



Water softening by combination of ultrasound and ion exchange

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ABSTRACT

Ion exchange resin used in this work was styrene-divinylbenzene co-polymer with sulfonic acid group as a strong acid cation resin. This resin is particularly well suited for the removal of water hardness. In water treatment, commonly used softening processes are chemical precipitation and ion exchange. In this study, a combination of ultrasound and ion exchange was applied for reducing the hardness of water. The rate of exchange or kinetics of ion exchange is governed by several parameters. Therefore, important variables such as intensity of ultrasound, amount of resin, concentration of ions and contact time were investigated. The experimental data related to the removal of magnesium and calcium ions were fitted properly with Langmuir model. The kinetic of removal for both ions was pseudo-first-order. In point of mechanism, the internal porous and film diffusion were both effective in the process. The capacity of sorption and the velocity of removal were higher in the presence of ultrasound than control method and this is related to the cavitation process.

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1. Introduction

Hardness in water is mostly due to cations such as calcium and magnesium. The hardness of water is important parameter for industries such as leather productions which influences on the quality of leather [1]. In vegetable tannage the higher level of hardness is undesirable, because calcium and magnesium cause formation of insoluble tannin salts. Water with low hardness levels is also suitable for dyeing and fat liquoring operation [2]. In the preventive approach to calcium nephrolithiasis, the extra meal intake of soft water is preferable to hard water, since it is associated with a lower risk for recurrence of calcium stones [3]. The common methods used for softening of water are chemical precipitation and ion exchange. In chemical precipitation method, the pH of water increased by adding the alkaline additives and bicarbonates converted into carbonates as the precipitates. Due to the limited solubility of carbonates of calcium and magnesium, the hardness of water cannot be removed completely with this method [4–6]. Ion exchange resins are found in numerous commercial and industrial uses and particularly suited for the removal of ionic impurities which can lead to problems in cooling and heating systems, steam generation, and manufacturing [7]. Ordinary polymeric resins are usually utilized in ion exchange processes where cations are removed from solution [8–10]. This kind of resin contains either strongly acidic sulfonic or weakly acidic carboxylic functionalities [11]. Polymeric resins are usually employed for industrial waste-

water treatment process [12]. It should be mentioned that the ion exchange is considered to be cost-effective if low-cost ion exchangers such as zeolites are used [13].

In ion exchange process, the rate of exchange is governed by several factors such as the concentration of ion, the structure of resin that is mostly affected by the amount of divinylbenzene which determines the porosity of the resin, mobility of ions, ion size, and the size of resin. The amount of divinylbenzene in resin also has an important role on the shrinking and swelling of the resin during the normal operation. As the exchange reaction is a diffusion process therefore, the diffusion rate of the ions has an effect on the rate of exchange. Owing to the high cost of ion exchange resin for the removal of ions from waste water especially in a large scale [14], it is necessary to study the other methods in order to reduce operating costs.

In this study we focused on the combination of ultrasound and ion exchange as a new method for the removal of hardness from water. It should be mentioned that the effect of ultrasound on sorption process was studied by different groups. Briethbach and Bathen [15] have done a good work on the influence of ultrasound on adsorption processes. Due to the importance of regeneration of the sorbent, they were focused on the desorption process. Ultrasound as an efficient method mostly used for desorption of species from sorbent such as desorption of phenol from activated carbon and polymeric resin [16], desorption of Cd^{2+} and Zn^{2+} from bentonite [17]. Generally, thermal and chemical methods are commonly used for the regeneration of the sorbent. These methods suffer from severe disadvantages. An alternative method for regenerating the sorbent is desorption by ultrasound [18–20].

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2. Experimental

2.1. Materials

Calcium chloride and magnesium nitrate were obtained from Merck in analytical grade. The stock solutions were prepared using de-ionized water. The resins used were a co-polymer of styrene and divinylbenzene with functional groups of $\text{SO}_3\text{-Na}$. (bulk density = 1.28 (g/l, approximately), bulk weight (820 g/l), and bead size = 0.6 mm) [21].

2.2. Apparatus

The ultrasonic irradiations were carried out with equipment operating at 20 kHz (XL-2020, Misonix). A Varian atomic absorption spectrophotometer (spectra-110-220/880 Australia Pty Ltd) equipped with a Zeeman atomizer was used to determine the concentration of Ca^{2+} and Mg^{2+} ions in the solution. The IR spectra were recorded by using Bomem B-154. The Fourier transform spectrometer was carried out in the region $500\text{--}4000\text{ cm}^{-1}$ in potassium bromide pellet with resolution of 2 cm^{-1} by co adding the results of 15 scans.

2.3. Procedure

The ultrasonic horn with standard tip (1.1 cm^2) was inserted to a depth of 10 mm to the Rosette cell containing 50 ml solution of ion with concentration of 50 mg l^{-1} . Acoustic power was measured by calorimetric method [22]. A circulating bath was used to maintain the temperature constant during the sonication. Classical experiments were performed in a batch reactor with continuous stirring fixed at 300 rpm without ultrasonic irradiation. At different interval times, the concentration of Ca^{2+} and Mg^{2+} ions were determined by atomic absorption spectrophotometer. As the behaviors of both ions were approximately the same, most of the work was focused on the magnesium ion.

3. Results and discussion

3.1. Amount of resin

The variation of magnesium ion removal with time for two different amounts of resin was shown in Fig. 1. In lower amount of resin (0.1 g), the removal of magnesium ion was different in the

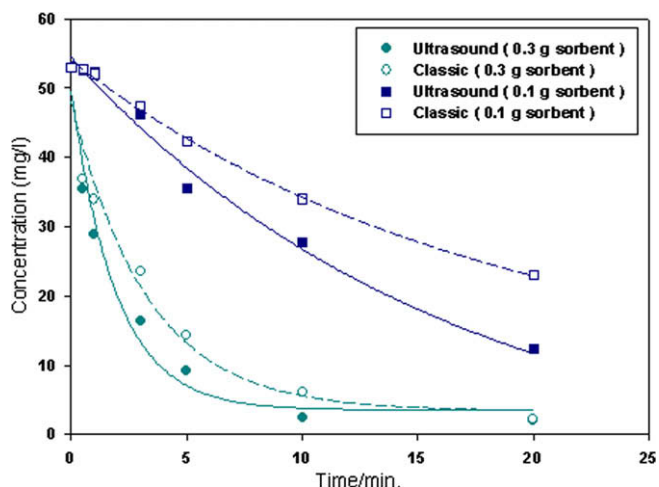


Fig. 1. Effect of amount of resin on the removal of magnesium (stirring speed, 300 rpm; C_0 , 50 mg l^{-1} ; temp., $35\text{ }^\circ\text{C}$; acoustic power at position 25%, 55.9 W).

presence and absence of ultrasound. By increasing the contact time, the difference was increased which is due to the lower site of sorption and lower concentration of the magnesium ion especially at higher contact times. This behavior could be attributed to the chemical and physical effects of ultrasound which arise from acoustic cavitation, i.e., the formation, growth, and implosive collapse of bubbles in the liquid medium. The collapse of the bubble generates localized hot spots through adiabatic compression or produce shock wave within the gas phase of the collapsing bubble. The extreme conditions attained during bubble collapse can increase the mass transfer and facilitate more removal of ions from aqueous solution. In higher amount of resin (0.3 g), the initial rate of removal was higher for both methods but, it was faster in the presence of ultrasound. In longer time, both methods reach to an equilibrium with the same amount of removal. This is due to the presence of higher sorption sites in higher amount of resin. In Fig. 1, the concentration of sorbate is constant and the amount of resin was changed from 0.1 to 0.3 g which led to the different behavior in the presence and absence of ultrasound. This means that the ratio of sorbate to sorbent is an important factor and our previous work confirmed this statement [23]. Regarding to the critical conditions produced during the cavitation process, the probable damage of resin was considered by the FT-IR spectrum. Fig. 2 confirms that the resin is stable under applied sonication. The spectrum is the same for the sample before sonication and after sonication with water or solution.

3.2. Sorption isotherm

Figs. 3 and 4 present the removal of calcium and magnesium ions from solution at three different temperatures, respectively. This figures show that the behavior of calcium and magnesium are approximately the same. By increasing the temperature, the isotherms shifted for both methods to the lower contact times. The difference of removal in the presence and absence of ultrasound was higher for the isotherm at lower temperature than isotherm at higher one. This behavior could be related to the different situation of the cavitation process at different temperatures. The vapor pressure of the liquid is one of the important parameters which affect the extreme conditions produced during the cavitation collapse. At low temperature, the vapor pressure is low and the collapse of the cavity is harsher than the collapse at higher temperature which has a high vapor pressure.

The Langmuir and the Freundlich models are often used to express the isotherm of ion removal from aqueous solutions. It is found that the isotherm of the two mentioned ions can be expressed well using the Langmuir model. It is possible to incorporate the concept of ion exchange into the Langmuir model. The difference is that the ion exchange model assumes that all sites to which the metal ions can be bound are initially occupied. The experimental data of magnesium ion were fitted properly to the Langmuir model in the applied range of initial concentration ($100\text{--}250\text{ mg l}^{-1}$). The linear form of the Langmuir model is presented by the following equation:

$$1/q_e = (1/q_m b) 1/C_e + (1/q_m) \quad (1)$$

where q_e is the amount of solute adsorbed per unit weight of sorbent at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of solute in the bulk solution (mg l^{-1}), q_m corresponds to complete coverage of available sites or the maximum amount of metal ions adsorbed per unit weight of sorbent (mg g^{-1}), and b (l mg^{-1}) is the equilibrium adsorption constant. Fig. 5 confirms that the experimental data fitted well with the linear form of Langmuir Eq. (1) at different temperatures. Various parameters such as sorption capacity (q_m), sorption efficiency (b), and correlation coefficient (R^2) were calculated from the isotherm and are shown in Table 1. The value of

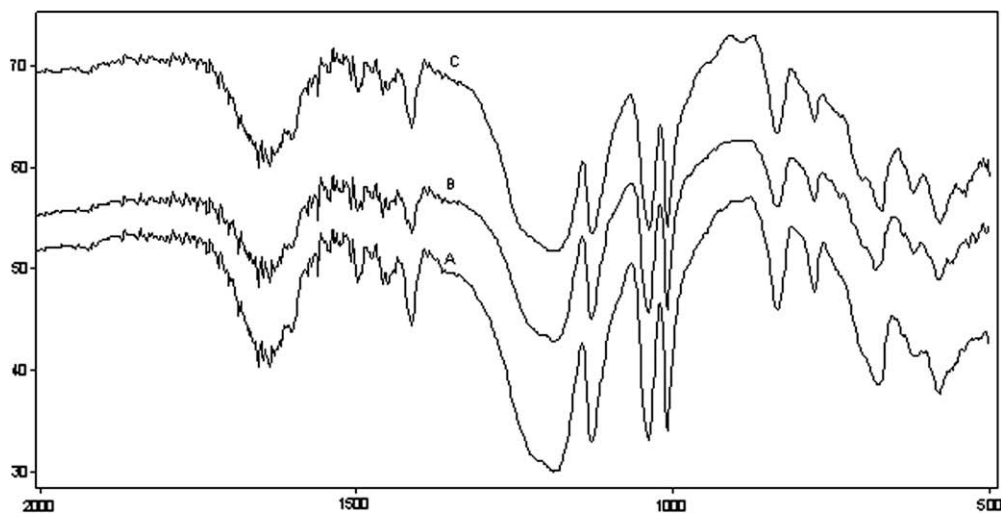


Fig. 2. FT-IR spectrum of the resin, A: original sample, B: sonicated with water (20 min.), C: sonicated with magnesium solution (20 min).

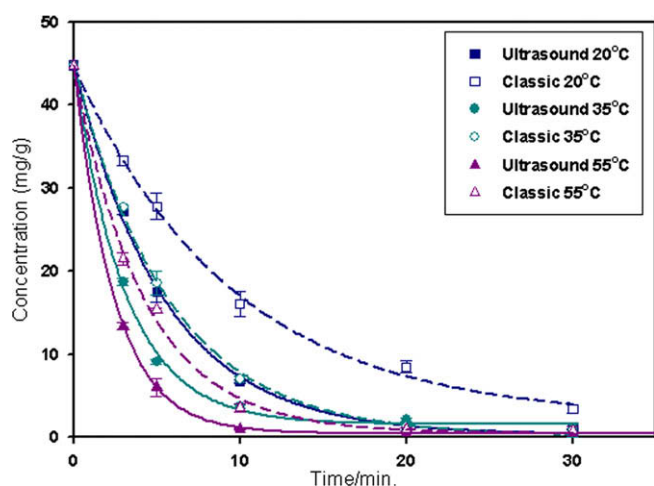


Fig. 3. Effect of contact time on the removal of calcium at different temperatures (stirring speed, 300 rpm; C_0 , 45 mg l⁻¹; dose of sorbent, 0.3 g; acoustic power at position 25%, 55.9 W).

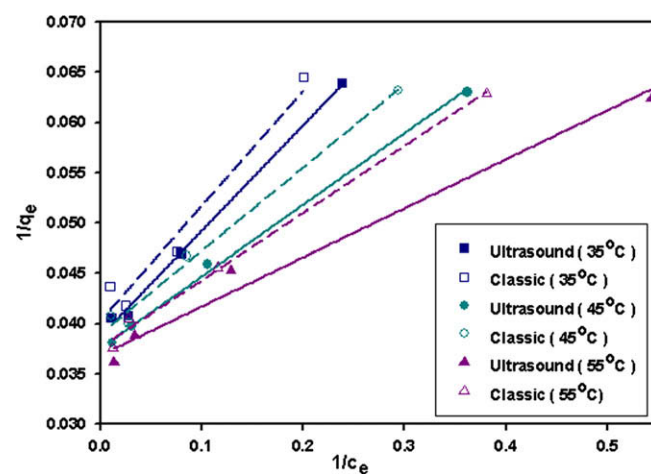


Fig. 5. Langmuir isotherms for magnesium ion in the presence and absence of ultrasound.

Table 1

Langmuir constants for the uptake of magnesium ion.

Method	Temp. (°C)	Langmuir		
		q_m (mg/g)	b (lit/mg)	R^2
Ultrasound	35	26.31	0.36	0.99
	45	27.02	0.52	0.99
	55	27.7	0.75	0.97
Classic	35	23.25	0.39	0.96
	45	25.64	0.47	0.99
	55	27.02	0.56	0.99

R^2 represents the goodness-of-fit of experimental data to the isotherm model which being close to unity.

3.3. Sorption kinetic

The pseudo-first-order kinetic model was applied for the sorption of Mg(II), according to the Lagergren equation [24]

$$\frac{dq_t}{dt} = k_{1,ad}(q_e - q_t) \quad (2)$$

where q_e and q_t are the amount of metal ions sorbed onto the resin (mg g⁻¹) at equilibrium and time t , respectively, and $k_{1,ad}$ is the rate

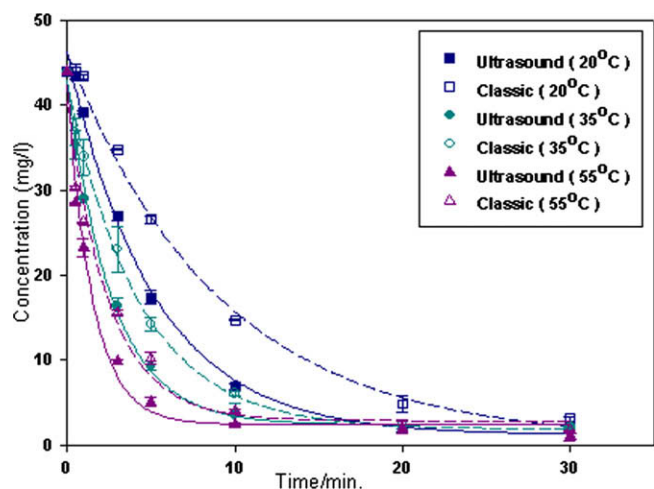


Fig. 4. Effect of contact time on the removal of magnesium at different temperatures (stirring speed, 300 rpm; C_0 , 45 mg l⁻¹; dose of sorbent, 0.3 g; acoustic power at position 25%, 55.9 W).

constant of pseudo-first-order (min^{-1}). After integration under the boundary conditions, the Eq. (2) changes to.

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

A plot of $\log(q_e - q_t)$ versus time gives a straight line as can be seen in Fig. 6, confirming the applicability of the pseudo-first-order rate expression of Lagergren. The slopes and the intercepts of these lines were used to determine the pseudo-first-order rate constant $k_{1,ad}$ and the capacity of sorption at equilibrium (q_e). The values of these parameters and the deviation (%) from the experimental values of q_e are presented in Table 2. The rate constant was higher in the presence of ultrasound than control method. This mostly related to the higher mass transfer and more contact of ions with sorbent sites which lead to the faster removal of magnesium ion from aqueous solution. The rate constant was increased for both methods with increasing the temperature. It is known that the temperature affects the viscosity, density, and diffusion term in the mass transfer correlations.

3.4. Sorption mechanism

In general, sorption may be described as a series of steps by the transfer of solute: (1) from the bulk of solution to the boundary film of sorbent, (2) from the boundary film to the sorbent surface (film diffusion), (3) from the sorbent surface to the intra-particle active sites (porous diffusion), and (4) interaction with the available sites on the internal surface [25]. One or more of the mentioned steps may control the rate of sorption. It has been observed that the ultrasonic waves and associated phenomena

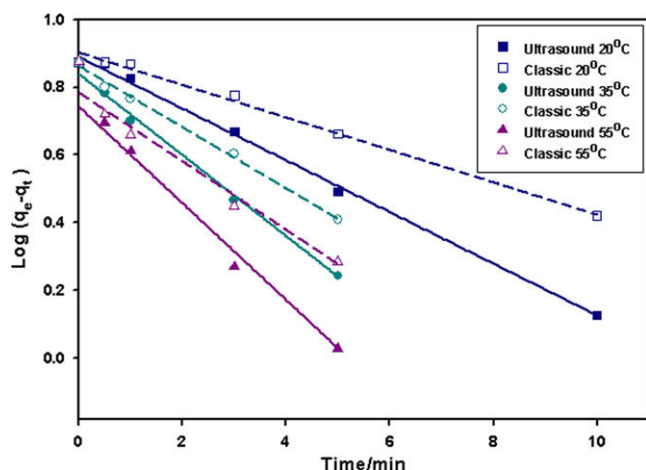


Fig. 6. Pseudo-first-order kinetic model for magnesium ion at different temperatures.

Table 2
(a, b). Pseudo-first-order kinetic model for the sorption of magnesium ion.

T (°C)	q_e (mg/g) Exp.	q_e (mg/g) Cal.	%dev	k_c l/min	R^2	
a. Classic						
20	6.69	7.24	0.15	0.13	0.98	
35	6.88	6.60	0.03	0.23	0.99	
55	7.22	6.02	0.11	0.27	0.97	
T (°C)	q_e (mg/g) Exp.	q_e (mg/g) Cal.	%dev	K_u l/min	R^2	k_{ul}/k_c
b. Ultrasound						
20	6.70	7.41	0.39	0.25	0.99	1.92
35	6.91	6.45	0.25	0.34	0.99	1.47
55	7.24	6.16	0.46	0.41	0.98	1.51

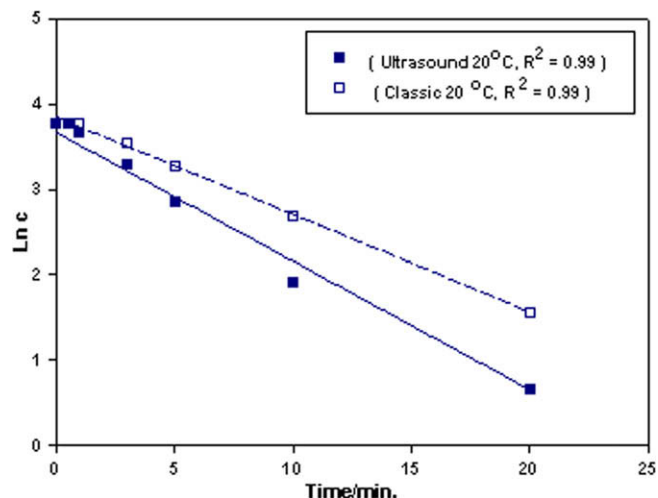


Fig. 7. Internal porous diffusion as a rate control step (magnesium ion).

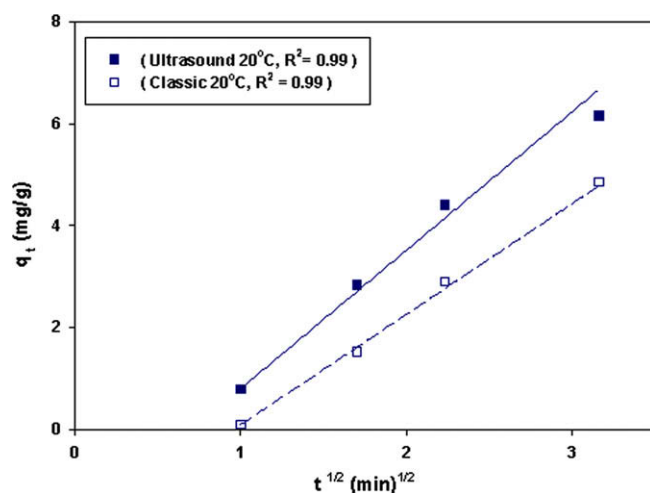


Fig. 8. Film diffusion as a rate control step (magnesium ion).

such as micro-disturbances of cavitation bubbles near the surface of solid reduce the boundary layer and lead to an efficient increase of the mass transfer [18,26]. If the process is controlled by the external resistance, the plot of $\ln c$ versus time must be linear [18,27]. According to Fig. 7, in the presence and absence of ultrasound the mentioned relationship was observed and therefore the external diffusion could be effective in the rate limiting step. In addition, Fig. 8 shows that the plot of sorbate uptake versus the root of time was linear and the lines did not pass through the origin [28]. This means that the pore diffusion was not the only rate controlling step. Therefore, both film diffusion and porous diffusion were effective in the removal of ions in the presence and absence of ultrasound.

4. Conclusion

The experimental data was fitted properly with Langmuir model and the kinetic of removal for both ions was pseudo-first-order. In point of mechanism, the internal porous and film diffusion were both effective in the sorption process. Finally, the capacity of sorption and the velocity of removal for both ions were higher in the presence of ultrasound than classical method especially in initial times.

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