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Removal of Water Hardness by Gas Sparged Dialysis Membrane Process

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ABSTRACT

Presence of high concentration of hardness in water is one of the major factors limiting its household and other uses. The main aim of this study was to determine the feasibility of dialysis membrane process over the conventional method for removing hardness (divalent ions) from saline water using lime stone to produce soft water with desalination by reverse osmosis. The rate of mass transfer of hardness salts such as calcium chloride and magnesium chloride across a regenerated cellulose acetate membrane in a gas-stirred batch dialysis cell were measured by the conductivity method. Two parameters namely velocity and initial concentration were investigated. An increase in the air velocity increased the overall mass transfer coefficient. The mass transfer coefficients ranged from 65.52 to 249.93% for calcium chloride and 67 to 251.14% for magnesium chloride over the natural convection value depending on the experimental conditions. An equation was obtained for the transfer of salt ions functions in a superficial velocity. The exponent of the superficial velocity agreed with the values reported in previous studies on heat and mass transfer in bubble stirred systems. The experimental data were fitted based on the formula. $J=0.026 \ (Re \ Fr)^{-0.252}$. In conclusion, the dialysis membrane process showed an excellent potential for hardness removal from saline water on cost effective method.

Key words: Water hardness, gas sparged dialysis, mass transfer coefficient, velocity, cellulose membrane

INTRODUCTION

Water has manifold uses such as domestic, industrial and agriculture etc. In chemical industries water is used as a coolant and to generate steam from boilers. Depending on its source, water may contain large amounts of dissolved calcium and magnesium salts that cause hardness. In boilers, water evaporates continuously and these dissolved salts form slimy precipitates or hard scales that deposit on the inner walls of the boiler. There are several disadvantages of these deposits. One of these is the corrosion that decreases the efficiency of the boiler unit by clogging of pipes, valves and condensers and through a decrease in the heat transfer rate. Furthermore, the excessive use of fuel might cause explosion. Therefore, water treatment is essential for safe operation of boilers. There are different methods to remove hardness from water such as ion-exchange and lime stone. In an ion-exchange process, some naturally occurring and synthetic materials can exchange one type of ion with another dissolved ion of similar charge, e.g., one positive ion for another positive ion and the number of charges on the ions removed from solution must equal the number of charges on the ions exchanged from the material. Also, ion exchange can be used as a pretreatment in desalination process to reduce the levels of sparingly soluble salts. A strong acid cation resin in the sodium form and a weak acid cation resin in the hydrogen form can be used. In both the processes, the level of alkaline earth metal cations, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}), are reduced. The use

of the strong acid cation resin in the sodium form is called water softening and the use of the weak acid cation resin in the hydrogen form in conjunction with a carbon dioxide degasifier is called dealkalization-softening.

One of the traditional methods of water softening is the lime-soda process which has some disadvantages such as leaving behind more sodium chloride dissolved in the raw water and the need of reaction tanks equipped with mechanical stirrers in addition of course to the main chemicals used by the process and coagulant to facilitate filtration of the formed precipitates.

A new approach to water softening is to use membrane separation. While most other types of membrane processes such as nanofiltration membrane are used principally for separations of hardness and softening the water based on pressure driven, dialysis membrane process is particularly well suited for the separation of inorganic ions such as both cations and anions, because the separation is based on the driving force of the concentration.

Dialysis process like other membrane separation processes has the unique advantage of not requiring energy to affect phase changes compared to distillation or crystallization and in contrast to other membrane processes, as the driving force for dialysis depends only on the solution concentration. Hence, it is economically attractive alternative in view of the fact that it is carried out at reduced energy costs. However, in dialysis, the flux through the membrane is limited by the membrane permeability and the resistances of the two stagnant diffusion layers present on each side of the membrane. Further reduction in the total cost of dialysis process could be achieved if the flux through the membrane is high enough to permit using small areas of membranes which result in low equipment cost. One possible mean of increasing the flux is employing efficient stirring of the solution at the membrane surface to decrease the thickness of the diffusion layers. Previously, gas stirring has proved to be more cost effective than the mechanical stirring in biochemical reactors, chemical reactors and electrochemical reactors (Shah *et al.*, 1982; Adam *et al.*, 1971). Recently, the use of gas bubbling to enhance the rate of ultrafiltration and microfiltration in membrane equipment of different geometries was reviewed and the examples of its application in biotechnology, bioseparations and water and wastewater treatment were discussed (Cui *et al.*, 2003). Recently, also, the effect of the presence of inert particles combined with mechanical stirring on the rate of mass transfer in dialysis of sodium chloride solutions was found to increase the mass transfer coefficient.

The main objective of this study is to investigate the feasibility of dialysis membrane in removing the hardness (divalent ions) from salt water as an alternative to conventional methods such as lime stone to produce low hardness waters that can be desalinated by reverse osmosis thus reducing the required energy. Also, to explore the possibility of using gas stirring in the near proximity of the membrane surface to enhance the rate of mass transfer of calcium and magnesium chloride salts in a dialysis membrane process with a flat sheet cellulose acetate membrane.

MATERIALS AND METHODS

Dialysis was carried out at room temperature (22±3°C) in a batch cell made of glass. The dialysis cell consisted of two identical compartments separated by a spectrapore regenerated cellulose acetate membrane sold by Coleparmer Company. Each compartment is rectangular shaped with a base of dimensions 17×17 cm with a height of 17 cm. The flat sheet membrane was sandwiched between two hollow Plexiglas frames. Holes were drilled all around the frame. Both frames were bolted together by means of screws and nuts. Strips of Teflon tape fitted in between the membrane surface at the top and the neighboring frame to prevent liquid leakage during an experimental run. The membrane-frame assembly was then slide length-wise into a channel
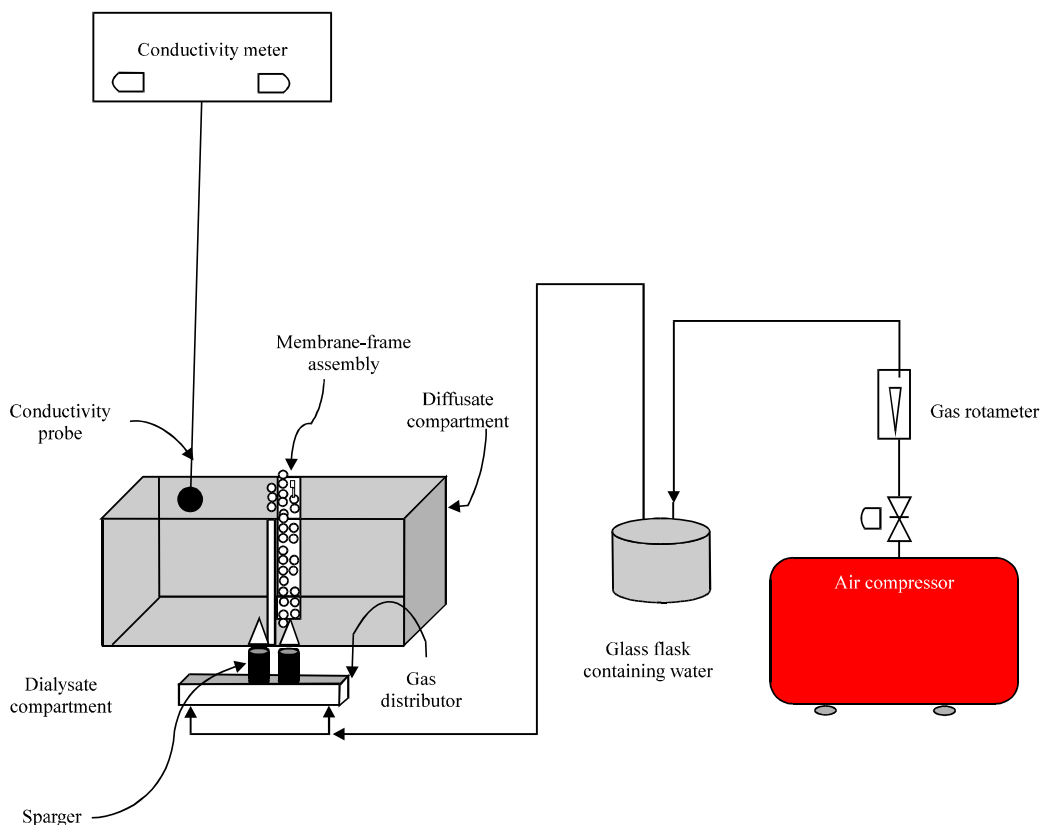
Fig. 1: Experimental set-up of sparged dialysis process

engraved around the cell base and walls. Two air stone spargers (used in aerating fish aquariums) were positioned at the bottom of the cell with each one on either side of the membrane.

At the start of an experiment, the diffusate compartment (compartment with more salt concentration) was filled with calcium chloride or magnesium chloride solution of a known concentration. The initial concentration of the solution varied between 1-5 g L^{-1} in the experiments. Before starting the experiment, conductivity, density and viscosity of the solution were measured. The experimental solutions of calcium chloride and magnesium chloride ions were prepared from calcium chloride and magnesium chloride purified LR supplied by BDH limited Poole, England.

The dialysate compartment (compartment with less salt concentration) was initially filled with distilled water. The density and viscosity of the distilled water were also measured and recorded before each experimental run. Air flowing out through the exit of a compressor was then saturated with water vapor in two glass flasks half-filled with distilled water being introduced by the air spargers into the solutions inside the dialyzer. The air velocity varied from 0-0.087 m sec^{-1}.

The salt concentration in the dialysate compartment was followed up by monitoring the conductivity of the dialysate solution continuously and a measurement recorded every 3 min. A schematic diagram of the experimental setup is presented in Fig. 1. The accuracy of the measurements was frequently checked by calibration of the conductivity meter against standard KCl solution. Each dialysis run lasted about 2-3 h. At the end of each run, the density and viscocity of the dialysate and diffusate solutions were determined using a pycnometer and a glass capillary viscometer. The diffusivity of the solution was measured using the Armfield diffusion of a liquid apparatus (model CER b). Both solutions were then discarded. The cell was finally cleaned

thoroughly and filled up with distilled water till the next run to avoid drying of the membrane, because its permeability may change upon drying.

Theory: The rate of dialysis of a solute is characterized by its overall mass transfer coefficient as defined by the following equation:

$$\frac{1}{K} = \frac{1}{K_1} + \frac{1}{K_2} + \frac{1}{P}$$

where, K_1 and K_2 are the mass transfer coefficients through the two stagnant liquid layers on both sides of the membrane, P is the permeability coefficient of the membrane. The equation used to calculate the overall mass transfer coefficient for a batch dialyzer is derived by considering the material balance on the salt as follows:

Rate of depletion of salt in the dialysate copmpartment = Rate of salt transfer across the membrane

$$-V\frac{dC_1}{dt} = KA(C_1 - C_2) \tag{1}$$

Substituting $C_1 = C_0 - C_2$, yields:

$$-V\frac{d(C_0 - C_2)}{dt} = KA(C_1 - C_2) \tag{2}$$

Integrating both sides of the above equation yields:

$$\ln\left[\frac{1}{1 - \dfrac{2C_2}{C_0}}\right] = \frac{2KA}{c}t \tag{3}$$

The ratio $2C_2/C_0$ was obtained under different conditions from the concentration data of the solution measured as conductivity at various times.

RESULTS AND DISCUSSION
According to Eq. 3, a plot of:

$$\left[\frac{1}{1 - \dfrac{2C_2}{C_0}}\right]$$

versus time (t) provided a straight line of a slope [K A/V] from which the overall mass transfer coefficient was calculated. A plot of the Eq. 3 is shown in Fig. 2a-e, 3a-e for all the initial concentrations, air velocity and types of salts studied in this study. In general, the data verified Eq. 3.
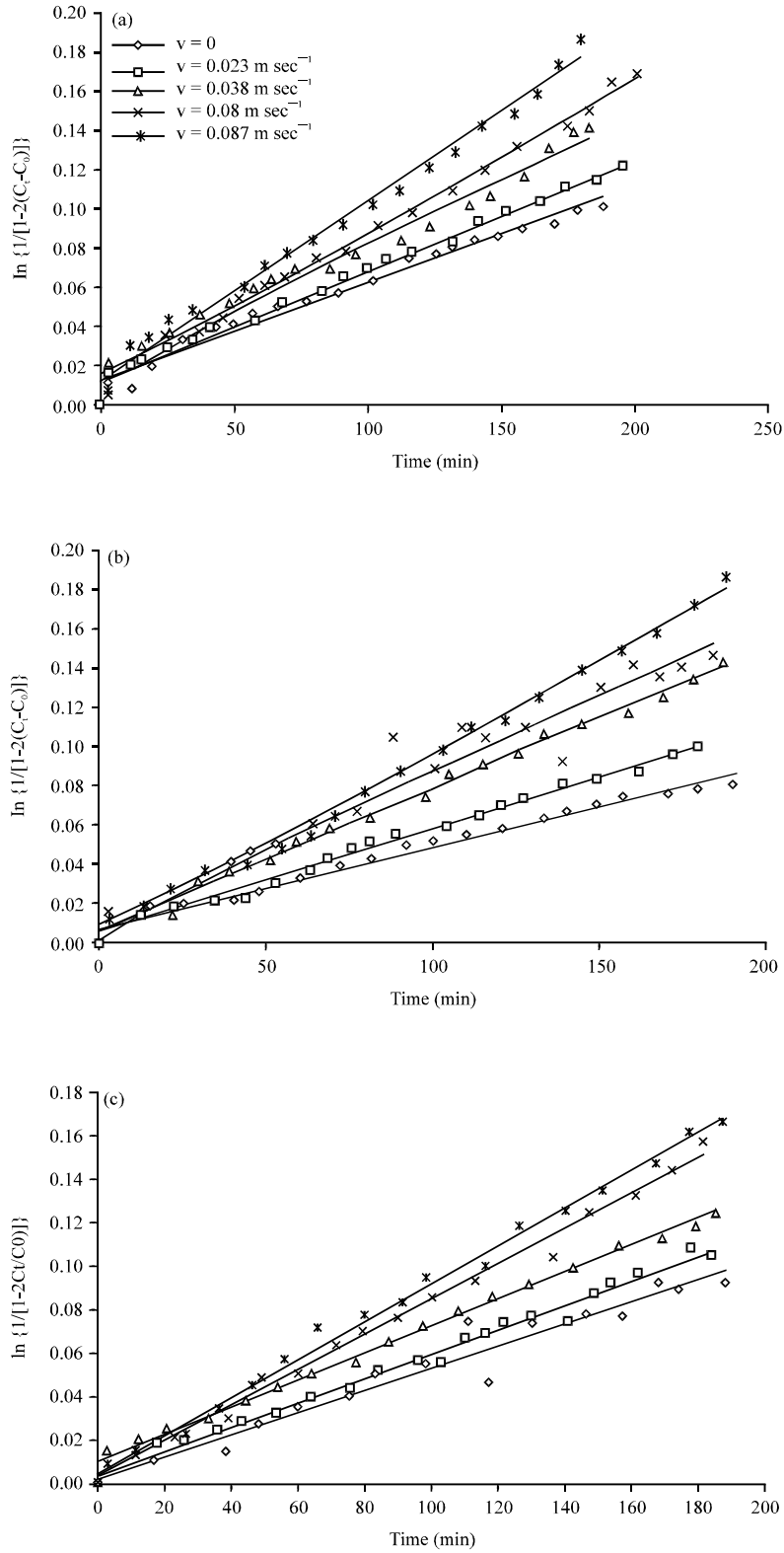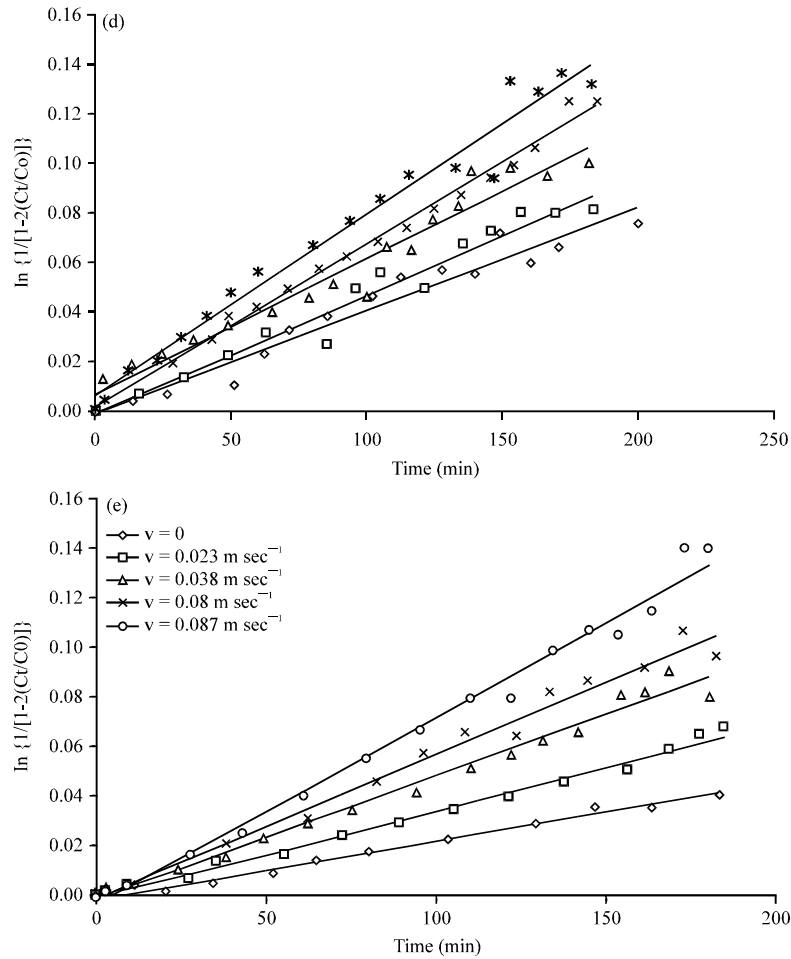
Fig. 2(a-e): Continue

Fig. 2(a-e): Plot of Eq. 3 for $CaCl_2$ at different air velocity (a) co = 1000 ppm, (b) co = 2000 ppm, (c) co = 3000 ppm, (d) co = 4000 ppm and (e) co = 5000 ppm

The effect of air velocity on the mass transfer coefficient is presented in Fig. 4a-b. The enhancement in the rate of mass transfer as depicted by the increase in the overall mass transfer coefficient with air sparging may be attributed to the convection effects induced by the rising swarm of air bubbles and the subsequent decrease in the thicknesses of the stagnant boundary layers adjacent to the membrane. The data fit the equation:

$$K = a \, V_g^{\,b}$$

Where:

a = Constant that depends on the initial concentration of the salt ions

V_g = Superficial air velocity based on sparger area

The exponent b is equal to 0.279 for calcium ions and 0.297 for magnesium ions. The exponent b, for these salt ions is in good agreement with the values obtained by different researchers who studied the rates of heat and mass transfer in bubble stirred systems (Sedahmed *et al.*, 1990; Deckwer, 1980; Hart, 1976).
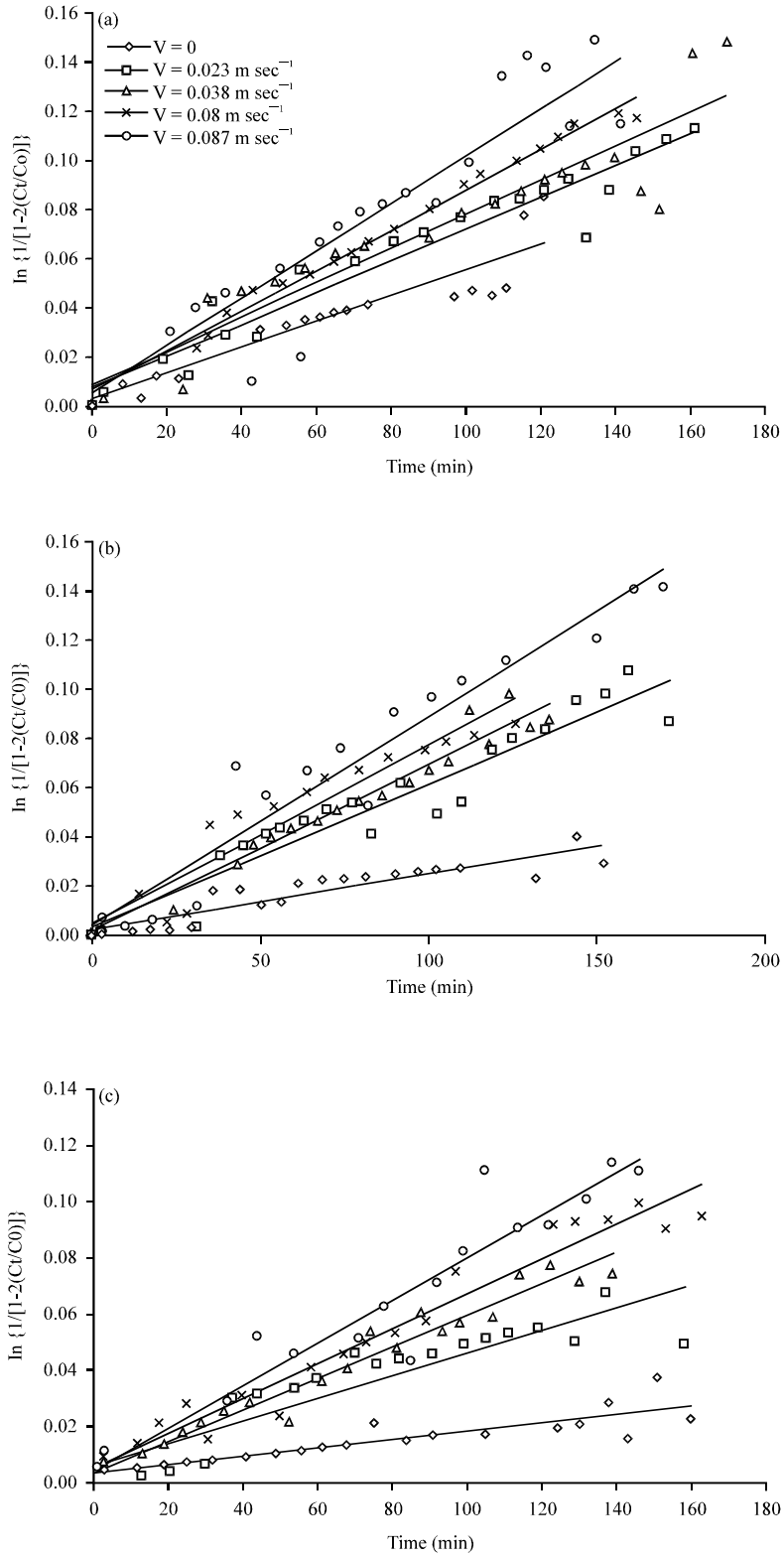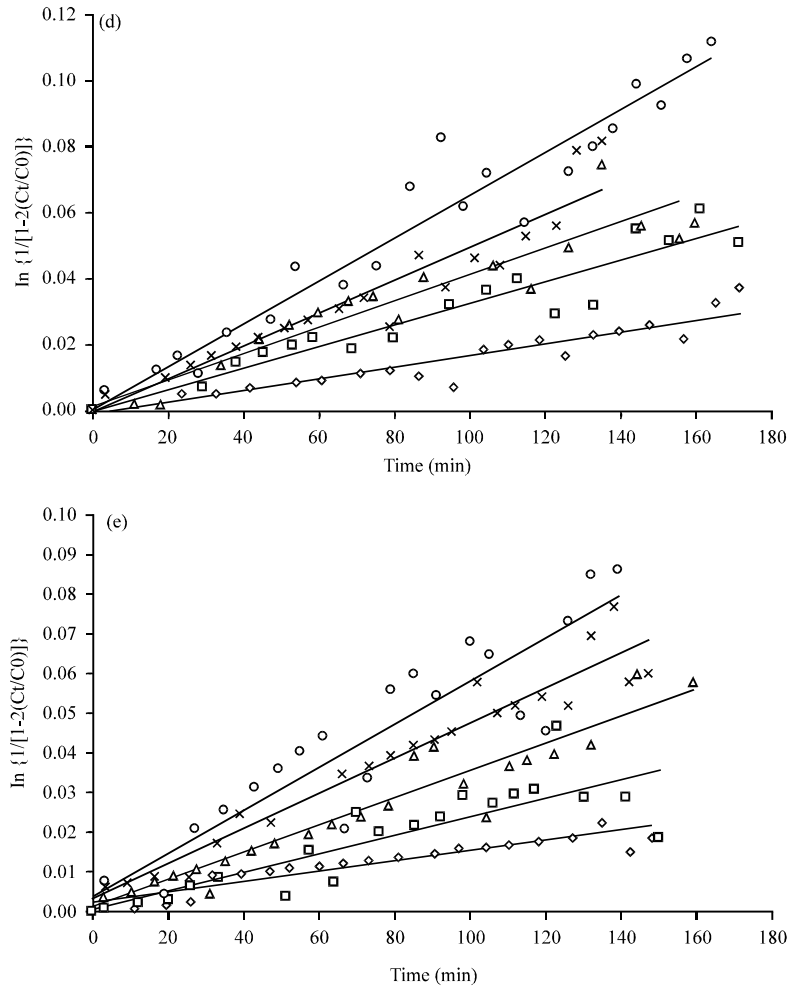
Fig. 3(a-e): Continue

Fig. 3(a-e): Plot of Eq. 3 for MgCl$_2$ at different air velocity (a) co = 1000 ppm, (b) co = 2000 ppm, (c) co = 3000 ppm, (d) 4000 ppm and (e) 5000 ppm

To assess the effectiveness of gas stirring in improving mass transfer, an enhancement factor was obtained from Fig. 5a-b for all the experiments carried out at different air velocities. The enhancement factor is defined as:

$$\frac{K_{\text{at some air velocity}} - K_{\text{without air sparging}}}{K_{\text{without air sparging}}}$$

and ranged from 65.52-249.93% for calcium chloride and 67-251.14% for magnesium chloride depending on experimental conditions. The improvement in the rates of mass transfer is clear by comparing the value of the mass transfer coefficient calculated without sparging with that calculated at the maximum air velocity by the experimental conditions.

An overall mass transfer correlation was used in terms of the dimensionless groups J, Re, Fr. Figure 6 shows that the data for the conditions 0.00122<Re Fr<0.066, 107996.9<Sc<130573.4
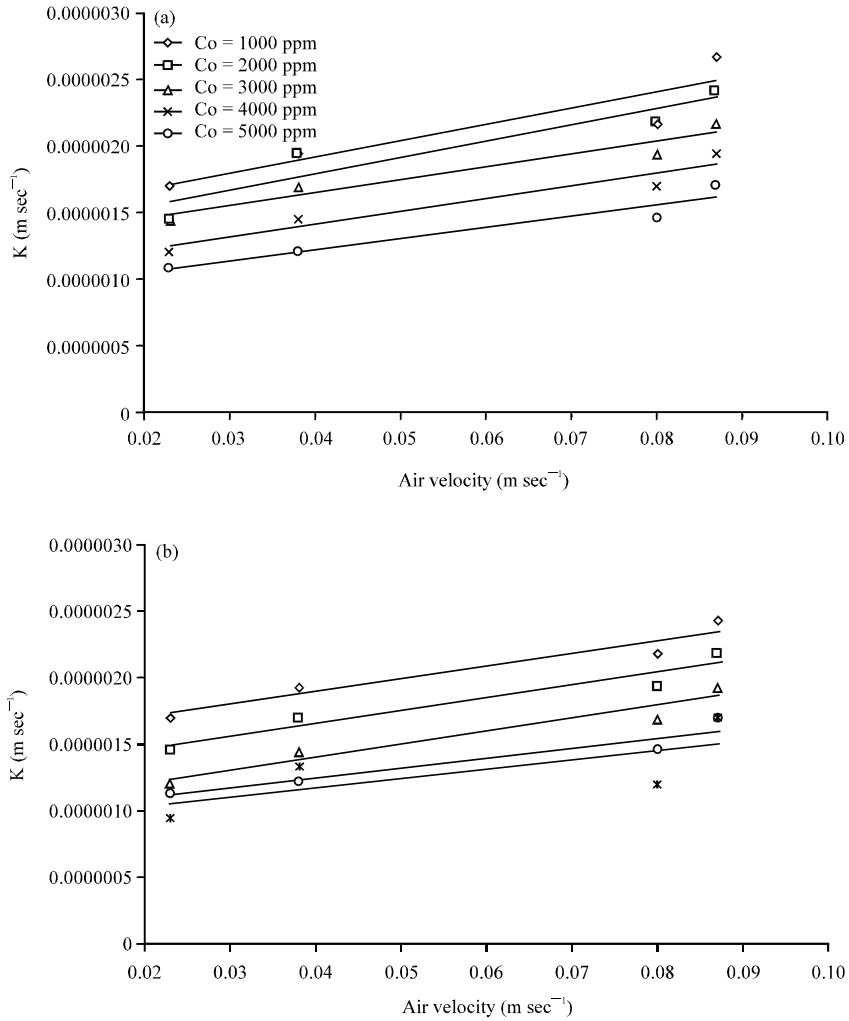
Fig. 4(a-b): Effect of air velocity on overall mass transfer coefficient (K) at different concentrations of the (a) $CaCl_2$ and (b) $MgCl_2$
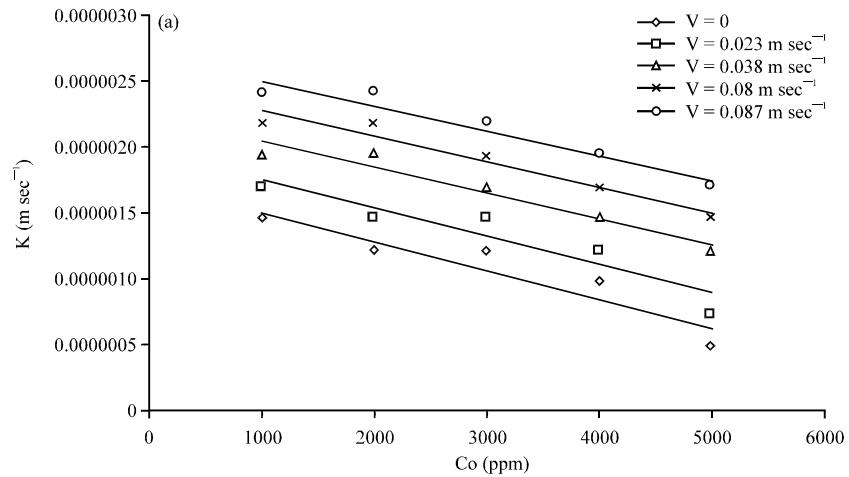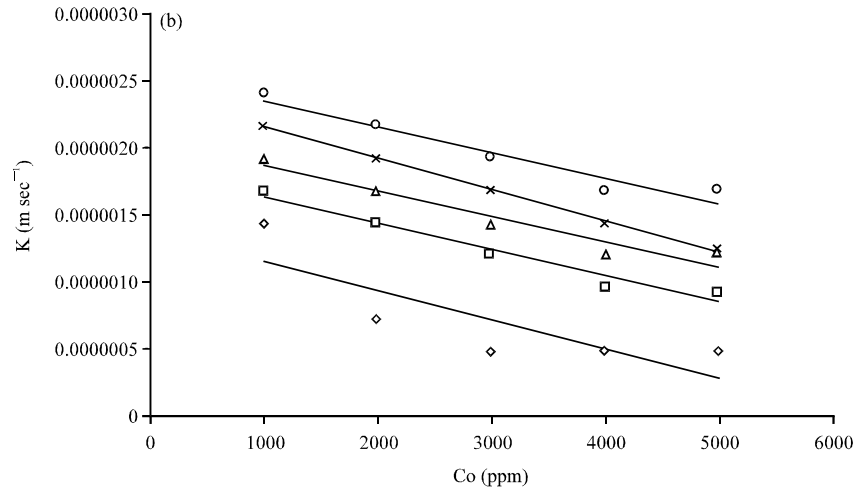

Fig. 5(a-b): Continue

Fig. 5(a-b): Effect of initial concentration of (a) $CaCl_2$ and (b) $MgCl_2$ on overall mass transfer coefficient (K) at different air velocity
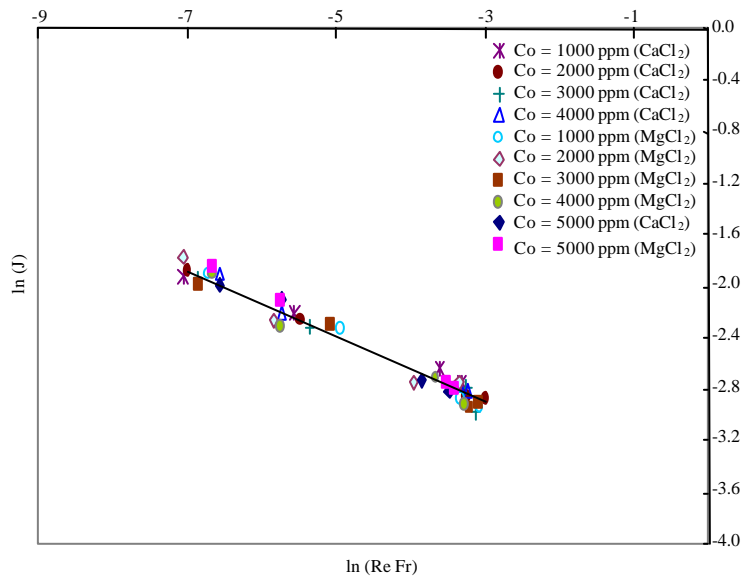

Fig. 6: Representation of the overall mass transfer correlation for $CaCl_2$ and $MgCl_2$ separation by dialysis membrane

and 8.75e-6<St<7.35e-5, fit the following equation J = 0.026 (Re. Fr)$^{-0.252}$ fairly with an average deviation of (±5.7%). The physical properties (ρ, μ) used in calculating the dimensionless groups were taken as the mean of time-averaged values for the diffusate and the dialysate compartments. From the comparison of present data with previous studies, it was found that the present data compare favorably with the data obtained by other researchers in the area of mass transfer (Deckwer, 1980; Hart, 1976; Cavatorta and Bohm, 1988).

CONCLUSION

- Gas stirring proved to have a favorable effect in increasing the rates of dialysis of calcium and magnesium chlorides representing the source permanent water hardness
- Use of gas stirring enhanced the rate of mass transfer of calcium chloride and magnesium chloride salts to a maximum value of 249.93 and 251.14%, respectively
- Overall the mass transfer coefficient was enhanced by reduction of the boundary layer thickness beside the membrane surface due to air sparging
- A mass transfer correlation was derived from the experimental data to show the effect of air sparged on mass transfer in dialysis cells
- The superficial velocity exponent approximately was equal to 0.28 and was in good agreement with the values obtained by other researchers in studying heat and mass transfer in bubble stirred systems

NOMENCLATURE

A : Membrane area
C1 : Salt concentration at time t in the diffusate compartment
C2 : Salt concentration at time t in the dialysate compartment
D : Diffusivity of salt solution
Fr : Froude number (v2/dp g)
g : Gravity acceleration
dp : Average particle diameter
J : Mass transfer J factor (St. $Sc^{0.66}$)
K : Overall mass transfer coefficient
Re : Reynolds number (ρ v dp/μ)
St : Stanton number (K/v)
Sc : Scmidt number (μ/ρ D)
t : Time of dialysis
v : Air velocity
V : Solution volume in each compartment
ρ : Solution density
μ : Solution viscosity

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