Ultrasonication-Assisted Sorption of Cadmium from Aqueous Phase by Wheat Bran

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · SEPTEMBER 2007

Impact Factor: 2.69 · DOI: 10.1021/jp0721393 · Source: PubMed

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Ultrasonication-Assisted Sorption of Cadmium from Aqueous Phase by Wheat Bran

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Received: March 17, 2007; In Final Form: June 25, 2007

In the present study, the sorption of cadmium from aqueous phase by wheat bran was investigated with and without the assistance of ultrasound. Kinetic data and sorption equilibrium isotherms were carried out in batch conditions. The influence of different operating parameters such as ultrasonic power, cadmium initial concentration, sorbent mass, temperature, and the combination of ultrasound and mechanical stirring on the kinetics of cadmium removal was studied. The obtained results show that the ultrasonic irradiation significantly enhances and improves the efficiency of the removal of cadmium, especially in the combined method. The sorption kinetic data were found to be well-represented by the pseudo-second-order rate equation, both in the absence and presence of ultrasound as well as in the combined process (stirring and ultrasonication). Ultrasonic power played a key role in the removal of cadmium. Equilibrium isotherm results could be well described by the Langmuir model both with and without the assistance of ultrasound. The effect of temperature on the sorption isotherms of cadmium in the absence and presence of ultrasound has been also studied and the thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ were determined. The monolayer sorption capacities were 51.81, 35.09, and 22.78 mg g^{-1} for experiments conducted by the combined process, in the presence of ultrasound, and in passive conditions, respectively. The combination ultrasound−stirring for the sorption process was shown to be of interest for the treatment of wastewaters contaminated with cadmium.

1. Introduction

Industrial wastewater is often characterized by considerable heavy metal content and, therefore, treatment is required prior to disposal in order to avoid water pollution. Heavy metals are prior toxic pollutants existent in industrial wastewater, while they also constitute common groundwater contaminants. Due to its acute toxicity, cadmium is a heavy metal with the greatest potential hazard to humans and the environment. Cadmium poses a serious threat to human health as it accumulates in the environment throughout the food chain. Besides, the industrial uses of cadmium are widespread and increasing in electroplating, paint pigments, plastics, alloy preparation, mining, ceramics, and silver−cadmium batteries.

Among the numerous treatment technologies developed for the removal of metal ions from industrial effluents, biosorption is receiving increasing attention in becoming an attractive and promising technology. The study of biosorption is of great importance from an environmental point of view, as it can be considered as an alternative technique for removing toxic pollutants from wastewaters.[1,2] Interest has recently been focused on agricultural wastes because of their high metal-sorbing capacity, low cost, and also ready abundance. The potential use of wheat bran as a low cost and easily available agricultural material for the removal of cadmium from aqueous phase is investigated in the present work.

Ultrasound represents mechanical waves, i.e., a variation of pressure or density with frequencies above the human hearing threshold (16 kHz). Ultrasound energy produces an alternating adiabatic compression and rarefaction of the liquid media being irradiated. In the rarefaction part of the ultrasonic wave, microbubbles form because of reduced pressure. These microbubbles contain vaporized liquid or gas that is 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. Cavitating ultrasound forms cavitation bubbles, which violently collapse on or near the sorbent surface and direct microjets of liquids toward it. Additionally, shock waves are also produced as the bubbles collapse, which have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles, also referred to as microstreaming. Acoustic streaming is the movement of the liquid induced by the sonic wave, which can be considered to be the conversion of sound to kinetic energy, and is not a cavitation effect.[3−6]

Many researchers have studied the effects of ultrasound on adsorption processes.[7−17] Ultrasonic waves accelerate mass transport phenomena and thus enhance and improve the sorption rate, but the influence of ultrasound on the sorbed amount at equilibrium and adsorption equilibrium isotherms is very controversial and contradictory. In an earlier work,[7] we have shown that the measured adsorption isotherms shifted toward lower loading in the presence of the ultrasonic field for the adsorption of *p*-chlorophenol onto granular activated carbon. Breitbach and Bathen,[8] Li et al.,[9,10] and Ji et al.[11] have obtained the same tendency for the adsorption of fructose on microporous resin, phenol onto polymeric resin, and Genipisode on polymeric resin, respectively. Schueller and Yang[12] have not found an ultrasonic effect on adsorption isotherms of a polymeric resin loaded with phenol. Qin et al.[13] have found a higher adsorption capacity of weak basic ion exchangers for acetic acids when

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10.1021/jp0721393 CCC: $37.00
Published on Web 08/03/2007

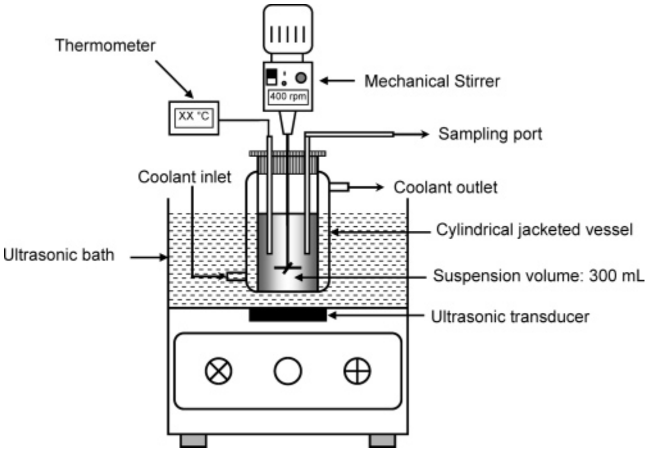

Figure 1. Scheme of experimental setup.

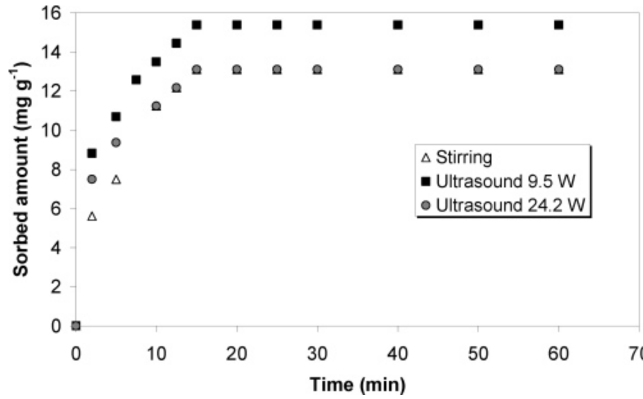

Figure 2. Sorption kinetics of cadmium by wheat bran in the absence and presence of ultrasound (C_0 = 100 mg L^{-1}, sorbent dose = 0.6 g/300 mL, T = 30 °C, pH 5).

applying ultrasound. Recently, the same result has been obtained by some researchers for different sorption systems.[14−17]

The primary objectives of this study are to investigate the sorption of cadmium from aqueous solution by an agricultural waste, wheat bran, in the absence and presence of ultrasound, and to clarify and explain the influence of ultrasound on the sorption kinetics and equilibrium isotherm. The main goal is to find an appropriate combination of ultrasonic irradiation and stirring that could provide maximum efficiency concerning the removal of cadmium from liquid phase by wheat bran.

2. Experimental Section

The wheat bran was obtained from a market as solid waste and was used for sorption experiments. The wheat bran was sieved repeatedly, in order to eliminate wheat semolina, non-wheat bran solids, and fine particles of the material, and dried to constant weight. Finally, the sorbent material was screened to eliminate fine particles (<0.5 mm) and stored in a vacuum desiccator before use.

Cadmium solutions of desired concentration have been prepared by dissolving the appropriate amount of its sulfate ($3CdSO_4 \cdot 8H_2O$, Fluka) in distilled water. All Chemicals used in this study were of analytical grade.

Batch sorption tests were conducted in the experimental setup shown in Figure 1. Experiments were performed in a 400 mL cylindrical jacketed glass vessel that was attached to an overhead mechanical stirrer. The agitator used was a 45°-pitch four-blades-down pumping impeller (diameter 5 cm), which have a good suspension characteristics for the solid particles. The vessel was immersed in an ultrasonic cleaning bath (Fungilab, Spain) operating at a frequency of 40 kHz and two electrical powers of 62.5 and 125 W (indirect sonication). Indirect sonication means that the vessel was immersed in the ultrasonic bath and the mixture was sonicated. For direct sonication, the ultrasonic transducer was mounted at the bottom of the vessel. Determination of the acoustical energy absorbed in the vessel was achieved following the calorimetric method.[5,18] For all the experiments, the cadmium solution volume treated was 300 mL. A predetermined mass of wheat bran was added to each 300 mL batch volume of cadmium ion solution. The mixture was stirred at a fixed agitation speed of 400 rpm (conventional method), sonicated or simultaneously stirred (400 rpm), and sonicated for 60 min. Samples from the mixture were withdrawn at suitable time intervals, filtered through a paper filter, and, if necessary (when wheat bran particles remain in the solution), centrifuged at 3500 rpm for 20 min. These were analyzed by flameless atomic absorption spectrophotometry (Perkin-Elmer A310) for the concentration of cadmium. The sorbed amount was calculated by mass balance. An ultrasonic procedure with the use of an ultrasonic bath was developed and compared with a conventional sorption protocol to assess whether ultrasonic agitation improves the sorption of the heavy metal. Experiments were carried out to study the effects of the cadmium initial concentration, wheat bran dose, and temperature on the sorption process.

Equilibrium isotherms were determined by contacting a fixed mass of wheat bran (0.6 g) with 300 mL of cadmium solutions. A range of cadmium concentrations (100−400 mg L^{-1}) was tested. The mixture was then agitated at a constant speed of 400 rpm or sonicated at different temperatures (20−50 °C). For the isotherm determined by associating stirring and ultrasonication, the mixture was simultaneously agitated and sonicated and the temperature was controlled at 30 °C. After a contact time of 60 min, the solutions were analyzed for the remaining cadmium concentration with atomic absorption spectrometry.

Experimental conditions used for the majority of experiments, such as a temperature of 30 °C, a cadmium initial concentration of 100 mg L^{-1}, and a sorbent dosage of 0.6 g/300 mL, were determined by preliminary tests. A temperature of 30 °C was selected because this was the lower temperature that can be perfectly controlled.

Each experiment was performed twice at least and the mean values were presented. The maximum standard deviation was ±2%.

Preliminary experiments had shown that cadmium sorption losses to the container walls and to the filter paper were negligible.

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

3. Results and Discussion

3.1. Kinetics. *3.1.1. Effect of Ultrasonic Power.* The sorption kinetics of cadmium by wheat bran was studied both in the presence of 40 kHz ultrasonic irradiation of two different power intensities (9.5 and 24.2 W) and in the absence of ultrasound (passive conditions) with simple mechanical stirring. Figure 2 shows the results of the sorption experiments. It was observed that metal sorption occurred rapidly, demonstrating that wheat bran is a good sorbent for cadmium. The sorption efficiency of Cd(II) increased gradually with increasing contact times up to 15 min and reached a plateau afterward. The comparison of the kinetic curves shows that at the beginning the rate of cadmium sorption in the presence of ultrasound is higher than that obtained by the conventional method. The observed variation decreases with time for an ultrasonic power of 24.2 W. The amount of cadmium sorbed at equilibrium in the absence of ultrasound by simple stirring of the wheat bran suspension is exactly equal to the sorbed amount obtained by sonication of the mixture for the higher acoustic power (24.2 W). Both the rate and the amount of cadmium sorption are significantly enhanced and improved in the presence of the ultrasonic field for an ultrasonic power of 9.5 W.

The enhanced sorption of cadmium by ultrasonication may be attributed to the extreme conditions generated during the violent collapse of cavitation bubbles. When the bubble is collapsing near the solid surface, symmetric cavitation is hindered and collapse occurs asymmetrically. The asymmetric collapse of bubbles in a heterogeneous system produces microjets with high velocity. Additionally, 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. Furthermore, 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 sorbent particles and within the pores. As a result, ultrasonication could produce not only high-speed microjets but also high-pressure shock waves and acoustic vortex microstreaming.[5−7,19−22] These actions lead to an improvement of the sorption by an enhancement of mass transfer across the boundary layer as well as into the pores. On the other hand, acoustic streaming, which is the movement of the liquid induced by the ultrasonic wave, enhances and improves the mass transfer into bulk solution as well as at the boundary layer.

The amount of cadmium sorbed by wheat bran decreases with increasing intensity (Figure 2), probably because more cavitation events occur and more ions are desorbed. Thus, it was concluded that high-intensity ultrasound leads to the breaking of bonds formed between metal ions and the sorbent surface and also to the enhancement of mass transfer by high-speed microjets, high-pressure shockwaves, and acoustic vortex microstreaming. Therefore, there is an optimum acoustic power, which can be applied during ultrasonic irradiation in order to obtain maximum sorption capacities.

The ultrasonic power was measured in the absence and presence of wheat bran. The obtained results show that, for the maximum electric power (100%), the measured acoustic powers are 24.2 and 26 W with and without the sorbent, respectively. The obtained ultrasonic powers for the medium electric power (50%) are, respectively, 16.7 and 9.5 W in the absence and presence of wheat bran. In both cases, the acoustic power measured in the presence of wheat bran is lower than that determined in its absence. This indicates that the biosorbent can absorb ultrasonic energy (43% for the medium electric power and 7% for the maximum power) and this absorption can lead to an increase of sorption.

Therefore, intensifying of mass transfer phenomena through acoustic vortex microstreaming, shockwaves, microjets, and thermal effects of ultrasound as well as the absorption of energy by the sorbent could be reasons for the enhancement of sorption at lower intensity.

The pseudo-second-order model proposed by Blanchard et al.[23] and linearized by Ho[24,25] can be represented by eq 1

$$\frac{t}{q} = \frac{1}{Kq_e^{\ 2}} + \frac{1}{q_e}t \qquad (1)$$

where q_e is the amount of cadmium sorbed at equilibrium (mg g^{-1}), q is the amount of cadmium (mg g^{-1}) on the surface of wheat bran at any time, t, and K is the pseudo-second-order rate constant (g mg^{-1} min^{-1}).

TABLE 1: Pseudo-Second-Order Equation Parameters Obtained in the Absence and Presence of Ultrasound and by the Combination of Stirring and Ultrasound

parameters	stirring	ultrasound 9.5 W	ultrasound 24.2 W	stirring + ultrasound: 9.5 W
$K \times 10^3$ (g mg^{-1} min^{-1})	34.59	43.96	54.56	40.99
q_e (mg g^{-1})	13.77	15.9	13.53	21.41
h (mg g^{-1} min^{-1})	6.56	11.11	9.99	18.8
R^2	0.997	0.999	0.999	0.999

The initial sorption rate h (mg g^{-1} min^{-1}) is given by the following equation

$$h = Kq_e^{\ 2} \qquad (2)$$

Linear regression analysis using the pseudo-second-order equation was used to determine the model parameters for the sorption of cadmium by wheat bran. The obtained results are shown in Table 1. The higher coefficients of determination suggest that the pseudo-second-order kinetic equation adequately represent the uptake of cadmium. It was observed that the theoretical sorbed amount at equilibrium and the initial sorption rate values decrease with an increase of acoustic power from 9.5 to 24.2 W. However, the rate constant increased with the rise of ultrasonic power from 9.5 to 24.2 W.

3.1.2. Effect of Sorbate Initial Concentration. The effect of initial cadmium concentration on the kinetics of sorption with and without the assistance of ultrasound (9.5 W) is shown in Figure 3. From this figure, it was observed that the sorption efficiency increased gradually with increasing contact time and reached a plateau afterward. In both cases, an increase in initial cadmium concentration leads to an increase in the sorption capacity of cadmium by wheat bran. Equilibrium uptake increased with the increasing of initial metal ions concentration, especially in the presence of ultrasound. The initial rate of sorption was greater for higher initial cadmium concentration, because the resistance to the metal uptake decreased as the mass transfer driving force increased. Additionally, both the sorbed amount and sorption rate in the presence of ultrasound is higher than that obtained in passive conditions independent of the sorbant initial concentration. This improvement may be explained by the intensification of mass transfer phenomena and thermal effects of ultrasound. Moreover, the sorbent absorbs ultrasonic energy, which is probably another reason for the increase of sorption.

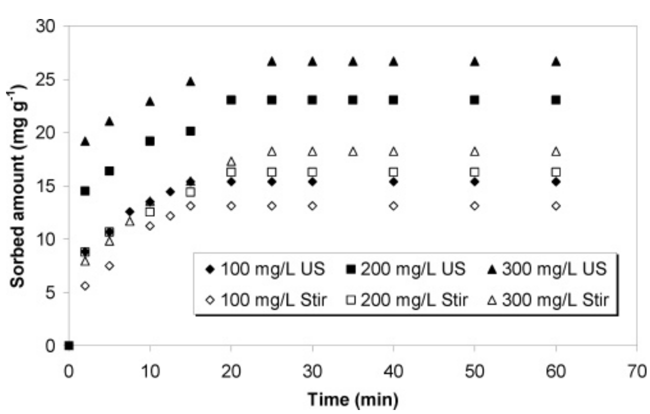

Figure 3. Effect of initial cadmium concentration on the sorption kinetics with and without the assistance of ultrasound (sorbent dose = 0.6 g/300 mL, T = 30 °C, pH 5).

TABLE 2: Pseudo-Second-Order Model Parameters Obtained for Different Operating Conditions Effects

parameters	initial concentration (mg L^{-1})			sorbent mass (g)				temperature (°C)		
	100	200	300	0.4	0.6	0.8	1	20	30	50
Stirring (400 rpm)										
$K \times 10^3$ (g mg^{-1} min^{-1})	34.59	25.6	13.13	37.23	34.59	36.52	26.93	30.24	34.59	46.19
q_e (mg g^{-1})	13.77	17.12	19.84	18.73	13.77	11.31	10.02	12.36	13.77	17.57
h (mg g^{-1} min^{-1})	6.56	7.51	5.17	13.05	6.56	4.67	2.7	4.62	6.56	14.27
R^2	0.997	0.998	0.997	0.999	0.997	0.997	0.994	0.996	0.997	0.999
Ultrasound (9.5 W)										
$K \times 10^3$ (g mg^{-1} min^{-1})	43.96	23.79	29.22	35.82	43.96	49.78	34.5	49.92	43.96	28.85
q_e (mg g^{-1})	15.9	23.98	27.4	25.91	15.9	13.99	11.45	14.9	15.9	20.66
h (mg g^{-1} min^{-1})	11.11	13.68	21.93	24.04	11.11	9.74	4.53	11.09	11.11	12.32
R^2	0.999	0.999	0.999	0.999	0.999	0.999	0.997	0.999	0.999	0.998

Table 2 shows the pseudo-second-order kinetic parameters for different initial concentrations of cadmium obtained by utilizing the linear regression analysis method. The sorption of cadmium by wheat bran for different solute initial concentrations was found to be adequately represented by the pseudo-second-order kinetic model. Increasing the initial metal concentration enhanced both the initial sorption rate and theoretical amount sorbed at equilibrium. Conversely, the pseudo-second-order rate constant decreased with initial cadmium concentration.

3.1.3. Effect of Sorbent Mass. The effect of a variation of sorbent mass on the sorption kinetics of cadmium by wheat bran in the absence and presence of ultrasound is reported in Figure 4. In both cases, the sorption of cadmium increases with an increase in sorbent dosage. This may be attributed to increased sorbent surface area and availability of more sorption sites resulting from the increased dose of the sorbent. But the amount of metal sorbed per unit mass of sorbent decreases with an increase in sorbent dose. At higher wheat bran to solute concentration ratios, there is a very fast superficial sorption onto the sorbent surface that produces a lower solute concentration in the solution than when the biomaterial to solute concentration ratio is lower. This is because a fixed mass of wheat bran can only sorb a certain amount of metal. Therefore, the higher the sorbent dosage is, the larger the volume of effluent that a fixed mass of wheat bran can purify. The decrease in the amount of cadmium sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentrations in the solution and on the sorbent surface.

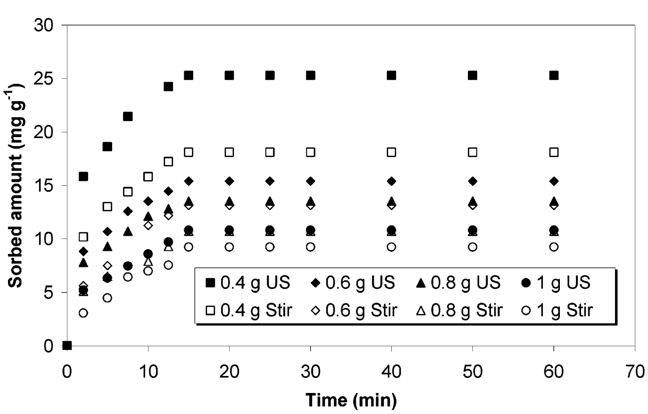

Figure 4. Effect of sorbent mass on the sorption kinetics with and without the assistance of ultrasound (C_0 = 100 mg L^{-1}, solution volume = 300 mL, T = 30 °C).

Both the rate of sorption and the amount of cadmium sorbed in the presence of the ultrasonic field are higher than those obtained in the classical method, whatever the sorbent dose is. This behavior could be related to the higher mass transfer in the presence of the ultrasonic irradiation. Microjets and shock-waves produced by the cavitation can disrupt the structure of the sorbate and lead to a higher sorption capacity.

A scanning electron microscope was used to look at the effect of ultrasound on the morphology of wheat bran particles. Figure 5 shows the SEM photographs of the biosorbent surface at two different magnifications (1000× and 5000×) before and after ultrasonication. Without ultrasonication, the particles are microscopically smooth and macroscopically rough. After 60 min of ultrasonication, ultrasound created a microscopically rough and pitted surface morphology. Shock waves and microjets should be the major mechanisms affecting particle morphology. On the other hand, shock waves created by cavitational collapse in the liquid and acoustic streaming may drive interparticle collisions with the speed of several hundred meters per second.[5] In addition, shock waves impinge on the particles, generating local surface pitting and microscopic erosion. On the basis of the surface morphology changes observed, an increase of surface area would be intuitively expected. Increased cadmium removal would be a consequence of newly formed sorption sites.

The experimental kinetic data were fitted to the pseudo-second-order equation using the linear regression analysis method. The determined parameters of the model are shown in Table 2. The sorption of cadmium by wheat bran was found to be well-represented by the pseudo-second-order kinetic equation. Increasing the dose of wheat bran enhances the rate constant. However, the initial sorption rate and theoretical normalized amount sorbed at equilibrium decrease with the increase of sorbent mass.

3.1.4. Effect of Temperature. Figure 6 presents the removal of cadmium as a function of time at different temperatures (20, 30, and 50 °C) without and with the assistance of ultrasound. In both cases, the sorption capacity of wheat bran increased with increasing temperature. This indicates that the sorption process is endothermic in nature. Similar results were reported for the biosorption of cadmium by spent grain,[26] natural and oxidized corncob,[27] rice husk,[28] and Kraft lignin.[29] As is known, the rate of diffusion of the sorbate ions is increased by increasing the temperature, owing to the decrease in the viscosity of the solution. This enhancement is felt to be due to the acceleration of the sorption process by the increased movement of metal

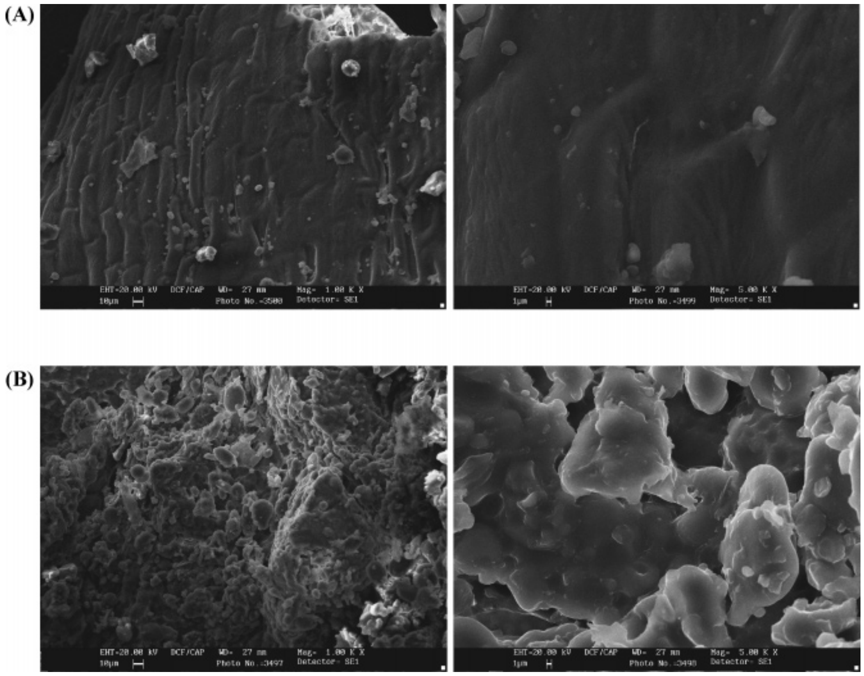

Figure 5. SEM images of particle morphology (1000× and 5000×): (A) without ultrasonication and (B) after 60 min of ultrasonication at power 9.5 W.

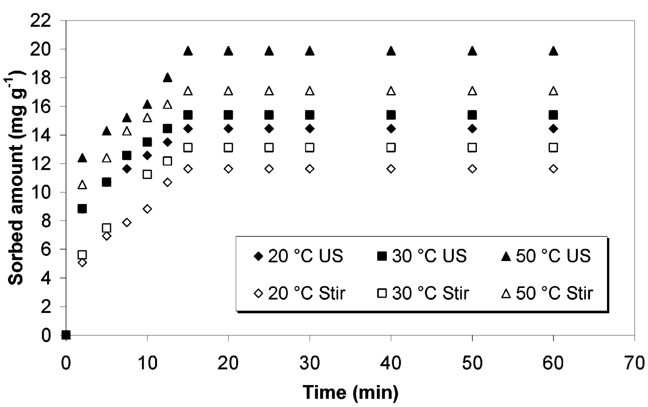

Figure 6. Effect of temperature on the sorption kinetics with and without the assistance of ultrasound (C_0 = 100 mg L^{-1}, sorbent dose = 0.6 g/300 mL, T = 30 °C).

ions from the bulk solution to the surface of the solid particles at higher temperatures. Additionally, in the presence of the ultrasonic irradiation, both the rate of sorption and the amount of cadmium sorbed are higher than those obtained in the conventional method for all the studied temperatures. Cavitating bubbles are more easily produced at high temperature because of the decrease of the liquid tensile stress and viscosity. In addition, sorption of cadmium by wheat bran, which is an endothermic process, is promoted if such bubble collapse occurs in the vicinity of the sorbent surface.

The above results indicate that the effects of ultrasound on the enhancement of sorption processes consist of both non-thermal effects and thermal properties. 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 is mostly produced by the acoustic vortex microstreaming and by the high-speed microjets and high-pressure shockwaves induced by acoustic cavitation.[20] This behavior shows that the influence of ultrasound on the sorption is highly dependent on the examined substance as the heat of sorption determines the quantum of energy required by a cavitation event to improve the interaction between a sorbate and a sorbent.

The kinetic results were correlated with the pseudo-second-order rate equation by using the linear regression method, and the obtained parameters are listed in Table 2. Both in the absence and presence of ultrasound, the theoretical amount sorbed at equilibrium and initial sorption rate increased with the increase in temperature. However, the pseudo-second-order kinetic constant increased with the rise in temperature in the absence of ultrasound and decreased in the presence of the ultrasonic field.

The Arrhenius equation for the pseudo-second-order kinetic model is given as follows

$$K = A_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (3)$$

where A_0 is the temperature-independent factor (g mg^{-1} min^{-1}), E_a the activation energy of sorption (kJ mol^{-1}), R the gas constant (kJ mol^{-1} K^{-1}), and T the solution temperature (K). The slope of the plot of ln K versus $1/T$ is used to evaluate the activation energy (figure not shown). The magnitude of activation energy gives an idea about the type of sorption that is mainly physical or chemical. Low activation energies (5−40 kJ mol^{-1}) are characteristic for physisorption, while higher activation energies (40−800 kJ mol^{-1}) suggest chemisorption.[30] The activation energy obtained in the absence of ultrasound is 11.19 kJ mol^{-1}, indicating that the sorption has a potential barrier and corresponds to physisorption. With the assistance of ultrasound, the determined activation energy is reduced and a negative value (−14.71 kJ mol^{-1}) is obtained. Central events of the ultrasonic action are the bubbles of cavitation that grow, pulsate, and suddenly collapse in the irradiated medium. On the microscale, high bubble temperatures up to 5000 K and pressures up to 1000 atm have been estimated.[5] Thus, ultrasound provides to the medium a lot of energy, leading to the reduction of the potential barrier of sorption, and thus a negative activation energy would imply that the sorption occurs without an energy barrier. Some results that support this conclusion were presented

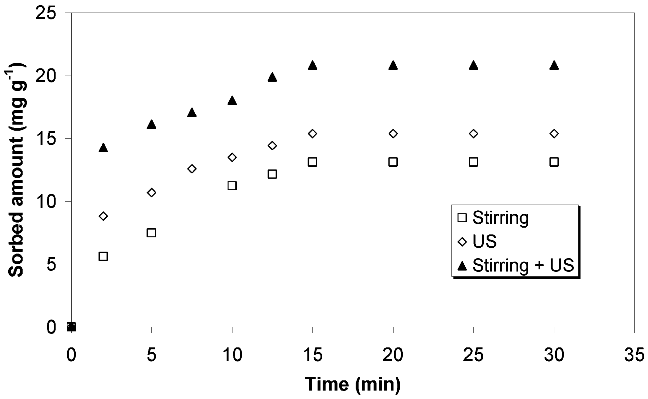

Figure 7. Effect of the combination stirring and ultrasound on the sorption kinetics of cadmium by wheat bran (C_0 = 100 mg L^{-1}, sorbent dose = 0.6 g/300 mL, T = 30 °C).

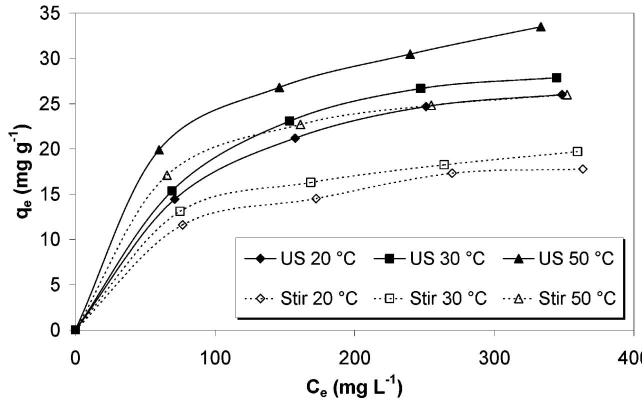

Figure 8. Sorption isotherms of cadmium by wheat bran in the absence and presence of ultrasound (C_0 = 100−400 mg L^{-1}, sorbent dose = 0.6 g/300 mL, pH 5, time = 60 min).

by Shimizu et al.,[31] who found that ultrasound lowered the activation energy of dye adsorbed on Nylon 6. Schueller et al.[12] and Hamdaoui et al.[22] also showed that acoustic waves could effectively lower the activation energy required for the mobility of phenolic compounds on an activated carbon surface.

3.1.5. Effect of the Combination of Ultrasound and Stirring. The influence of the combination of ultrasonic irradiation (9.5 W) and mechanical stirring (400 rpm) on the sorption of cadmium ions by wheat bran was investigated at 30 °C. The obtained results compared with the sorption kinetics obtained in the presence of ultrasound and by simple stirring (passive conditions) are presented in Figure 7. From this figure, it is clearly showed that the application of ultrasound enhances the rate and the amount of sorption. An appropriate combination of the ultrasonic irradiation and mechanical stirring provides maximum efficiency concerning the removal of cadmium from liquid phase by the biosorbent. This behavior could be explained by the strong convective currents occurring within the reactor. These effects associated with the hydrodynamic phenomenon due to cavitation and mechanical stirring are responsible for the perfect mixing of the vessel content. It was thereby established that under ultrasonic irradiation the used vessel is a completely stirred tank reactor (CSTR).[22] The thickness of the boundary layer between the fluid and the solid decreases as the mass-transfer coefficient increases. Microjets and shockwaves produced by the cavitation can disrupt the structure of the sorbent and lead to a higher sorption capacity. Additionally, extreme conditions produced by acoustic cavitation lead to high pressure and high temperature on the surface of the solid that can change the morphology of the surface and the biosorbent granulometry.[7,8,21,22] These phenomena might produce new sites for sorption that cause a higher removal of pollutant from aqueous solution.

3.2. Equilibrium Isotherms. The analysis and design of the sorption process require the relevant sorption equilibria, which is the most important piece of information to understand the sorption process. The sorption equilibrium provides fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation.

Figure 8 presents the amount of cadmium sorbed at 20, 30, 40, and 50 °C plotted against its concentration in the aqueous phase at equilibrium determined in the absence of ultrasound and in the presence of an ultrasonic field with a calorimetric power of 9.5 W at a frequency of 40 kHz. In both cases, isotherm data obtained with a range of initial cadmium concentration showed an increase in the amount of cadmium sorbed when the initial metal concentration was raised. Additionally, the amount of metal sorbed increased following an increase in temperature from 20 to 50 °C. The shape of the curves clearly indicated that the isotherms for all temperatures are L-type according to the classification of equilibrium isotherms in solution by Giles et al.[32]

The comparison between the sorption isotherms of cadmium by wheat bran shows that the plateaus of sorbent saturation obtained in the presence of ultrasound are higher than those obtained in passive conditions, whatever the solution temperature is. Ultrasound does not appear to modify the sorption process but shifts the equilibrium toward higher sorption capacities.

The enhancement of sorption capacity with the assistance of ultrasound is related to hydrodynamic and thermal processes generated by acoustic cavitation as well as to the strong convective currents occurring within the vessel here and there along the transducer axis. These actions lead to an improvement of the sorption of cadmium by the biomaterial. In our previous work,[7] we have shown that the adsorption equilibrium was shifted to lower adsorbed amounts when investigating the adsorption of 4-chlorophenol onto granular activated carbon using an ultrasonic reactor operating at a frequency of 21 kHz. Similar results were reported by Breitbach and Bathen,[8] Li et al.,[9,10] and Ji et al.[11] for the adsorption of fructose on microporous resin, phenol onto polymeric resin, and Genipisode on polymeric resin, respectively. In all cases, ultrasound is able to intensify both the mass transfer as well as the rate of sorption. The increase or decrease of the sorbed amount at equilibrium is a function of the applied ultrasonic power. In these studies,[7−11] the used ultrasonic power is high, which enhances the sorption rate but decreases the sorption capacity. The stronger the acoustic power delivered to the sorption system, the lower the corresponding isotherm. Thus, ultrasonication intensifies the sorption rate in all cases but reduces the sorption capacity for higher ultrasonic power and enhances the sorption amount at equilibrium for lower acoustic power.

The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes. The sorption data for cadmium by wheat bran at different temperatures in the absence and presence of ultrasound were analyzed using the linear forms of the Langmuir and Freundlich models (eqs 4 and 5).

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{bq_m} \qquad (4)$$

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (5)$$

where q_e is the amount of pollutant sorbed per unit weight of

TABLE 3: Parameters of the Langmiur and Freundlich Models at Different Temperatures and Thermodynamic Parameter Values

parameters	stirring, 400 rpm 20 °C	30 °C	50 °C	ultrasound, 9.5 W 20 °C	30 °C	50 °C	stirring + ultrasound, 9.5 W, 30 °C
b (L mg^{-1}) × 10^3	14.68	16.42	20.83	11.4	11.93	15.66	11.86
q_m (mg g^{-1})	21.19	22.78	29.5	32.79	35.09	39.37	51.81
R^2	0.995	0.997	1	0.999	0.998	0.997	0.999
$\Delta G°$ (kJ mol^{-1})	−18.05	−18.95	−20.83	−17.43	−18.14	−20.07	−
$\Delta H°$ (kJ mol^{-1})	9.26			8.76			−
$\Delta S°$ (J mol^{-1} K^{-1})	93.1			89.1			−
n	3.48	3.84	3.3	2.63	2.63	3.3	2.49
K_F (mg$^{1-(1/n)}$ L$^{(1/n)}$ g^{-1})	3.34	4.27	6.01	2.95	3.19	5.81	4.24
R^2	0.983	0.999	0.977	0.97	0.957	0.997	0.971

sorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of the solute in the bulk solution (mg L^{-1}), q_m is the maximum sorption capacity (mg g^{-1}), b is a constant related to the free energy of adsorption (L mg^{-1}), K_F is a constant indicative of the relative sorption capacity of the sorbent (mg$^{1-(1/n)}$ L$^{(1/n)}$ g^{-1}), and n is a constant indicative of the intensity of the sorption.

Table 3 shows the isotherm parameters obtained using the linear regression method. The obtained results indicate that the Langmuir model gave a more acceptable fit to the experimental data than the Freundlich equation.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L[33]

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where b is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration of cadmium (mg L^{-1}).

The parameter R_L indicated the shape of isotherm as follows: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$, favorable; $R_L = 0$, irreversible.

The value of R_L in the range of 0−1 at all initial metal concentrations and for all solution temperature conditions confirms the favorable uptake of cadmium.

3.2.1. Thermodynamic Parameters. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change ($\Delta G°$) is the basic criterion of spontaneity, and a negative value indicates the reaction to be spontaneous. By using the equilibrium constant (b_M) obtained for each temperature from the Langmuir model using the linear method (Table 3), $\Delta G°$ can be calculated according to eq 7.

$$\Delta G° = -RT \ln b_M \tag{7}$$

$$\Delta G° = \Delta H° - T\Delta S° \tag{8}$$

where $\Delta G°$, $\Delta H°$, and $\Delta S°$ are the changes in free energy, enthalpy, and entropy, respectively.

The thermodynamic parameter, $\Delta G°$, is shown in Table 3. $\Delta G°$ is negative and decreases with an increase in temperature, indicating that sorption of cadmium by wheat bran is spontaneous and spontaneity increases with an increase in temperature. From Table 3, the values of the enthalpy change indicate that the sorption is physical in nature, involving weak forces of attraction, and is also endothermic, thereby demonstrating that the process is stable energetically. Positive values of the entropy change show the increased randomness at the solid/solution interface during the sorption of metal ions and an affinity of the sorbent toward cadmium. The values of standard entropy change are not very large and indicate an increase due to sorption. Normally, adsorption of gases leads to a decrease in entropy due to orderly arrangement of the gas molecules on a solid surface. However, the same may not be true for the complicated system of sorption from solution onto wheat bran.

3.2.2. Effect of the Combination of Ultrasound and Stirring. Equilibrium isotherm for the sorption of cadmium by wheat bran obtained at 30 °C by the combination of ultrasound (9.5 W) and mechanical stirring (400 rpm) is compared with those determined in the absence of ultrasound by simple stirring and obtained in the presence of the ultrasonic field (Figure 9). It can be seen that the sorption isotherm of cadmium for the combined method is much higher than that determined in the presence of ultrasound. A correct combination of ultrasonic irradiation and mechanical stirring provides maximum efficiency concerning the removal of cadmium from liquid phase by the biosorbent. The reason is that the effects associated with the hydrodynamic phenomena due to ultrasound and mechanical stirring are responsible for the ideal mixing of the vessel content. Microjets, shockwaves, and microstreaming as well as extreme conditions of high temperature and pressure produced by acoustic cavitation can disrupt the structure of the sorbent and may create new sites for sorption, which leads to a higher sorption capacity. According to the classification of Giles et al.,[32] the isotherm obtained by the combined process displayed an L curve pattern.

The analysis of the isotherm data is performed by fitting them to Langmuir and Freundlich models using the linear regression method. Table 3 shows the isotherms' parameters and the coefficient of determination. As shown in this table, the determination coefficients indicate that the Langmuir isotherm properly fits the equilibrium data better than the Freundlich equation. The monolayer sorption capacities are 51.81, 35.09,

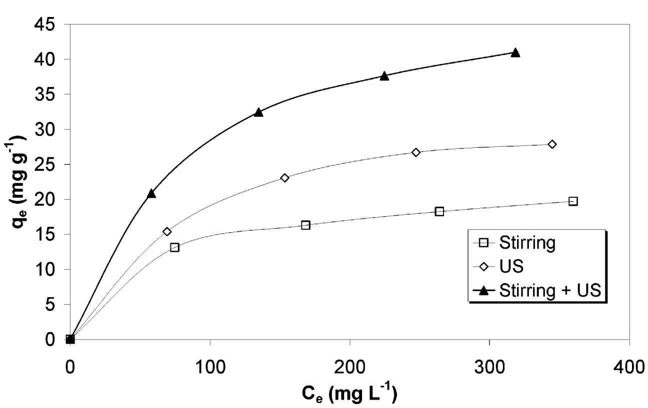

Figure 9. Effect of the combination of stirring and ultrasound on the sorption isotherms of cadmium by wheat bran ($C_0 = 100{-}400$ mg L^{-1}, sorbent dose = 0.6 g/300 mL, 30 °C, pH 5, time = 60 min).

and 22.78 mg g^{-1} for experiments conducted by the combined process, in the presence of ultrasound, and in passive conditions, respectively.

4. Conclusion

The removal of cadmium ions from aqueous phase by wheat bran was significantly enhanced and improved in the presence of ultrasound, especially by the combined method. Ultrasonic power played a key role in the removal of cadmium. In all cases, i.e., stirring, ultrasonication, and its combination, equilibrium and kinetic data fit the Langmuir model and the pseudo-second-order expression, respectively. The combination ultrasound−stirring for the sorption process was shown to be of interest for the treatment of wastewaters contaminated with cadmium.

Acknowledgment. The authors are grateful to the Ministry of Higher Education and Scientific Research of Algeria for financial assistance (Project No. J 0101120060043).

References and Notes

(1) Veglio, F.; Beolchini, F. Removal of metals by biosorption: A review. *Hydrometallurgy* **1997**, *44*, 301−316.

(2) Vieira, R. H. S. F.; Volesky, B. Biosorption: A solution to pollution? *Int. Microbiol.* **2000**, *3*, 17−24.

(3) Suslick, K. S. *The Yearbook of Science and the Future;* Encyclopedia Britannica: Chicago, 1994; pp 138−155.

(4) Mason, T. J.; Lorimer J. P. *Applied Sonochemistry;* Wiley-VCH Verlag GmbH: Weinheim, Germany, 2002.

(5) Mason T. J. *Practical Sonochemistry: User's Guide to Applications in Chemistry and Chemical Engineering;* Ellis Horwood: Chichester, 1991.

(6) Thompson, L. H.; Doraiswamy, L. K. Sonochemistry: Science and engineering. *Ind. Eng. Chem. Res.* **1999**, *38*, 1215−1249.

(7) Hamdaoui, O.; Naffrechoux, E.; Tifouti, L.; Pétrier, C. Effects of ultrasound on adsorption−desorption of *p*-chlorophenol on granular activated carbon. *Ultrason. Sonochem.* **2003**, *10*, 109−114.

(8) Breitbach, M.; Bathen, D. Influence of ultrasound on adsorption processes. *Ultrason. Sonochem.* **2001**, *8*, 277−283.

(9) Li, Z.; Li, X.; Xi, H.; Hua, B. Effects of ultrasound on adsorption equilibrium of phenol on polymeric adsorption resin. *Chem. Eng. J.* **2002**, *86*, 375−379.

(10) Li, Z.; Xu, K.; Li, X.; Xi, H.; Hua, B.; Li, F. Effect of ultrasound on desorption kinetics of phenol from polymeric resin. *Ultrason. Sonochem.* **2006**, *13*, 225−231

(11) Ji, J. B.; Lu, X.-h.; Xu, Z.-C. Effect of ultrasound on adsorption of Geniposide on polymeric resin. *Ultrason. Sonochem.* **2006**, *13*, 463−470.

(12) Schueller, B. S.; Yang, R. T. Ultrasound enhanced adsorption and desorption of phenol on activated carbon and polymeric resin. *Ind. Eng. Chem. Res.* **2001**, *40*, 4912−4918.

(13) Qin, W.; Wang, D.; Dai, Y. Effect of ultrasound on resin adsorption dynamics of acetic acids. *Qinghua Daxue Xuebao, Ziran Kexueban* **2001**, *41*, 28−31.

(14) Entezari, M. H.; Ghows, N.; Chamsaz M. Combination of ultrasound and discarded tire rubber: removal of Cr(III) from aqueous solution. *J. Phys. Chem. A* **2005**, *109*, 4638−4642.

(15) Entezari, M. H.; Ghows, N.; Chamsaz M. Ultrasound facilitates and improves removal of Cd(II) from aqueous solution by the discarded tire rubber. *J. Hazard. Mater. B* **2006**, *131*, 84−89.

(16) Entezari, M. H.; Rohani Bastami, T. Sono-sorption as a new method for the removal of lead ion from aqueous solution. *J. Hazard. Mater. B* **2006**, *137*, 959−964.

(17) Juang, R. S.; Lin, S. H.; Cheng, C. H. Liquid-phase adsorption and desorption of phenol onto activated carbons with ultrasound. *Ultrason. Sonochem.* **2006**, *13*, 251−260.

(18) Mason, T. J.; Lorimer, J. P.; Bates, D. M. Quantifying sonochemistry: Casting some light on a 'black art'. *Ultrasonics* **1992**, *30*, 40−42.

(19) Adewuyi, Y. G. Sonochemistry: Environmental science and engineering applications. *Ind. Eng. Chem. Res.* **2001**, *40*, 4681−4715.

(20) Hamdaoui, O.; Naffrechoux, E. An investigation of the mechanisms of ultrasonically enhanced desorption. *AIChE J*. **2007**, *53*, 363−373.

(21) Hamdaoui, O.; Naffrechoux, E.; Suptil, J.; Fachinger, C. Ultrasonic desorption of p-chlorophenol from granular activated carbon. *Chem. Eng. J.* **2005**, *106*, 153−161.

(22) Hamdaoui, O.; Djeribi, R.; Naffrechoux, E. Desorption of metal ions from activated carbon in the presence of ultrasound. *Ind. Eng. Chem. Res.* **2005**, *44*, 4737−4744.

(23) Blanchard, G.; Maunaye, M.; Martin, G. Removal of heavy metals from waters by means of natural zeolites. *Water Res.* **1984**, *18*, 1501−1507.

(24) Ho, Y. S. Adsorption of heavy metals from waste streams by peat. Ph.D. thesis, 1995, University of Birmingham, Birmingham, UK.

(25) Ho, Y. S.; McKay, G. The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* **2000**, *34*, 735−742.

(26) Low, K. S.; Lee, C. K.; Liew, S. C. Sorption of cadmium and lead from aqueous solutions by spent grain. *Process Biochem.* **2000**, *36*, 59−64.

(27) Leyva-Ramos, R.; Bernal-Jacome, L. A.; Acosta-Rodriguez, I. Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob. *Sep. Purif. Technol.* **2005**, *45*, 41−49.

(28) Ajmal, M.; Rao, R. A. K.; Anwar, S.; Ahmad, J.; Ahmad, R. Adsorption studies on rice husk: Removal and recovery of Cd(II) from wastewater. *Bioresour. Technol.* **2003**, *86*, 147−149.

(29) Mohan, D.; Pittman, C. U. J.; Steele, P. H. Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin−A biosorbent. *J. Colloid Interface Sci.* **2006**, *297*, 489−504.

(30) Nollet, H.; Roels, M.; Lutgen, P.; Van der Meeren, P.; Verstraete, W. Removal of PCBs from wastewater using fly ash. *Chemosphere* **2003**, *53*, 655−665.

(31) Shimizu, Y.; Yamamoto, R.; Shimizu, H. Effects of ultrasound on dyeing of Nylon 6. *Textile Res. J.* **1989**, *59*, 684−687.

(32) Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurements of specific surface areas of solids. *J. Chem. Soc.* **1960**, *10*, 3973−3993.

(33) Hall, K. R.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T. Pore and solid diffusion kinetics in fixed-bed adsorption under constant pattern conditions. *Ind. Eng. Chem. Fundam* **1966**, *5*, 212−223.