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RESEARCH NOTES

Effect of Ultrasound on Desorption Equilibrium*

QIN Wei(秦炜), YUAN Yonghui(原永辉) and DAI Youyuan(戴猷元)**
Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Abstract Effects of ultrasound on intensification of separation process were investigated through the experiment of desorption equilibrium behavior. Tri-butyl phosphate (TBP) on NKA-Ⅱ resin and phenol on a solvent impregnated resin, CL-TBP resin, were used for desorption processes. The desorption rate was measured with and without ultrasound. Desorption equilibrium was studied under various ultrasonic power densities or thermal infusion. Results showed that the desorption rate with ultrasound was much higher than that with normal thermal infusion. Both ultrasound and thermal infusion broke the desorption equilibrium existed at room temperature. However, after the systems were cooled down, the amount of solute desorbed in the liquid phase in the presence of ultrasound was much higher than that at the temperature corresponding to the same ultrasound power. It is proved that the initial desorption equilibrium was broken as a result of the spot energy effect of ultrasound.
Keywords ultrasound, sorption equilibrium, desorption

1 INTRODUCTION

It is known that the application of ultrasound to mass transfer operations such as solvent extraction could improve process efficiency and yield. The result of the extensive research in the area of solid-liquid extraction is the evidence to this effect[1−5]. Many chemical engineers and specialists have devoted themselves to find efficient processes with low energy input, but the study on intensification of separation processes utilizing ultrasound seems remaining at its primary stage. That might be the reason of few published reports on this subject[6]. One of the ways of intensifying separation process using ultrasound is generally accepted as ultrasound cavitation with high local temperature (about 3000℃) and pressure (500 Pa) in an ultrasound field[4].

We have proposed four additional effects for intensifying separation process using ultrasound based on the mass transfer pathways of liquid-liquid extraction and solid-liquid extraction, and chemical effect of ultrasound, namely, turbulence effect, micro- disturbance effect, new interface effect and spot energy effect[7,8]. For a solid-liquid system, the shock wave and blast flow from ultrasound cavitation could result in the macro-turbulence in the liquid phase and collisions between particles at high speed to reduce the boundary layer thickness and increase the rate of mass transfer. The micro-turbulence effect from ultrasound cavitation could accelerate molecular diffusion in micro holes of solid phase. Micro jet produced by ultrasound cavitation stripes and erodes the solid surface to make new active surface and enlarge the mass transfer interface, which is called new interface effect. The bonds of the solute bonded to resin may be broken by local high temperature and high pressure caused by energy accumulation from ultrasound cavitation to reduce the amount of solute on the resin, which is called energy spot effect.

One of the effects, spot energy effect, is discussed through the effect of ultrasound on desorption equilibrium in this paper. Desorption processes of tri-butyl phosphate (TBP) from NKA-Ⅱ resin and phenol from CL-TBP resin were measured. Desorption equilibria with and without ultrasound as well as different ultrasonic power densities were studied to find out the potential rule of sorption equilibrium and their mechanisms in the presence of ultrasound.

2 EXPERIMENTAL

2.1 Materials

The resins used were NKA-Ⅱ resin from the Chemical Factory of Nankai University of China and CL-TBP resin, an extraction-elution resin, from the Fifth Research Institute of National Nuclear Corporation of China. The chemicals used were ethanol, acetone and phenol from Beijing Chemical Plant, and TBP from the First Chemical Plant of Tianjin.

2.2 Solute loading

NKA-Ⅱ resin, a polar resin, is made from crosslinked-polystyrene with particle diameters of 0.3—1.25 mm and an average pore diameter of 14.5—15.5 nm. All the resins were pretreated first by infusing in deionized water, ethanol and acetone success-

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** To whom correspondence should be addressed. E-mail: qinw@chemeng.tsinghua.edu.cn

ively for 24 h, followed by stoving for 24 h at 40℃. The pretreated resins were infused for 24 h in TBP solution to load TBP on the resins, then filtrated and washed with 50% ethanol to remove the residual TBP on the surface of the resins. Finally, the resins were stoved for 24 h at 40℃.

CL-TBP resin is a solvent impregnated resin with an average particle diameter of 0.3 mm, and contains TBP about 50%. The active functional group —P=O bonds phenol with hydrogen bond[9]. All the loading preparation was conducted in 500 ml conical flasks at room temperature. 20 g of resin and 400 ml of phenol solution ($9.8\,g\cdot L^{-1}$) were added to each flask. The resins were infused in phenol solution for 24 h, then filtrated and washed with deionized water to remove the residual phenol on the surface, followed by stoving for 24 h at 40℃.

2.3 Desorption procedure

All desorption experiments were conducted in 250 ml conical flasks. 5 g of the loaded resin and 100 g of desorption solution, 50% alcohol for NKA-II resin/TBP resin and deionized water for CL-TBP resin/phenol resin, were added to each conical flask. The conical flask containing the resin and desorption solution was shaken to equilibrate for about 20 min and 24 h for CL-TBP resin and NKA-II resin respectively, then put into a water bath or an ultrasound field for experiments of thermal infusion effect and ultrasonic effect respectively. The aqueous samples were taken regularly for analyzing the amount of solute desorbed.

The experiments for the effect of thermal infusion on desorption equilibrium were carried out in a water bath shaker with a rotation speed of $100\,r\cdot min^{-1}$. The experiments for the effect of ultrasound on desorption equilibrium were in a self-made ultrasound generator of 10 × 10 × 10 mm in volume with the power of 0 to 500 W and frequency of 40 kHz.

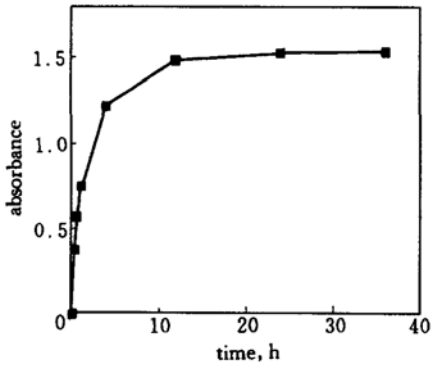
2.4 Analysis

The amount of TBP in desorption solution was analyzed by HP8452 ultraviolet analyzer at wavelength of 200 nm[10]. The concentration of phenol in desorption solution was analyzed by using the 4-aminoantipyrine spectrophotometric method (GB 7490-87).

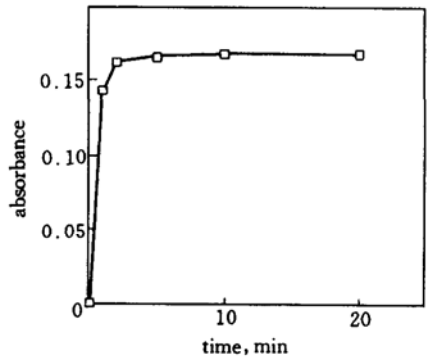
3 RESULTS AND DISCUSSION

3.1 Desorption equilibrium process

Figure 1(a) shows the amount of solute desorbed *versus* time for NKA-II resin loaded with TBP in 50% alcohol solution at 15℃. It can be seen that desorption rate was quite low. It took 24 h to reach equilibrium. Fig. 1(b) illustrates the desorption of CL-TBP resin loaded with phenol in deionized water at 20℃, which was quite different from NKA-II resin-TBP-50% alcohol system. The desorption rate of phenol was very fast, and it only took 10 min to reach equilibrium.



(a) NKA-II resin



(b) TBP resin

Figure 1 Desorption kinetics

3.2 Effect of thermal infusion

It is known that the temperature of solution increases if ultrasound is introduced, and the thermal infusion affects the sorption equilibrium apparently. A study of effect of temperature on desorption equilibrium was carried out in order to isolate the thermal infusion effect when ultrasound is introduced. The results are presented in Fig. 2. The amount of solute desorbed increases with temperature for both resin systems. By regression method, the correlated equations for the amount of solute in desorption equilibrium with temperature were obtained as follows:

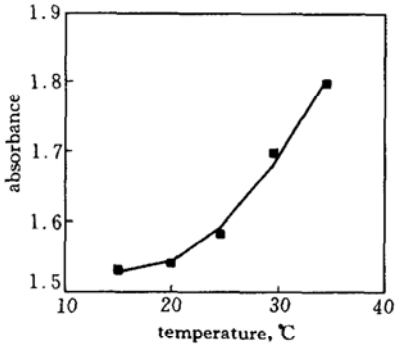
NKA-II resin-TBP-50% ethanol system

$$C = 1.7085 - 2.3465 \times 10^{-2}T + 7.6512 \times 10^{-4}T^2 \quad (1)$$

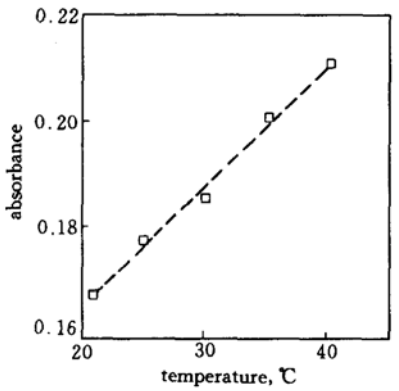
CL-TBP resin-phenol-water system

$$C = 0.1202 + 2.2712 \times 10^{-3}T \quad (2)$$

where C is the spectrophotometer absorbance of solute, and T is temperature (℃).



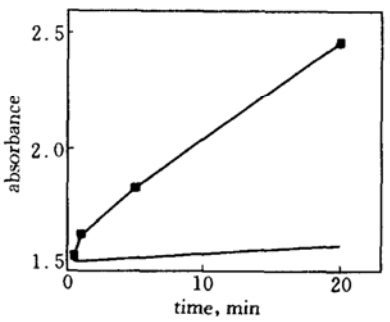
(a) NKA-Ⅱ resin



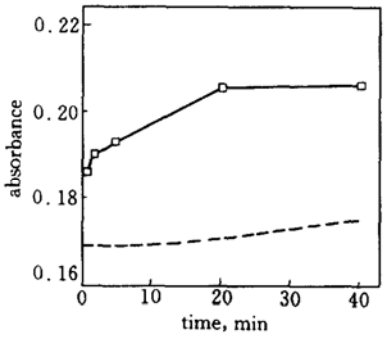
(b) TBP resin

Figure 2 Effect of temperature on desorption equilibrium

■ experimental data for NKA-Ⅱ resin;
□ experimental data for CL-TBP resin
——Eq. (1); - - - -Eq. (2)



(a) NKA-Ⅱ resin



(b) TBP resin

Figure 3 Effect of ultrasound on desorption equilibrium

(ultrasonic power density=0.46 W·cm^{-2})
■ experimental data for NKA-Ⅱ resin;
□ experimental data for CL-TBP resin
——Eq. (1); - - - -Eq. (2)

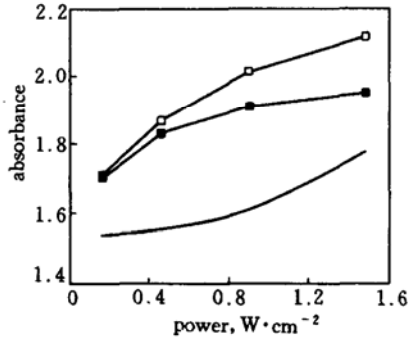
3.3 Effect of ultrasound

The flask containing the resin and desorption solution in equilibrium from shaking test was put inside an ultrasound field with 0.46 W·cm^{-2} of ultrasonic power density for further desorption. The amount of solute desorbed *versus* time is shown in Fig. 3. It can be seen that the interference of ultrasound breaks the existing equilibrium, so that more loaded substances are desorbed from the resin for both resin systems. The longer the desorption time, the more the amount of solute desorbed.

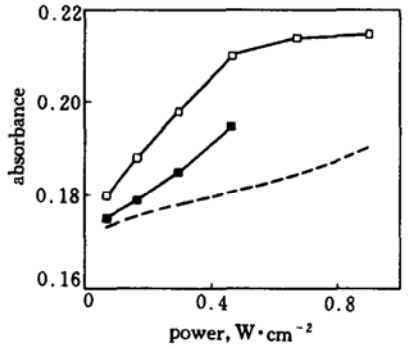
The temperature in infusing vessel was measured regularly in the presence of ultrasound, to isolate the thermal infusing effect. The amount of solute desorbed from thermal infusion with ultrasound could be calculated according to the measured temperature with Eq. (1) and Eq. (2) for NKA-Ⅱ resin and CL-TBP resin respectively. As shown in Fig. 3, the desorption rate with ultrasound is much faster than that under normal thermal infusion. Therefore, the primary improvement in desorption process was not from the thermal infusion of ultrasound, which proves further that ultrasound is more effective than normal thermal infusion for the process.

The effect of ultrasonic power density on desorption process was investigated with both resin systems. The samples were taken when ultrasound was introduced for 10 min and followed by cooling for 24 h, and the temperature in the vessel was also measured. As shown in Fig. 4, the amount of solute desorbed and the vessel temperature increase with ultrasonic power density, and the efficiency of ultrasound effect depends on the kinetic process. For the fast desorption process, *e.g.* CL-TBP resins-phenol system, the effect of ultrasound is not apparent in the range of higher ultrasonic power density (> 0.4 W·cm^{-2}) because of approaching to desorption thoroughly. However, for the normal desorption process, *e.g.* NKA-Ⅱ resin-TBP system, the efficiency of ultrasound effect increases with ultrasonic power density in this experimental region. In comparison with the system of CL-TBP resins-phenol, the extent of improvement on amount of solute desorbed is lower for the system of NKA-Ⅱ-TBP.

However, the absorbance values after cooling are higher than the calculation value for thermal infusion, which indicates that the adsorption process is irreversible in the presence of ultrasound. Based on the four additional effects of ultrasound, turbulence and micro-disturbance effects probably improve the mass



(a) NKA-Ⅱ resin



(b) TBP resin

Figure 4 Effect of ultrasound power density on desorption equilibrium (Time=10 min)
□ experimental data with ultrasound;
■ experimental data cooled
——Eq. (1); - - - -Eq. (2)

transfer rate only, while new interface and spot energy effects could shift the existing thermodynamic equilibrium. It is proposed that the associated hydrogen bonds between polar molecules and adsorbent broken by the high local temperature and pressure from ultrasonic cavitation results in the change in desorption equilibrium.

In general, sorption equilibrium depends on the active interface area and the amount of the active groups on the resin[11]. In this study, the porosity of resins is higher in the presence of ultrasound than that in the original one[10], presenting the increase of the active interface. However, with the ultrasound introduced and the system cooled down the amount of solute desorbed are more than that in the original one, which indicates further that the active adsorbent groups on the resin is reduced, and broken into desorption solution by the ultrasound. Therefore, the change in existing equilibrium in the presence of ultrasound is dependent on the spot energy of ultrasound primarily.

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