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Desorption of Metal Ions from Activated Carbon in the Presence of Ultrasound

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The aim of the present work is to explore the effects of ultrasound on desorption of metal ions from activated carbon. The desorption of Cu(II), Mn(II), Hg(II), and Cr(VI) from activated carbon in the absence and the presence of ultrasound is investigated. Desorption studies are performed under various conditions of temperature and intensity. Results indicate that ultrasonic irradiation considerably improves the desorbed amount and the rate of desorption. The amount of desorbed metal ions increases with increasing temperature and ultrasound intensity. The addition of ethanol to the desorption system leads to an enhancement of the desorption rates, especially in the presence of ultrasound. Acidification of the regenerating solution to pH 1 leads to an enhancement of the desorption of Cu(II). This improvement is more obvious in the presence of ultrasound. Modeling of desorption kinetics shows that ultrasound enhances surface diffusivity. This can be attributed to the phenomena induced by acoustic cavitation: acoustic vortex microstreaming, high-speed microjets, high-pressure shock waves, and intense localized heating.

1. Introduction

Contamination of the environment from a variety of sources has become an increasingly serious problem in recent years. The strong release of metal ions into the environment by several industries has meant that their recovery from wastewater has become a major topic of research in wastewater treatment. The main techniques that have been used to reduce the metal ion content of liquid effluents include lime precipitation, ion exchange, membrane processing, and electrolytic methods, but adsorption seems to be an economical alternative method for removing trace metals from water.

Adsorption processes using activated carbon represent a highly effective method to remove low concentrations of metal ions from water and industrial effluents. Numerous studies describe the adsorption of metal ions onto activated carbon.^{1–6} After exhaustion, activated carbon is regenerated or replaced by fresh carbon. The first option is preferred due to the high cost of this adsorbent. However, studies on desorption of metal ions are less numerous.^{7,8}

Recently, the use of ultrasound has been investigated as a means to improve desorption processes.^{9–18} Ultrasound refers to sound waves of 16 kHz to 500 MHz frequency that can be transmitted in the form of mechanical energy through any medium having elastic properties, such as water, gas-saturated water, and aqueous particle suspensions. Effects induced by ultrasonic waves in aqueous solution have been attributed to acoustic cavitation, which not only leads to a mechanical action between solid and liquid interfaces, but also to chemical effects. Bubbles are nucleated and knocked in the liquid phase during ultrasonic irradiation. High temperature (several thousand kelvin) and pressure (few hundred bars) are produced for a few

microseconds in the liquid phase during the adiabatic collapse of cavitation bubbles. These extreme conditions promote chemical reactions, such as the cracking of water into hydrogen and hydroxyl radicals. The collapse of cavitation bubbles also produces liquid jets which are driven to the solid surface at 100 m s⁻¹. Shock waves from cavitation in liquid–solid slurries produce high-velocity interparticle collisions; these impacts are sufficient to melt most metals. Ultrasound also improves transport in liquid systems by acoustic streaming. Acoustic waves produce time-independent vortices in the pores of suspended solid in aqueous solution as well as at solid–liquid interfaces.^{9,19–21}

There are some studies where power ultrasound is successfully used for cleaning of different particle surfaces from organic or inorganic matter.^{22–29} Newman et al., using granular pieces of brick as a model for contaminated soil, noticed a 40% reduction in copper content by using an ultrasonic shaker operating at 20 kHz.²⁸ Vinatoru et al. have shown the usefulness of ultrasound in the extraction of bioactive compounds from plant material.²⁹

Some authors have also explored the effects of ultrasound on the elution of ions.^{30,31} Ultrasonication at 40 kHz was demonstrated to enhance the elution of gold, cadmium, and sulfate ions from polymeric resins.³⁰ Feng et al. have studied the elution of gold cyanide from activated carbon by ultrasound. They found that elution of both laboratory and plant loaded carbon with different eluants was considerably enhanced by sonication at 40 kHz.³¹

The efficiency of the desorption depends on the parameters also affecting the cavitation process, such as temperature and pressure of the irradiated system, viscosity of the solvent, power of the ultrasound generator, amplitude and frequency of the ultrasonic wave, and the geometry of the employed reactor vessel.^{9,32} In our previous work, low-frequency ultrasound was successfully used for enhancing desorption of *p*-chlorophenol from granular activated carbon.⁹ Low-frequency ultra-

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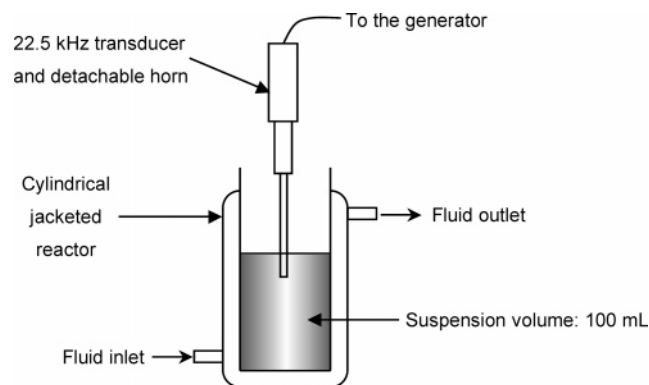


Figure 1. Scheme of experimental device used for ultrasonic desorption experiments.

sonic devices can be considered an attractive way to perform desorption.

Ultrasound appears to be a promising alternative method for the desorption of metal ions from activated carbon. This work focuses on desorption of metal ions (Cu(II), Mn(II), Hg(II), and Cr(VI)) from activated carbon in the absence and presence of ultrasound at 22.5 kHz. The stability of the activated carbon in the presence of the ultrasonic field is studied, and the effects of parameters such as temperature, acidification, addition of ethanol, and power intensity are discussed. Furthermore, an attempt is made to model the kinetics of desorption.

2. Materials and Methods

2.1. Reagents and Activated Carbon. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, MnSO_4 , HgCl_2 , and $\text{K}_2\text{Cr}_2\text{O}_7$ (from Merck, analytical grade) were used to prepare Cu(II), Mn(II), Hg(II), and Cr(VI) solutions, respectively. Analytically pure H_2SO_4 and ethyl alcohol were obtained from Prolabo. Distilled water was used in all the experiments.

The activated carbon (Prolabo) used in this study has a BET surface area of $1046 \text{ m}^2 \text{ g}^{-1}$. The carbon was pretreated by boiling in distilled water for 1 h and washed thoroughly with distilled water until the UV absorbance and the conductivity were equal to zero. Finally, the washed activated carbon was dried in an oven at 110°C to constant weight, and stored in a desiccator until use.

The particle size analysis of the activated carbon was determined after sonication and after mechanical stirring. For these experiments, 100 mL of distilled water was added to 2.5 g of activated carbon and the suspension was exposed to ultrasound of different power intensities or stirred in silent conditions at 300 rpm for 3.5 h. The suspension was then filtered ($0.45 \mu\text{m}$) and dried at 110°C for 24 h. The size distribution was determined by passing the samples through a battery of various opening size sieves, followed by weighing the size fractions.

2.2. Ultrasonic Reactor. Desorption experiments were carried out using an ultrasonic reactor (9 cm height and 5 cm internal diameter), shown in Figure 1. It consists of a double glass cylindrical jacket, allowing water cooling of the reactor. In all cases, the volume treated was 100 mL. The 22.5 kHz irradiations were carried out with a commercial supply Microson equipped with an ultrasonic probe mounted at the top of the cylindrical glass reactor.

For adsorption experiments, activated carbon (5 g) was added to 1 L of 200 mg L^{-1} metal ion solution at

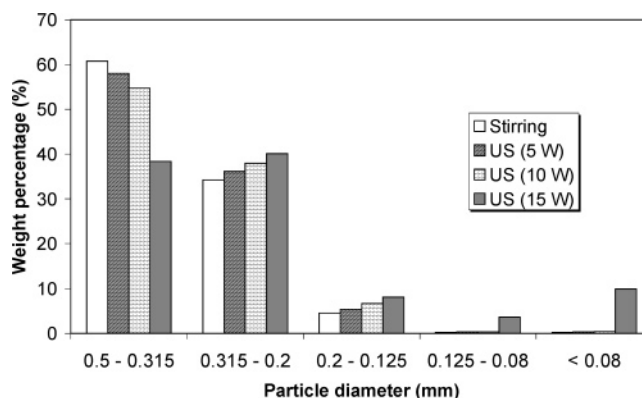


Figure 2. Weight distribution of activated carbon particle size after sonication or stirring.

25°C in sealed bottle. The bottle was stirred (300 rpm) until equilibrium was reached. The carbon loaded with metal ion was then separated from the solution. The concentrations of metal ions in solution were determined by atomic absorption spectroscopy (Perkin-Elmer A310). The activated carbon loading was determined by the difference of the ion concentrations in solutions. The activated carbon loaded with metal ions (33.98 , 29.42 , 24.75 , and 23.35 mg g^{-1} for Hg(II), Cr(VI), Cu(II), and Mn(II), respectively) was dried in air.

2.3. Desorption Procedure. About 0.5 g of metal ion loaded activated carbon was tested for desorption by adding 100 mL of distilled water and placing the sample in a low-frequency (22.5 kHz) ultrasonic reactor. The desorption rate was determined by metal concentration measurement in the aqueous phase. Ethyl alcohol and/or sulfuric acid was added to the regenerating solution to determine the effect on the ultrasonic desorption process.

Identical experiments were repeated in silent conditions using a mechanical stirrer with a stirring rate of 300 rpm.

All the experiments were carried out in duplicate, and the mean values are presented. The maximum standard deviation was $\pm 2\%$.

3. Results and Discussion

3.1. Stability of the Activated Carbon. The eroding effect of ultrasound is significant for some materials because of the high-pressure shock waves and high-speed microjets resulting from cavitation implosions.⁹ Thereby the particles can be completely destroyed or pieces can be torn off the surface. To propose a reasonable alternative process to existing regeneration processes, it is essential that no attrition of the activated carbon occurs when treated with ultrasound. Hence, the stability of the activated carbon particles was experimentally determined. The activated carbon was irradiated with ultrasound of different power intensities for 3.5 h in the same reactor employed for the desorption experiments. A procedure similar to the previous one was followed in order to obtain the particle size distribution without ultrasound at a stirring rate of 300 rpm. Figure 2 shows the size distribution of the activated carbon with and without the use of ultrasound. Sonicated activated carbon showed a decrease in the large size fraction (0.5–0.315 mm), with a corresponding increase in smaller size fractions. With increasing ultrasound intensity, the large size fraction decreases, because with high intensities more cavitation events occur and stronger high-speed microjets and high-

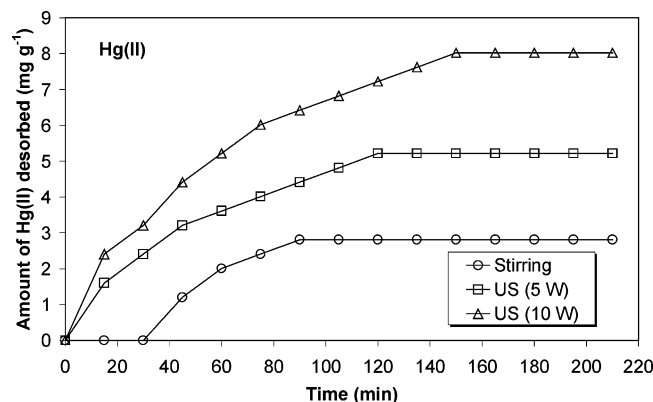


Figure 3. Desorption of Hg(II) from activated carbon versus time in the absence and presence of ultrasound at 25 °C.

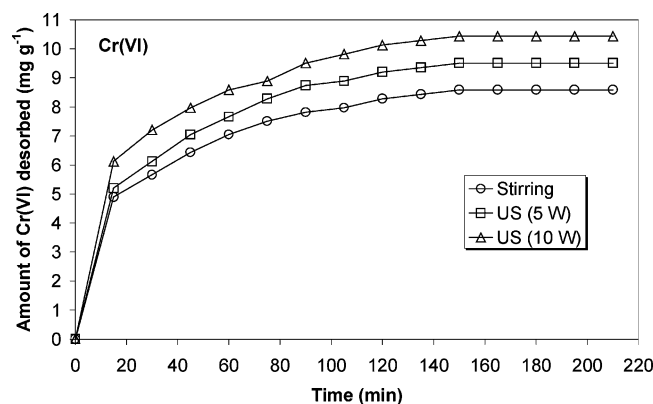


Figure 4. Desorption of Cr(VI) from activated carbon versus time in the absence and presence of ultrasound at 25 °C.

pressure shock waves are formed, leading to greater mechanical stress on the adsorbent surface. The size fraction of 0.5–0.315 mm, when compared with that for the not sonicated activated carbon, decreased of 4.5, 9.9, and 36.8% for intensities of 5, 10, and 15 W, respectively. Hence ultrasound with a power of 15 W destroys the particles and is unsuitable for the used activated carbon and experimental device. The size fractions of 0.315–0.2 and 0.2–0.125 mm increased from 34.2 and 4.54%, in silent conditions, to 37.95 and 6.63% for an ultrasonic power of 10 W.

A particle analysis was also performed using the same mass of activated carbon (0.5 g) employed for desorption experiments. The size distribution after 3.5 h of sonication was only shifted 1.7% for an ultrasonic power of 10 W, showing the stiffness of the activated carbon, in these conditions, toward ultrasonic application.

Consequently, ultrasonic desorption experiments were conducted at two intensities of 5 and 10 W.

3.2. Ultrasonic Desorption of Metal Ions at 25 °C.

The concentration of metal ions in the distilled water regenerating the activated carbon was monitored with time, both in the presence of ultrasound of different intensities (5 and 10 W) and in silent conditions with stirring. The results of the desorption experiments are shown in Figures 3–6. The rate of metal ion desorption is significantly increased in the presence of ultrasound.

The action modes of ultrasound on desorption are related to hydrodynamic and thermal processes generated by acoustic cavitation. Cavitation bubbles, growing over one or several sound cycles, act like energy transformers. When a critical size is reached, they violently collapse during the compression cycle with the release of large amounts of energy. Cavitation collapse

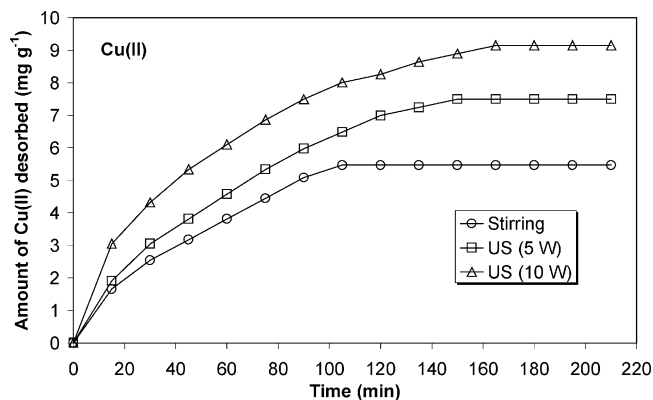


Figure 5. Desorption of Cu(II) from activated carbon versus time in the absence and presence of ultrasound at 25 °C.

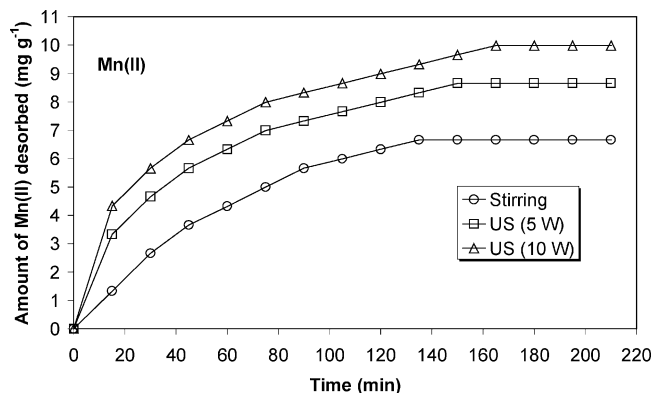


Figure 6. Desorption of Mn(II) from activated carbon versus time in the absence and presence of ultrasound at 25 °C.

promotes desorption, an endothermic process, by generating localized high temperature and pressure near the carbon surface. An asymmetric collapse also occurs in the vicinity of this surface and leads to high-speed microjets impinging it and shock waves creating microscopic turbulence or microstreaming at interfacial films surrounding nearby solid particles and within the pores. The effects of ultrasound on the desorption process are thus due to mass transport and bond breaking enhancement, leading to more metal ions released in the regenerating solution.^{9,19,21}

The desorbed amount of metal ions increases with increasing ultrasound intensity (Figures 3–6), because with high intensity more cavitation events occur and more ions are desorbed. Indeed, the number of cavitation events, the intensities of the high-speed microjets and of the high-pressure shock waves produced by acoustic cavitation are mostly dependent on the power delivered to the system. The stronger the acoustic power is, the greater the intensity of ultrasonic field is, that led to the breaking of more bonds between metal ions and the adsorbent surface and thus increased the amount of desorbed ions. This indicates that the desorption of metal ions from exhausted activated carbon is dependent on the intensity of the ultrasonic field.

For all metal ions the desorbed amounts are small, compared to that adsorbed, because the adsorbent reached equilibrium with the solution in the reactor. For an ultrasonic power of 10 W, the percentages of desorbed metallic ions are approximately 24, 35, 37, and 43% for Hg(II), Cr(VI), Cu(II), and Mn(II), respectively.

As can be observed from Figures 3–6, the use of ultrasound appreciably improves desorption. The

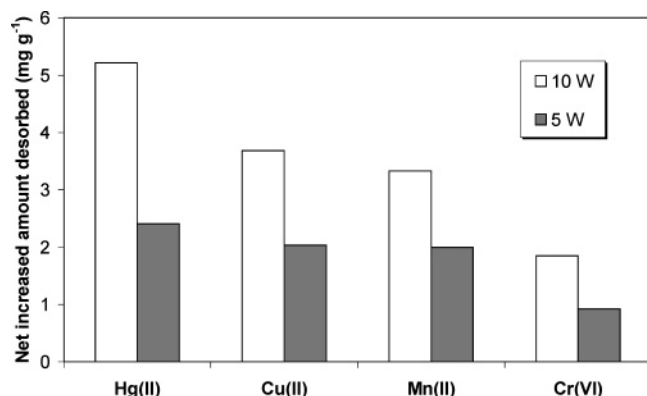


Figure 7. Net increased amounts of desorption due to ultrasonic irradiation.

Table 1. Net Enhanced Amounts of Desorption of Metal Ions by Ultrasonic Watt at 5 and 10 W

metal ion	net enhanced amt (mg g ⁻¹ W ⁻¹)	
	at 10 W	at 5 W
Hg(II)	0.52	0.48
Cr(VI)	0.18	0.18
Cu(II)	0.37	0.41
Mn(II)	0.33	0.40

amounts of Hg(II), Cr(VI), Cu(II), and Mn(II) desorbed without ultrasound are 2.81, 8.58, 5.47, and 6.66 mg g⁻¹, respectively, whereas the desorption amounts in the presence of ultrasound of 10 W are respectively 8.02, 10.43, 9.15, and 9.99 mg g⁻¹.

The net increased amounts of desorption due to the 10 W ultrasonic irradiation (Figure 7) are 5.22, 1.85, 3.69, and 3.33 mg g⁻¹ for Hg(II), Cr(VI), Cu(II), and Mn(II), respectively. The net desorption yields due to the contribution of ultrasound are Hg(II) (15%) = Cu(II) (15%) > Mn(II) (14%) > Cr(VI) (6%). It appears that ultrasonication is not selective for the bivalent metal ions (Hg(II), Cu(II), and Mn(II)); indeed, the desorption yields are almost identical. On the other hand, the desorption yield calculated for Cr(VI) is 3 times less than that of bivalent metal ions.

The net enhanced amounts of desorption by ultrasonic Watt for two different powers (5 and 10 W) are presented in Table 1. For a given metal ion, it seems that the enhancement of desorbed amounts by ultrasonication is identical in both cases; it can be concluded that the increase in ultrasonic power applied enhances the number of cavitation events and therefore the amount of desorbed metal ion. The net increased amount by ultrasonic Watt obtained for Hg(II) is 3 times greater than that for Cr(VI), whereas that for Cu(II) and Mn(II) is 2 times greater than that for Cr(VI).

Among the four metal ions the most significant improvement of desorption amounts is obtained for Hg(II). In the presence of ultrasound the amount of Hg(II) desorbed is about 2 (5 W) to 3 (10 W) times the corresponding amount without ultrasound.

As shown in Figure 3, 8.02 mg g⁻¹ Hg(II) was desorbed from the activated carbon after 150 min in the presence of an ultrasonic wave of 10 W. For a sonication time of 120 min and an intensity of 5 W, 5.22 mg g⁻¹ Hg(II) was desorbed, while only 2.81 mg g⁻¹ Hg(II) was desorbed from the activated carbon after 90 min without ultrasound. The desorption of Hg(II) in the absence of ultrasound starts very slowly, showing the high affinity of Hg(II) ions to the activated carbon surface.

The classification of the affinity of metal ions to the activated carbon surface is Hg(II) > Cr(VI) > Cu(II) >

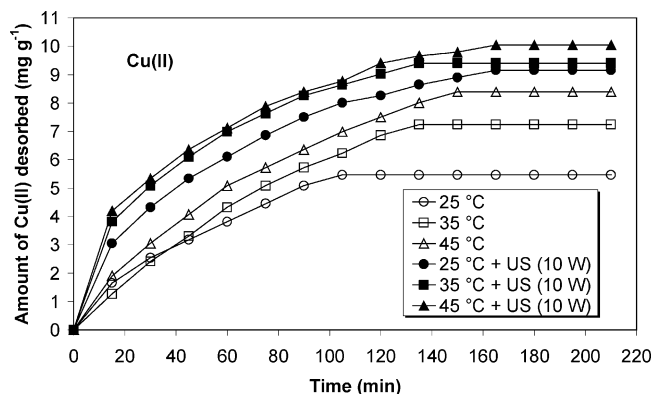


Figure 8. Influence of temperature on desorption of Cu(II) from activated carbon in the absence and presence of ultrasound.

Mn(II), whereas the order of metal ion desorption yields in the presence of ultrasound is Mn(II) > Cu(II) > Cr(VI) > Hg(II) for an ultrasonic power of 10 W. It is very important to note that Hg(II) has the highest affinity to the surface of the activated carbon and consequently the lowest yield of desorption. In contrast, Mn(II) has the highest yield of desorption because of the relatively weak affinity of the metal ions to the adsorbent surface. This behavior shows that the influence of ultrasound on desorption is highly dependent on the examined substances 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.

3.3. Effect of Temperature on Desorption of Metal Ions. The results of the desorption of Cu(II) in the absence and presence of ultrasound at temperatures of 25, 35, and 45 °C are shown in Figure 8. It can be seen that the rates of desorption at 45 °C are much higher than the corresponding rates observed at lower temperatures. It is interesting to note that the enhancement in desorption rate in the absence of ultrasound is appreciably greater at high temperature.

In the presence of ultrasound, it was observed that the desorption rates and the desorbed amounts at equilibrium increased as the temperature was increased. 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 metal ions at this spot go into solution.

The above results indicate that the effects of ultrasound on the enhancement of desorption processes consist of both its nonthermal effect and its thermal effect. The thermal effect is mostly given by localized hot spots formed when bubbles cavitating as well as by piezoelectric transducer heating. The nonthermal 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 microjets and high-pressure shock waves induced by acoustic cavitation.

Figure 9 shows the time variation for Mn(II), Hg(II), and Cr(VI) desorption from activated carbon at different temperatures, in silent conditions. It is obvious from this figure that desorption increases with time until equilibrium. The desorption of respectively Mn(II), Hg(II), and Cr(VI) increases from 6.66, 2.81, and 8.58 mg g⁻¹ to 8.66, 6.42, and 9.51 mg g⁻¹ by a 20 °C increase of the temperature of the regenerating solution. This shows

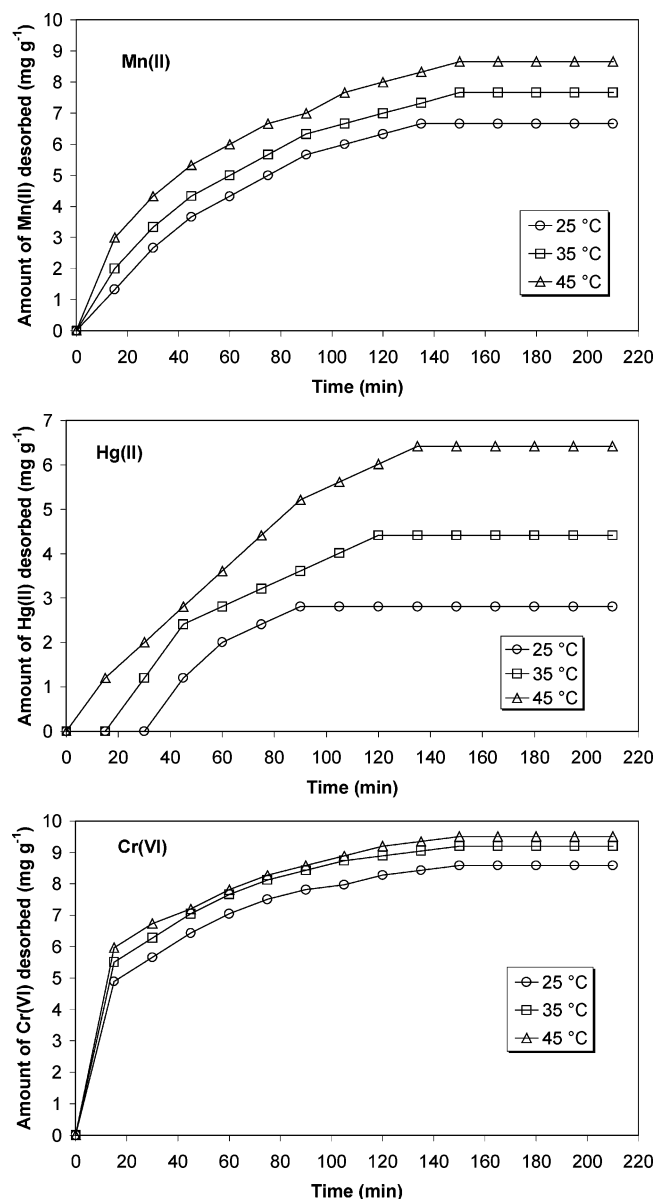


Figure 9. Influence of temperature on desorption of Mn(II), Hg(II), and Cr(VI) from activated carbon in silent conditions.

that the desorption is highly temperature dependent. Further, the equilibrium time increases with increasing temperature (Figures 8 and 9), except for Cr(VI) where the desorption equilibrium time is constant (150 min) whatever the temperature is.

In all cases, 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 sorbate ions and activated carbon surface and/or the increase of the pore intraparticle diffusion rate of sorbate ions into the pore at higher temperature as diffusion is an endothermic process.

3.4. Effect of Acidification and/or Addition of Ethanol. The pH is one of the most important parameters controlling the metal ion sorption process. The effect of pH of the solution on the adsorption of Cu(II) ions on the activated carbon was determined. The pH of the solution was controlled by the addition of H₂SO₄ or NaOH. Adsorption of copper ions onto activated carbon at different initial pH values is shown in Figure 10. This figure demonstrates that the copper adsorption

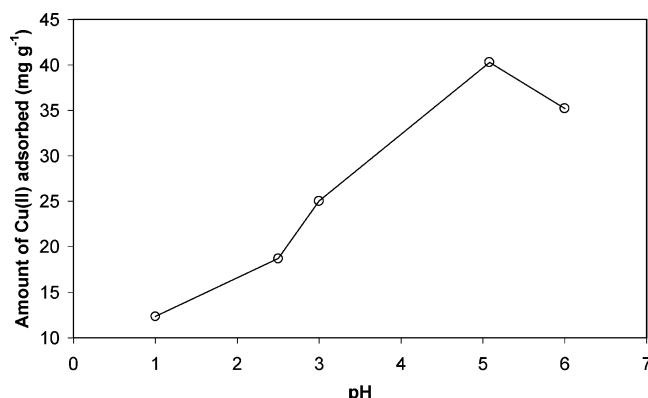


Figure 10. Adsorption of Cu(II) onto activated carbon as a function of pH. Conditions: contact time = 2 h; 0.5 g of activated carbon L⁻¹; C₀ = 200 mg L⁻¹; T = 25 °C.

by the activated carbon is strongly pH dependent. It can be observed that the removal of Cu(II) by activated carbon adsorption increases with increasing pH, from its minimum at pH 1 to its maximum at pH 5. After that, the adsorption decreases in pH range of 5–6. A similar result was gained by several workers.^{7,33,34}

The copper adsorption increases when the solution pH is increased from 1 to 5. It appears that a change in pH of the solution results in the formation of different ionic species and the increase of the negative charge on the carbon surface; thus, the electrostatic attraction force between the sorbent surface and sorbate ions increases.

At pH values less than 3, there is excessive protonation of the activated carbon surface resulting in a decrease in the adsorption of Cu(II) ions. Above pH 5, the preponderance of OH⁻ generates a competition between the activated carbon surface and the solution OH⁻ ions for Cu(II) ions, which causes a decrease in the adsorption of Cu(II) ions on the activated carbon surface.

At pH 5, maximum adsorption is observed, which might be due to a partial hydrolysis of Cu(II), leading to the formation of CuOH⁺ and Cu(OH)₂. Cu(OH)₂ should adsorbed to a greater extent on the activated carbon surface compared to Cu(OH)⁺. Low solubilities of hydrolyzed copper (II) species may be another reason for maximum adsorption at pH 5. In the acidic pH range of 1–3, copper should be predominantly present as Cu(II). Above pH 6, precipitation of Cu(OH)₂ prevents adsorption studies.

Adsorption of metal ions on activated carbons from aquatic environments is governed by electrostatic (Coulombic) and nonelectrostatic interactions. The electrostatic interactions come mainly from the surface charges generated on carbon after its immersion into water and the ions in solution. Nonelectrostatic interactions can be of a different nature, predominantly of van der Waals type.³⁵

Ethyl alcohol and/or sulfuric acid was added into the desorption system (distilled water and exhausted activated carbon) in the absence and presence of the ultrasonic field, and the concentration of Cu(II) was monitored with time.

Experimental results show that the acidification of the regenerating solution to pH 1 obviously leads to the enhancement of the amount of Cu(II) desorbed, especially in the presence of ultrasound, as shown in Figure 11.

The enhancement of copper ion desorption by the addition of sulfuric acid (pH 1) can be explained by the increase of the positive charge on the activated carbon

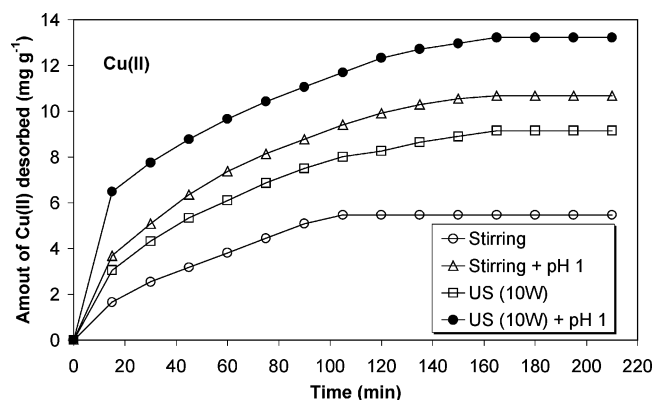


Figure 11. Influence of acidification (pH 1) on desorption of Cu(II) from activated carbon in the absence and presence of ultrasound at 25 °C.

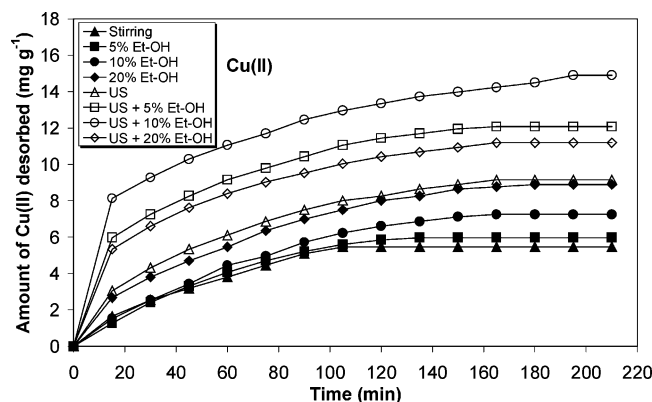


Figure 12. Influence of addition of ethanol on desorption of Cu(II) from activated carbon with and without application of ultrasound (10 W) at 25 °C.

surface and the predominance of Cu(II) ions at this pH ($[\text{Cu}(\text{OH})^+] = 1.44 \times 10^{-9} \text{ M}$). Thus, the electrostatic force of repulsion between the sorbent surface and sorbate ions increases. The high solubility of Cu(II) may be another reason for the improvement of the desorption by acidification to pH 1. Since the desorption of metal ions from activated carbon is the reverse of their adsorption, chemical and physical factors that inhibit adsorption enhance desorption. As a consequence, the acidification of the distilled water regenerating the activated carbon should benefit the desorption of Cu(II).

In the presence of different concentrations of ethanol, the results of Cu(II) desorption experiments conducted in silent conditions as well as with ultrasound are presented in Figure 12. It can be seen that the addition of ethanol considerably enhances the desorption of Cu(II). This effect is more dominant in the presence of ultrasound.

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 hydrodynamic and thermal effects.

As can be seen from Figures 12 and 13, the amount of Cu(II) desorbed in the absence of ultrasound increases with increasing ethanol concentration in the regenerating solution. In the presence of ultrasound, the desorption rates of Cu(II) from the activated carbon are enhanced with the raise of ethanol concentration from 5 to 10% (v/v). Surprisingly, for 20% (v/v) ethanol concentration, the rates of desorption are lower than

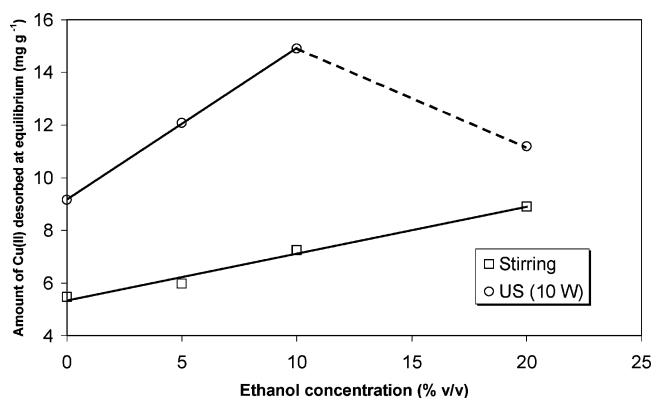


Figure 13. Effect of ethanol concentration on amount of Cu(II) desorbed at equilibrium in the absence and presence of ultrasound at 25 °C.

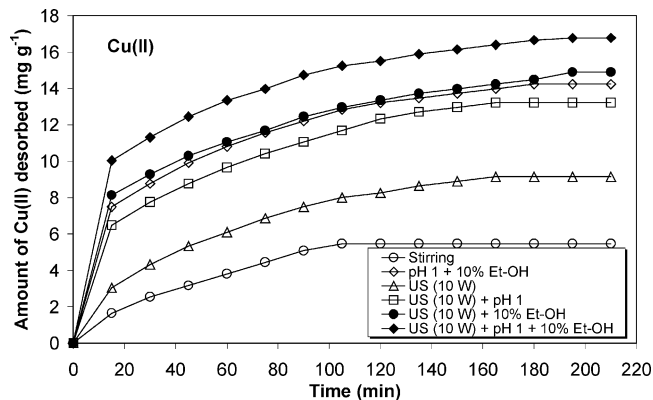


Figure 14. Effect of acidification (pH 1) and addition of ethanol on desorption of Cu(II) in the absence and presence of ultrasound at 25 °C.

corresponding rates obtained by lower concentration (5 and 10%). A possible explanation for this decrease is the generation in the solution of a great number of cavitation bubbles due to lowering of cavitation threshold. Their coalescence forms larger and more stable bubbles. These numerous stable bubbles dampen the passage of sound energy through the liquid and also remove many of the smaller bubbles that would have collapsed.

In the presence of a mixture of ethanol (10% v/v) and sulfuric acid, the concentration of Cu(II) in the solution (pH 1) regenerating the activated carbon was monitored with time, both in the presence of ultrasound and in silent conditions with simple stirring. The results of the desorption experiments are shown in Figure 14. Experimental results show that the adding of a mixture of ethanol and sulfuric acid considerably enhances the kinetics of desorption, especially in the presence of ultrasound.

The improvement of desorption by the addition of a mixture of ethanol and sulfuric acid in the presence of ultrasonic irradiation can be explained by the lowering of the cavitation threshold and the creation of repulsion forces between the activated carbon surface and sorbate ions.

3.5. Modeling of Desorption Kinetics. The desorption of sorbate from the adsorbent surface is limited by the strength of the surface bonds, and by the rates of sorbate diffusion through the micropores. For liquid-phase desorption of strongly or moderately adsorbed species, surface diffusion is the controlling step.⁵ This is probably true for the studied system (metal ions from

Table 2. Values of Surface Diffusion Constant and Correlation Coefficient

	D_s/r^2 (s ⁻¹)	R
stirring, 25 °C	6.976×10^{-7}	0.994
stirring, 35 °C	1.068×10^{-6}	0.986
stirring, 45 °C	1.240×10^{-6}	0.995
US (5 W), 25 °C	1.006×10^{-6}	0.996
US (10 W), 25 °C	1.240×10^{-6}	0.995
US (10 W), 35 °C	1.536×10^{-6}	0.995
US (10 W), 45 °C	1.574×10^{-6}	0.994
stirring + 5% ethanol	7.761×10^{-7}	0.985
stirring + 10% ethanol	9.236×10^{-7}	0.992
stirring + 20% ethanol	1.148×10^{-6}	0.996
US (10 W) + 5% ethanol	1.874×10^{-6}	0.975
US (10 W) + 10% ethanol	2.024×10^{-6}	0.952
US (10 W) + 20% ethanol	1.584×10^{-6}	0.976
stirring, pH 1	1.721×10^{-6}	0.995
US (10 W), pH 1	2.374×10^{-6}	1.000
stirring, pH 1 + 10% ethanol	2.189×10^{-6}	0.961
US (10 W), pH 1 + 10% ethanol	2.702×10^{-6}	0.932

activated carbon), and a surface diffusion model was used to describe the desorption kinetics. The model assumes that the sorbate adsorbs to the surface and then migrates from site to site along the surface. For isothermal diffusion in a spherical adsorbent particle, the transfer can be represented by the following equation:^{36,37}

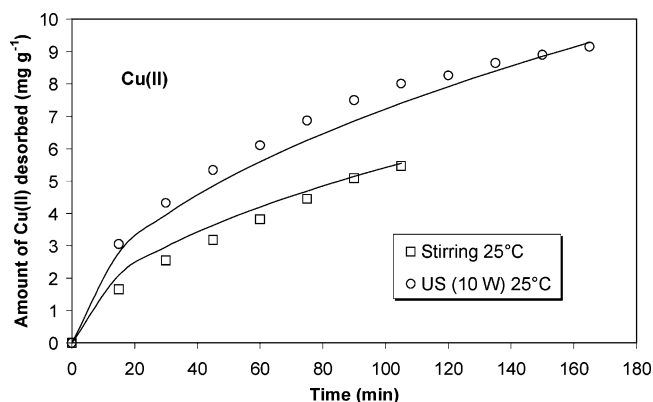
$$\frac{q_d}{q_0} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2 \pi^2 D_s}{r^2} t\right) \quad (1)$$

where q_d is the amount of sorbate desorbed at time t (mg g⁻¹), q_0 is the total amount of sorbate adsorbed (mg g⁻¹), n is an integer that defines the infinite series solution, D_s is the surface diffusion coefficient (cm² s⁻¹), t is the time (s), r is the adsorbent particle radius (cm), and q_d/q_0 is the desorbed fraction.

In the short-time region, eq 1 approaches the limiting parabolic solution form and can be expressed as

$$\frac{q_d}{q_0} = 6 \sqrt{\frac{D_s t}{\pi r^2}} \quad (2)$$

The diffusivity constant (D_s/r^2) is obtained by plotting q_d/q_0 versus $t^{1/2}$ and by determining the slope. The values of the diffusivity constant and the linear correlation coefficient are given in Table 2. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients. A relatively high value of correlation coefficient (close to unity) indicates that the model successfully describes the kinetics of desorption. In addition, the values of the diffusivity constant calculated using the model (Table 2) are in good agreement with the experimental results. It is noticed that the surface diffusion, which is an endothermic process, increases with the temperature rise in both the absence and the presence of ultrasound. Also, the stronger the power intensity of the ultrasonic field is, the higher the value of the surface diffusivity is. The addition of ethanol to the desorption system leads to an enhancement of the surface diffusivity, especially in the presence of ultrasound. For 20% (v/v) ethanol concentration, the diffusivity constant is less than the corresponding one obtained by lower concentrations (5 and 10%). Acidification of the regenerating solution to pH 1 leads to an enhancement of the Cu(II) diffusivity constant. This improvement is more obvious in the presence of the ultrasonic field. In the presence

**Figure 15.** Experimental and simulated results by the surface diffusion model in the absence and presence of ultrasound (10 W) at 25 °C.

of 10% (v/v) ethyl alcohol, pH 1, regenerating solution, the diffusivity constant for Cu(II) is appreciably enhanced, especially in the presence of ultrasound.

Results indicate that surface diffusion is the rate-limiting step for the desorption of metal ions from activated carbon. The values of the surface diffusivity constant in the presence of the ultrasonic field are greater than that obtained in the absence of ultrasound. We assign this behavior to asymmetric cavitation bubble collapse in the vicinity of the sorbent surface leading to the formation of high-speed microjets targeted to the solid surface, high-pressure shock waves generated by cavitation collapse, acoustic vortex microstreaming produced within the pores as well as at the solid–liquid interface, and localized hot spots generating high temperatures and pressures at the surfaces of carbon. The surface diffusivity increases with increasing ultrasound intensities.

As expected, surface diffusivity increases with temperature. The temperature dependence of surface diffusivity may be expressed by the Arrhenius equation:³⁸

$$D_s = D_0 \exp\left(\frac{-E_d}{RT}\right) \quad (3)$$

where E_d is the activation energy of desorption (kcal mol⁻¹), R is the ideal gas constant (kcal mol⁻¹ K⁻¹), T is the absolute temperature (K), and D_0 is the frequency factor.

From eq 3, using the surface diffusivities summarized in Table 2, it can be shown that a plot of $\ln D_s$ versus $1/T$ is linear with a slope of E_d/R . The activation energy for surface diffusion at an ultrasonic power of 10 W is 2.28 kcal mol⁻¹, instead of 5.48 kcal mol⁻¹ in the absence of ultrasound. Ultrasound effectively lowers the energy required for moving sorbate adsorbed from a site to adjacent sites.

The courses of concentration for the desorption experiments conducted at different temperatures in the absence and presence of ultrasound are simulated with the surface diffusion model. An example of the modeling results and the corresponding experimental results are illustrated in Figure 15. The model gives a very good representation of the experimental data and well describes the desorption.

4. Conclusions

The goal of this work was to explore the effects of ultrasound on metal ion desorption from activated carbon.

Ultrasonic irradiation considerably improves the desorbed amounts of metal ions and their kinetics of desorption. The stronger the power intensity of the ultrasonic field is, the higher the amount of metal ions desorbed from the activated carbon is. The rates of desorption increase with increasing temperature.

The addition of ethanol into the regenerating solution increases the desorbed amounts of metal ions, especially in the presence of ultrasound.

The acidification of the regenerating solution to pH 1 enhances the desorption of Cu(II). This rise is more noticeable in the presence of the ultrasonic field.

In the presence of 10% (v/v) ethyl alcohol pH 1 regenerating solution, the desorption of Cu(II) is appreciably enhanced, especially in the presence of ultrasound. The enhancement of repulsive forces and the lowering of the cavitation threshold can explain this behavior.

The improvement of metal ion desorption from activated carbon by ultrasound stems from the enhancement of the surface diffusivity. This improvement is due to both thermal and nonthermal effects of the ultrasonic field; the latter effect is produced by hydrodynamic processes of ultrasound and the former effect is produced by localized hot spots.

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