ELSEVIER

Chemical Engineering Journal 86 (2002) 375–379

Chemical Engineering Journal

www.elsevier.com/locate/cej

Short communication

Effects of ultrasound on adsorption equilibrium of phenol on polymeric adsorption resin

Zhong Li*, Xiangbin Li, Hongxia Xi, Ben Hua

Research Institute of Chemical Engineering, South China University of Technology, Guangzhou 510640, China

Received 4 December 2000; received in revised form 5 November 2001; accepted 12 November 2001

Abstract

Adsorption equilibrium experiments of phenol on NKA II resin were separately conducted in the presence and absence of ultrasound at ambient temperature. The isotherm of phenol on the polymer adsorbent in the presence of an ultrasonic field is reported. Results indicate that the adsorption of phenol determined in the presence of ultrasound is less than that in the absence of ultrasound. In addition, experimental results also show that the use of ultrasound in the adsorption system of the phenol aqueous solution + NKA II resin could cause a rise in temperature of the system. The effect of ultrasound on the isotherm of phenol on the NKA II resin is due both to the thermal and non-thermal effects of the ultrasonic field, and the role of the latter is much greater than that of the former. The addition of surfactant substance, ethanol or ethyl acetate, to the adsorption system of the phenol aqueous solution + the NKAII resin in the existence of the ultrasonic field would cause the equilibrium adsorbed amounts of phenol to decrease.

Keywords: Ultrasound; Adsorption; Isotherm; Polymeric resin; Phenol

1. Introduction

Ultrasound has been proved to be a very useful tool in enhancing the reaction rates in a variety of reacting systems. It has successfully increased the conversion, improved the yield, changed the reaction pathway and/or initiated the reaction in biological, chemical and electrochemical systems [1,2]. In addition, the use of ultrasound may enable operation at milder operating conditions (lower temperatures and pressures), eliminate the need for extra-costly solvents, reduce the number of synthesis steps while simultaneously increasing end yields, permit the use of lower purity reagents and solvents, and/or increase the activity of existing catalysts. On recent years, the study of ultrasonics and sonochemistry has expanded considerably. A rapidly growing area is that of 'environmental sonochemistry', which deals mainly with destruction of organics in an aqueous solution [3,4]. Besides, the use of ultrasound to enhance desorption of phenol from adsorbents is of sufficient importance to merit consideration [5,6]. Phenol is a model pollutant in waste water. One of the popular technologies for removal and recovery of organic pollutants from waste water is by adsorption. Although the adsorption of phenolic compounds onto the adsorbents is relatively simple, the process of regenerating the adsorbents by using organic solvents or thermal fluid still poses a major challenge in this field, notably because of the high affinity of the phenolic compounds to the sorbent surface. Qin et al. [5] investigated the effect of ultrasound on the desorption of phenol from NKA II resin, and pointed out that ultrasound had "spot energy effects", which would enhance the desorption of phenol from the NKA II resin and make the concentration of phenol of fluid phase in the presence of ultrasonic field higher than that in the absence of ultrasonic field, but the cause was not very clear in their work. Rege et al. [6] used ultrasound to enhance the desorption rate of phenol from activated carbon and polymeric resins. It was found that the desorption rates were increased by decreasing the temperature and increasing the ultrasonic intensity. However, the phase equilibrium of liquid/solid adsorption system in the presence of the ultrasonic field has not been studied systematically yet. To have a clear understanding of the desorption of phenol from the solid adsorbent by using ultrasound, it is necessary to study liquid/solid adsorption equilibrium under ultrasound. The objective of this work is to investigate the adsorption equilibrium of phenol on the NKA II polymeric resin under the ultrasonic field.

* Corresponding author. Tel.: +86-2087-113-501; fax: +86-2087-113-735.
E-mail address: cezhli@scut.edu.cn (Z. Li).

1385-8947/02/$ – see front matter
PII: S1385-8947(01)00301-1

Nomenclature

C_0	initial concentration of solute in fluid phase (mg/l)
C^*	equilibrium concentration of solute in fluid phase (mg/l)
M	amount of adsorbent used (g)
q_a^*	amount adsorbed in equilibrium with the concentration of solute in fluid phase (mg/g)
t	time (min)
V	volume of aqueous solution (l)

2. Adsorption equilibrium in the presence and absence of ultrasound

Suppose that M grams of adsorbent is put into V liters of phenol aqueous solution whose initial concentration is C_0 (mg/l), and thus the adsorption of phenol on the adsorbent takes place at $t > 0$. When the time of the adsorption is long enough, the adsorption system reaches a state of equilibrium, and then the phenol solutions in the flasks is analyzed for the phenol content. And thus the equilibrium amount adsorbed can be calculated by Eq. (1):

$$q_a^* = \frac{(C_0 - C^*)V}{M} \quad (1)$$

For the system of liquid/solid adsorption which has been in a state of equilibrium in the absence of ultrasound, if ultrasound is exerted on it, a great many transient cavitation bubbles would be produced. As the bubbles collapse, microjets of solvent are formed perpendicular to the solid surface. When the microjets continually impinge on the surface at high speed, it results in breaking of some chemical bonds between the adsorbate and the adsorbent surface, and thus causes the part of molecules of phenol adsorbed on the adsorbent to be desorbed. Finally, the system of the liquid/solid adsorption would reach a new equilibrium state, and then the equilibrium amount of phenol adsorbed on the adsorbent under the ultrasonic field can be calculated by using Eq. (1) as well.

3. Experimental section

3.1. Materials and instruments

Reagent: phenol (AR); polymeric resin: the NKA II resin, which was purchased from Nankai Chemicals Plant, Tianjin. Diameters of the resin ranged from 0.3 to 1.0 mm. Instruments: 751-GW Varian UV–visible spectrophotometer at 270 nm wavelength was used; an ultrasonic producer (Model 39 kHz, HN1006) was used, which belongs to the ultrasonic bath system, as ultrasonic cleaner. It can operate at a frequency of 39 kHz with maximum instrument power of 500 W, and its power was adjustable. This ultrasonic producer was different from probe (Horn) ultrasonic system in that it can be run incessantly while the latter can be operated only intermittently.

3.2. Experimental methods

For liquid/solid phase adsorption equilibrium experiments under normal condition, eight samples, each of 5 g of the NKA II resin, were separately added to the solutions in eight sealed conical flasks with different contents of phenol. The volumes of the solutions were 500 ml each. In order to determine the time required to have the system of liquid/solid adsorption reach the equilibrium state, preliminary experiments were needed. The result of the preliminary experiments had shown that 24 h were long enough to make the adsorption systems be in a state of equilibrium. In this work, the conical flasks were placed on a shaker maintained at 22 or 28 °C for 3 days. After the adsorption systems reached equilibrium, samples of 1 ml were withdrawn for analysis using UV–visible spectrophotometer to determine the concentration of phenol in the fluid phase, and thus the equilibrium amount adsorbed, q_a^*, can be calculated using Eq. (1). Finally, the isotherms of phenol on the resin at 22 and 28 °C can be obtained.

In order to get the isotherms of phenol on the resin under ultrasonic field, firstly, the same experiments as described above were repeated in the absence of ultrasound. Then, after the adsorption systems had been in a state of equilibrium, the ultrasonic field was exerted on the systems for 60 min to shift from adsorption equilibrium of this system in the absence of ultrasound to new adsorption equilibrium of this system in the presence of ultrasound. The preliminary experiments had shown that 40 min were long enough to make the adsorption systems remain in equilibrium in the presence of the ultrasonic field. Finally, samples of 1 ml were separately withdrawn from the eight sealed conical flasks for analysis using UV–visible spectrophotometer. The amount adsorbed remains in equilibrium with the concentration of phenol in the fluid phase under the ultrasonic field calculated by using Eq. (1), and thus the isotherms of phenol on the resin under ultrasonic field can be obtained.

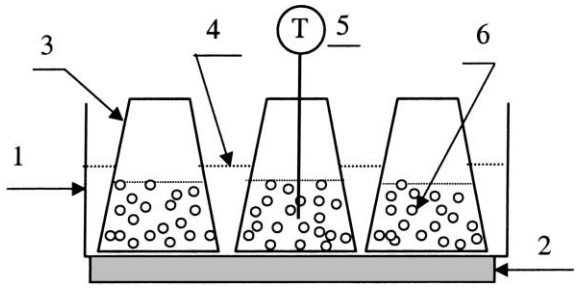

Fig. 1. Scheme of the experimental set-up of bath ultrasonic producer (Model 39 kHz, HN1006) for the phase equilibrium experiment under ultrasound field: (1) ultrasound bath producer, (2) piezoelectric transducers, (3) conical flasks, (4) water, (5) thermometer, and (6) phenol aqueous solution + NKA II resin.

Fig. 1 showed the scheme of the experimental set-up for the phase equilibrium experiment under ultrasound field.

4. Results and discussion

4.1. The effect of ultrasonic field on isotherms of phenol on the NKA II resin

Fig. 2 showed isotherms of phenol on three kinds of polymeric resins in the absence of ultrasound. It can be seen that the isotherm of phenol on NKA II resin was much higher than the isotherms of phenol on AB-8 and D4006 resin, while the isotherm of phenol on the AB-8 resin was slightly higher than the isotherm of phenol on the D4006 resin. The reason is that the NKA II resin was polar resin, AB-8 resin was weak polar resin, and D4006 resin was non-polar resin. The stronger the polarity of a resin, the greater the amount adsorbed of phenol on the resin was. As a result, the NKA II resin was chosen as the adsorbent for adsorption of phenol.

It was found that when ultrasound was incessantly exerted into the adsorption system of the phenol aqueous solution + NKA II resin, which had already been in a state of equilibrium under normal condition, it could cause the concentration of phenol in the fluid phase to rise and then reach a new equilibrium. That is to say, the use of ultrasound could change the equilibrium state of the system. Fig. 3 showed the comparison between the isotherms of phenol on the NKA II resin obtained separately in the absence of ultrasound and in the existence of ultrasound (39 kHz). It can be seen that the isotherms of phenol on the NKA II resin obtained in the presence of ultrasound are lower than that obtained in the absence of ultrasound. It indicated that after the ultrasound was exerted into the adsorption system for 60 min, it caused some parts of the adsorbates adsorbed on the resin to be desorbed and enter into the fluid phase. Finally, it made the concentration of phenol rise in the fluid phase and descend in the resin, and hence made the adsorption system reach a new equilibrium state from an original equilibrium state. The cause for this was mainly the action of acoustic cavitation,

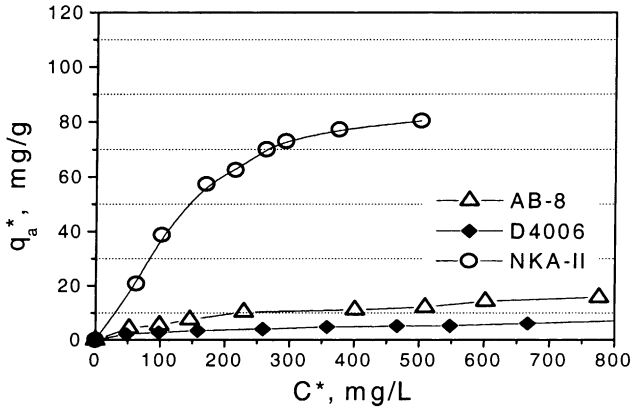

Fig. 2. Isotherms of phenol on three kinds of polymeric resins at 22 °C.

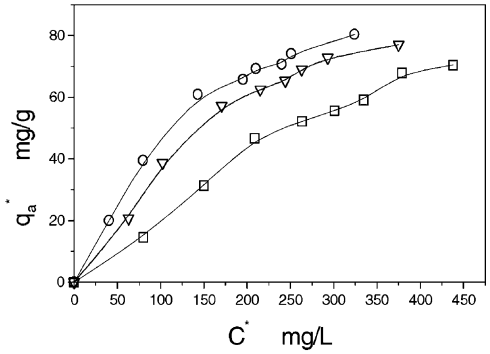

Fig. 3. Comparison between isotherms of phenol on NKA II resin in the presence of ultrasonic field and in the absence of ultrasonic field: (○) 22 °C, no ultrasound; (▽) 28 °C, no ultrasound; (□) 28 °C, ultrasound, 0.038 W/cm^2.

especially its transient cavitation bubbles. A transient cavitation bubble usually existed only for a few acoustic cycles; so upon implosion, it created extreme temperature and pressure within the transient collapsing bubble [1]. When the bubble was collapsing near the solid surface, which was several orders of magnitude larger than the cavitating bubble, symmetric cavitation was hindered and collapse occurred asymmetrically [7]. As the bubble collapsed, localized areas of high temperatures and pressures were generated in the fluid. The former would make the temperature of the system increase slightly and the latter would have microjets of solvent to be formed. The microjets were perpendicular to the solid surface, and impinged on the surface at a high speed of 100 m/s [8], which led to pitting and erosion of the surface. Its behavior was similar to the well-known cleaning effects associated with ultrasound, and resulted in enhancing the breaking of the hydrogen bonds in desorption of phenol from the resin. In addition, shock waves were also produced as the bubbles collapsed, which had the potential of creating microscopic turbulence within interfacial film surrounding nearby solid particles. As a result, the acoustic cavitation could produce not only high-speed microjects but also the high-pressure shock waves that impinged incessantly on the surface and eroded the adsorbate. This action led to enhancing the breaking of chemical bonds between the adsorbate and the adsorbent surface, and caused more molecules of phenol adsorbed on the adsorbent be desorbed. Its final result was that the equilibrium amounts of the adsorbate on NKA II resin in the presence of ultrasound were smaller than that in the absence of ultrasound, as shown in Fig. 3.

4.2. The effect of ultrasonic power on the isotherm of phenol on the NKA II resin

From the foregoing discussion, it is known that the application of ultrasound can change the equilibrium state of the liquid/solid adsorption system. Fig. 4 showed the effect of ultrasonic power on the isotherms of phenol. It was seen that the stronger the acoustic power delivered

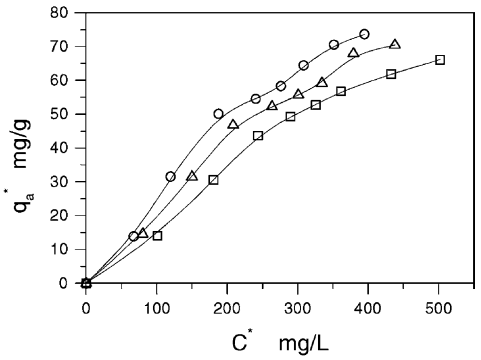

Fig. 4. Effect of ultrasonic intensity on isotherms of phenol on NKA II resin. (○) 0.022 W/cm^2; (□) 0.038 W/cm^2; (△) 0.057 W/cm^2.

to the liquid/solid adsorption systems, the lower was the corresponding isotherms, which meant that the equilibrium amount adsorbed on the resin decreased. It indicated that the magnitude of the influence of the ultrasound on the isotherms of phenol on the resin was dependent on the intensity of ultrasonic field because the intensity of the high-speed microjects and high-pressure shock wave produced by acoustic cavitation was mostly dependent on the acoustic power delivered to the system. The stronger the acoustic power, the greater the intensity of ultrasonic field [1] which led to the breaking of more hydrogen bonds formed between phenol and the adsorbent surface and thus increased the amount of phenol desorption.

4.3. Influence of non-thermal effect on the isotherm of phenol on NKA II resin

It was found in our experiments that when ultrasound was exerted, the temperature of the liquid/solid adsorption system gradually rose and then remained constant. For example, when the acoustic power delivered to the system was 0.038 W/cm^2, there was a rise in temperature of the liquid in the ultrasonic bath of the order 6 °C. That is to say, when the adsorption system reached a new equilibrium state in the presence of the ultrasonic field from its original equilibrium state in the absence of ultrasound, its final temperature became 28 °C from its initial temperature 22 °C. It meant that the influence of ultrasound on the phase equilibrium of the adsorption system is partly ascribed to its thermal effect, at least as the temperature did usually. This thermal effect was mostly given by localized hot spots formed when bubbles cavitated [1] as well as heating up of piezoelectric transducers [6]. In addition, the non-thermal effect of ultrasound possibly played an important role in affecting the phase equilibrium of the adsorption system. Therefore, it was necessary to identify and compare the thermal and non-thermal effects of ultrasound on the isotherm. Firstly, the adsorption equilibrium experiments separately at 22 and 28 °C were conducted without ultrasound. It was seen from Fig. 3 that the isotherm at 28 °C was slightly lower than that at 22 °C in the absence of ultrasound. The difference between these two isotherms was caused by the variance of system temperature, which was equivalent to the variance of the equilibrium amounts adsorbed which was caused only by the thermal effect of ultrasound in this work. Then, the adsorption equilibrium experiments were conducted with ultrasound. After ultrasound was incessantly exerted into the adsorption systems of the phenol aqueous solution + NKA II resin which had already been in a state of equilibrium under normal condition at 22 °C for 60 min, the adsorption systems reached a new equilibrium state. Its final temperature became 28 °C from 22 °C. Fig. 3 showed the isotherms of phenol on the resin obtained in the absence and the presence of ultrasound. It can be seen that the isotherm at 28 °C in the presence of ultrasonic field was much lower than that at 28 °C in the absence of ultrasonic field. Such difference was obviously caused by the non-thermal effect of ultrasonic field. The non-thermal effect was mostly produced by the high-speed microjets and high-pressure shock waves caused by acoustic cavitation. In order to get good understanding of the impact of the thermal effect and non-thermal effect of the ultrasonic field on the isotherm of phenol, it is necessary to compare the thermal and the non-thermal effect. On the basis of the equilibrium amounts of phenol adsorbed on the resin at 22 °C without ultrasound, Fig. 5 showed quantitatively the decreases of the equilibrium amounts of phenol adsorbed on the resin, $\Delta q_a{}^*$, respectively caused by the thermal effect and non-thermal effect of ultrasound. It was obvious that the $\Delta q_a{}^*$ caused by the latter is much greater than that caused by the former. The results above indicated that the effect of ultrasound on the adsorption phase equilibrium consisted of its thermal and its non-thermal effect, and that its non-thermal effect is dominant. On the other hand, it was also found in this work that when the acoustic

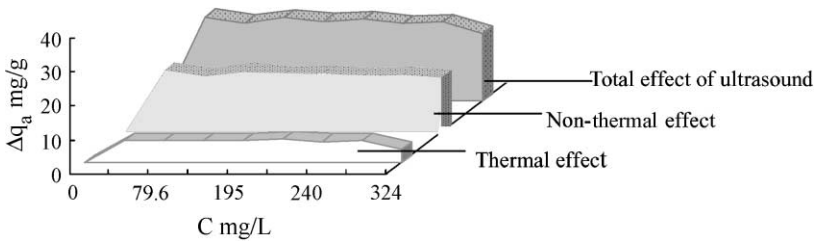

Fig. 5. Comparison between thermal and non-thermal effect of ultrasound on $\Delta q_a{}^*$.

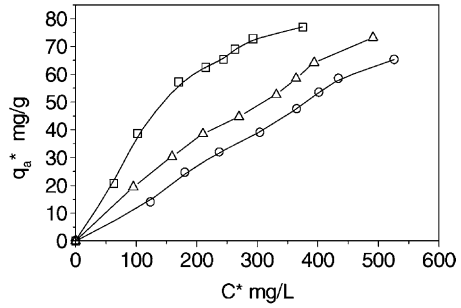

Fig. 6. Effect of addition of 5% (v/v) ethanol on isotherm of phenol in the presence and absence of ultrasonic field: (□) 28 °C; (Δ) 28 °C + ethanol; (○) ethanol + 0.038 W/cm^2.

power increased to 0.057 W/cm^2, slight pulverization of the NKA II resin occurred, which should be avoided in application of ultrasound. Therefore, the intensity of ultrasound exerted should be limited in order to avoid breaking adsorbents.

4.4. Effect of addition of surfactant substances on the isotherm of phenol on NKA II resin

In this work, ethanol or ethyl acetate as the third component was put into the adsorption system of the phenol aqueous solution + the NKA II resin in the absence and existence of the ultrasonic field. Its dosage was 5% (volume ratio of fluid). Experimental results showed that the accession of ethanol or ethyl acetate would obviously cause the adsorption capacity of phenol on the NKA II resin to decrease, especially in the presence of ultrasonic field, as shown in Figs. 6 and 7.

The cause for this was that since both ethanol and ethyl acetate belonged to the surfactant substance which can reduce the surface tension of the liquid, the addition of the surfactant substances to the adsorption system under the ultrasonic field would reduce the surface tension of the liquid, and thus reduce the cavitation threshold and facilitate the generation of bubbles. The generation of more transient cavitation bubbles helped to produce easily the high-speed microjets and high-pressure shock wave of solvent as they collapsed. Since the high-speed microjets and high-pressure shock wave continually impinged on the surface of the adsorbent, it resulted in the breaking of more hydrogen bonds between phenol and surface of the resin. The final result was that the adsorbed amounts of phenol decreased. It meant that ultrasound and the surfactant substances could produce a synergetic effect to enhance the desorption of phenol from the resin.

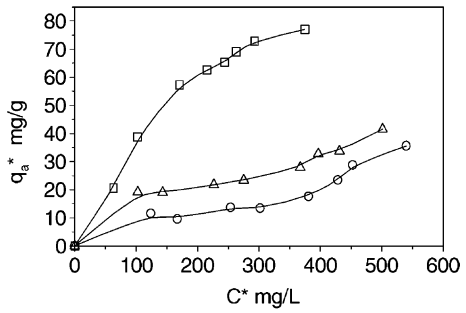

Fig. 7. Effect of addition of 5% (v/v) ethanol on isotherm of phenol in the presence and absence of ultrasonic field: (□) 28 °C; (Δ) 28 °C + ethyl acetate; (○) ethyl acetate + 0.038 W/cm^2.

5. Conclusions

The adsorption of phenol in the presence of ultrasound is lower than that in its absence, and the stronger the power intensity of the ultrasonic field, the smaller the adsorption capacity of phenol on the NKA II resin. Experimental results show that the application of the ultrasound to the adsorption system of the phenol aqueous solution + NKA II resin would result in a rise in temperature of the system. The effect of ultrasound on the isotherm of phenol on the NKA II resin is caused both by thermal and non-thermal effects. The role of the latter is much larger than that of the former. The addition of ethanol or ethyl acetate to the adsorption system of the phenol aqueous solution + the NKA II resin in the existence of the ultrasonic field would have the adsorbed amounts of phenol on the resin decrease obviously.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 29936100), the Major State Basic Research Development Program (G20000263) and the Natural Science Foundation of Guangdong Province.

References

[1] L.H. Thompson, L.K. Doraiswamy, Sonochemistry: science and engineering, Ind. Eng. Chem. Res. 38 (1999) 1215–1249.
[2] G. Ondrey, I. Kim, G. Parkinson, Reactors for 21st century, Chem. Eng. 103 (1996) 39–45.
[3] M.R. Hoffmann, I. Hua, R. Hochemer, Application of ultrasonic irradiation for the degradation of chemical contaminants in water, Ultrason. Sonochem. 3 (1996) S163–S172.
[4] K. Hirai, Y. Nagata, Y. Maeda, Decomposition of chlorofluorocarbons and hydrofluorocarbons in water by ultrasonic irradiation, Ultrason. Sonochem. 3 (1996) S205–S207.
[5] W. Qin, Y. Yuan, Y.Y. Dai, Study on the spot energy effect of ultrasound—influence of ultrasound on desorption equilibrium for hydrogen association system, J. Tsinghua Univ. (Sci. Technol.) 38 (2) (1998) 84–887.
[6] S.U. Rege, R.T. Yang, C.A. Cai, Desorption by ultrasound: phenol on activated carbon and polymeric resin, AIChE J. 44 (7) (1998) 1519–1528.
[7] F.A. Neppiras, Acoustic cavitation, Phys. Rep. 61 (3) (1980) 159–251.
[8] K.S. Suslic, Sonochemistry, Science 247 (1990) 1439–1445.