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Mass transfer characteristics of single heavy metal ions in air-sparged dialysis cells

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ABSTRACT

The rate of mass transfer of three heavy metal ions such as Cu, Ni, and Zn across a regenerated cellulose membrane in a batch dialysis cell was measured by conductivity method by air-sparging. Air-spargingenhanced the rate of mass transfer depending on the air velocity. The increase in mass transfer coefficient ranged from 83.3 to 125%, 149.83 to 200%, and 99.4 to 201.52% for Cu, Ni, and Zn, respectively. The exponent values of superficial velocity agreed with the values obtained in previous studies on heat and mass transfer in bubble-stirred systems. The ranges of exponents were $0.0093 < \mathrm{Re}\ \ \mathrm{Fr} < 0.0467$, $110{,}584.3 < \mathrm{Sc} < 240214.9$,$2.11\mathrm{e}{-5} < \mathrm{St} < 9.45\mathrm{e}{-5}$. The overall mass transfer correlation came to $J = 0.027\ (\mathrm{Re\ Fr})^{-0.261}$

Keywords: Heavy metal ions; Regenerated cellulose membrane; Batch dialysis cell; Air-sparged; Mass transfer

1. Introduction

Among the various heavy metal ions, some metals such as copper (Cu), nickel (Ni), and zinc (Zn) are considered as potential wastewater pollutants due to their toxic nature both for water and animals. Presently, chemical precipitation, ion flotation, and evaporation are used for removing heavy metal ions from wastewater, but need high capital costs for implementation [1].

Currently, application of membrane separation processes has witnessed a large growth over the years in diverse areas such as medicine, desalination, pollution control, and chemical and petrochemical industries. The unique advantage of these processes is that these do not need energy for phase changes as compared to distillation or crystallization. Therefore, the membrane separation processes seem economically feasible alternative as these are carried at low energy costs than the conventional techniques. In particular, dialysis is a simple conventional membrane process that has some commercial uses [2]. Besides, other membrane processes, the driving force depends only on the solution concentration. Because, in dialysis, the flux through the membrane is limited by the membrane permeability and the resistance of diffusion layer on each side of the membrane. One possible approach to increase the flux is by stirring the solution at the membrane surface to decrease the thickness of the diffusion layers. The use of fluidized beds as turbulence promoters in tubular membrane systems were found useful in combating concentration polarization for ultrafiltration purposes [3]. Some researchers found the surface active agents to decrease the rate of mass transfer by an amount ranging from 54 to 84% depending on surfactant concentration [4]. A critical analysis of the literature suggests that the liquid side mass transfer coefficient (K_La) is significantly reduced in the presence of electrolytes. The combined effect of these factors resulted in the achievement of K_L values as high as 0.028/s at a superficial velocity of 0.03 m/s [5]. Increasing the sparging flow rate simply directed more of the sparged bubbles to the side of the membrane modules which resulted heterogenous distribution of the shear forces within the system. No correlation was observed between the sheer force and bubble count or rise velocity. The distribution of sparged bubbles, the bulk liquid flow, and the surface shear forces in the system were highly affected by the system geometry (e.g., module spacing, tank configuration, and diffuser nozzle size) [6].

The main objective of this study was to investigate the effect of air-sparged as a means of enhancing the rate of mass transfer in a batch dialyzer with flat-sheet membrane.

2. Experimental work

Dialysis of single heavy metal ion solution was carried out at room temperature (25˚C) in a batch cell made of Plexiglas. The cell consisted of two identical compartments separated by a flat-sheet regenerated cellulose membrane. Each compartment was rectangular and had dimensions of 15 cm × 20 cm for the base and 15 cm high. The membrane was assembled between two hollow Plexiglas frames and joined by screws and nuts. The net membrane dimension was 13×13 cm^2. The membrane–frame assembly was then slided into a groove made on the cell base and walls. The experimental setup is shown in Fig. 1. Air was driven by two distributors to the surface of the membranes with each stirring the solution near to the membrane surface in one of the cell compartments. The heavy metal ion solutions used in the experiments were copper (Cu), nickel (Ni), and zinc (Zn). The individual metal ion solution was prepared from copper chloride ($CuCl_2$), nickel chloride ($NiCl_2$), and zinc nitrate [$Zn(NO_3)_2$] and LR reagent grade salts supplied by SD Fine-chem. Limited (Laboratory Rasayan).

At the start of an experiment, the diffusive compartment (compartment with more heavy ions concentration) was filled with a specific heavy metal ions such as copper chloride ($CuCl_2$), nickel chloride ($NiCl_2$), or zinc nitrate ($Zn(NO_3)_2$) solution of a desired concentration. The pH of the experimental solution varied for each metal used in the study and was 5.48 for Ni solution, 4.53 for Cu, and 5.70 for Zn. The initial concentration of the experimental solutions varied from 300 to 1,000 mg/L. Each experimental run was started by placing 500 mL of concentrated solution of one metal ion simultaneously in one compartment and 500 mL distilled water in the other compartment. The two compartments were filled with the liquid at the same rate and time to avoid any difference in solution level between the two compartments. Gas sparging was started immediately after filling the two compartments. The dialysate compartment (compartment with low heavy metal ions concentration) was initially filled with distilled water. The air velocity of the gas sparged ranged between 0 and 0.087 m/s in both the compartments. The air distributor orientation was adjusted to ensure liquid

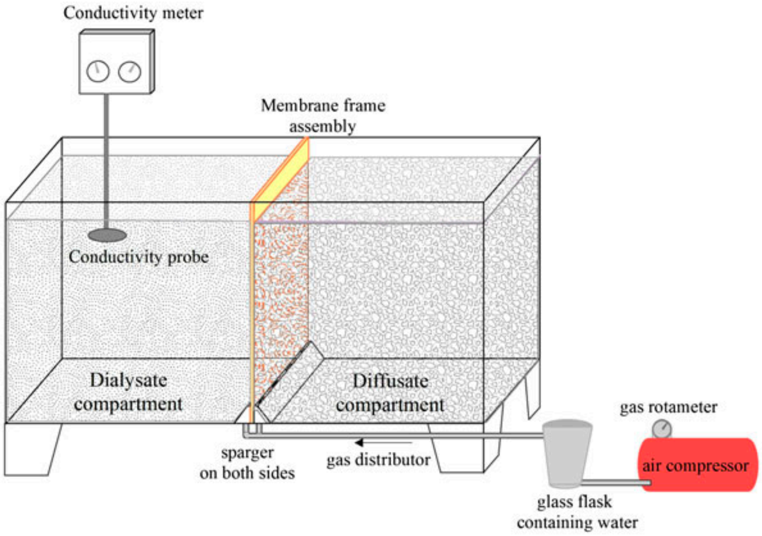

Fig. 1. Experimental setup.

circulation sweeping the membrane surface from bottom to top all the time. The concentration of heavy metal ions (dialysate solution) in the dialysate compartment was monitored continuously. The data was recorded after 3 min interval. Total period of each dialysis run was about one and half hours. The density and viscosity of the dialysate and the diffusate solutions were determined by pycnometer and a glass capillary viscometer at the end of each run. The diffusivity of the solution was measured by Armfield diffusion apparatus (Model CER b). The dialysis cell was finally cleaned thoroughly and filled with distilled water before the next run to avoid drying of the membrane which might affect the membrane permeability.

The experimental treatments were replicated three times with average values, removing the experimental errors.

3. Theory

The rate of dialysis of a solute is related to its overall mass transfer coefficient (K) for the membrane to two liquid phase mass coefficients (K_1 and K_2) and the membrane permeability (P) by the following equation:

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

where K_1 and K_2 are two liquid phase mass transfer coefficients on both sides of the membrane and P is the permeability coefficient of the membrane. The equation used to calculate the overall mass transfer coefficient for a batch dialyzer was derived by considering material balance on the heavy metal ions by considering that the system has two equal compartments where the experimental solution was well agitated by the mechanism of the system as follows:

$$-V\,\frac{\mathrm{d}C_1}{\mathrm{d}t}=KA\,(C_1-C_2) \tag{2}$$

Substituting $C_1 = C_\mathrm{o} - C_2$, yield:

$$-V\,\frac{\mathrm{d}(C_\mathrm{o}-C_2)}{\mathrm{d}t}=KA\,(C_1-C_2) \tag{3}$$

Integrating both sides of the above equation:

$$\int_{C_2=0}^{C_2}\frac{\mathrm{d}C_\mathrm{o}}{(C_\mathrm{o}-C_2)}-\int_{C_2=0}^{C_2}\frac{\mathrm{d}C_2}{(C_\mathrm{o}-C_2)}=-\frac{KA}{V}\int_0^t \mathrm{d}t \tag{4}$$

The first integral on the left-hand side of the equation is zero, where C_o is the initial concentration of the heavy metal ions in the diffusive compartment. The result of the integration is as follows:

$$\ln\left[\frac{1}{1-\frac{2C_2}{C_\mathrm{o}}}\right]=\frac{2KA}{V}\,t \tag{5}$$

the ratio $\frac{2C_2}{C_\mathrm{o}}$ was obtained under different conditions from concentration data taken in terms of conductivity at various times. According to Eq. (5), a plot of $\ln\left[\frac{1}{1-\frac{2C_2}{C_\mathrm{o}}}\right]$ vs. time (t) would give a straight line of a slope $[K\,A/V]$.

From the slope, the overall mass transfer coefficient can be calculated.

4. Results and discussion

In general, the experimental data fit very well with Eq. (5) as shown from the coefficient of determination, R-squared for the metal ions under experimental investigation at different initial concentrations and air velocities by Table 1.

The overall mass transfer coefficient was obtained from the plots of Eq. (5). The effect of air velocity on the mass transfer coefficient is shown in Figs. 2–4. Data in figures showed that the overall mass transfer coefficient increased with increasing the air velocity which caused an enhancement in the rate of mass transfer. This increase in the transfer coefficient might be due to reduction in the thickness of the diffusion layer that was adjusted to the membrane surface by the air-sparged. The study results contradict with the findings of (8) who found a decrease in the mass transfer coefficient by an amount ranging from 5 to 30% depending on triton concentration and superficial air velocity. However, the study results agree with the findings of (9) who observed an increase in the rate of mass transfer across the membrane from 18 to 360% depending on the superficial gas velocity and the physical properties of the solution. The effect of air velocity on the overall mass transfer coefficient at different initial concentrations of the heavy metal ions is presented in Figs. 2–4.

The experimental data fit very well with the following equation:

$$K = aV_\mathrm{g}^{b}$$

where a = constant that depends on the initial concentration of the metal ions; V_g = superficial air velocity based on sparger area.

The exponent (b) is equal to 0.276 for Cu ion, 0.276 for Ni ions, and 0.254 for Zn ion. The equal values of

Table 1
The slope and coefficient of determination, R-squared for the metal ions under experimental investigation at different initial concentrations and air velocities

		Cu		Ni		Zn	
Conc. (PPM)	v (m/s)	Slope	R^2	Slope	R^2	Slope	R^2
300	0.000	0.302	0.973	0.196	0.977	0.196	0.977
	0.023	0.247	0.961	0.207	0.987	0.207	0.987
	0.048	0.449	0.984	0.213	0.989	0.213	0.989
	0.800	0.447	0.991	0.285	0.963	0.285	0.963
	0.870	0.546	0.979	0.330	0.962	0.330	0.962
500	0.000	0.293	0.975	0.282	0.982	0.282	0.982
	0.023	0.290	0.978	0.363	0.986	0.363	0.986
	0.048	0.352	0.990	0.454	0.988	0.454	0.988
	0.800	0.505	0.984	0.474	0.984	0.474	0.984
	0.870	0.949	0.949	0.561	0.988	0.561	0.988
700	0.000	0.450	0.973	0.276	0.980	0.276	0.980
	0.023	0.490	0.980	0.326	0.989	0.326	0.989
	0.048	0.719	0.997	0.423	0.994	0.423	0.994
	0.800	0.610	0.955	0.460	0.980	0.460	0.980
	0.870	0.683	0.988	0.526	0.980	0.526	0.980
1,000	0.000	0.439	0.981	0.493	0.972	0.493	0.972
	0.023	0.483	0.989	0.595	0.983	0.595	0.983
	0.048	0.531	0.992	0.736	0.995	0.736	0.995
	0.800	0.630	0.986	0.816	0.963	0.816	0.963
	0.870	0.868	0.987	1.197	0.979	1.329	0.984

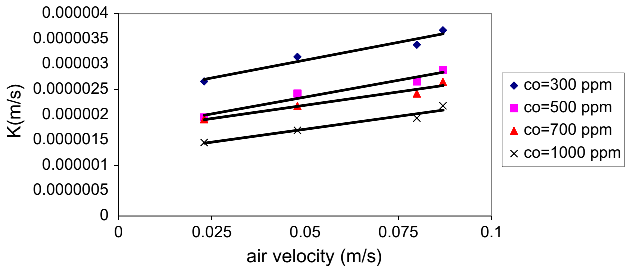

Fig. 2. Effect of air velocity on overall mass transfer coefficient at different initial concentrations of the copper ions.

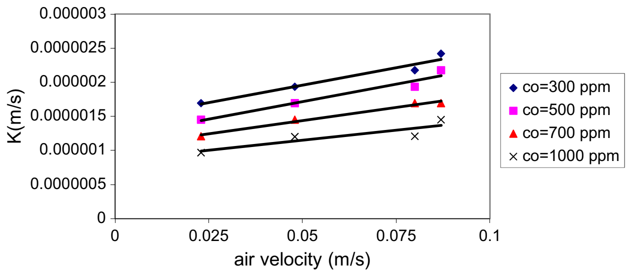

Fig. 3. Effect of air velocity on overall mass transfer coefficient at different initial concentrations of the nickel ions.

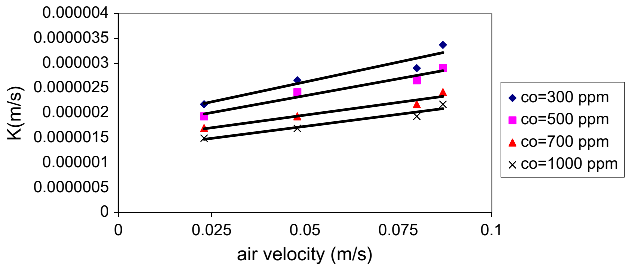

Fig. 4. Effect of air velocity on overall mass transfer coefficient at different initial concentrations of the zinc ions.

b components for Cu and Ni might be related to the ionic radius of each metal ion which is very close (0.72 for Cu and 0.69 for Ni) and the electronegativity of the atoms (almost equal i.e., 1.90 for Cu and 1.91 for Ni) in the diffusion phase where the membrane configuration is the same. The exponent (b), for these metal ions, is in good agreement with the values obtained by different researchers who studied rates of heat and mass transfer in bubble-stirred systems [7–10]. For example, Sedahmed et al. reported the value of b constant as 0.22 which is very close to the b value obtained in this study. The small variation in b constant may be attributed to the experimental solution. As in the present study, experimental solution was prepared from Cu, Ni, and Zn salts, while it was NaCl salt used by Sedahmed et. al. in their investigation [10].

In order to assess the effectiveness of gas stirring in improving the mass transfer, an enhancement factor (EF) was obtained from Figs. 5–7 for all the experiments carried out at different air velocities. The EF is defined as $[(K_{\text{at some air velocity}} - K_{\text{without air-sparging}})/(K_{\text{without air-sparging}})]$ and ranged from 83.3 to 125%, 149.83 to 200% and 99.4 to 201.52% for Cu, Ni, and Zn metal ions, respectively. This variability in EF for different metal ions might be attributed to the difference in the ionic radius, atomic weight, coordinator number, electron configuration, pH of solution, and the electronegativity among different metals used in the experiment. The improvement in rates of mass transfer was pronounced as compared to the calculated value of mass transfer coefficient without sparging to that calculated at the maximum air velocity.

Furthermore, to clarify the effect of all variables such as physical properties of heavy metal ions and the air velocity, an overall mass transfer correlation was determined for the pertinent dimensionless groups, namely J, Re, Fr. Fig. 8 shows that the data fitted well to the following equation:

$$J = 0.027\,(\mathrm{Re\ Fr})^{-0.261}$$

Reasonably with an average deviation of (±5.8%) for the conditions

$$0.0093 < \mathrm{Re\ Fr} < 0.0467,\ 110{,}584.3 < \mathrm{Sc} < 240214.9,$$
$$2.11\mathrm{e}{-5} < \mathrm{St} < 9.45\mathrm{e}{-5}$$

The value of constants a and b in the above equation came to 0.027 and −0.261, respectively, based on its geometry and the experimental conditions of the system. These values do not agree with those of [4] who found 0.096 and −0.14 values for a and b, respectively, due to the different geometry and experimental conditions to remove pollutants such as SO_2, Cl_2, H_2S, and nitrogen oxide. In another study [11], the value of a and b was 0.12 and −0.25, respectively. In another study [12], the values of a and b constants were 0.126 and −0.226, respectively. These values do not agree with the values of a and b obtained in the present study due to the difference in the experimental setup where different apparatus and an electrode were used.

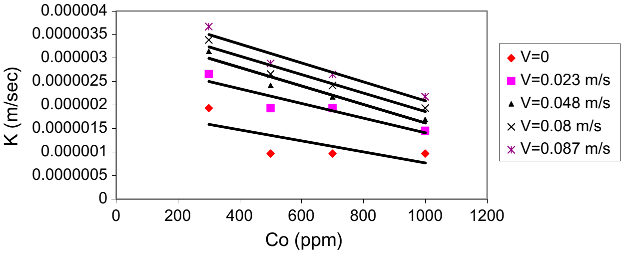

Fig. 5. Effect of initial total ion concentration of copper ions on overall mass transfer coefficient at different air velocity.

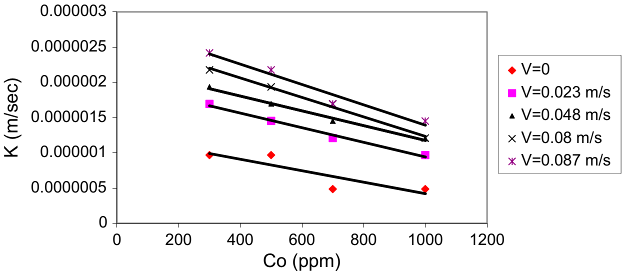

Fig. 6. Effect of initial total ion concentration of nickel ions on overall mass transfer coefficient at different air velocity.

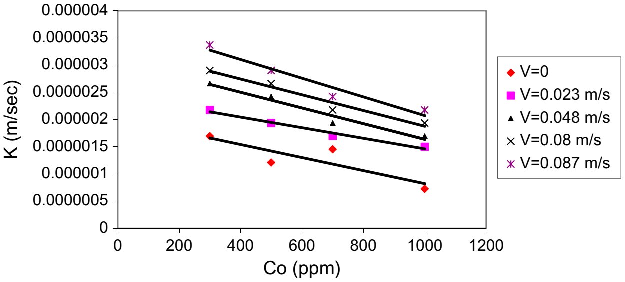

Fig. 7. Effect of initial total ion concentration of zinc ions on overall mass transfer coefficient at different air velocity.

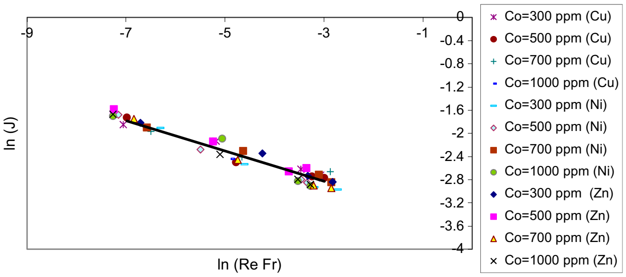

Fig. 8. Representation of the overall mass transfer correlation for copper, nickel, and zinc ions separation by dialysis membrane.

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. A comparison of the present data with previous studies showed that the present data compared favorably with the data of other researchers dealing with mass transfer [8,9,13].

5. Conclusions

1. Overall mass transfer coefficient was enhanced by reducing the boundary layer thickness beside the membrane surface by air-sparging. The maximum increase in the rate of mass transfer of the metal ions was 125, 200, and 201.52% for Cu, Ni, and Zn ions, respectively, by gas stirring.
2. A mass transfer correlation was derived from experimental data to show the effect of air-sparged on mass transfer in dialysis cells. In practice, the above correlation can be used to predict the overall mass transfer coefficient needed in the design or the operation of continuous dialyzers.
3. The superficial velocity exponent was approximately 0.276. This value agreed with the values obtained by other researchers while studying heat and mass transfer in bubble-stirring systems.
4. Air-sparging is expected to have similar effect on other membrane separation processes such as reverse osmosis which can eliminate concentration polarization and enhance their rate of mass transfer.

Acknowledgments

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Nomenclature

A — membrane area (cm^2)
C1 — heavy metal ions concentration at time t in the diffusate compartment (g/cm^3)
C2 — heavy metal ions concentration at time t in the dialysate compartment (g/cm^3)
D — diffusivity of heavy metal ions solution (cm^2/s)
Fr — Froude number ($v^2/dp\,g$)
g — acceleration due to gravity (cm/s^2)
Dp — average particle diameter (cm)
J — mass transfer J factor ($St.\ Sc^{0.66}$)
K — overall mass transfer coefficient (m/s)
Re — Reynolds number ($\rho\, v\, dp/\mu$)
St — Stanton number (K/v).
Sc — Scmidt number ($\mu/\rho\, D$)
t — time of dialysis (s)
v — air velocity (cm/s)
V — solution volume in each compartment (cm^3)
ρ — solution density (gm/cm^3)
μ — solution viscosity (gm/cm s)

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