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A Method for The Removal of Trace Iodine from Wet process Phosphoric Acid

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Abstract: An effective method for extracting trace iodine from wet-process phosphoric acid (WPA) was designed. The iodine content in WPA was determined using an iodide-selective electrode. In addition, in this method, the sample solution, which contained approximately 2 ppm iodide, was phosphoric acid (PA) from WPA. The optimal extraction conditions were as follows: the PA/H_2O_2 volume ratio was 1:24, the PA/simethicone volume ratio was 1:3, the reaction time was 1 h, the reaction temperature was 45 °C, and no stirring was needed. The extraction yield of iodine reached 95%. A kinetic model was established based on bubbles with different rising velocities, and the characteristic viscosities of the gases as well as the heat flow rates of the bubbles were determined to simulate bubble movement. Then, the extraction principle was discussed, and the effect of bubble movement on extractability was analysed. The extractant (simethicone) can be recycled. Therefore, the proposed method can be considered a rapid, simple, and environmentally friendly method of extracting trace iodine from WPA.

Keywords: Wet-process phosphoric acid; Extraction process of iodine; Gas bubble motion; Dynamic model.

Introduction

Iodine is an essential micronutrient for human health, and insufficient iodine intake can lead to goitre, cretinism or other iodine-deficiency disorders [1]. Iodine and its compounds are important strategic resources in the military industry and in advanced technologies, with broad applications in the fields of metallurgy, agriculture, printing, photography, medicine, environmental health, and others [2] . The content of iodine in phosphorite is extremely high. In particular, iodine is relatively enriched in the phosphorite of Guizhou Province, with a concentration of approximately 0.01% [3,4]. Most factories devoted to the production of phosphoric acid (PA) from phosphorite use the so-called “wet process” [5] . Since the 1950s, the extraction of iodine can not only purify PA but also achieve iodine resource recovery. Many extensive studies have investigated methods for extracting iodine from WPA [6] . However, the process flow is complicated, and the production cost is too high to realize industrialized production. Based on research on the iodine extraction process, four methods have been widely used and developed for industrial applications. In 1932, K. Hiroshi et al. [7-9]reported the extraction of iodine by air-blowing, and this method is one of the most widely used methods of extracting iodine in factories. In 1961, G. Toth et al. [10-13]used an activated carbon adsorption method to extract iodine. As early as 1972, Y. Hatazakiy [14] applied a strongly alkaline anion resin to adsorb molecular iodine and iodide ions. The advances in iodine extraction methods represent a major achievement in large-scale iodine resource use in recent years. According to T. Cristian et al [15], the precipitation method of extracting iodine mainly uses iodide ions and copper ions to form insoluble copper iodide precipitates [16], which are then purified by dissolution–precipitation and decomposed at high temperature to obtain iodine; the recovery rate is approximately 80%. E.R. Vance et al. [17] and H. I. Kim [18] outlined a process to recover iodine from wastewater using oxidative precipitation followed by a solvent extraction (SX) technique. P. Samaddar et al. [19] described a newly designed block copolymer-based aqueous biphasic system (ABS, composed of two immiscible aqueous phases) to extract iodine. Y. Nan et al. [20] and AV. Korobeinyk et al. [21] reported the adsorption of iodine from solutions by Ag-zeolite materials. S. Wang et al. [22] used a zwitterionic surfactant as an extractant to extract organic and inorganic iodine under microwave irradiation. Worldwide extraction of resources is increasing dramatically; as a result, increasing resource consumption is expected. Overall, these methods are neither easy to control in terms of operation nor suitable for extracting trace iodine from waste solutions. With respect to economic and ecological sustainable development, the circular economy plays an essential and useful role in China [23]. The method proposed in this paper can be applied to industry to establish circular resource use and an economical form of environmental protection. This article describes a method for the extraction of iodine from WPA in which iodine-containing PA is directly treated with H_2O_2 to liberate iodine as a free element that can then be transferred to the organic phase by bubble transport and molecular diffusion. This method can be applied to the extraction of solutions with low iodine concentrations. Simethicone is used as the extractant because its chemical stability and recovery efficiency are high, and it combines economic performance with social performance. Unlike the extractants of other methods, this extractant (simethicone) can be recycled.

Experimental Methods

Reagents.

Phosphate ore was used as an experimental raw material. Sulfuric acid was supplied by Chuandong Chemical Co., Ltd. (Chongqing, China), and 30% hydrogen peroxide (H_2O_2) was provided by the Chengdu Jinshan Chemical Reagent Co., Ltd. (Chengdu, China). For the first time [24], a method was developed for obtaining purified ammonium phosphates with preliminary concentration of magnesium-containing EPA to a P_2O_5 content of 50-55% and its further ammonization. It was assumed that ammonium nitrate ions and molecules destroy the hydration shell of magnesium sulfate etc., and also prevent the association of water around crystalline hydrates, thereby the acid acquires fluidity and does not thicken even when cooled to minus 30-32°C. The other reagents, including potassium iodide, iodine, phosphoric acid, sodium hydroxide, sodium sulfite, sodium citrate, citric acid, simethicone, liquid paraffin, bromocresol green, 95% ethanol, tributyl phosphate (TBP), sodium fluoride and lauryl alcohol, were purchased from the Macklin Reagent Co., Ltd. (Shanghai, China). All reagents except for sulfonated kerosene were of analytical-reagent grade.

Apparatus.

An automatic potentiometric titrator (Samotor, ZD-2A, Shanghai, China) was used to measure the iodine potential and pH in the WPA sample solution. A tensiometer (NJUWH, DMPY-2C, Nanjing, China) was used to measure the liquid surface tension coefficient. An iodide-selective electrode (Leici, PI-1, Shanghai, China) and reference electrode (Leici, 232-01, Shanghai, China) were used to determine the contents of iodine in sample solutions. UV-visible spectra were recorded using a UV spectrophotometer (Hitachi, 722 Hitachi, Japan) to analyse the form of iodine present in PA. A polarizing microscope (Optec, BK-POLr, Chongqing, China) was used to observe the bubble size of iodine vapour formed by oxidation during extraction.

Experimental procedures.

PA preparation.

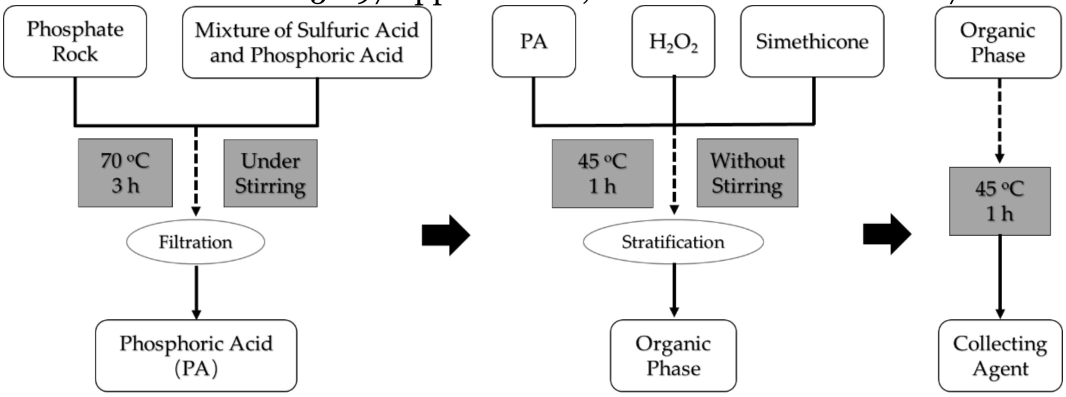
According to the practical process of the production line, to prepare a sample solution of PA, the phosphate ore was placed in a dry box at 110 °C for 48 h. The dried sample was placed in a ball mill, ground and then passed through a 100 mesh sieve. Powdered phosphate ore (50–55 g, < 0.12 mm) was completely mixed with concentrated PA (40–45 mL) and deionized water (200–250 mL), and the sample was placed in a water bath at 75–80 °C for approximately 2.5 h. Concentrated sulfuric acid (30–35 mL) was added to the sample for 0.5 h at 75–80 °C [25]. After cooling, the iodine was leached with deionized water, followed by filtration to remove residues, and the volume was adjusted to 500 mL with deionized water. The iodine in PA was determined by an iodide-selective electrode, and a calibration curve was prepared using iodide ion standards. The iodine standard curve was used to calculate the iodine concentration, which was approximately 2 ppm, and the pH value of the PA solution was 1.21.

Extraction procedure of iodine.

Varying volume ratios of 30% H_2O_2 were added to the sample and completely mixed. Iodine was extracted into the organic phase as elemental iodine with different extractants. The extraction Journal Pre-proof Journal Pre-proof 3 procedure was repeated with varying experimental conditions (i.e., different temperatures, reaction times and stirring intensities). The iodide ion potentials of the sample solution were determined by using an iodide-selective electrode and the calculated iodine concentration (Figure 1).

Preparation of simulated PA (SPA) solutions for solvent extraction testing.

Contrast experiments were used to determine the influence of concentrated acid on the iodine loss rate, while the effect of bubble movement on the extractability was analysed. According to the preparation procedure of PA (2.3.1.), the iodine content in the tested potassium iodine liquid was 61.788 ppm (potassium iodide was 3.012 $mol\cdot L^{-1}$). The iodine content was 56.976 ppm in SPA, and the loss rate was 0.078%.



Results And Discussion

UV-vis spectrophotometric analysis.

The absorbances of the samples were measured via UV-vis spectrophotometry [26-28]. The concentration of KI was 0.05 mol·L^{-1} , and the concentration of I_2 was 0.0005 mol·L^{-1} . The absorbance curves are given in Figure 2A and B. For the Iand I_2 samples, the highest absorbance was registered in the UV range. The UV-vis spectrum of I_2 in concentrated acid possessed an absorption peak at approximately 205 nm as well as very weak peaks at approximately 288 and 455 nm. In addition, I^- had strong absorption at 226 nm. The UV-vis spectra of I^-+ I_2 solutions in concentrated acid were recorded at different volume ratios. As shown in Figure 2C and D, the spectrum obtained immediately after mixing I_2 with Iresulted in two strong absorption bands in the 200–450 nm region. Because I^- has a strong absorption peak at 226 nm, it is difficult to obtain the absorption of I_3^- . The first absorption peak, located at approximately 290 nm, corresponds to a charge-transfer band, and the second peak, at approximately 360 nm, is a blueshifted iodine band brought about by the rapid formation of I_3^- species in solution. The UV spectra in Figure 2E show that iodine exists in the forms of I^- , I_3^- and I_2 in the acid hydrolysate of PA.

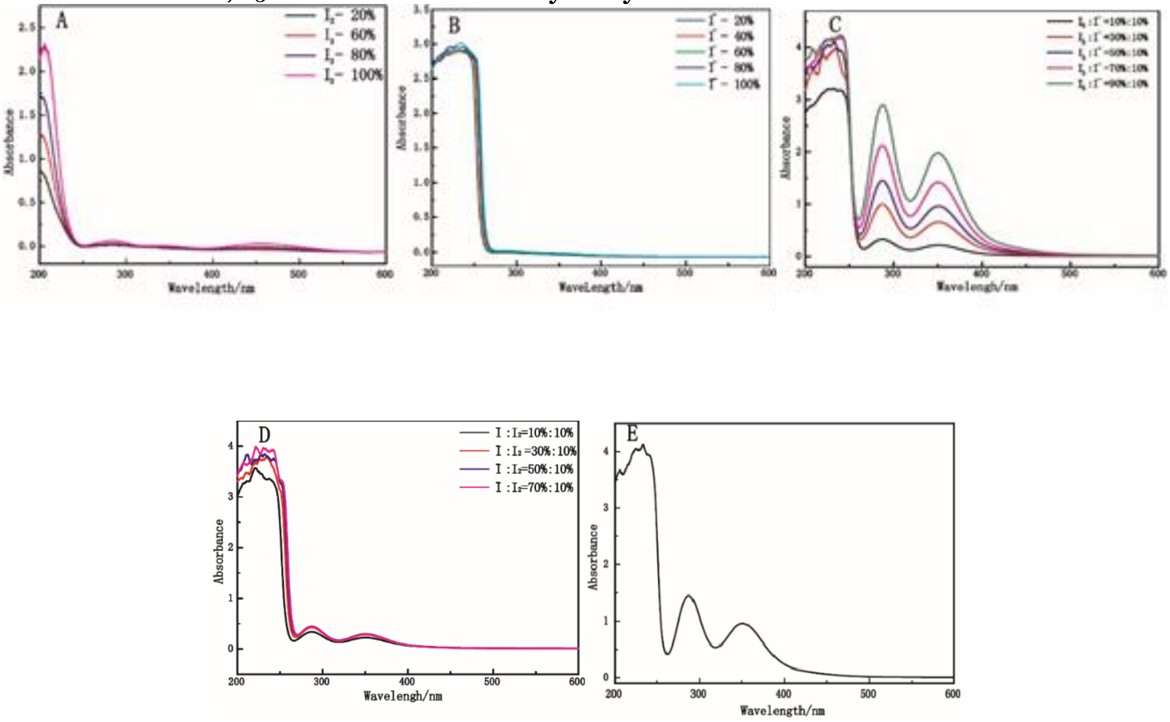
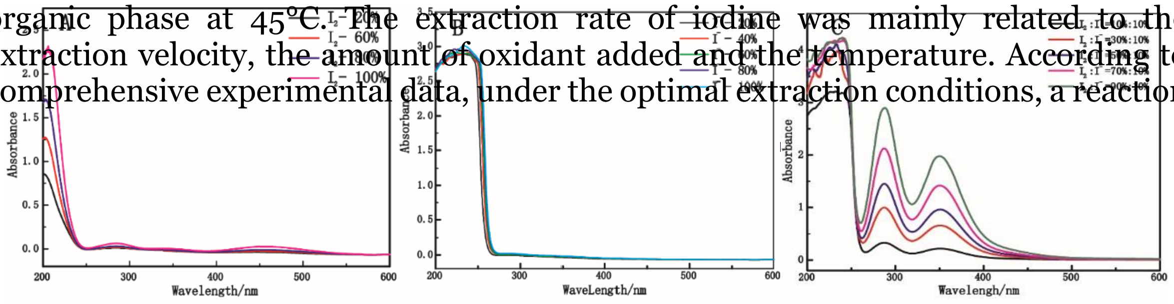


Figure 2 (a) UV-vis spectra of the I2 :concentrated acid solutions (v/v, 20%, 60%, 80%, and 100%); (b) UV-vis spectra of the I^-:concentrated acid solutions (v/v 20%, 40%, 60%, 80%, and 100%); (c) UV-vis spectra of the I^-:I_2:concentrated acid solutions (v/v/v, 10%:10%:80%, 10%:30%:60%, 10%:50%:40%, 10%:70%:20%, and 10%:90%:0%); (d) UV-vis spectra of the I_2 :I^- :concentrated acid solutions (v/v/v, 10%:10%:80%, 10%:30%:60%, 10%:50%:40%, 10%:70%:20%, and 10%:90%:0%); (e) UV-vis spectrum of PA.

Conclusions

During the extraction process, when the iodide ions in PA were oxidized to I_2 by H_2O_2, iodine- containing bubbles moved from the aqueous phase to the viscous organic phase at 45℃. The extraction rate of iodine was mainly related to the extraction velocity, the amount of oxidant added and the temperature. According to comprehensive experimental data, under the optimal extraction conditions, a reaction



temperature of 45 °C, a volume ratio of PA/simethicone of 1:3, a volume ratio of PA/H_2O_2 of 1:24, and a reaction time of 1 h, the extraction rate of iodine from PA in WPA reached 99% without stirring. Compared with other extractants, simethicone has the highest viscosity and mass transfer resistance and thus causes iodine to be trapped in the organic phase for a long period. Because simethicone has high stability, it did not react with iodine at high temperature and could be recycled. Due to the large viscosity of the organic solution, large mass transfer resistance, and small distance between molecules, the iodine-containing bubbles were temporarily trapped in the organic phase. When the temperature rises to 185 °C (boiling point of iodine), the molecules in the organic phase move violently with increasing temperature, and the distance between molecules increases. The bubbles overcome the mass transfer resistance of the organic phase by having enough buoyancy and energy and escape from the viscous phase. The extractant simethicone could be recycled. This process is simple, causes little environmental pollution and provides good economic benefits.

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