrane into the acceptor in the extraction process, magnetic stirring is commonly used, which speeds up the process [17]. Effective mixing of the sample also decreases the extraction time by

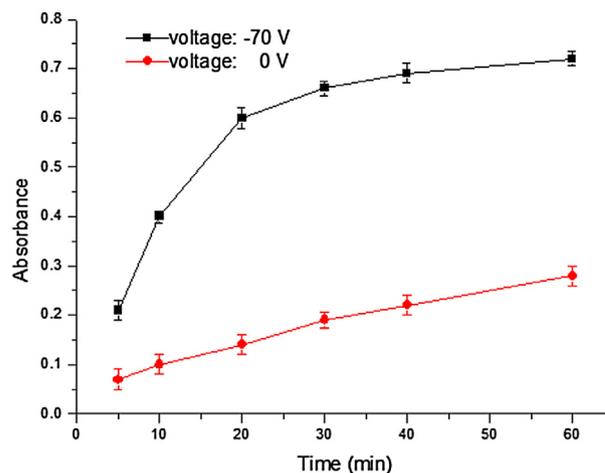


Fig. 3 – Effect of extraction time under 0 and -70 V electrical voltages. Extraction conditions: neutral red, 5 mg/L; pH 7; stirring speed, 300 rpm; and extraction time 20 minutes.

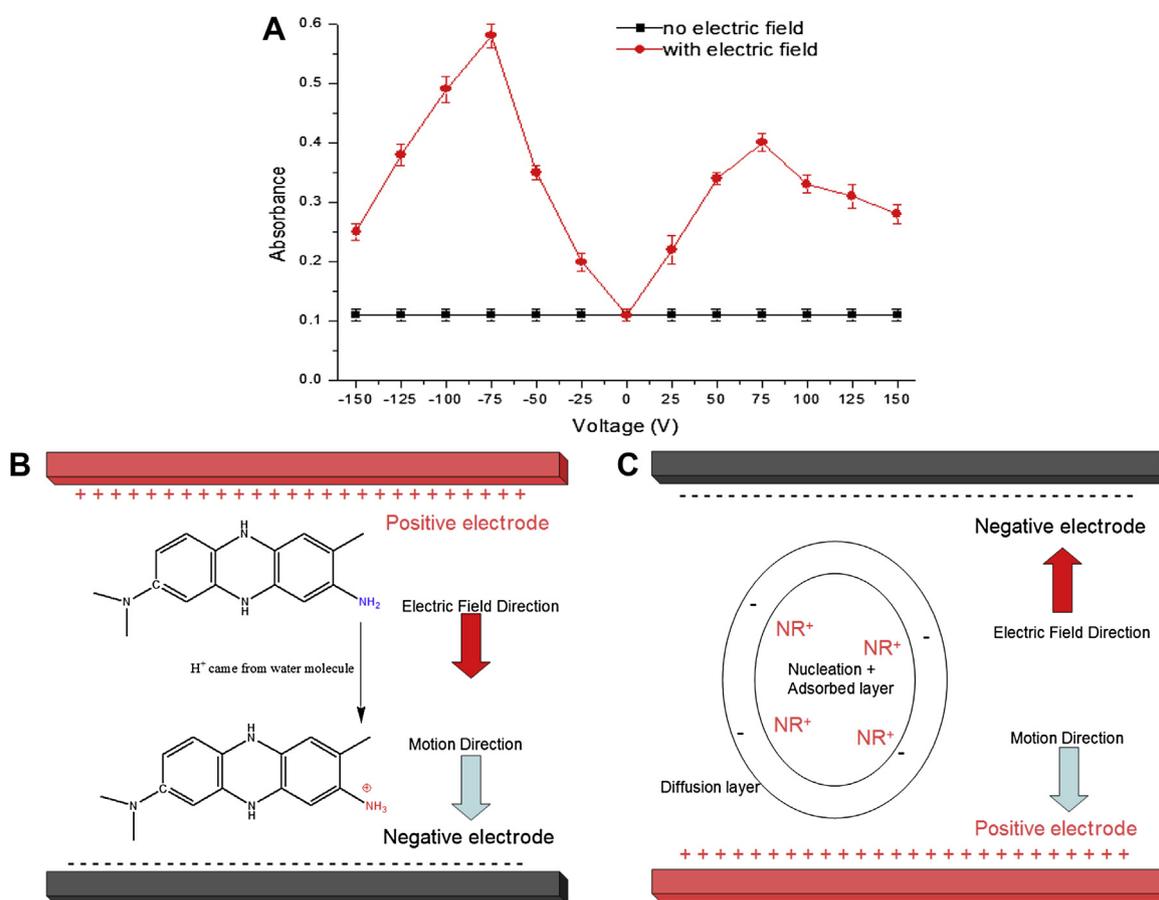


Fig. 4 – (A) Effect of voltage. Extraction conditions: neutral red, 5 mg/L; pH 7; stirring speed 300 rpm; and extraction time 20 minutes. (B) electrical voltage -70 V. (C) electrical voltage $+70$ V.

increasing the diffusion rate of the analyte from the donor phase into the acceptor phase. Therefore, the highest speed of the magnetic stirrer should be selected for stirring. At high rates of stirring, however, air bubbles produced on the surface of the HF hinder the transfer of the analyte into the fiber and, therefore, decrease the extraction efficiency. Hence, the effect of stirring rate on NR dye extraction was investigated in the range of 50–300 rpm by another series of experiments. The results showed that a stirring rate of 300 rpm was optimized in our work.

3.4. Effect of electrical field

The electrical field conditions are also an important factor influencing the extraction efficiency, because they are capable of driving and accelerating target molecules to migrate to the opposite electrode surface. To examine the effect of the electrical field on dye extraction, the voltage is applied across the stainless steel in the range of -150 to 150 V. As shown in Fig. 4A, both anodic and cathodic polarization can increase the amount of extraction of NR. It may be due to the interactions of the adsorbent and adsorbate under the different voltages. With no electric field, NR was extracted into the hollow fiber-supported ionic liquid membrane through intermolecular forces and diffusion. As the electric field was applied, the extractant surface would accumulate the significant amount

of charge because of the “capacitive charge”. The charge and the ionic state of NR would generate additional electrostatic force, resulting in the increase of extraction rate and capacity.

An interesting fact was that two kinds of electric filed modes ($+70$ V and -70 V) could enhance the extraction efficiency. Our reasoning for this is as follows: the hydrogen ion coming from the ionized water could lead to protonation of the amino group in the NR molecule, and then the molecules would be accelerated to move toward the cathode (Fig. 4B). In the solvation shell, the negative charge of the diffusion layer surrounding the cationic molecules would be beneficial for moving toward the anode (Fig. 4C). Because the volume of the solvation molecule was larger than that of the cationic molecule, the movement was slower and the extraction efficiency was relatively lower under the same conditions. However, the underlying fact should be further researched in the future. Based on the results of Fig. 4A, we selected the voltage of -70 V and performed another experiment to present the effect of electrical field. The results (Fig. 4) showed that the electrical potential as driving force can be beneficial for the extraction.

3.5. Salt effect

The ionic strength would influence the nature and extent of the electrostatic interactions and hydrophobic properties

between the adsorbent and the analyte [17]. With no electric field, the experiments were carried out using 5.0 mg/L NR solutions containing various concentrations of NaCl ranging from 0% to 20% (wt/vol). The results showed that the presence of an external electrolyte only has a slight effect on the extraction efficiency. However, the stability of ionic liquid-based hollow fiber would get worse and may even influence the application of electrical voltage, exposed to high ionic strength. Therefore, the strong electrolyte was not added in this research work.

3.6. Eluent and elution time

We selected a strong acid (0.1 mol/L HCl), a strong base (0.1 mol/L NaOH), ethanol (95%), and acetone as eluents to remove the targeted dye from the uploaded ionic liquid-based hollow fiber. The results showed that the four kinds of eluting reagents can effectively remove the uploaded NR. However, longer extraction time and larger eluent volume are needed when using a strong acid or base as the eluent. Moreover, acetone is relatively toxic and expensive than ethanol. Therefore, 1 mL 95% ethanol was selected as the eluting reagent.

Effect of elution time was evaluated in the range of 10–60 minutes, and the results showed that complete elution of NR occurs after 30 minutes. The static eluting process was relatively longer, because the eluent volume was too small to be stirred easily. However, the ultrasonic-assisted elution or vortex mixing elution shortened the eluting time to 3 minutes.

3.7. Analysis characteristics

The standard solutions of NR were dealt with the aforementioned operation procedure, and the concentrations were determined and calculated by UV–Vis spectrophotometer. The working curve was made, and the linear equation was Y (mg/L) = $-0.01336 + 0.0584X$ (Abs) with the linear correlation coefficient $r = 0.9982$ and the linear range = 1.0–10.0 mg/L.

As described earlier, at lower levels of NR, ECL was used to determine the concentration of NR dye solution. Under the aforementioned optimal conditions, the standard curve for NR was measured. The quenched ECL intensity (ΔI) has good linear relationship with the logarithm of the concentration of NR, with C_{NR} in the range of 0.001–1.0 mg/L. The regression equation was $\Delta I = 1325 \times \log C_{NR} + 4267$, and the correlation coefficient (r) was 0.9903. The DL was 0.36 $\mu\text{g/L}$ at a signal-to-noise ratio of 3, indicating that the ECL method is very sensitive for determining NR.

To investigate the interference effects of coexisting substances in the real samples, the effect of foreign substances was tested by analyzing a standard solution of NR (1.0 mg/L) and interfering substances. The upper limit of an interfering species was estimated under the optimized conditions (relative error was <10%). The results showed that the proposed method would be feasible under the following conditions: 1000-fold Na^+ , K^+ , NO_3^- , Cl^- , SO_4^{2-} ; 500-fold Ca^{2+} , Mg^{2+} , Zn^{2+} ; 30-fold lemon yellow, sunset yellow, amaranth, carmine; fivefold basic orange, basic fuchsin; twofold malachite green, methylene blue, crystal violet (average values of three determinations).

Intraday and interday precision and accuracy were determined by triplicate analysis of the samples at three concentrations (0.1, 1.0, and 5.0 mg/L) on the same day and 3 consecutive days. Means and relative standard deviations (RSDs) were calculated. RSDs were used as estimates of intraday and interday precision, and the accuracy was assessed by comparison of calculated mean concentrations with known concentrations. The results showed that intra-assay RSDs were 8.64%, 4.75%, and 2.90%; interassay RSDs were 9.43%, 6.04%, and 4.58%, respectively, for these three concentrations. Intra-assay and inter-assay accuracy for NR were 93.45–108.3% and 87.85–119.1%, respectively. For trace analysis, these results could be accepted.

The HF-LPME enhanced electrically was successfully applied to the analysis of three soft drink samples collected from local markets (Table 1). After the soft drink samples were filtered with 0.22- μm cellulose acetate membrane filters to eliminate any solid particles and debris, the samples were tested immediately under the optimized experimental conditions without any other pretreatment. To evaluate the accuracy of this method, these samples were spiked with NR standards at the concentrations of 0.1, 1.0, and 5.0 mg/L, respectively. For every concentration level, five repeated experiments were performed and the mean values were taken. The data indicate that the recoveries ranged from 90% to 115%, and the RSDs were less than 10.0%, which shows good reproducibility. Thus, this method shows potential application for the fast determination of NR in soft drink samples.

4. Conclusions

A method of ionic liquid-based HF-LPME enhanced electrically was successfully developed and applied to the extraction and determination of NR dye combined with UV–Vis or ECL determination. The advantages of this eco-friendly method are its simplicity, sensitivity, and low cost. The method was applied to the analysis of NR in real samples with satisfactory

Table 1 – Determination results of NR in soft drink samples utilizing standard addition method.

Samples	Standard added (mg/L)	Founded amount (mg/L)	RSD (%)	Recovery (%)
1	0	0.0	ND	—
	1	0.11 \pm 0.04	9.2	110.0
	2	1.12 \pm 0.05	6.5	112.0
	3	4.91 \pm 0.09	4.7	98.2
2	0	0.0	ND	—
	1	0.09 \pm 0.05	7.4	90.0
	2	1.01 \pm 0.03	3.6	101.0
	3	5.29 \pm 0.06	5.8	105.8
3	0	0.0	ND	—
	1	0.10 \pm 0.04	7.9	100.0
	2	0.95 \pm 0.05	8.6	95.0
	3	5.34 \pm 0.09	4.3	106.8

ND = not detected; RSD = relative standard deviation.

results, and would be a green and potential method for the analysis of NR.

Conflicts of interest

All contributing authors declare no conflicts of interest.

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REFERENCES

- [1] Ravikumar K, Ramalingam S, Krishnan S, et al. Application of response surface methodology to optimize the process variables for reactive red and acid brown dye removal using a novel adsorbent. *Dyes Pigments* 2006;70:18–26.
- [2] Robinson T, Chandran B, Nigam P. Removal of dyes from a synthetic textile dye effluent by biosorption on apple pomace and wheat straw. *Water Res* 2002;36:2824–30.
- [3] Iram M, Guo C, Guan YP, et al. Adsorption and magnetic removal of neutral red dye from aqueous solution using Fe₃O₄ hollow nanospheres. *J Hazard Mater* 2010;181:1039–50.
- [4] Abdel-Aziz HM, El-Zahhar AA, Siyam T. Sorption studies of neutral red dye onto poly(acrylamide-co-maleic acid)-kaolinite/montmorillonite composites. *J Appl Polym Sci* 2012;124:386–96.
- [5] Zhou Q, Gong WQ, Xie CX, et al. Removal of neutral red from aqueous solution by adsorption on spent cottonseed hull substrate. *J Hazard Mater* 2011;185:502–6.
- [6] Mahmoodi NM, Najafi F, Neshat A. Poly(amidoamine-co-acrylic acid) copolymer: synthesis, characterization and dye removal ability. *Ind Crop Prod* 2013;42:119–25.
- [7] Rauf MA, Shehadi IA, Hassan WW. Studies on the removal of neutral red on sand from aqueous solution and its kinetic behavior. *Dyes Pigments* 2007;75:723–6.
- [8] Alnuaimi MM, Rauf MA, Ashraf SS. Comparative decoloration study of neutral red by different oxidative processes. *Dyes Pigments* 2007;72:367–71.
- [9] Yua SC, Liu MH, Ma M, et al. Impacts of membrane properties on reactive dye removal from dye/salt mixtures by asymmetric cellulose acetate and composite polyamide nanofiltration membranes. *J Memb Sci* 2010;350:83–91.
- [10] Panahi HA, Feizbakhsh A, Karimpour M, et al. Determination of gemfibrozil in drug matrix and human biological fluid by dispersive liquid-liquid microextraction with high performance liquid chromatography. *J Food Drug Anal* 2013;21:109–14.
- [11] Chen HL, Chang SK, Lee CY, et al. Preconcentration of aqueous dyes through phase-transfer liquid-phase microextraction with a room-temperature ionic liquid. *Anal Chim Acta* 2012;742:54–8.
- [12] Ghaedi M, Hossainian H, Montazerzohori M, et al. A novel acorn based adsorbents for the removal of brilliant green. *Desalination* 2011;281:226–33.
- [13] Vidal L, Riekkola ML, Canals A. Ionic liquid-modified materials for solid-phase extraction and separation: a review. *Anal Chim Acta* 2012;715:19–41.
- [14] Pei YC, Liu J, Yan ZN, et al. Association of ionic liquids with cationic dyes in aqueous solution: a thermodynamic study. *J Chem Thermodyn* 2012;47:223–7.
- [15] Ma JY, Hong XP. Application of ionic liquids in organic pollutants control. *J Environ Manage* 2010;99:104–9.
- [16] Pedersen-Bjergaard S, Rasmussen KE. Electrical potential can drive liquid-liquid extraction for sample preparation in chromatography. *Trend Anal Chem* 2008;27:934–41.
- [17] Abulhassani J, Manzoori JL, Amjadi M. Hollow fiber based-liquid phase microextraction using ionic liquid solvent for preconcentration of lead and nickel from environmental and biological samples prior to determination by electrothermal atomic absorption spectrometry. *J Hazard Mater* 2010;176:481–6.
- [18] Sira N, Pakorn V, Manuel M. Hybrid flow analyzer for automatic hollow-fiber-assisted ionic liquid-based liquid-phase microextraction with in-line membrane regeneration. *Anal Bioanal Chem* 2013;405:3279–88.
- [19] Sun P, Armstrong DW. Ionic liquids in analytical chemistry. *Anal Chim Acta* 2010;661:1–16.
- [20] Wu CX, Liu Y, Wu QH, et al. Combined use of liquid-liquid microextraction and carbon nanotube reinforced hollow fiber microporous membrane solid-phase microextraction for the determination of triazine herbicides in water and milk samples by high-performance liquid chromatography. *Food Anal Methods* 2012;5:540–50.
- [21] Sevgi E, Melike B, Gönül D. Treatment of dye-rich wastewater by an immobilized thermophilic cyanobacterial strain: *Phormidium* sp. *Ecol Eng* 2008;32:244–8.
- [22] Deng AN, Wei J, Zhang N, et al. Electrically enhanced extraction of nitrobenzene in water by epoxy resin-based polymer membrane. *Acta Sci Circumst* 2012;32:2422–7 [in Chinese].
- [23] Wang S, Deng AN, Wei J, et al. Electrosorption-enhanced micro-column solid-phase extraction for traces of cresol red in water using electrodes of stainless steel wire coated with nonconductive polymer. *Adsorp Sci Technol* 2012;30:241–53.
- [24] Chen RC, Wei KJ, Wang TM, et al. Simultaneous quantification of antibiotic dyes in aquatic products and feeds by liquid chromatography–tandem mass spectrometry. *J Food Drug Anal* 2013;21:339–46.
- [25] Vachirapatama N, Maitresorasun S. Simultaneous determination of melamine, ammeline, ammeline and cyanuric acid in milk products by micellar electrokinetic chromatography. *J Food Drug Anal* 2013;21:66–72.
- [26] Yao HC, Xu EJ, Zeng WY, et al. Determination of doxorubicin in pharmaceutical preparation and rat plasma with luminol-K₃Fe(CN)₆ chemiluminescence system. *J Food Drug Anal* 2013;21:279–85.
- [27] Wang SJ, Neshkova MT, Miao WJ. EQCM study of the ECL quenching of the tris(2,2'-bipyridyl)ruthenium(II)/tris-*n*-propylamine system at a Au electrode in the presence of chloride ions. *Electrochim Acta* 2008;53:7661–7.
- [28] Choi JP, Bard AJ. Electrogenerated chemiluminescence 73: acid–base properties, electrochemistry, and electrogenerated chemiluminescence of neutral red in acetonitrile. *J Electroanal Chem* 2004;573:215–25.
- [29] Chao YY, Tu YM, Jian ZX, et al. Direct determination of chlorophenols in water samples through ultrasound-assisted hollow fiber liquid–liquid–liquid microextraction on-line coupled with high-performance liquid chromatography. *J Chromatogr A* 2013;1271:41–9.
- [30] Zeng CJ, Hu Y, Luo JW. Ionic liquid-based hollow fiber supported liquid membrane extraction combined with

- thermospray flame furnace AAS for the determination of cadmium. *Microchim Acta* 2012;177:53–8.
- [31] Wu Q, Wu DP, Geng XH, et al. Hollow fiber-based liquid–liquid–liquid micro-extraction with osmosis: I. Theoretical simulation and verification. *J Chromatogr A* 2012;1248:32–40.
- [32] Tao Y, Liu JF, Hu XL, et al. Hollow fiber supported ionic liquid membrane microextraction for determination of sulfonamides in environmental water samples by high-performance liquid chromatography. *J Chromatogr A* 2009;1216:6259–66.