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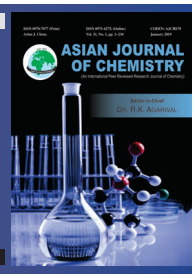

Comparative Spectroscopic Studies on Flotation Rate of Low Toxic Mixed Solvents

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The application of hydrophilic mixed solvents provides a new direction for the study of green air flotation technology. In this test, a mixture of *n*-propanol and anhydrous ethanol (4:1) was selected as solvent, sodium chloride as phase separator, sodium hydroxide solution was used to maintain acidity and hydrophobic associations formed by Fe(III) and doxycycline were flotated to the organic phase. After flotation, the hydrophobic associations were analyzed by spectrophotometry and high performance liquid chromatography. The results showed that the hydrophilic mixed solvent maintained good flotation rate without toxicity.

Keywords: Hydrophilic mixed solvent, Doxycycline, Flotation.

INTRODUCTION

Doxycycline is a derivative of hydrogenated biphenyl ring. It is a semi-synthetic broad-spectrum tetracycline antibiotic [1]. As a feed additive, it is widely used in veterinary medicine. In clinic, it is mainly used for upper respiratory tract infection caused by sensitive Gram-positive and Gram-negative bacteria, and chronic bronchitis in the elderly persons. Doxycycline is well absorbed orally and widely distributed in the body. It can be enriched in liver tissue and cause liver injury. With the international community's concern for environmental safety, the sensitivity of doxycycline residue detection method in the environment is becoming increasingly demanding. At present, the reported methods for determination of doxycycline residues in foods such as HPLC [2-6], fluorescence method [7,8], ultraviolet spectrophotometry [9], TLC [10], capillary electrophoresis [11,12], microbial method [13], *etc*. In the above determination methods, either it takes a long time or requires a high purity of the separation matrix.

In this study, the solvent sublation was utilized to separate trace doxycycline in wastewater, simultaneously, the hydrophilic mixed solvents *n*-propanol and anhydrous ethanol was used. This way effectively overcomes the problems of slow analysis speed and secondary pollution. The effects of different hydrophilic organic solvents on the results of solvent flotation were studied in detail. At the same time, the results of flotation separation and enrichment were evaluated by ultraviolet spectrophotometry and HPLC, respectively. Other factors affecting impact analysis were also studied one by one.

EXPERIMENTAL

Doxycycline (National Medicines and Chemical Reagents Ltd.) standard solution 1×10^{-4} mol L^{-1}; ferric nitrate (Tianjin Yuehua Chemical Plant) standard solution: 1×10^{-2} mol L^{-1} $Fe(NO_3)_3$ reserve solution was prepared with water and diluted to 1×10^{-4} mol L^{-1} when used. NaOH solution 0.01 mol L^{-1}; HCl solution 0.01 mol L^{-1}, anhydrous ethanol, *n*-propanol and tetrahydrofuran (Zhengzhou Pini Chemical Reagent Factory); Sodium chloride, sodium nitrate and potassium hydrogen phosphate (Tianjin Jinbei Fine Chemical Co. Ltd.). The experimental water was secondary distilled water and the other reagents used were of analytical grade.

UV-265 Ultraviolet-visible spectrophotometer (Shimadzu Corporation, Japan); high performance liquid chromatography (Aglient Technology 1200 series), 722 grating spectrophotometer (Sichuan Instrument Factory 9), 320-S acidity meter (Maitre-Toledo Instrument Co. Ltd.), electronic analytical balance (Metler, Switzerland). The hydrophilic solvent air flotation test device is self-made (sublation principle is shown in Fig. 1).

Generral procedure: A standard solution of doxycycline (5 mL, 1×10^{-4} mol L^{-1}) was drawn accurately and put into a

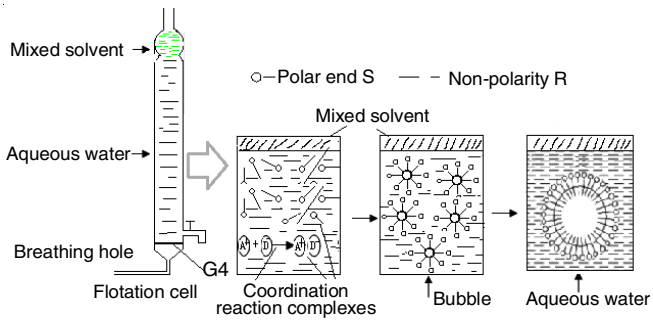

Fig. 1. Sublation principle

beaker, added 0.5 mL of 0.01 mol L^{-1} NaOH and 6 mL of mol L^{-1} $Fe(NO_3)_3$ and then wait for the standing response for 5 min followed by the diversion of the solution into a floatation equipment. The beaker should be washed for 2 to 3 times and the washed water was also transferred into the floatation device. The solution was diluted with saturated NaCl to 200 mL and then 5 mL mixture of *n*-propanol and anhydrous ethanol (4:1) was added and finally nitrogen gas was passed for 5 min @ 10 mL/min). The organic phase and water phase were transferred into a 1 cm comparison tube and then the absorbency was determined at wavelength of 383 nm (blank reagent as comparison solution) and floatation rate was calculated (%).

Next, using diamonsil C_{18} column, acetonitrile-water as mobile phase, flow rate of 0.8 mol L^{-1} and VWD1A detector, the organic phase after flotation was analyzed at 383 nm. The flotation rate of doxycycline was calculated by standard curve method, which was consistent with the results of photometric method.

RESULTS AND DISCUSSION

Absorption spectrometry: According to the experimental method, the absorption of organic phase was scanned by UV-265 UV-visible spectrophotometer in the wavelength range of 200-600 nm. The results indicated that the maximum absorption band of complex was observed at 383 nm (Fig. 2), henceforth the determination was carried out at wavelength of 383 nm in this study.

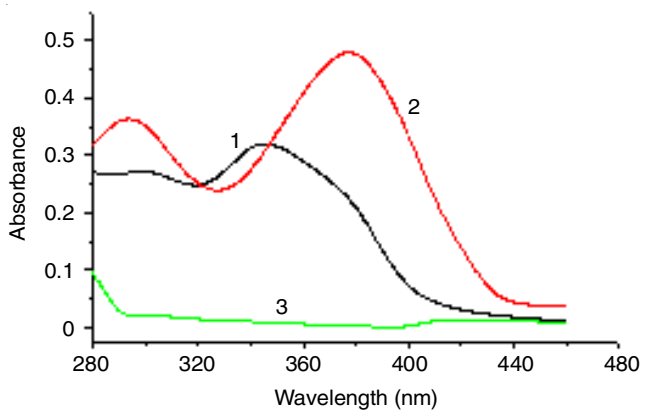

Fig. 2. Absorption spectra of doxycycline (1); Fe(III)-doxycycline (2); Reagent blank (3)

Effect of acidity: By optimizing the experimental process, the effect of acidity for the floating outcome was investigated. The results showed that the floating effect of Fe(III)-doxycycline complex was good when the pH value was 8. Hence, 0.5 mL of 0.01 mol L^{-1} NaOH was added.

Effect of reagent dosage: According to the experimental method, other conditions were fixed, the absorption of organic phase was investigated after flotation by changing the dosage amount of Fe(III). The results showed that the flotation effect was the best when the dosage of Fe(III) is 6 mL simultaneously, the absorbance was large and stable, so 6 mL of Fe(III) was chosen in this experiment. Similarly, studying the absorbance of organic phase with the change of sorts and dosage of inorganic salt and hydrophilic solvent, we obtained that the absorbance of organic phase was maximum and stabilization when 10 % NaCl was used for adjusting ionic strength of testing solution and *n*-propanol and anhydrous ethanol mixture (4:1) was used as solvent. Therefore, 10 % NaCl solution and 5 mL volume ratio of *n*-propanol and anhydrous ethanol are chosen as mixed solvents in the experiment.

Impacts of reaction time, floatation time and nitrogen flow: According to the experimental method, the impacts of reaction time, floatation time and nitrogen flow were investigated. The results showed that the floating rate of doxycycline was over 99.2 % when reaction time was 5 min, floatation time was 5 min and nitrogen flow was 10 mol L^{-1}. Hence, 5 min reaction time, 5 min floatation time and 10 mL/min N_2 flow were optimized in this experiment.

Working curve and correlation coefficient: Several standard solutions of doxycycline (3, 4, 5, 6 and 7 mL) were prepared and operated according to the experimental method. The absorbance of organic phase after flotation was determined and the working curve was made. The linear regression equation was obtained according to the least square method as follows:

$$A = 2.546 \times 10^5 C - 0.0566, r = 0.9996$$

The linear range was $1.1 \times 10^{-6} \sim 2.0 \times 10^{-4}$ mol L^{-1}; detection limit was 2.62×10^{-6} mol L^{-1}; average recovery rate was 93.85 %; apparent molar absorption coefficient was fond to be 2.546×10^5 L mol^{-1} cm^{-1}.

Impact of foreign ions: When the relative error is less than 5 %, the following foreign ions do not interfere with the determination: Cl^-, Na^+, NO_3^-, K^+, NH_4^+, SO_4^{2-} did not interfere with the determination. It was also found that 900 times of D-tryptophan and D-threonine; 600 times of L-histidine, L-albumin and L-isoalbumin; 400 times of L-cystine and glycine; 300 times of ascorbic acid; 100 times of starch; 20 times of glucose and hydroxymethyl cellulose sodium; 10 times of Cu^{2+}, Ca^{2+}; 5 times of Ba^{2+}, Mg^{2+}; 3 times of Pb^{2+}, $S_2O_3^{2-}$ and F^- also do not interfere during the determination of doxycycline.

Chromatographic analysis: Diamonsil (diamond) C_{18} column with acetonitrile-water as mobile phase, flow rate of 0.8 mL/min^{-1}, VWD1A detector was used to analyze the flotation organic phase at 383 nm. According to Fig. 3, Fe-doxycycline complex with an aqueous concentration of 2.31×10^{-6} mol L^{-1} was effectively floated into a mixed solvent of *n*-propanol and ethanol. The flotation rate of doxycycline was 92.3 % calculated by standard curve method, which was consistent with the result of photometric method. Chromatographic analysis further proved that the mixed solvent of *n*-propanol and absolute ethanol had good solubility to Fe-doxycycline complex because

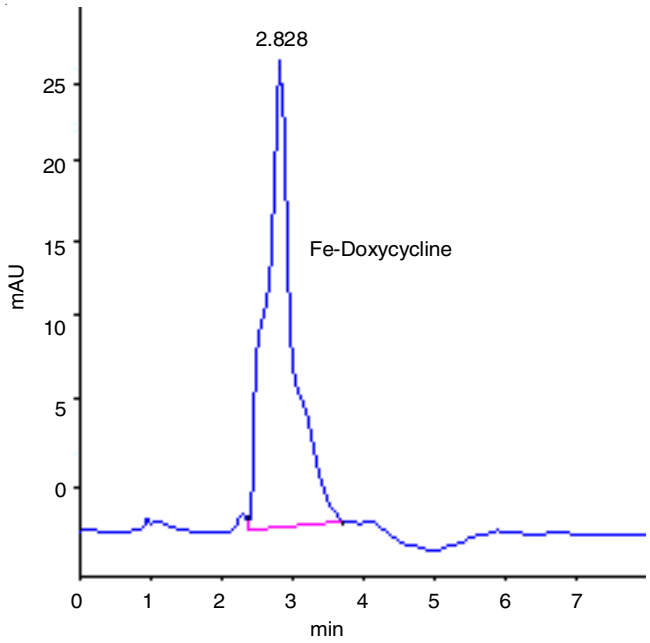

Fig. 3. Total chromatogram of organic phase

Fe-doxycycline complex had good hydrophobicity, which is one of the key conditions for the effective flotation of complex.

Applications: Accurate removal of 100 mL Baiguishan reservoir water samples, simulated water sample and a hospital drainage was achieved according to the experimental method. The results are shown in Table-1 using UV-visible and HPLC techniques.

TABLE-1
CONTRAST DETERMINATION OF
DOXYCYCLINE IN WATER SAMPLES (n = 5)

	Sample	A	B	C
UV-vis	Found mean value (× 10^{-6} mol/L)	–	1.39	1.68
	Standard added (× 10^{-6} mol/L)	–	1.5	2.0
	RSD (%)	–	1.6	1.6
	Reflection (%)	–	92.6	84
HPLC	Found mean value (× 10^{-6} mol/L)	–	1.36	1.76
	Standard added (× 10^{-6} mol/L)	–	1.5	2.0
	RSD (%)	–	3.1	2.8
	Reflection (%)	–	90.6	88

A = Baiguishan reservoir water samples, B = Simulated water sample, C = Hospital drainage

Conclusion

The key technology for the determination of trace pollutants by hydrophilic solvent flotation was the selection of organic solvents. Several commonly used organic solvents were either volatile or low solubility. This study proposed the concept of using mixed solvents. In this work, the performance of mixed solvent (*n*-propanol and anhydrous ethanol) in a ratio of 4:1 solvent flotation process was studied by UV-vis and HPLC techniques. In short, this work provides a new direction for the development and utilization of green solvent in flotation technology.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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