# Combination of Ultrasound and Discarded Tire Rubber: Removal of Cr(III) from Aqueous Solution

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Ground discarded tire rubber is an interesting and inexpensive medium for the sorption of toxic metals, including chromium, from water. The batch sorption tests were conducted to investigate the sorption capacity of Cr(III) from aqueous solution by ground tire in the presence and absence of ultrasound. The research parameters included ultrasonic waves, solution temperature, aqueous chromium concentration, particle size of the ground tire, contact time, and others. The Langmuir model was applied to the sorption equilibrium to determine the maximum metal sorption capacity in the presence and absence of ultrasound. The Langmuir constants were also obtained from the isotherms under different conditions. The results indicated that the tire rubber was a more efficient sorbent for the removal of chromium in the presence of ultrasound. Because there are several stages in the sorption process, it is important to find out which step or steps control the rate of sorption. According to the results, the internal porous diffusion is the rate-controlling step. The diffusion coefficient of Cr(III) in ground tire rubber in the presence of ultrasound was about two times greater than that in the absence of ultrasound. The effect of ultrasound on the sorption process could be explained by the thermal and nonthermal properties of acoustic cavitation.

## Introduction

Industrial wastewaters often contain considerable amounts of heavy metals that would endanger public health and the environment. Pollution by chromium is of considerable concern because its use is widespread in electroplating, leather tanning, metal finishing, textile industries, and chromate preparation. Chromium is considered by the IARC[1] as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberrations.[2,3] The National Institute for Occupational Safety and Health (NIOSH) recommends that the level of chromium in water should be reduced to $10^{-3}$ mg/m$^3$.[4] Several treatment methods including ion exchange, reduction, precipitation, and activated-carbon adsorption have been used to remove chromium from wastewaters.[5−7] Activated carbon is an efficient adsorbent for chromium, but its high cost has led to an extensive search for low-cost adsorbents such as natural moss,[8] agricultural residues, and organic wastes.[9−11] Discarded tire rubber has caused many public health and environmental problems, and it can be used as an inexpensive sorbent. This sorbent provides a convenient method for removing a broad range of inorganic pollutants.[12,13] This paper focuses on the removal of Cr(III) by ground discarded tire rubber in the presence and absence of ultrasound. Acoustic cavitation produced by ultrasonic waves strongly affects the mass transfer between two phases; it is well understood that it has a greater efficiency on the interface mixing than conventional agitation,[14,15] and therefore ultrasound enhances the kinetics of the sorption process.[16−18] In addition, ultrasonic waves can also change the morphology and the size of the sorbent particles, which can lead to a change of the equilibrium position.

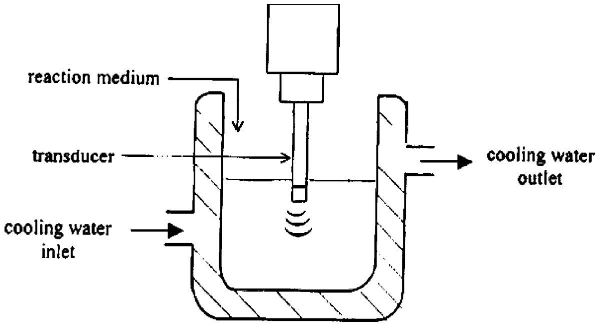

**Figure 1.** Scheme of the experimental setup for sorption under an ultrasonic field.

## Materials and Methods

**Materials.** Ground discarded tire rubber with a particle size of 0.4 mm was prepared from the Yazd Tire Company, Iran. Chromium(III) nitrate (98−100%) was from BDH. A stock solution of chromium was prepared in deionized distilled water with a concentration of 1000 ppm. This solution was diluted as required to obtain standard solutions.

**Apparatus.** The ultrasonic irradiation was carried out with equipment operating at 20 kHz. Ultrasonic waves were emitted from a titanium horn with a diameter of 1.2 cm. The cylindrical sonochemical reactor (volume = 100 mL) was thermostated by a water jacket (Figure 1). The ultrasonic energy dissipated in the reactor was estimated to be 30 W by the calorimetric method.

**Analysis.** The chromium concentration was determined by an atomic absorption spectrophotometer (Shimadzu-AA-670).

**Procedure.** The batch experiments were conducted by adding 1.0 g of ground tire to 60 mL of a chromium aqueous solution of desired concentration and stirred continuously at different temperatures. Equilibrium was achieved after 4 h. In the case

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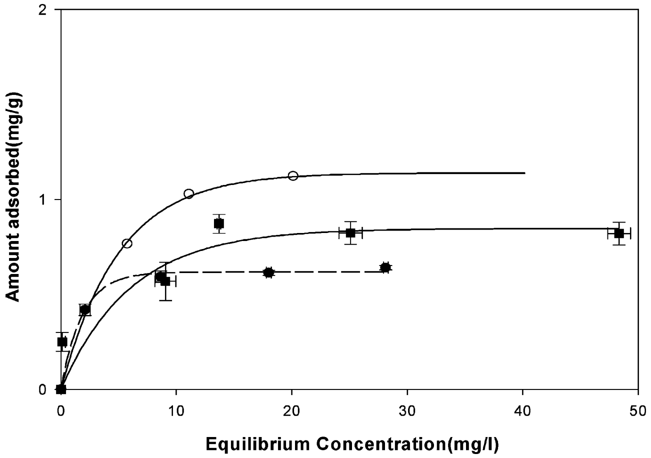

**Figure 2.** Sorption isotherms of Cr(III) on tire powder in the presence of ultrasound, stirring and a combination at 30 °C: (■) stirring, (●) sonication, (○) stirring + sonication.

of sonication, two methods were applied to determine the sorption isotherm of Cr(III) on the powder of tires under an ultrasonic field. In one method, the system was conducted to equilibrium under classical conditions and then ultrasound was applied. In another method, the ultrasonic waves were applied continuously on the system from the initial time. Aliquots were withdrawn at different interval times for analysis.

## Results and Discussion

**Sorption Isotherms.** Figure 2 shows the experimental results obtained for the sorption of chromium on the discarded tire rubber powder at 30 °C in the presence and absence of ultrasound. The isotherms exhibit a Langmuir shape for the three studied cases (stirring, sonicating, and its combination). By stirring, the contact time was 4 h and for sonication it was 1 h. In the combined method, the suspension was stirred for 4 h and then ultrasound was applied for 20 min. In the presence of ultrasound, the isotherms also exhibited a Langmuir shape but it was shifted. The comparison of the stirred and combined method clearly showed that the applying of ultrasound changed the equilibrium for each point to the higher sorption. This behavior could be explained by the cavitation process. During sonication, cavitation bubbles transfer energy by growing and then reach a critical size and collapse. As the bubble collapses, localized high temperature and pressure are produced in the bubble. Ultrasonic cavitation has an influence on the adsorption and desorption processes. Because the concentration of chromium in the solution during sonication was reduced, it is concluded that the effect of ultrasound on adsorption was higher than that on desorption. The enhancement of sorption in the presence of ultrasound could be related to the asymmetric collapse of the bubble near the solid particles of tire, which are much larger than the size of bubble. This collapse leads to microjets of solvent and shock waves that have the potential of creating microscopic turbulence within the interfacial film surrounding nearby solid particles. This is supposed to increase the external mass transfer and thus enhance the sorption kinetics. The critical conditions produced by acoustic cavitation lead to high pressure on the surface of the tire particles that can change the morphology of the surface and the size of the particles.[16−18] This process might produce new sites for sorption that cause a higher removal of pollutant from aqueous solution and change the equilibrium position.

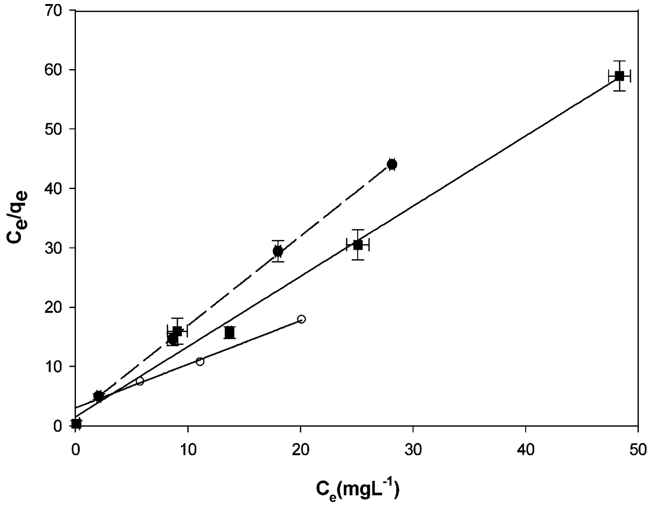

**Figure 3.** Linear form of the Langmuir model at 30 °C: (■) stirring, (●) sonication, (○) stirring + sonication.

**TABLE 1: Langmuir Constants for the Uptake of Cr(III) from Solution by Different Methods**

| | | Langmuir | | |
|---|---|---|---|---|
| method | $t$ (°C) | $Q_o$ (mg g$^{-1}$) | $b$ (lit mg$^{-1}$) | $R^2$ |
| stirring | 30 | 0.85 (±0.13) | 0.77 | 0.98 |
| | 40 | 2.21 | 1.75 | 0.99 |
| | 50 | 2.34 | 3.75 | |
| st + us | 30 | 1.36 (±0.12) | 0.24 | 0.99 |
| ultrasound | 30 | 0.82 | 0.66 | 0.99 |
| | 40 | 1.50 | 1.30 | 0.99 |
| | 50 | 2.06 | 2.65 | |

The data for sorption of Cr(III) on rubber were better fitted to a Langmuir isotherm than to a Freundlich isotherm. The linear form of the Langmuir model is represented by eq 1

$$\frac{c_e}{q_e} = \left(\frac{1}{Q_o b}\right) + \left(\frac{1}{Q_o}\right) c_e \tag{1}$$

where $q_e$ is the amount of solute sorbed per unit weight of sorbent (mg g$^{-1}$) at equilibrium, $c_e$ is the equilibrium concentration or concentration in the bulk fluid phase (mg l$^{-1}$), $Q_o$ is the solid-phase concentration corresponding to complete coverage of available sorption sites (mg g$^{-1}$), and $b$ is a characteristic constant that is related to the free energy ($b \propto e^{-\Delta G/RT}$) and the intensity of sorption. A linear plot of ($c_e/q_e$) against $c_e$ was employed to give the values of $Q_o$ and $b$ from the slope and the intercept of the line. Figure 3 shows the applicability of the Langmuir model, and its parameters are given in Table 1.

**Effect of Temperature.** Figure 4 shows the effect of temperature on the sorption of Cr(III) in the presence and absence of ultrasound. The sorption capacity of rubber in the presence of ultrasound was increased with increasing temperature. In addition, the slope of the curves (rate of sorption) at the initial times was bigger at higher temperatures. For a comparison, the curves obtained with the stirring method in the same period of time were showed in the same Figure. Higher temperature was also more effective than lower temperature in the absence of ultrasound for the removal of the chromium ion. This indicates that the sorption process was endothermic in nature. According to the concentration of pollutant in the solution and the amount of sorbent in the studied range of temperature, the enhancement induced by temperature increase was 53−100% in the presence of ultrasound, and 25−82% in the absence of ultrasound (stirring) in 60 min.

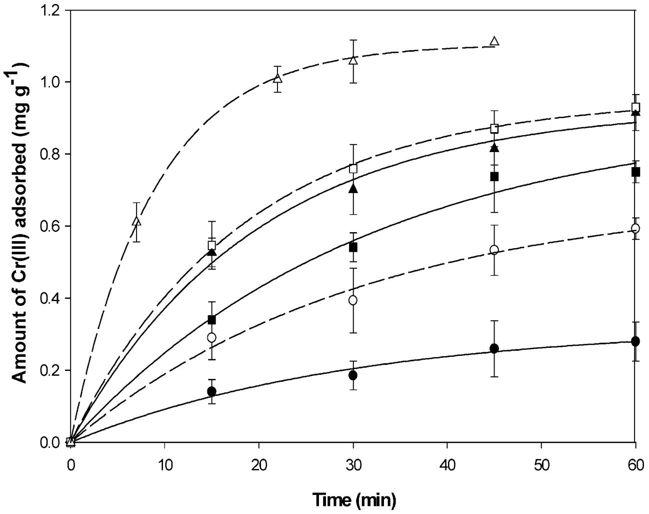

**Figure 4.** Effect of temperature on the sorption of Cr(III) in the presence and absence of ultrasound (sorbent = 1 g, pollutant = 18.50 ppm): (●) stirring (30 °C), (■) stirring (40 °C), (▲) stirring (50 °C), (○) sonication (30 °C), (□) sonication (40 °C), (△) sonication (50 °C).

**TABLE 2: Effects of Rubber Particle Size on Removal of Pollutant**[a]

| % adsorbed (ultrasound) | % adsorbed (stirring) | size |
|---|---|---|
| 33.71 (±0/08) | 11.88 (±0.04) | 0.353−0.500 mm |
| 41.39 (±0.34) | 26.12 (±0.34) | 0.177−0.250 mm |
| 46.60 (±0.32) | 30.37 (±0.92) | 0.088−0.125 mm |

[a] Temperature = 30 °C, pollutant concentration = 18.51 ppm, time = 30 min.

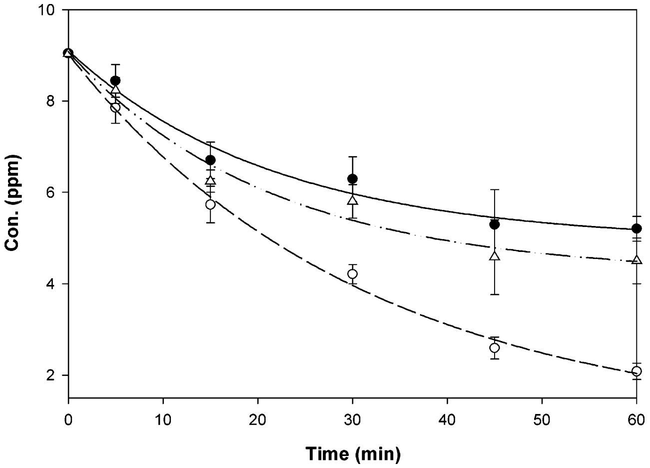

**Figure 5.** Rate of removal in different methods at 30 °C: (●) stirring with pollutant (△) sonication of powder with water then contact with pollutant by stirring, (○) sonication with pollutant.

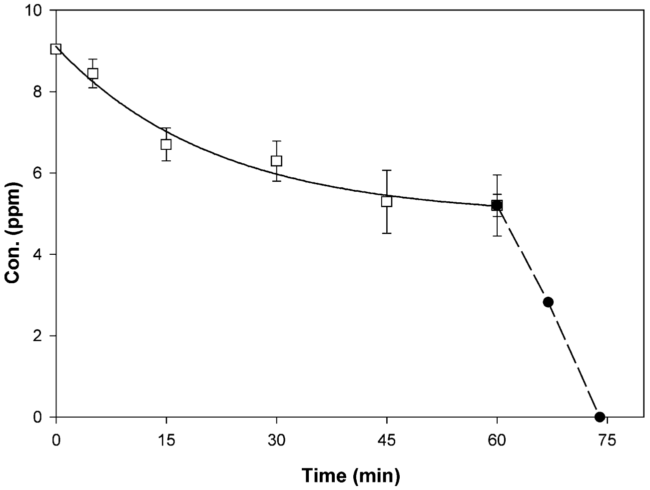

**Figure 6.** Rate of removal in another order at 30 °C: (□) stirring with pollutant, (●) sonication after stirring the mixture for 60 min.

**Effect of Rubber Particle Size.** The sorption efficiency was increased in both methods as the particle diameter decreased (Table 2). Theoretically, the observed rate and extent of sorption are related to the available sorbent sites of the surface. By assuming that the particles have a spherical shape, we can show that the total surface area is inversely proportional to the diameter of the particles present for a given mass of sorbent. Thus, if only surface sorption sites were utilized for Cr(III) removal, then the extent of sorption should be proportional to the reciprocal of the sorbent particle diameter. Crank[19] stated that the variation of uptake rate relates to a higher power reciprocal of the sorbent particle diameter when considering diffusion to be the rate-limiting step. This might be related to the breaking of particles and open tiny cracks and channels on the particle surface that could be employed in the sorption process.[20] For each size of particle, the presence of ultrasound enhanced the extent of sorption. The asymmetrical collapse of bubbles impose locally high pressures at the sorbent's surface that lead to the breakage of particles and change the morphology of the surface.[18] Therefore, ultrasonic waves can increase the surface area and mass transfer, both of which enhance the amount of sorption.

**Effect of the Method of Sonication.** The mixture of deionized water and tire rubber powder was sonicated for 30 min. Then the powder was separated from water by filtration. This powder was stirred with 60 mL of chromium aqueous solution (9.0 ppm). Figure 5 demonstrated that the amount of removal of the chromium ion was higher in the mentioned method (ultrasound + stirring) than it was in stirring alone. This might be related to the change of surface and particle size by ultrasonic waves. But it was much lower than the sonication of powder in the presence of pollutant. This is due to the effect of ultrasound on the powder and the enhancement of mass transfer in the medium. In another method, the mixture of powder and pollutant was stirred for 1 h and then the ultrasonic waves were applied for 15 min (Figure 6). It is showed that the ultrasonic waves can remove the remaining pollutant from solution.

**Sorption Kinetics.** The sorption kinetics can be described by the Lagergren equation[21]

$$\frac{dq_t}{dt} = k(q_e - q_t) \tag{2}$$

Equation 2 can be written in the form of eq 3 by integration under the boundary conditions

$$\log(q_e - q_t) = \log q_e - \frac{k}{2.303}t \tag{3}$$

where $q_e$ and $q_t$ are the amounts of metal ions sorbed onto the rubber (mg g$^{-1}$) at equilibrium and at time $t$, respectively, and $k$ is the first-order rate constant of sorption (min$^{-1}$). A plot of $\log(q_e - q_t)$ versus time gave a straight line, as can be seen in Figure 7. Therefore, the sorption is first-order in both methods. The rate constants were determined from the slope of the plot at different temperatures, and the values were presented in Table 3. The sorption rates in the presence of ultrasound were 2.8−4.3 times greater than those without ultrasound in the studied range of temperature.

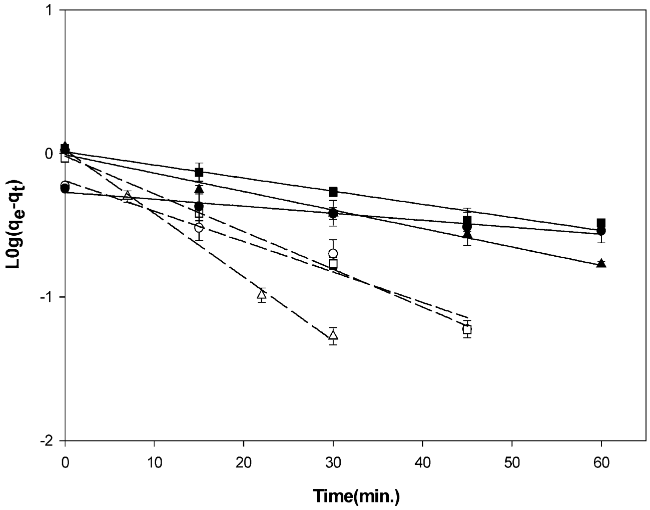

**Figure 7.** Pseudo-first-order kinetic model at different temperatures (power = 32.38 W, pollutant = 18.51 ppm, sorbent = 1 g): (●) stirring (30 °C), (■) stirring (40 °C), (▲) stirring (50 °C), (○) sonication (30 °C), (□) sonication (40 °C), (△) sonication (50 °C).

**TABLE 3: Comparison of the Rate Constants and Amount of Sorption at Equilibrium in the Presence and Absence of Ultrasound**[a]

| method | $t$ (°C) | $q_{e(\mathrm{exptl})}$ (mg/g) | $q_{e(\mathrm{calcd})}$ (mg/g) | %dev[b] | $k$ (min$^{-1}$) | $R^2$ | $k/k_{t=30}$ | $k$(us)/ $k$(st) |
|---|---|---|---|---|---|---|---|---|
| stirring | 30 | 0.57 | 0.54 | 5.26 | 0.011 | 0.98 | 1.00 | 4.35 |
| | 40 | 1.07 | 1.02 | 4.67 | 0.021 | 0.98 | 1.87 | 2.88 |
| | 50 | 1.08 | 0.98 | 9.26 | 0.030 | 0.99 | 2.64 | 3.44 |
| ultrasound | 30 | 0.60 | 0.64 | 6.66 | 0.049 | 0.98 | 1.00 | |
| | 40 | 0.93 | 0.95 | 2.15 | 0.061 | 0.99 | 1.24 | |
| | 50 | 1.11 | 1.06 | 4.50 | 0.102 | 0.99 | 2.08 | |

[a] $q_{e(\mathrm{exptl})}$ was found from the experimental measurements, and $q_{e(\mathrm{calcd})}$ was found from the interception of the lines in Figure 7.

[b] $$\Delta q_e(\%) = \frac{\sum_{i=1}^{N} |[(q_e,i)^{\mathrm{calcd}} - (q_e,i)_{\mathrm{exptl}}]/(q_e,i)_{\mathrm{exptl}}|}{N} \times 100$$

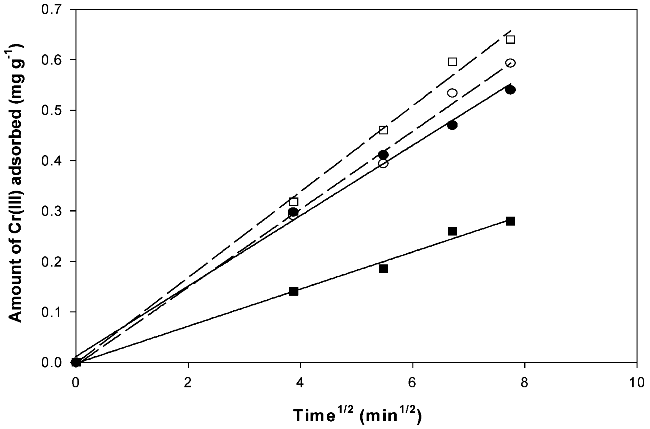

**Figure 8.** Determination of the pour diffusion coefficient at 30 °C (sorbent = 1 g): (■) stirring (18.51 ppm), (●) stirring (38.8 ppm), (○) sonication (18.51 ppm), (□) sonication (38.8 ppm)

**TABLE 4: Pore Diffusion Coefficient in the Presence of Ultrasound and Stirring**

| | stirring | | | ultrasound | | | |
|---|---|---|---|---|---|---|---|
| $t$ (°C) | $k_w$ (mg l$^{-1}$ min$^{-1/2}$) | $R^2$ | $k_w$(st)/ $k_w$(st)$_{t=30}$ | $k'_w$ (mg l$^{-1}$ min$^{-1/2}$) | $R^2$ | $k'_w$ /$k'_{w(t=30)}$ | $k'_w$(us)/ $k'_w$(st) |
| 30 | 0.61 | 0.99 | 1.00 | 1.29 | 0.99 | 2.09 | 1.00 |
| 40 | 1.71 | 0.99 | 2.79 | 2.06 | 0.98 | 1.20 | 1.60 |
| 50 | 1.98 | 0.99 | 3.23 | 3.31 | 0.99 | 1.67 | 2.57 |

**Sorption Mechanism.** In general, sorption may be described as a series of steps: mass transfer from the fluid to the particle surface, diffusion within the pores of the particle surface, and sorption itself onto the surface. It has been observed that the ultrasonic waves and associated phenomena, such as microdisturbances of cavitation bubbles near the particle surface, reduce the boundary layer and therefore give rise to an efficient increase of mass transfer.[22] If the process is controlled by external resistance, then the plot of ln $c$ versus time must be linear.[23] In the presence and absence of ultrasound, the relation was not linear and proved that the external diffusion was not the limiting step. Weber and Moris[21,24−26] reported that if a plot of sorbate uptake versus the square root of time is linear and passes through the origin then pore diffusion will be the rate-controlling step of sorption. Such a linear relationship, presented in Figure 8, indicated that pore diffusion was the rate-limiting step. The pore diffusion coefficient can be determined using the Weber and Morris model

$$C = C_o - k_w t^{1/2} \tag{4}$$

or

$$q = \frac{k_w}{w} t^{1/2} \tag{5}$$

where

$$w = \frac{C_o - C}{q}$$

$C_o$ is the initial concentration (mg l$^{-1}$), $C$ is the concentration at any time (mg l$^{-1}$), $t$ is the time (min), $q$ is the amount of sorption at any time (mg g$^{-1}$), $w$ is the weight of sorbent per volume of reactor (g l$^{-1}$), and $k_w$ is the Weber pore diffusion coefficient (mg l$^{-1}$ min$^{-1/2}$).

The pore diffusion coefficient can be found by drawing $q_t$ against $t^{1/2}$. The values of $k_w$ were determined from the slope of the plots, and they were tabulated in Table 4. The values in the presence of ultrasound were 1.2−2 times greater than those obtained in the absence of ultrasound, that is, ultrasound enhances the mass transport in the pores. This behavior could be attributed to the induced turbulence and additional convective mass transport inside the pores caused by microjets.[16]

The data in Table 4 also showed an increase (up to 3 times) in the pore diffusion coefficient by increasing the temperature for both methods. This enhancement can be attributed to the higher mobility of ions and mass transfer at higher temperatures.

## Conclusions

Discarded tire rubber can be used as a low-cost sorbent for the removal of chromium from aqueous solution. This sorbent was more effective in the presence of ultrasound. The experimental data fit properly with the Langmuir model in the presence and absence of ultrasound. The kinetics of sorption was first-order, and the sorption process was controlled by the porous diffusion step.

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