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Ultrasonic desorption of *p*-chlorophenol from granular activated carbon

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Abstract

In this study ultrasound was used as an alternative method to regenerate granular activated carbon saturated with *p*-chlorophenol. Desorption experiments of exhausted activated carbon have been conducted in the presence of ultrasound of different frequencies (21, 800 and 1660 kHz) and in silent conditions with stirring. The desorption rates were significantly increased by ultrasound. The ultrasonic effects increase with increasing acoustic intensity at frequencies of 21 and 800 kHz. The rates of desorption of *p*-chlorophenol from activated carbon appreciably increase by increasing temperature. In all cases, this rise is more noticeable as ultrasonic power increases. The stability of activated carbon was not affected until an ultrasonic power of 38.3 W showing the adsorbent stiffness towards ultrasonic application. The addition of NaOH to the desorption system causes an enhancement in the amount of *p*-chlorophenol desorbed, especially in the presence of ultrasound. The rate of desorption was significantly increased by the addition of ethanol to the regenerating solution. This behaviour was higher in the presence of ultrasonic irradiation, with the exception of that at 1660 kHz. In general, a synergetic enhancement of the desorption rate was observed when ultrasonic irradiation was coupled with chemical regeneration.

Keywords: Activated carbon; Ultrasound; Desorption; *p*-Chlorophenol; Frequency; Intensity

1. Introduction

Adsorption processes using granular activated carbons (GAC) are widely employed for the removal of trace organic contaminants such as phenolic compounds from drinking waters and industrial effluents. The United States Environmental Protection Agency (USEPA) has designated GAC adsorption as a 'best available technology' for removing organic pollutants [1,2]. Phenols constitute the 11th of the 126 chemicals, which have been designated as priority pollutants by USEPA [3,4]. Also, the European Union has classified several phenols as priority contaminants [4]. There is a considerable amount of data in the literature concerning adsorption of phenols onto GAC [5–9]. After adsorption saturation, the activated carbon can either be replaced or regenerated, and indeed its high cost makes a regeneration treatment an attractive possibility. Studies on desorption are, however, less numerous.

A variety of regeneration techniques [10–17] for exhausted GAC, especially carbon saturated with phenols, are suggested. The most common methods employed are thermal regeneration, chemical regeneration and biological treatment. Thermal regeneration suffers from severe drawbacks such as the requirement of high-energy consumption to keep the temperature between 800 and 850 °C and frequently the leading to loss of carbon surface area mainly by destruction of micropores, although efforts are now under way to lower the temperature [17]. Thermal methods using heat of low potential (parametric pumping) as regenerant have been investigated by Rodrigues and co-workers [18–20]. The cost and toxicity of organic solvents make the chemical method prohibitive. Moreover, the use of organic solvents or inorganic chemicals (i.e. addition of NaOH to desorb phenols from carbon [21]) requires further treatment to destroy or to recuperate the extracted pollutants, and it is relatively difficult to make the regeneration efficiency of activated carbon over 70%. Biological treatment is not efficient and shows several limitations concerning the non-biodegradability, the toxicity of phenols

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to microorganisms and the high time-consumption since most biological activities are slow.

As these techniques present drawbacks, it is of interest to explore other methods of desorption of phenols from GAC surface. Currently, one of the regeneration ways which is considered is the desorption by ultrasound [22]. Ultrasound has been used for decontamination of soil and sediments [23–26] and for regeneration of polymeric resin [27–32]. However, few works have been regarded for the desorption of phenols from activated carbon [22,33,34]. Ultrasound (40 and 1440 kHz) was used by Rege et al. [33] to realize the desorption of phenol from activated carbon in deionised water. It was found that there was an enhancement in the rate of desorption at high frequency, but to a smaller extent compared to that at low frequency. Schueller and Yang [34] have studied the effects of ultrasound (40 and 1000 kHz) on the adsorption and desorption of phenol on activated carbon. It was found that the improvement of desorption by ultrasound is due to the enhancement of surface diffusivity.

The effect of ultrasound on desorption phenomena is controversial:

- Breitbach et al. [28,32] have suggested that the improvement in desorption upon ultrasonic application results only from thermal effects.
- Rege et al. [33] and Schueller and Yang [34] have shown that the desorption rate enhancement is due to the acceleration of mass transport by cavitation and acoustic vortex microstreaming.
- Qin et al. [35] have found higher desorption rates by ultrasonication due to an ultrasonic ‘spot energy effects’.
- Yu et al. [36] have shown that the desorption rate is increased by acoustic vortex microstreaming.
- Bässler et al. [37] have found that the enhancement of desorption by ultrasound is explained by acoustic cavitation phenomenon.
- Hamdaoui et al. [22] have indicated that the improvement of the desorption rate is attributed to high-speed microjets (microstreaming) and high-pressure shock waves produced by acoustic cavitation.

The aim of this work is to determine to what extent the desorption of *p*-chlorophenol (*p*-CP) from GAC could be enhanced by ultrasound. Desorption experiments under ultrasonic field of various frequencies (21, 800 and 1660 kHz) and intensities (15.2–38.3 W) were studied using three different ultrasonic reactors optimized on the basis of our knowledge for each used frequency. The objective of this paper is not to determine an effect of frequency but to describe the results obtained in various experimental configurations (reactor of different geometry), knowing that:

- The reactor geometry is very important for an effective cavitation field. Each reactor was optimized on the basis of our knowledge according to the used frequency and the transducer nature available for this frequency. It is indeed known that the lower the frequency, the more divergent is the ultrasonic field.
- The size of the cavitating bubbles varies with the frequency. However, the particles of GAC are about 3 mm whereas effective cavitating bubbles have a radius lower than the ambient radius (about 100 μm at low frequency). At a frequency of about 20 kHz, for acoustic pressures varying between 1 and 1.5 bars, the instability threshold of a cavitating bubble is about few microns, which means that the existence of larger bubbles can be only fortuitous. This discriminates often-advanced argument, according to which bubbles producing sonochemical effects would be resonant bubbles. Indeed, the resonance radius at this frequency is about 160 μm, which is quite higher than the threshold mentioned above. To produce effects, a bubble owes simply implose (inertial bubble), which is the case above Blake threshold (about 1 μm for an acoustic pressure of 1.5 atm), therefore for very small bubbles [38].

This paper describes studies showing the improvement of desorption provided by ultrasound of various frequencies and intensities by varying experimental configuration using reactors optimized on the basis of our knowledge for each used frequency. The stability of the sorbent under the action of ultrasonic field is discussed and the influence of power intensity and temperature are investigated. Furthermore, the ultrasound effect on the desorption of *p*-CP from GAC is coupled with chemical regeneration method in order to evaluate the efficiency of the combined process.

2. Materials and methods

The granular activated carbon (Prolabo) has a BET surface area of 929 $m^2 g^{-1}$ and a mean granulometry of 3 mm. The carbon was pretreated by boiling in ultra-high quality (UHQ) water for 1 h and washed thoroughly with UHQ water until the UV absorbance intensity was equal to zero. Finally, the washed GAC was dried in an oven at 110 °C to constant weight before use.

The particle size analysis of GAC was conducted before and after treatment. A suspension of GAC (0.6 g) in pure water (90 mL) was exposed to ultrasound of different frequencies (21, 800 and 1660 kHz) and intensities (15.2 and 38.3 W) or stirred at 400 rpm during 7 h. The suspension was then filtered (0.45 μm) and dried at 110 °C for 24 h. The particle size distribution was performed with a laser granulometer (Mastersizer 2000 – Malvern Instruments). The size measurement range and detection limit were 0.02–5000 and 0.01 μm, respectively.

Analytically pure ethanol and 2-methyl-2-propanol (*tert*-butanol) from Acros Organics and sodium hydroxide from Prolabo were employed. UHQ water (Elga elgastat 18 MΩ) was used in all the experiments. *p*-CP for analysis (Sigma) and UHQ water were used to prepare the aqueous solutions for the adsorption tests.

Analysis of *p*-CP in the solution was done by a Hewlett Packard 8453 diode array spectrophotometer in 1 cm suprasil quartz cell. Determined concentrations were corrected taking into account nitrate and nitrite perturbation [39–41]. These analyses were confirmed by HPLC apparatus using C18 (4 mm) column. The eluent was an aqueous mixture of acetonitrile (40%) and acetic acid (1%).

2.1. Apparatus

Desorption experiments were carried out using three different ultrasonic reactors as shown in Fig. 1. They consist of a double glass cylindrical jacket, allowing water-cooling of the reactors. In all cases, the volume treated was 90 mL.

The 21 kHz ultrasonic wave was emitted from a titanium horn (3.5 cm diameter) connected to a commercial supply Sinaptec Nexus II. The top of the glass reactor (7.9 cm height and 4.1 cm internal diameter) received the ultrasonic transducer.

The 800 kHz reactor was cylindrical (6.15 cm diameter) jacketed glass vessel (14.5 cm height). The ceramic transducer (5.4 cm diameter) is located at the bottom of the reactor and connected to a high frequency supply.

The 1660 kHz irradiations were carried out with a high frequency commercial supply EF 1534 equipped with an ultrasonic transducer (diameter 1.8 cm) mounted at the base of a jacketed cylindrical glass reactor (3.2 cm diameter, 32 cm height).

Determination of the acoustical energy absorbed in the reactors was achieved following the calorimetric method [42–45].

2.2. Desorption procedure

For adsorption experiments, GAC (1 g) was added to 1 L of 100 mg L^{-1} of *p*-CP solution at 21 °C in sealed flask. The flask was stirred (400 rpm) for 4 days. The carbon was then separated from the solution. The *p*-CP concentration in the supernatant was analysed by absorbance measurement. The activated carbon loaded with *p*-CP (99.5 mg g^{-1}) was dried under air.

After adsorption experiments, about 0.6 g of exhausted GAC was tested for regeneration by adding 90 mL UHQ water and placing the sample in the low frequency (21 kHz) ultrasonic reactor. At high frequency (800 and 1660 kHz), activated carbon (0.6 g) was regenerated by adding the same quantity (90 mL) of 10% (volume ratio fluid) *tert*-butanol (*t*-butanol) in UHQ water. Ethyl alcohol or sodium hydroxide solution was added to the aqueous regenerating solution to determine their effects on the desorption under ultrasonic field. Identical experiments were repeated in the absence of ultrasound using a magnetic stirrer with a stirring rate of 400 rpm.

3. Results and discussion

3.1. Resistance of the activated carbon to ultrasound

In order to propose a reasonable process alternative to existing regeneration processes, it is essential that no attrition of the activated carbon occurs when treated with ultrasound. To determine the stability, the activated carbon was exposed to ultrasound of different frequencies (21, 800 and 1660 kHz)

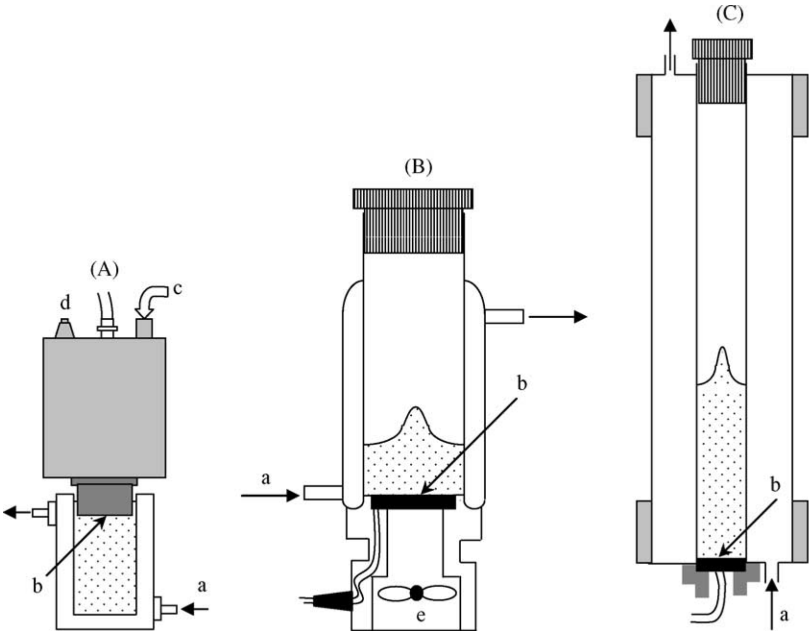

Fig. 1. Schematic description of the ultrasonic reactors: (A) 21 kHz; (B) 800 kHz; (C) 1660 kHz; (a) cooling fluid; (b) ultrasonic transducer; (c) air inlet; (d) air outlet; and (e) fan.

and intensities (21.5 and 38.3 W) for 7 h in the same reactors used during the desorption experiments. GAC particle size distributions showed same characteristics with and without the application of ultrasound. The mean granulometry has only shifted to 3% at 21 kHz for a calorimetric power of 38.3 W. Size distribution determined after sonication at high frequencies (800 and 1660 kHz) indicates that an erosion of the activated carbon is not evident until an ultrasonic power of 38.3 W. At 800 and 1660 kHz no attrition (erosion) of the activated carbon was observed because the cavitating bubbles size and the duration of the collapses decrease with the increase of the frequency. Cavitation collapses are fewer but more violent at lower frequencies, and more frequent and less violent at higher frequencies. These results evidence stiffness of the activated carbon towards ultrasonic application.

3.2. Degradation of p-chlorophenol by ultrasound

Numerous authors have studied the degradation of chlorophenols in aqueous solution by ultrasound [46–51]. Exposure of 90 mL of *p*-CP solution (100 mg L^{-1}) to ultrasound at 21, 800 and 1660 kHz was carried out for 3 h at 21 °C (Fig. 2). At 21 kHz, *p*-CP degradation was not noticeable until a calorimetric power of 38.3 W. At high frequency, the degradations in the initial stage for the employed concentration corresponds to a pseudo-first-order reaction kinetics. Initial rate of degradation were 13.51 and 3.12 μM min^{-1} at 800 and 1660 kHz, respectively. Degradation rate was faster at 800 kHz than at 1660 kHz: 81% of starting *p*-CP were degraded by 50 min and virtually 100% by 63 min for sonolysis at 800 kHz, whereas it was 11% by 50 min and 13–15% by 65 min for sonication at 1660 kHz.

Degradation rate of *p*-CP is higher at 800 kHz than at 1660 kHz. This difference can be explained by the size of the cavitating bubbles and the duration of the collapse. Hydroxyl radical as well as homolytic oxygen (reactions 1 and 2) are produced in the bubble during the implosion. Radicals combine in the bubble (reactions 3–5) or escape from the bubble, which conducts to H_2O_2 release in the medium (reactions 6–8). Diameter of cavitating bubbles is more important at 800 kHz than at 1660 kHz as a consequence, the build up of energy at the final stage of the collapse is more elevated at 800 kHz. At very high frequency (higher than the megahertz), rarefaction (and compression) cycles are becoming extremely short, the finite time required for the rarefaction cycle becomes too short to permit the molecules to be pulled apart sufficiently to generate a bubble. Consequently, the duration of implosion and the number of hydroxyl radicals formed decrease with the increase of frequency:

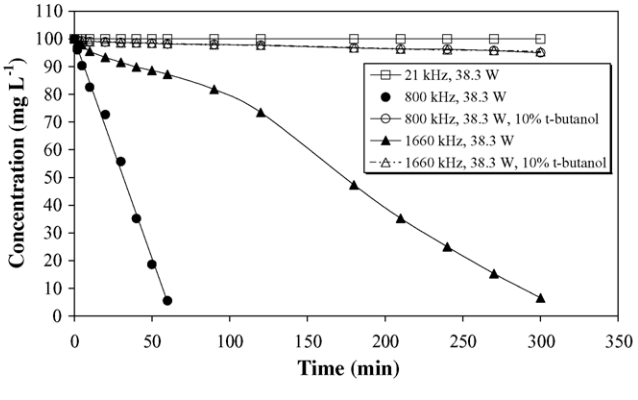

Fig. 2. Evolution of *p*-chlorophenol concentration for ultrasonic treatment at different frequencies.

$$H_2O \rightarrow H^{\bullet} + HO^{\bullet} \tag{1}$$

$$O_2 \rightarrow 2O \tag{2}$$

$$O + H_2O \rightarrow 2HO^{\bullet} \tag{3}$$

$$H^{\bullet} + HO^{\bullet} \rightarrow H_2O \tag{4}$$

$$2HO^{\bullet} \rightarrow O + H_2O \tag{5}$$

$$H^{\bullet} + O_2 \rightarrow HOO^{\bullet} \tag{6}$$

$$2HO^{\bullet} \rightarrow H_2O_2 \tag{7}$$

$$2HOO^{\bullet} \rightarrow H_2O_2 + O_2 \tag{8}$$

The scavenging effect of *t*-butanol (10% volume ratio fluid) on the degradation of *p*-CP is shown in Fig. 2. The degradation was effectively quenched, but not completely, by the addition of *t*-butanol, which is known as an efficient OH radical scavenger in aqueous solution. This low degradation could be attributed to a thermal reaction at the interface of the cavitation bubbles because of the hydrophobic character of *p*-CP. Thermal reaction in the cavities was negligible due to the low volatility of *p*-CP.

To distinguish degradation and desorption of *p*-CP from exhausted GAC, desorption experiments at high frequency were conducted using 10% (v/v) *t*-butanol solution as regenerating solution.

3.3. Regeneration of activated carbon

The concentration of *p*-CP in the solution (UHQ water for low frequency and 10% *t*-butanol for high frequency) regenerating the activated carbon was monitored with time, both in the presence of ultrasound of different frequencies (21, 800 and 1660 kHz) and in silent conditions with stirring. The results of the desorption experiments are shown in Fig. 3. The rate of *p*-CP desorption is significantly increased in the presence of ultrasound.

We explain this phenomenon by a superimposed dynamic process on microscopic level. Cavitation bubbles act like energy transformers by growing over several sound cycles until they reach a critical size. Then they collapse during a fraction of a cycle and a lot of energy is set free [43]. When the bubble is collapsing near the solid surface, which is several orders of magnitude larger than the cavitating bubble, symmetric cavitation is hindered and collapse occurs asymmetrically. As the bubble collapsed, localized areas of high temperatures

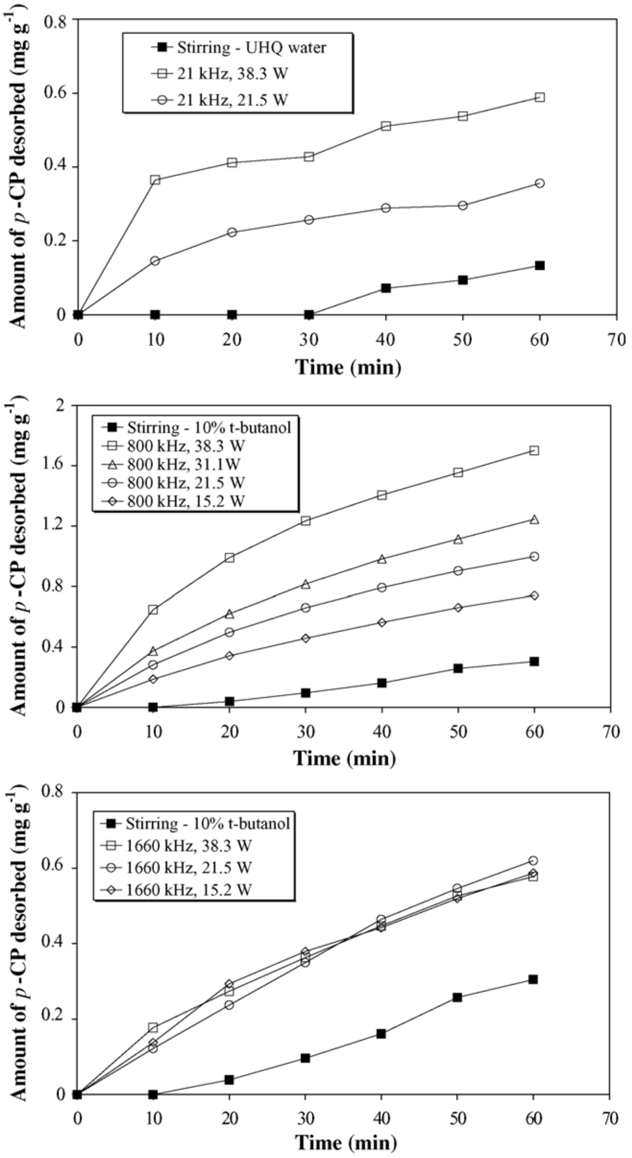

Fig. 3. Amount of *p*-chlorophenol desorbed from activated carbon vs. time at 21 °C in stirring or ultrasound conditions.

and pressures are 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 perpendicular to the solid surface [52]. In addition, shock waves are also produced as the bubbles collapsed, which have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles, also referred to as microstreaming. As a result, the acoustic cavitation could produce not only high-speed microjets but also high-pressure shock waves that impinged incessantly on the surface [43,52]. This action leads to enhancing the breaking of bonds between the adsorbate and the adsorbent surface, and causes more molecules of *p*-CP adsorbed on the adsorbent to get into the liquid phase.

At frequencies of 21 and 800 kHz, the amount of *p*-CP desorbed increases with increasing ultrasound intensities, because with high intensities more cavitation events occur and more molecules are desorbed. Indeed, the number of cavitation events, the intensity of the high-speed microjets and high-pressure shock waves produced by acoustic cavitation are mostly dependent on the power delivered to the system. The stronger the acoustic power, the greater the intensity of ultrasonic field which led to the breaking of more bonds between *p*-CP and the adsorbent surface and thus increased the amount of *p*-CP desorbed. It indicates that the desorption of *p*-CP from exhausted GAC is dependent on the intensity of ultrasonic field.

It can be noticed from Fig. 3 that the rate of *p*-CP desorption is independent on the intensity of the 1660 kHz ultrasonic field. As the most pertinent effects of ultrasound on desorption systems are mechanical and are attributed to symmetric and asymmetric cavitation, the reason could be a lower microscopic turbulence production, because of the size of cavitating bubble and the duration of the collapse. At high frequency, acoustic periods are shorter, size of cavitating bubble is lower and duration of the collapse is shorter [43,52]. The explanation in qualitative terms is that at very high frequency (megahertz region), where the rarefaction (and compression) cycles are becoming extremely short, the finite time required for the rarefaction cycle becomes too short to permit the molecules to be pulled apart sufficiently to generate a bubble. It should be recognized that the transducers, which operate at these high frequencies are not mechanically capable of generating very high ultrasonic power. When a large amount of ultrasonic power enters a system a great number of cavitation bubbles are generated in the solution. Many of these will coalesce, forming larger, more stable bubbles. These may dampen the passage of sound energy through the liquid and also remove many of the smaller bubbles, which would have collapsed to give effects.

The comparison of desorption experiments at high frequencies shows that the rates of desorption at 800 kHz are much higher than corresponding rates observed at 1660 kHz. Differences are more noticeable at high ultrasonic intensities. When the ultrasonic frequency is increased towards the megahertz region the production of cavitation in liquids decreases, which led to the decrease of the amount of *p*-CP desorbed. At 1660 kHz, the cavitational effect is reduced because either the rarefaction cycle of the sound wave produces a negative pressure which is insufficient in its duration and/or intensity to initiate cavitation or the compression cycle occurs faster than the time required for the microbubble to collapse.

The influence of frequency on the desorption process is highly dependent on the examined substance as the heat of adsorption determines how much energy is required by a cavitation event to overcome the affinity between adsorbed molecules and adsorbent. Because of the high affinity of *p*-CP to the activated carbon surface, high-energy of the cavitation event is necessary for the desorption. Consequently there is a great potential for process optimisation in changing the frequency and intensity.

3.4. Effect of temperature of the regenerating solution

The results of the desorption of *p*-CP in the presence of different frequencies ultrasound at 21 and 63 °C with calorimetric powers of 21.5 and 38.3 W are shown in Fig. 4. It can be seen that the rates of desorption at 63 °C are much higher than the corresponding rates observed at lower temperature (21 °C). It is interesting to note that the enhancement in desorption rate at 63 °C, due to the ultrasound, is appreciably greater at high acoustic power for the three frequencies applied. In general, cavitating bubbles are more easily produced at high temperature because of the decrease of the liquid tensile stress and viscosity. In addition, desorption, which is an endothermic process, is promoted if such bubble collapse occurs in the vicinity of the adsorbent surface wherefore adsorbed molecules at this spot go into solution. Thus, it was concluded that high intensity of ultrasound leads to the breaking of bonds between *p*-CP and the adsorbent surface.

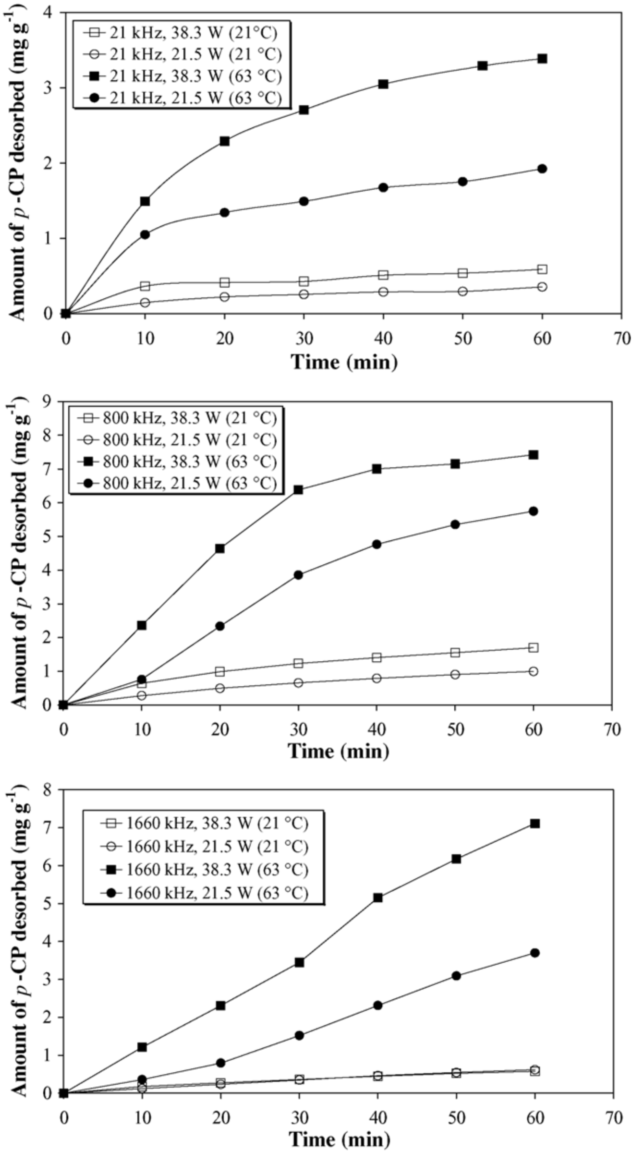

Fig. 4. Effect of temperature on the desorption of *p*-chlorophenol from activated carbon in the presence of ultrasound.

At 1660 kHz (Fig. 4), contrary to the desorption rates at low temperature, there is a significant enhancement of the amount of *p*-CP desorbed with increasing ultrasound intensity, because of the lowering of the cavitation threshold.

Desorption rates obtained at high frequencies (Fig. 4) show that the desorbed *p*-CP amounts were comparable for an ultrasonic power of 38.3 W. For an intensity of 21.5 W, it can be seen that the rates of desorption at 800 kHz were much higher than the corresponding rates observed at 1660 kHz. Thus, it was concluded that the ultrasonic frequency and intensity plays an important role in enhancing desorption.

The results above indicated that the effect of ultrasound on the enhancement of desorption processes consisted of its non-thermal effect and its thermal effect, and that its non-thermal effect is dominant. The thermal effect was mostly given by localized hot spots formed when bubbles cavitated as well as heating up of piezoelectric transducers. The non-thermal effect was mostly produced by the high-speed microjets and high-pressure shock waves caused by acoustic cavitation.

3.5. Effect of addition of alcohol and/or NaOH on the desorption

Ethyl alcohol and/or NaOH (1 M) was added into the desorption system (regenerating solution + exhausted GAC) in the absence and presence of the ultrasonic field. The proportion was 5 and 20% (volume ratio fluid) for NaOH and ethanol, respectively.

Experimental results show that the addition of NaOH would obviously cause the enhancement of the amount of *p*-CP desorbed, especially in the presence of ultrasound, as shown in Fig. 5.

The addition of NaOH to the desorption system increases the pH value, and thus the fraction of phenolate ion. Therefore, *p*-CP, a weak acid ($pK_a = 9.20$), will be desorbed to a greater extent due to the repulsive forces prevailing at high pH values. The final result is that the desorbed amounts of *p*-CP increase with NaOH addition.

For an ultrasonic frequency of 21 kHz (Fig. 5), the desorbed *p*-CP amount under ultrasound with alkaline condition ($0.76\,\mathrm{mg\,g^{-1}}$) is exactly the sum of desorbed *p*-CP quantity under ultrasound ($0.58\,\mathrm{mg\,g^{-1}}$) and the desorbed *p*-CP quantity at alkaline pH under stirring ($0.18\,\mathrm{mg\,g^{-1}}$). As can be seen from Fig. 5, the rates of desorption was noticeably increased by the addition of NaOH to the regenerating solution in the presence of high frequency ultrasound (800 and 1660 kHz). The stronger the acoustic power delivered to the desorption system, the higher was the desorption rate. It meant that ultrasound of high frequency and NaOH could produce a synergetic effect to enhance the desorption of *p*-CP from the activated carbon.

In the presence of ethanol, the results of the desorption experiment conducted in silent conditions as well as with ultrasound of different frequency are presented in Fig. 6. It

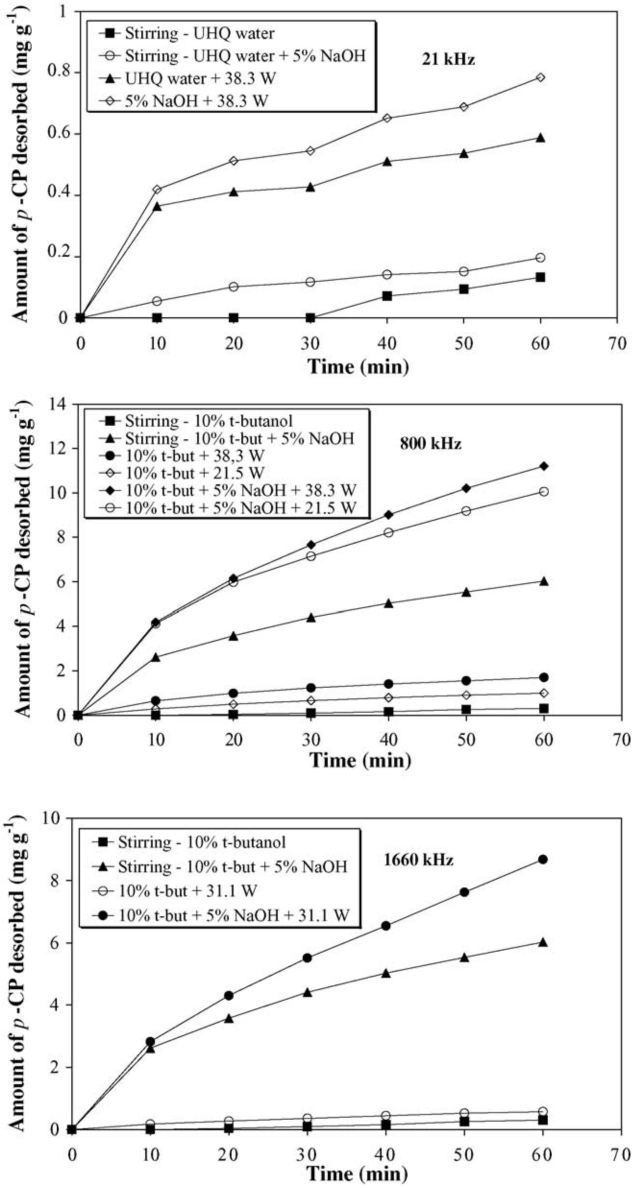

Fig. 5. Effect of addition of NaOH (1 M, 5% (v/v)) on the desorption of *p*-chlorophenol in the absence and presence of ultrasound at 21 °C.

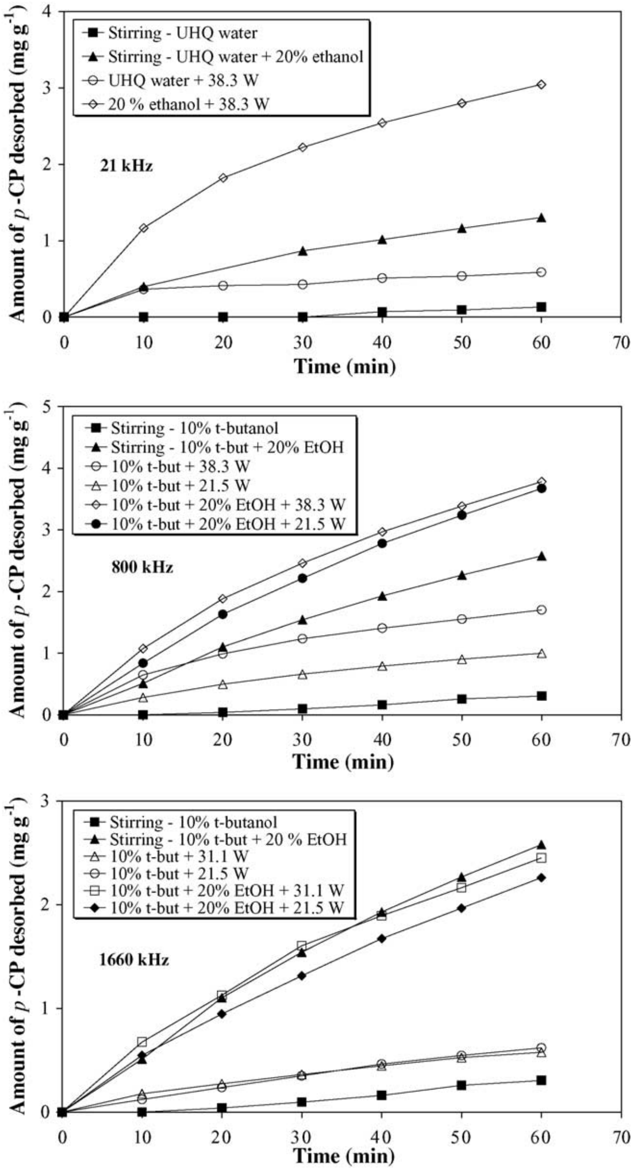

Fig. 6. Effect of addition of 20% (v/v) ethanol on the desorption of *p*-chlorophenol in the absence and presence of ultrasound at 21 °C.

can be seen that the addition of ethanol considerably enhances the desorption of *p*-CP. This effect is more dominant in the presence of ultrasound, with the exception of that obtained at 1660 kHz.

Ethanol, a surfactant substance, can 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 helps to produce easily the high-speed microjets and high-pressure shock waves of solvent as they collapse.

At low frequency (21 kHz), ultrasound and ethanol produce a synergistic effect: the desorption of *p*-CP from the activated carbon is greater than the sum of the two separate processes.

At 800 kHz, ultrasound and ethanol generate a synergetic result for an ultrasonic power of 21.5 W, which was not the case for an intensity of 38.3 W. Moreover, the amount of *p*-CP desorbed raises with increasing ultrasound intensity.

For a frequency of 1660 kHz, the rates of desorption in the absence of ultrasound are higher than corresponding rates obtained in the presence of ultrasound, which is surprising. A possible explanation for the observed decrease is the formation of dense cloud of cavitation bubbles near the transducer tip which acts to block the energy transmitted from the transducer to the fluid.

In the presence of a mixture of 20% ethanol and 5% NaOH, the concentration of *p*-CP in the solution regenerating the activated carbon was monitored with time, both in the presence of ultrasound and in silent conditions with simple stir-

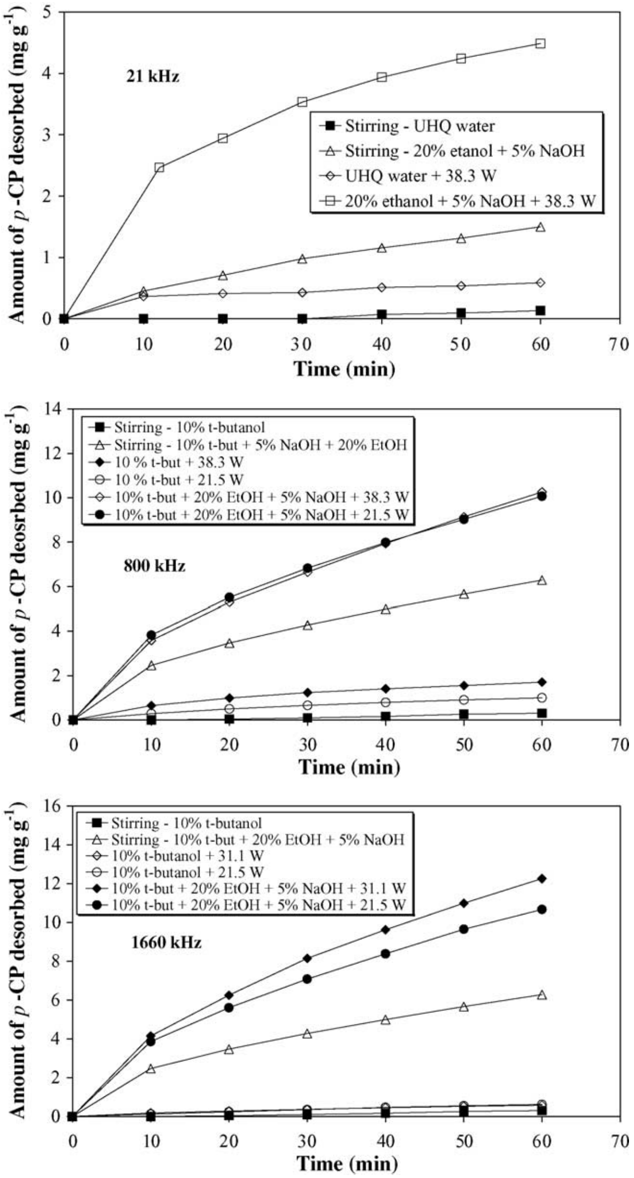

Fig. 7. Effect of addition of a mixture of 20% (v/v) ethanol and 5% (v/v) NaOH on the desorption of *p*-chlorophenol in the absence and presence of ultrasound at 21 °C.

ring. The results of the desorption experiments are shown in Fig. 7. Experimental results show that the adding of a mixture of ethanol and NaOH considerably enhances the kinetics of desorption, especially in the presence of ultrasound. It was interesting to note that the *p*-CP desorption rate enhances with rising ultrasonic intensity, with the exception of that at 800 kHz. In all cases, ultrasound and the mixture of 20% ethanol and 5% NaOH generate a synergetic effect to enhance the desorption rates.

The improvement of desorption rates by the addition of a mixture of 20% ethanol and 5% NaOH in the presence of ultrasonic irradiation can be explained by the lowering of cavitation threshold and the creation of repulsion forces between activated carbon surface and phenolate anions.

4. Conclusions

The influence of ultrasound of different frequency and intensity on the desorption of *p*-chlorophenol from granular activated carbon were studied.

The rates of desorption of *p*-chlorophenol from GAC in the presence of ultrasound is much higher than in the absence of ultrasound. The stronger the power intensity of the ultrasonic field, the higher is the amount of *p*-chlorophenol desorbed from the activated carbon. However, this behaviour was not observed at 1660 kHz, because of the size of cavitating bubble and the duration of the collapse.

The rate of desorption increases with the temperature (between 21 and 63 °C). The ultrasonic effects increase with increasing acoustic intensity for the three frequencies applied. The addition of NaOH to the desorption system obviously increases the desorbed amount of *p*-chlorophenol, especially in the presence of ultrasound. The rate of desorption was significantly increased by the addition of ethanol to the regenerating solution. This behaviour was higher in the presence of ultrasonic irradiation, with the exception of that obtained at 1660 kHz.

In the presence of a mixture of NaOH and ethyl alcohol, desorption rate was appreciably enhanced, particularly in the presence of ultrasound.

Contrary to the addition of ethanol at a frequency of 1660 kHz and NaOH at 21 kHz, a synergetic enhancement of the desorption rate was obtained when ultrasonic irradiation was coupled with chemical regeneration. This effect can be explained by the enhancement of phenolate ion fraction and the lowering of the cavitation threshold.

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