An Investigation of the Mechanisms of Ultrasonically Enhanced Desorption

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In this work, the mechanisms underlying ultrasonic desorption of 4-chlorophenol from granular activated carbon have been explored. Desorption experiments are investigated in the absence and presence of 516 kHz ultrasound of different intensities. Using three regenerating solutions and two temperatures, it has been shown that ultrasonic irradiation considerably improves both the amount and the rate of desorption. Desorption increases with increasing temperature and ultrasound intensity. The addition of sodium hydroxide or a mixture of sodium hydroxide and ethanol to the regenerating medium leads to an enhancement of the desorption, especially in the presence of ultrasound. The mechanisms of ultrasonically enhanced desorption is due both to the thermal and non-thermal (hydrodynamical) effects of ultrasound. Hydrodynamical phenomena are principally produced by the acoustic vortex microstreaming within porous solids as well as at the solid-liquid interface and by the high-speed micro-jets and high-pressure shock waves produced by acoustic cavitation. The thermal effects are evaluated as localized hot spots formed when bubbles cavitated as well as by global heating of the medium and piezoelectric transducer heating-up. Additionally, the non-thermal effect of ultrasound is greater than the thermal effect, and it is more noticeable when the ultrasonic irradiation is carried out in a high temperature regenerating medium. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 363–373, 2007
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Introduction

Phenolic compounds are common contaminants in water effluents in many industries, such as oil refineries, plastics, and leather and paint industries. Almost all phenolic compounds are highly toxic at the concentration discharged into the receiving effluents. Important substances in this class include chlorinated phenols. Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of specific pollutants.

4-Chlorophenol (4-CP) is released into the environment as a by-product of various industrial activities, including the chlorinated bleaching of paper and chlorination of drinking water, drug decay, and via waste from the coal, gas, and oil industries.[1] The U.S. Environmental Protection Agency (EPA)[2] and the European Union (EU)[3] have labeled chlorophenols as "priority pollutants," which means that they need to be constantly monitored in the aquatic environment and that a value of 0.5 mg L^{-1} is the upper permissible limit of these compounds in publicly supplied water.[4] The removal of this compound is currently performed by conventional treat-

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ment methods. However, in water treatment, adsorption has been found to be highly efficient in terms of initial cost, simplicity of design, ease of operation, and insensitivity to toxic substances. Indeed, the USEPA has designated adsorption onto granular activated carbon (GAC) as a "best available technology" for removing organic pollutants.[5]

After the exhaustion of its adsorption capacity, GAC can either be replaced or regenerated, and indeed its high cost makes regeneration an attractive possibility. Moreover, from an environmental viewpoint, regeneration is recommended because the exhausted spent carbon could be landfilled. The process of regenerating the adsorbent poses a major challenge because of the high affinity of phenols to the sorbent surface. The objective of the regeneration is to recover the adsorption capacity of virgin adsorbent without loss of its active structure and to enable its reuse. Various regeneration processes have been proposed.[6] The most common 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 underway to lower the temperature. The cost and toxicity of organic solvents make the chemical method prohibitive. Moreover, the use of organic solvents or inorganic chemicals (that is, addition of NaOH to desorb phenols from carbon) 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 to microorganisms, and the high time consumption since most biological activities are slow.[6]

Recently, ultrasound has been investigated as a means to improve desorption processes.[6–19] Ultrasound are waves at frequencies above those within the hearing range of the average person, that is, at frequencies above 16 kHz. Ultrasonic energy (high frequency sound waves) produces an alternating adiabatic compression and rarefaction of the liquid media being irradiated. In the rarefaction part of the ultrasonic wave (when the liquid is unduly stretched or "torn apart"), microbubbles form because of reduced pressure. These microbubbles contain vaporized liquid or gas that was previously dissolved in the liquid. The microbubbles can be either stable about their average size for many cycles or transient when they grow to certain size and violently collapse or implode during the compression part of the wave. The critical size depends on the liquid and the frequency of sound. The energy put into the liquid to create the microvoids is released in this part of the wave, creating high local pressures up to 1000 bars and high transitory temperatures up to 5000 K. This energy-releasing phenomenon of the bubble formation and collapse is simply called acoustic cavitation. Two different modes of action of ultrasound can exist at different reaction conditions (intensity, pressure, and so forth): cavitating and noncavitating ultrasound (acoustic streaming). Cavitating ultrasound forms cavitation bubbles, which violently collapse on or near the adsorbent surface and direct micro-jets of liquids toward it. Asymmetric collapses produce not only high-speed micro-jets but also high-pressure shock waves, which impinge on the sorbent surface. Acoustic streaming is the movement of the liquid induced by the sonic wave, which can be considered to be the conversion of sound to the kinetic energy, and is not a cavitation effect.[20–23]

There are some studies where the effects of ultrasound on adsorption and desorption have been explored.[7,12,24,25] Many researchers have successfully used power ultrasound for recovery of organic and inorganic matter from different particle surfaces.[17,19,26–30] It is well understood that ultrasonic waves accelerate mass transport phenomena, but the influence of ultrasonication on adsorption equilibrium is very contradictory: (i) Schueller and Yang[12] have not found an ultrasonic effect on adsorption isotherms of a polymeric resin loaded with phenol; (ii) Qin et al.[31] have found a higher adsorption capacity of weak basic ion exchangers for acetic acids when applying ultrasound; (iii) Breitbach and Bathen,[24] Li et al.,[25] and Hamdaoui et al.[7] have shown that the measured adsorption isotherms shifted toward lower loading in the presence of ultrasonic field for the adsorption of phenol onto polymeric resin, fructose on microporous resin, and *p*-chlorophenol onto granular activated carbon, respectively.

Additionally, the effects of ultrasound on desorption are yet badly known and controversial. Bässler et al.[32] have found that the improvement of desorption by ultrasound is explained by the acoustic cavitation phenomenon. Rege et al.[9] and Schueller and Yang[12] have shown that the desorption rate enhancement by sonication is due to the acceleration of mass transport by cavitation and acoustic vortex microstreaming. Yu et al.[11] have mentioned that the desorption rate in the presence of ultrasound is increased by acoustic vortex microstreaming. Feng and Aldrich[14] and Feng et al.[18] have indicated that ultrasonic radiation considerably improves the desorption recovery and kinetics and attributed this to an increase in diffusive transport caused by acoustic vortex microstreaming and micro-jets. Qin et al.[13] have found higher amounts of solute desorbed by ultrasonication due to ultrasonic "spot energy effects." Breitbach et al.[15] have concluded that an important factor of ultrasound enhanced desorption is the temperature rise due to ultrasonication. Another ultrasonic effect, such as cavitation or ultrasonic energy dissipation, is supposed to increase the process. In another article, Breitbach et al.[16] have suggested that the improvement in desorption upon ultrasonic application results only from thermal effects. Hamdaoui et al.[6–8] have indicated that the improvement of the desorption rate by ultrasonic irradiation is due both to thermal and nonthermal effects of the ultrasonic field; the latter is produced by hydrodynamical processes of ultrasound and the former by localized hot spots. Zhang et al.[33] have attributed the increase of desorption by ultrasonic waves to "cavitation." He et al.[19] have indicated that the adsorbed molecules may be released into solution by breaking chemical bonds through shock waves, micro-jets, and thermal effects from cavitational collapse. Lim and Okada[34] have mentioned that the enhancement of desorption by ultrasonication is due to high-speed micro-jets, high-pressure shock waves, and acoustic vortex microstreaming.

The purpose of this study is to identify and clarify the effects of 516 kHz ultrasound on the intensification of the desorption of 4-CP from activated carbon surfaces. This frequency was selected among others tested (21, 800, and 1600 KHz)[8] owing to the fact that it gave, under used experimental conditions, the highest efficiency for the desorption of 4-chlorophenol.

Experimental Section

Materials

The GAC used in this study was purchased from Prolabo. Prior to use, the carbon was pretreated by boiling in ultra-high quality (UHQ) water for 1 h and washed repeatedly with UHQ water until the electric conductivity and the UV absorbance were equal to zero, and the pH remained constant. Finally, the washed activated carbon was dried in an oven at 110°C to constant weight and stored in a desiccator until use. The BET (Brunauer-Emmett-Teller) surface area of the carbon (929 m^2 g^{-1}) was obtained from N_2 adsorption isotherms at 77 K. The GAC has an average granulometry of 3 mm.

4-CP was purchased from Sigma with purity greater than 99.5%, and UHQ water (Milli-Q 18.2 MΩ) was used to prepare the aqueous solutions for the adsorption tests. Analytically pure ethyl alcohol, 2-methyl-2-propanol (tert-butanol), and sodium hydroxide from, respectively, Acros Organics, Merck, and Prolabo, were employed in this study.

Ultrasonic reactor

Desorption tests were conducted using an ultrasonic reactor, shown in Figure 1, operated at a frequency of 516 kHz. It consists of a double glass cylindrical jacket, allowing water cooling of the reactor. The 516 kHz reactor has an internal diameter and a height of 6.1 and 15 cm, respectively. The ceramic transducer (lead titanate zirconate piezoelectric, diameter 4 cm) is located at the bottom of the reactor and connected to a high frequency supply. In all cases, the treated volume was 90 mL for a liquid height of about 3.1 cm.

Determination of the acoustical energy absorbed in the reactor was achieved following the calorimetric method.[22]

Desorption experiments

The adsorption of aqueous 4-CP onto activated carbon was performed for an initial bulk concentration of 100 mg L^{-1}. Initially, 1 g of activated carbon was placed in a sealed flask containing 1 L of 4-CP aqueous solution. The flask was stirred at 400 rpm for 4 days. The carbon was then separated from the solution, and the 4-CP concentration in the supernatant was analyzed by absorbance measurement. From the bulk concentration, the amount of adsorption could be determined. The activated carbon loaded with 4-CP was dried under air until constant weight.

For sonolytic desorption, about 0.6 g of 4-CP-laden GAC was transferred to the 516 kHz ultrasonic reactor with 90 mL of 10% (volume ratio fluid) tert-butanol (t-butanol) in UHQ water. The 516 kHz ultrasonic wave was used for sonication experiments at four different power input intensities (15.2, 21.5, 31.1, and 38.3 W) as measured by calorimetry. The reactor was water jacketed to control the solution temperature at 21°C. Strong convective currents occur within the reactor here and there along the transducer axis. These effects associated with the hydrodynamic phenomenon due to cavitation are responsible for the perfect mixing of the reactor content. It was thereby established that under ultrasonic irradiation the used reactor is a completely stirred tank reactor (CSTR).

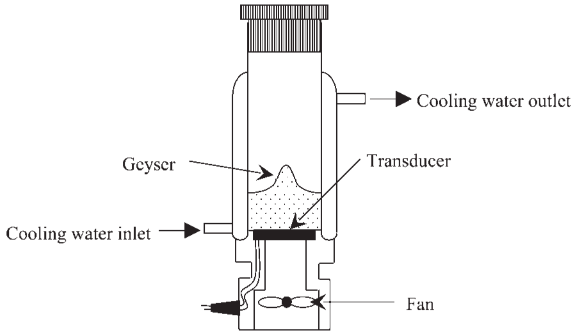

Figure 1. Scheme of the experimental set-up for the desorption under an ultrasonic field.

Sodium hydroxide (1 M) solution or a mixture of sodium hydroxide and ethyl alcohol were added to the regenerating solution to determine their effects on the desorption under an ultrasonic field.

Identical experiments were repeated in the absence of ultrasound (silent conditions) using a glass reactor (with the same geometry as the sonication reactor) and a magnetic stirrer with a stirring rate of 400 rpm. The reactor provides uniform mixing conditions due to continuous agitation. All other conditions, such as temperature and pH, were the same as those used with ultrasonic desorption.

After selected times of sonication (or stirring), the desorption kinetics was determined by following the concentration change in the reactor.

The amount of 4-CP desorbed (mg g^{-1}) at time t was calculated by using Eq. 1:

$$q_d = \frac{(C - C_0)\,V}{W} \tag{1}$$

where C_0 is the initial concentration of 4-CP ($C_0 = 0$ in this study), C is the concentration of 4-CP at any time t (mg L^{-1}), V is the volume (L), and W is the weight of the adsorbent (g) in the mixture.

In this study, all experiments were performed in triplicate, and the mean values are presented.

Measurements

The particle size analysis of the GAC was determined before and after ultrasonication treatment. Volume of 90 mL of UHQ water was added to 0.6 g of GAC, and the obtained suspension was exposed to ultrasound of different power intensities for 9 h. The suspension was then filtered (0.45 μm) and dried at 110°C for 48 h. The size distribution was determined using a laser granulometer (Mastersizer 2000—Malvern instruments).

Scanning electron micrographs (SEM) were obtained by using a Leo (type Stereoscan 440) scanning electron microscope.

4-CP samples were analyzed by a Hewlett Packard 8453 diode array spectrophotometer in a 1 cm suprasil quartz cell. These analyses were confirmed by an HPLC apparatus Waters (pump 515, detector 996, column C18) with UV254 detection. The used eluent was an aqueous mixture of acetonitrile (40%) and acetic acid (1%).

Results and Discussion

Effect of ultrasonication on GAC granulometry

Theoretically, when bubbles collapse in homogeneous solution, the shape of the bubbles remains spherical and sym-

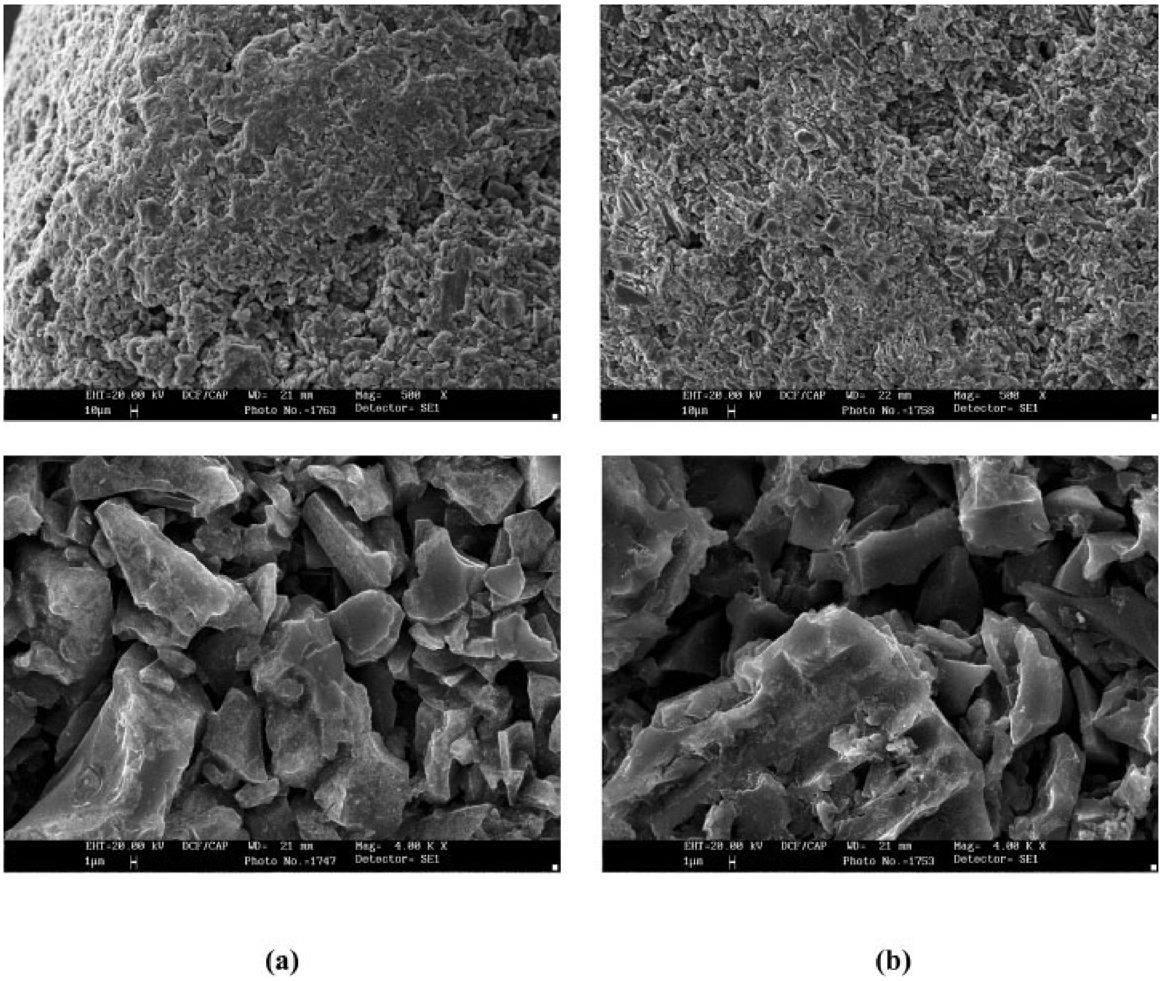

Figure 2. SEM micrographs of GAC surface (500× and 4,000×): (a) before ultrasonication and (b) after 9 h of ultrasonication at 38.3 W.

metrical during their lifetime. However, in heterogeneous solution (that is, when solid particles exist), the bubbles collapse near a solid surface; thus, the dynamics of cavitation bubbles change significantly. In this situation, the bubbles collapse asymmetrically producing a high-speed jet of liquid, which passes through the interior of the cavitation bubble and toward the solid surface, called a micro-jet.[20,23] It has been reported that the speed of the liquid jet may reach speeds of more than 100 m s^{-1}.[22] Such a powerful jet will produce dramatic effects on the solid surface, and is responsible for pitting and erosion of the solid surface. In addition, fracturing and melting of particles has been observed resulting from bubble implosion and shockwaves at the surface of particles.[8]

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. In addition, changes in the size of the particles are important factors to understand the mechanisms of desorption of 4-CP from GAC into the aqueous phase. Hence, the resistance of the activated carbon granules in the presence of an 516 kHz ultrasonic field was experimentally determined. The activated carbon was irradiated with ultrasound of different power intensities (15.2–38.3 W) for 9 hours in the same reactor employed for the desorption tests. Size distribution determined after sonication indicates that no attrition (erosion) of the activated carbon was observed, whatever the power intensity is. This is due to cavitating bubbles size and the duration of the collapses that 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.

The scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of the activated carbon. The SEM enables the direct observation of changes in the surface microstructures of the carbon due to ultrasonication. Figure 2 shows the SEM photographs of the GAC surface at two different magnifications (500× and 4,000×) before and after sonication. These photographs clearly reveal the surface texture and different levels of porosity of the carbon. The carbon looks like a random pile of crystallized blocks of various sizes and shapes. It can be seen from the micrographs that the activated carbon showed similar surface morphologies before and after ultrasonication.

These results evidence stiffness of the activated carbon towards ultrasonic application.

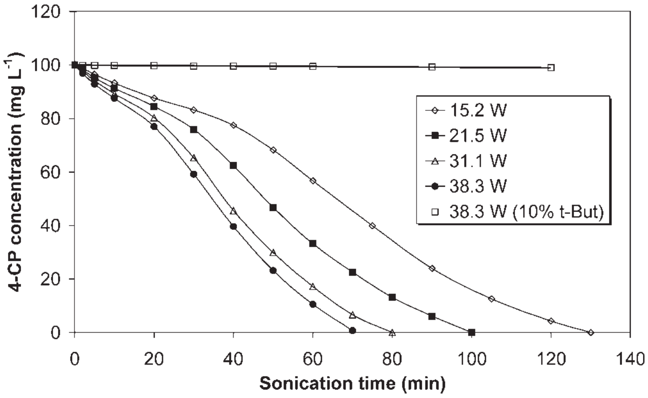

Figure 3. Sonochemical degradation of 4-CP.

Sonochemical degradation of 4-CP

The effect of ultrasound on the degradation of 4-CP was studied using an ultrasonic reactor operating at 516 kHz. Exposure of 90 mL of 4-CP solution at a concentration of 100 mg L^{-1} to 516 kHz ultrasonic irradiation was carried out under isothermal conditions (21°C). Initial pH of the solution was 5.5. Figure 3 shows the evolution of 4-CP concentration versus sonication time. The degradation in the initial stage for the employed concentration corresponds to a pseudo-first order reaction kinetics. Initial rates of degradation were 9.64, 9.38, 6.83, and 5.30 μM min^{-1} for 38.3, 31.1, 21.5, and 15.2 W, respectively. The results of 4-CP sonooxidation clearly show that the degradation of the pollutant increases with intensity. An increase in the ultrasound intensity results in an increase in the acoustic amplitude, which favors more violent cavitation bubble collapse because the bubble collapse time, the transient temperature, and the internal pressure in the cavitation bubble during collapse are all dependent on the acoustic amplitude.[35] That is, high enough acoustic power results in transient cavitation. Hence, the results of an increase in the sound intensity are greater sonochemical effects, resulting in higher 4-CP degradation rates.

Figure 3 also shows the scavenging effect of t-butanol on the sonolysis of 4-CP. The degradation was effectively quenched by the addition of 10% (v/v) t-butanol but not completely. It has been reported that t-butanol is an effective OH radical scavenger in water sonolysis.[6] This low degradation could be attributed to a thermal reaction at the interface of the cavitation bubbles because of the hydrophobic character of 4-CP. Thermal reaction in the cavities was negligible due to the low volatility of 4-CP.[6]

Consequently, in this work, desorption experiments were conducted using 10% (v/v) t-butanol solution as regenerating solution in order to distinguish degradation and desorption of 4-CP from GAC.

Sonolytic desorption at 21°C

The desorption kinetics of 4-CP from GAC using 10% t-butanol solution as regenerating medium was studied, both in the presence of 516 kHz ultrasonic irradiation of different power intensities (15.2–38.8 W) and in the absence of ultrasound (silent conditions) with simple stirring. Figure 4 shows the results of the desorption experiments. The amount of 4-CP desorbed in the absence of ultrasound by simple stirring of the GAC suspension is small. Both the rate and the amount of 4-CP desorption are significantly enhanced and improved in the presence of the ultrasonic field.

The mechanism by which sonication promotes desorption in a heterogeneous system may be due to an altered chemical equilibrium and/or improved kinetics of release. The enhanced desorption of 4-CP from the GAC surface by sonication may be attributed to the extreme conditions generated during the violent collapse of cavitation bubbles. As the bubble collapses, a localized high pressure and temperature are produced in the fluid. Desorption, which is an endothermic process, is promoted if such a bubble collapse occurs in the vicinity of the adsorbent surface wherefore adsorbed molecules at this spot are desorbed and released into the solution. In addition, the asymmetric collapse of bubbles in a heterogeneous system produces micro-jets with high velocity on the surface of the adsorbent. This action leads to an improvement of the breaking of bonds between the adsorbent surface and adsorbate molecules and also to an enhancement of mass transfer into the pores. Furthermore, symmetric and asymmetric collapses generate shockwaves, which cause extremely turbulent flow at the liquid-solid interface, increasing the rate of mass transfer near the solid surface. The cavitation event also gives rise to acoustic microstreaming or formation of miniature eddies that enhance the mass and heat transfer at interfacial films surrounding nearby adsorbent particles and within the pores.[21–23,36] Thus, the number of cavitational events, the intensity of microstreaming, high-speed micro-jets, and high-pressure shockwaves produced by acoustic cavitation are mostly dependent on the power delivered to the system, explaining why the higher sonication power produced a higher amount of desorption.

With such cavitational events, the available active sites for adsorption and the number of adsorbate molecules in solution will reach a new equilibrium. In our previous work,[7] we have shown that the adsorption equilibrium was shifted to lower adsorbed amounts when investigating the adsorption of 4-CP onto GAC using an ultrasonic reactor operating at a frequency of 21 kHz. The stronger the acoustic power delivered to the adsorption system, the lower is the corresponding isotherms. Similar results were reported by Breitbach and Bathen[24] and Li et al.[25] for the adsorption of fructose on a microporous resin and of phenol on polymeric resin, respectively.

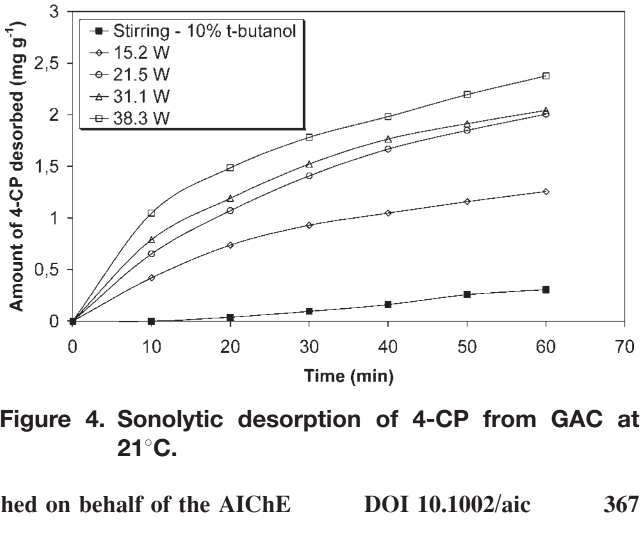

Figure 4. Sonolytic desorption of 4-CP from GAC at 21°C.

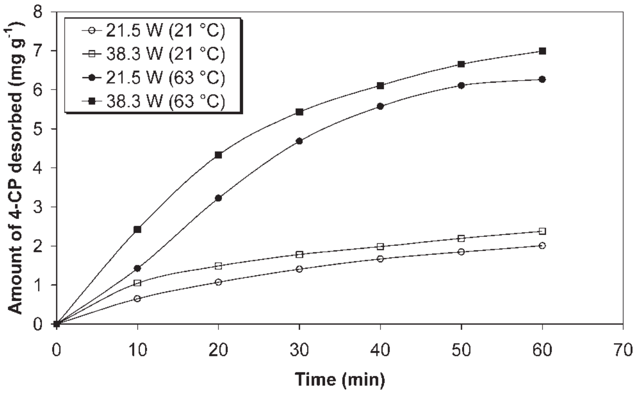

Figure 5. Effect of temperature on the sonolytic desorption of 4-CP from GAC.

The desorption increases with increasing acoustic power of the ultrasound (Figure 4), because with high intensities more cavitation events occur and more molecules are desorbed. An increase in ultrasound intensity means an increase in the acoustic amplitude. The collapse time, the temperature, and the pressure on collapse are all dependent on acoustic amplitude; the cavitation bubble collapse will be more violent at higher acoustic amplitudes. An increase in intensity will thus result in greater ultrasonic effects in the collapsing bubble.[36] Additionally, when the acoustic power increases and simultaneously increases amplitude of vibration, the maximum radius of the cavity bubble also increases, as well as its time of collapse, and this bubble is not able to collapse within time equal to half of the period—that is, before the sound field reverses itself and the rarefaction phase begins acting on the collapsing bubble.[22,36] Thus, it was concluded that high intensity of ultrasound leads to the breaking of bonds formed between 4-CP and the adsorbent surface and also to the enhancement of mass transfer by high-speed micro-jets, high-pressure shockwaves, and acoustic vortex microstreaming. Therefore, these effects of ultrasound could be reasons for the enhancement of desorption at higher intensity.

In conclusion, the adsorbed molecules may be released into solution by breaking chemical bonds and intensifying mass transfer phenomena through acoustic vortex microstreaming, shockwaves, micro-jets, and thermal effects from cavitational collapse.

Effect of temperature on sonolytic desorption

Figure 5 shows the effect of temperature on the desorption of 4-CP from GAC in the presence of ultrasound. The desorption kinetics of 4-CP from GAC increased with increasing temperature.

This indicates that the desorption process is endothermic in nature. The amount of desorption increased from 2.37 to 6.99 mg g^{-1} for an ultrasonic power of 38.3 W and from 2.01 to 6.26 mg g^{-1} for an ultrasonic power of 21.5 W after 60 min of sonication when the temperature is increased from 21 to 63°C. This enhancement is felt to be due to the acceleration of the desorption process by the increased movement of adsorbate molecules from the adsorbent surface to the bulk solution at higher temperatures. Additionally, cavitating bubbles are more easily produced at high temperature because of the decrease of the liquid tensile stress and viscosity.

Furthermore, it is interesting to note that the enhancement in desorption rate at 63°C, due to ultrasonication, is appreciably greater at higher acoustic power. The stronger the acoustic power is, the greater the intensity of the ultrasonic field, which led to the breaking of more bonds between adsorbate molecules and the adsorbent surface and thus increased the amount of desorbed molecules.

Thus, the desorption increases with increasing temperature, indicating that high temperature favors the desorption. The enhancement of desorption with temperature may be due to the increase of the breaking of bonds between adsorbate molecules and the activated carbon surface and/or the increase of the diffusion rate of adsorbate molecules into the pore at higher temperature as diffusion is an endothermic process.

This behavior shows that the influence of ultrasound on desorption is highly dependent on the examined substance as the heat of adsorption determines the quantum of energy required by a cavitation event to overcome the affinity between an adsorbate and an adsorbent.

The above results indicate that the effects of ultrasound on the enhancement of desorption processes consist of both non-thermal effects and thermal effects. The thermal effect is mostly given by localized hot spots formed when bubbles cavitated as well as by piezoelectric transducer heating. The non-thermal effect was mostly produced by the acoustic vortex microstreaming within porous solids as well as at the solid-liquid interface and by the high-speed micro-jets and high-pressure shockwaves induced by acoustic cavitation.

Effects of NaOH or a mixture of NaOH and ethyl alcohol

Sodium hydroxide (1 M) or a mixture of NaOH and ethyl alcohol were added into the desorption system (10% t-butanol solution and exhausted activated carbon) in the presence of the ultrasonic field and in silent conditions by magnetic stirring, and the concentration of 4-CP was monitored with time.

As shown in Figure 6, the addition of NaOH (5% v/v, 1 M) to the regenerating solution evidently leads to the intensification of both the rate and the amount of desorption, especially in the

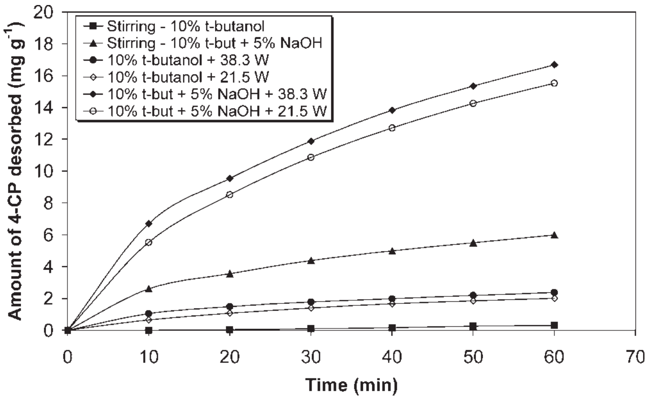

Figure 6. Influence of addition of NaOH (5% v/v, 1 M) on the desorption of 4-CP from GAC with and without application of ultrasound at 21°C.

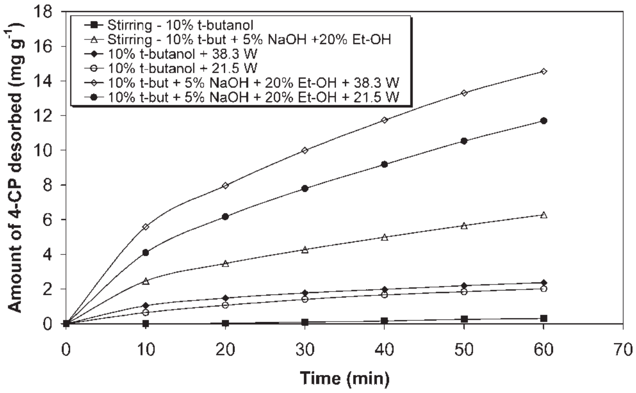

Figure 7. Influence of addition of mixture of 5% (v/v) NaOH (1 M) and 20% (v/v) ethanol on the desorption of 4-CP from GAC at 21°C.

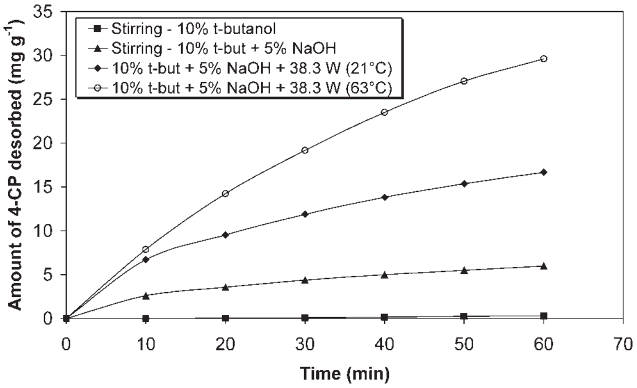

Figure 8. Influence of temperature on the desorption of 4-CP from GAC in the absence and presence of ultrasound (regenerating solution 10% t-butanol + 5% NaOH).

presence of ultrasound. This improvement can be explained by the increase of negative charge on the activated carbon surface, because the solution pH (12.7) is much higher than the point of zero charge (PZC = 4.1), and the predominance of phenolate ions at this pH (99.97%). Therefore, the electrostatic repulsion forces between the adsorbent surface and adsorbate anions increase. On the other hand, it seems that 4-CP solubility, which varied considerably with the solution pH, may be another reason for this enhancement. The stronger the acoustic power delivered to the desorption system is, the higher the desorption rate is. It means that ultrasonic irradiation and NaOH could produce a synergetic effect to enhance the desorption of 4-CP from the activated carbon surface.

The influence of the addition of a mixture of 20% ethanol and 5% NaOH (1 M) on the desorption of 4-CP from saturated GAC is examined in the absence and presence of ultrasonic irradiation for two different sonication powers. The experimental results, presented in Figure 7, show that the addition of a mixture of ethanol and NaOH increases considerably the desorption kinetics, especially in the presence of ultrasound. Also, the desorption rate enhances with rising ultrasonication intensity. Ethanol reduces the tensile stress of the liquid and thus reduces the cavitation threshold and facilitates the generation of cavitating bubbles. The generation of more transient cavitation bubbles helps to produce easily hydrodynamical (high-speed micro-jets, high-pressure shockwaves, and acoustic vortex microstreaming) and thermal effects. Studying the ultrasonic elution of gold from activated carbon, Feng et al.[18] have indicated that ethanol could not only reduce the threshold for cavitation, but also capture the primary radicals ($HO^{\bullet}$ and $H^{\bullet}$) to form secondary radicals ($C_2H_4OH^{\bullet}$) beneficial for the desorption of gold. Ultrasound and the mixture of 20% ethanol and 5% NaOH produce a synergistic effect involving a significant intensification of the rate and the amount of desorption.

When an ultrasonic wave traverses a medium, part of the energy that it transports is dissipated in the form of heat. The movements due to the passage of the ultrasonic wave engender frictions that induce a heating of the liquid because of the solution viscosity. We will make profitable this property to study the influence of temperature on desorption in the presence of ultrasonic irradiation using different regenerants.

In the presence of a 516 kHz ultrasonic field, desorption experiments of 4-CP from exhausted GAC were carried out in two different regenerating solutions, at two temperatures of 21 and 63°C, for a calorimetric power of 38.3 W. The employed regenerating mediums are: (i) solution of 10% t-butanol and 5% NaOH (1 M); and (ii) solution of 10% t-butanol, 5% NaOH (1 M), and 20% ethanol.

The obtained results, presented in Figures 8 and 9, show that both the rate and the amount of desorption are improved considerably in the presence of ultrasonic irradiation. This increase is much more significant at high temperature (63°C). This can be explained by: (i) the creation, in the presence of NaOH, of repulsion electrostatic forces between the activated carbon surface (negatively charged at this pH) and phenolate anions; (ii) the reduction of the tensile stress of the liquid in the presence of ethanol, which facilitates the generation of cavitating bubbles; and (iii) the decrease of the liquid tensile stress and viscosity at high temperature, which involves the reduction of the cavitation threshold.

Comparison of the effect of temperature on the desorption in the presence of an ultrasonic field using different regenerating solutions is shown in Figure 10. Desorption rates and

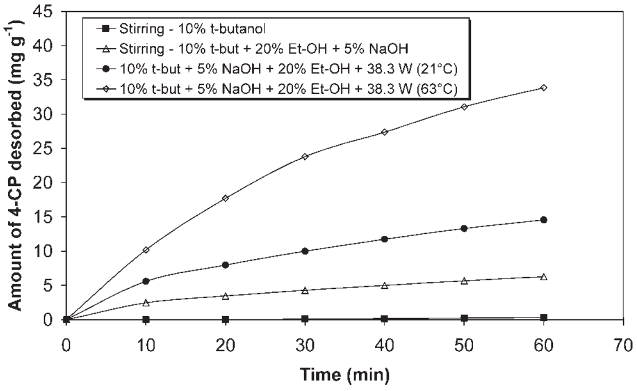

Figure 9. Influence of temperature on the desorption of 4-CP from GAC in the absence and presence of ultrasound (regenerating solution 10% t-butanol + 5% NaOH + 20% ethanol).

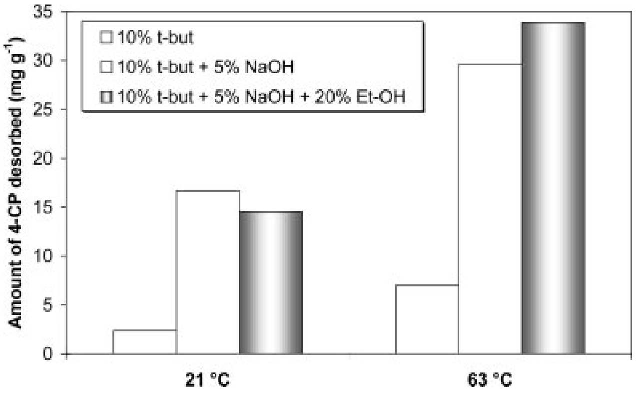

Figure 10. Comparison of the effect of temperature on the ultrasonic desorption in different regenerating solutions.

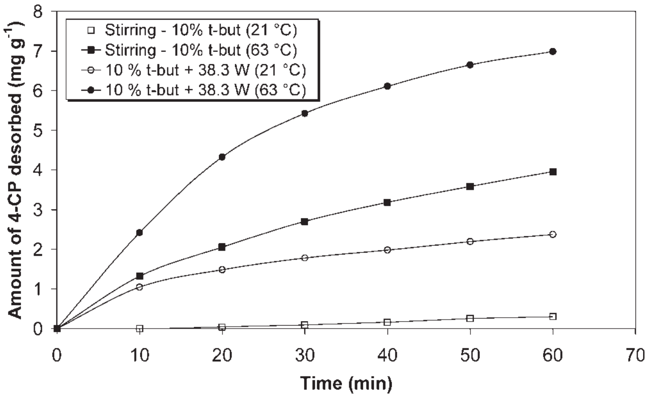

Figure 11. Desorption kinetics at 21 and 63°C in the absence and presence of 516 kHz ultrasonic irradiation (regenerating solution: 10% t-butanol).

desorbed amounts at 63°C are much higher than those obtained at 21°C, whatever the regenerating solution is. The amounts of 4-CP desorbed at 63°C are 2 to 3 times those obtained at 21°C.

Desorption of 4-CP from the adsorbent surface is limited by the strength of the surface bonds and/or by the rates of adsorbate diffusion through the micropores. Schueller and Yang[12] and Hamdaoui et al.[8] have indicated that the improvement of desorption by ultrasound stems from the enhancement of the surface diffusivity.

Thus, several significant mechanisms can be identified for the desorption at high temperature. First, localized hot spots are created in the liquid, where the temperature and pressure of the gas in the cavity rise enormously, owing to the expansion and implosive collapse of bubbles at nucleation sites within the liquid irradiated with ultrasound. These high temperatures enhance the breaking of bonds between the adsorbate molecules and the adsorbent surface. Second, acoustic cavitation produces high-speed micro-jets and high-pressure shockwaves that impinge on the adsorbent surface and desorb the adsorbate. Finally, ultrasound produces acoustic vortex microstreaming within the pores of the solid particles, as well as the solid-liquid interface. This phenomenon arises owing to the increase in momentum brought about as the liquid absorbs energy from the propagating soundwaves and occurs even in the absence of cavitation, previously found to accelerate mass transport,[8] and could possibly be the cause of enhanced desorption rates.

Effects of ultrasonication on the desorption (mechanisms)

Desorption tests of 4-CP from the activated carbon surface were conducted in the absence and presence of ultrasonic irradiation of 516 kHz and 38.3 W for two temperatures of 21 and 63°C. The used regenerating solutions are: (i) 10% t-butanol; (ii) 10% t-butanol + 5% NaOH (1 M); and (iii) 10% t-butanol + 5% NaOH (1 M) + 20% ethanol.

The results of the desorption experiments are presented in Figures 11–13. In all regenerating solutions, the desorbed amounts increase with the temperature rise. The enhancement of the desorption rate is more significant in the presence of the ultrasonic field. It seems that the desorption rates in the presence of ultrasound at 21°C are higher than those obtained at 63°C in silent conditions by simple stirring, except for the regenerating solution composed of 10% t-butanol and 5% NaOH.

The influence of ultrasonication on desorption is partially attributed to the thermal effect of ultrasound. The thermal effect is mostly given by localized hot spots formed when bubbles cavitated as well as by piezoelectric transducer heating. Moreover, the non-thermal effect of ultrasound plays a significant role in the intensification of the desorption process. Thus, it is necessary to clarify the mechanisms of sonolytic desorption.

As can be seen from Figures 11–13, desorption rates obtained at 63°C in the absence of ultrasound are higher than those observed at 21°C. This difference can be explained by the improvement of diffusion phenomena and the breaking of bonds formed between 4-CP molecules and the activated carbon surface at high temperature.

On the other hand, Figures 11–13 show that the desorption kinetic at 63°C in the presence of the ultrasonic field are much higher than obtained in the absence of ultrasound at 63°C. The same remarks are noted for the results obtained at 21°C. These differences are obviously caused by the non-thermal effect of the ultrasonic field. The non-thermal effect

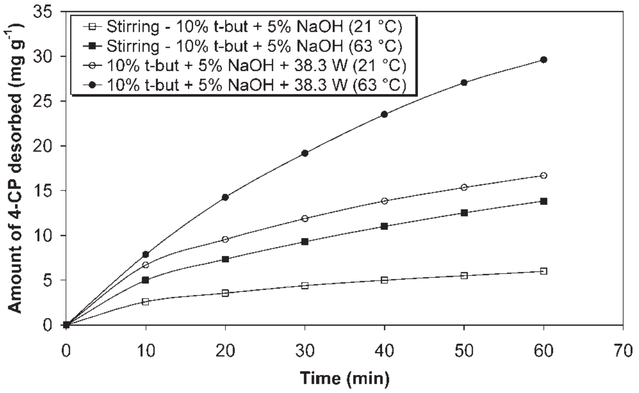

Figure 12. Desorption kinetics at 21 and 63°C in the absence and presence of 516 kHz ultrasonic irradiation (regenerating solution: 10% t-butanol + 5% NaOH (1 M)).

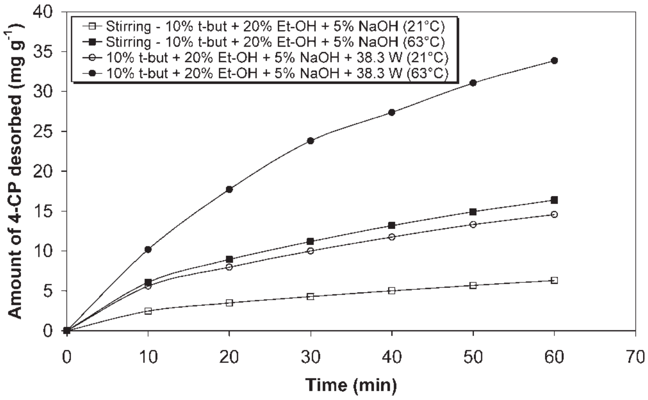

Figure 13. Desorption kinetics at 21 and 63°C in the absence and presence of 516 kHz ultrasonic irradiation (regenerating solution: 10% t-butanol + 5% NaOH (1 M) + 20% ethanol).

is principally produced by acoustic vortex microstreaming, high-speed micro-jets, and high-pressure shockwaves produced by acoustic cavitation. For better comprehension of the impact of thermal and non-thermal effects on desorption, it is necessary to compare them. On the basis of the amounts of 4-CP desorbed from activated carbon in the absence of ultrasound at 21°C, Figure 14 shows the net increase of the amount of desorption, $\Delta q_{\text{desorbed}}$, caused by thermal and non-thermal effects of ultrasound.

The obtained results (Figure 14) indicate that the influence of ultrasound on desorption consists of thermal and non-thermal effects. The non-thermal effect of ultrasound is higher than the thermal effect, except for the experiments conducted in 10% t-butanol regenerating medium. The non-thermal effect of the ultrasonic irradiation at 63°C is more significant than that obtained at 21°C.

All these observations show that the effects of temperature on ultrasonic desorption are complex. The increase in temperature is evidently harmful to cavitation but beneficial to desorption. Indeed, increasing temperature induces a reduction of dissolved gas concentration, and thus a decrease of gas pressure in the bubbles, but also an increase of the vapor pressure and a damping of implosion by the presence of vapor in cavities. The rise in temperature generates rupture of bonds between adsorbate and adsorbent and enhances diffusion phenomena. In addition, the hydrodynamical (non-thermal) effect of cavitation depends on the size and the number of cavitation bubbles, and also on their contents in gas and vapor.

Comparison of desorption at high temperature

The results of desorption obtained in different regenerating solutions at high temperature (63°C) in the absence and presence of ultrasonic irradiation (516 kHz and 38.3 W) are presented and compared in Figure 15.

Classification of different regenerating solutions according to the amount of desorption is identical in the absence and presence of ultrasound. This indicates that the desorption process at high temperature is not modified by ultrasonic irradiation. Desorption rates in the presence of an ultrasonic field are higher than those obtained in silent conditions, except for the regenerating solution formed of 10% t-butanol.

Mixed regenerants offer the possibility of synergistically combining multiple mechanisms to enhance desorption efficiencies. In order to explore this possibility, the effectiveness of the NaOH-ethanol mixture at high temperature was studied. As can be seen from Figure 15, ultrasound and the mixture of 20% ethanol and 5% NaOH produce a synergistic effect, generating a significant intensification of both the rate and the amount of desorption. The enhancement of desorption by the addition of a mixture of ethanol and NaOH in the presence of ultrasonic irradiation can be explained by the lowering of the cavitation threshold and the establishment of repulsion forces between the activated carbon surface and phenolate ions.

Additionally, ultrasonic irradiation and NaOH produce a synergetic effect to enhance the desorption of 4-CP from the activated carbon surface.

Ultrasonic regeneration of GAC

Another aspect that concerned us was the effectiveness of ultrasonic irradiation on the regeneration of the adsorption capacity of the GAC. We have found that both the rate and the amount of desorption of 4-CP from the GAC surface

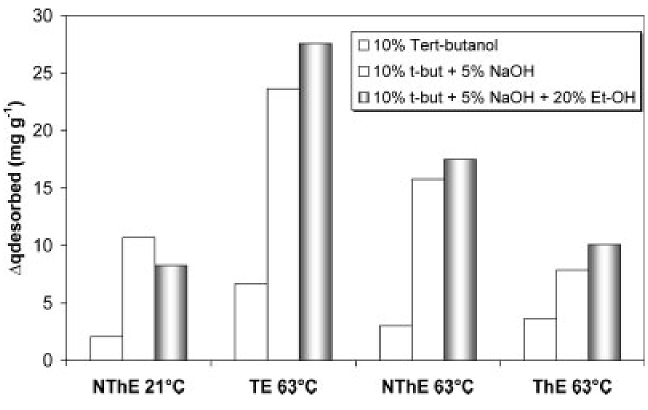

Figure 14. Thermal and non-thermal effects of ultrasound on the intensification of the desorption (NThE: non-thermal effect, TE: total effect, ThE: thermal effect).

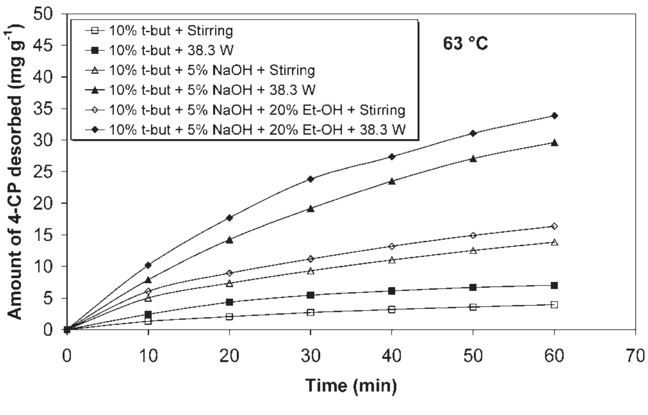

Figure 15. Comparison of the desorption at high temperature in different regenerating solutions in the absence and presence of 516 kHz ultrasonic irradiation for 38.3 W power intensity.

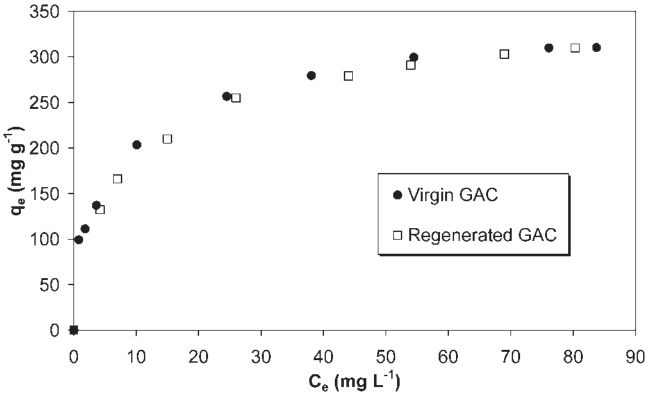

Figure 16. Adsorption isotherms of 4-CP onto virgin and regenerated GAC.

increase significantly in the presence of ultrasonic irradiation. Additionally, the phenolic compound is effectively degraded in aqueous solution by ultrasound. These results encouraged us to study the regeneration of 4-CP-loaded GAC by ultrasonic irradiation. In this process, both desorption and degradation of 4-CP steps are combined in one stage, which led to simultaneous regeneration of GAC and elimination of 4-CP.

The adsorption isotherms of 4-CP onto virgin GAC and ultrasound treated activated carbon after 7 cycles of adsorption-regeneration are presented in Figure 16. In both cases, the isotherms exhibit a shape of type L. From this figure, it clearly appears that adsorption capacities of the activated carbon regenerated by ultrasound and that of the virgin carbon remained the same. This indicates that recovery of the initial adsorption capacity of activated carbon was obtained and regeneration of GAC was complete (approximately 100%). Additionally, these results demonstrated that the proposed method can be used as an alternative to traditional techniques. However, additional research should be conducted to evaluate the scale-up and the cost of this process.

Conclusion

In this study, the mechanisms underlying the ultrasonic desorption of 4-CP from granular activated carbon have been explored. It has been demonstrated that ultrasonically enhanced desorption is due both to thermal and non-thermal effects of the ultrasonic field. The thermal effect is mostly given by localized hot spots formed when bubbles cavitated as well as by global heating of the medium and piezoelectric transducer heating-up. The non-thermal effect is principally produced by the acoustic vortex microstreaming within porous solids as well as at the solid-liquid interface and by the high-speed micro-jets and high-pressure shockwaves produced by acoustic cavitation. The non-thermal effect of ultrasound is greater than the thermal effect, and it is more marked when the ultrasonic irradiation is carried out in a high temperature regenerating medium.

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