

Mass Transfer Study of Heavy Metal Removal by Ion Exchange in Batch Conical Air Spouting Bed

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Abstract

The performance of a batch conical air spouting vessel for conducting ion exchange reactions involving heavy metal removal has been investigated. The performance was measured in terms of volumetric mass transfer coefficient (K). The effect of various parameters such as type of heavy metal ion (Ni²⁺, Pb²⁺), superficial air velocity and initial heavy metal concentration has been investigated. It has been found that volumetric mass transfer coefficient increases as air superficial velocity increases. Initial Ni²⁺ concentrations have two opposing effects on the volumetric mass transfer coefficient, whereas initial Pb²⁺ concentrations have negligible effect. Dimensional analysis of the present mass transfer data led to the following correlations:

$$\text{For Ni}^{+2} J_D = 49 (\text{Re} \cdot \text{Fr})^{-0.215}$$

$$\text{For Pb}^{+2} J_D = 117.71 (\text{Re} \cdot \text{Fr})^{-0.24}$$

The importance of these mass transfer correlations in the design and operation of gas spouting vessels used for conducting diffusion-controlled reactions was highlighted.

Keywords: Ion exchange; Zeolites; Heavy metals; Kinetics; Conical gas spouting bed; Mass transfer

Introduction

Water plays an important role in human beings, natural environment, and social development, but the subsequences of water use are municipal wastewaters and industrial wastewaters. Therefore, how to treat wastewaters and make them reusable is not only an important task but also an urgent problem to be solved [1]. Industrial wastewaters such as those produced by metal plating facilities, mining operations, metallurgical engineering, battery manufacturing processes, the production of paints and pigments, electroplating, nuclear power plants, and ceramic and glass industries contain heavy metals such as copper, zinc, cadmium, lead, nickel, and chromium.

These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, thereby causing health problems in animals, plants, and human beings [2]. In the case of liquid effluents, there are many methods available for the removal of these heavy metals such as chemical precipitation, coagulation, solvent extraction, membrane processes, adsorption, and ion exchange [3]. Among the heavy metals removal processes, ion exchange process is very effective to remove various heavy metals and the ion exchange resin can be easily recovered and reused by regeneration operation [4].

Ion exchange is the process through which ions in solution are transferred to a solid matrix which, in turn releases ions of a different type but of the same polarity [5]. Ion exchange is a physical separation process in which the ions exchanged are not chemically altered [6]. The main advantages of ion exchange are recovery of metal value, selectivity, less sludge volume produced and the meeting of strict discharge specifications. Ion-exchange resins are variety of different types of exchange materials, which are distinguished into natural or synthetic resins.

Furthermore, it can be as well categorized on the basis of functional groups such as cationic exchange resins, anion exchange resins, and

chelating exchange resin. Among the materials used in ion exchange processes, synthetic resins are commonly preferred as they are effective and inexpensive [7]. Ion exchange is a mass transfer process. There are two main rate-determining steps which are considered in most of the ion exchange reactions [8]. Diffusion of ions inside the material defined as intra- particle diffusion or diffusion of ions through the liquid film surrounding the particle defined as film diffusion.

The rate of ion exchange is determined by both or the slower of these two processes [9]. Industrially ion exchange reactions are conducted in either fixed bed or fluidized bed columns. In spite of the good hydrodynamic flow characteristics of spouted bed column, no attempt has been made before to investigate its performance in conducting ion exchange reactions. However a single study in literature has studied the performance of batch air sparged vessel in conducting ion exchange reactions [10].

In that study the flow pattern resembles fluidization of resin particle in solution by the aid of air sparging. An alternative flow behavior is spouted bed. Spouted beds are gas-particle contactors in which the gas is introduced through a single nozzle at the center of a conical or flat base [11]. Unlike the fluidized bed the high-velocity spout of gas penetrates the bed and carries the particles upward. The other sections of the particle move downwards at slow speed so that a fairly uniform circulation of particles is obtained as illustrated [12].

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Received June 12, 2013; **Accepted** July 31, 2013; **Published** August 02, 2013

Citation: Yousef NS, Darwish S, Zewail TM, El-Tawail YA (2013) Mass Transfer Study of Heavy Metal Removal by Ion Exchange in Batch Conical Air Spouting Bed. J Chem Eng Process Technol 4: 168. doi: [10.4172/2157-7048.1000168](https://doi.org/10.4172/2157-7048.1000168)

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This hydrodynamic behavior could achieve more intense heat- and mass-transfer conditions. The spouted bed technique has been applied in many industrial processes, such as drying of granular materials, blending of polymer chips, coating of tablets, and granulation of fertilizers and other materials [13]. Conical spouted beds have the properties of conventional spouted beds (cylindrical conical base), while also allowing for strong gas-solid contact since they operate stably in a wide range of gas flow rates [14].

The main objective of the present work is to investigate the performance of a batch conical air spouted bed in the removal of heavy metal ions by strong cation exchange resin. To this end the following parameters have been investigated: Type of heavy metal ion: Ni^{+2} and Pb^{+2} , initial concentration of Ni^{+2} and Pb^{+2} and different air superficial velocity. In addition the present mass transfer data were correlated in terms of dimensionless correlation, which may be useful in the design and operation of such ion exchange conductors.

Materials and Methods

Materials

Fresh strong cation exchange resins, macro-porous AMBERJET 1200 Na a product of ROHM and HAAS were used for each run. (Table 1) shows the specifications of the used ion exchange resin. Nickel Sulfate, Lead Nitrate and Hydrochloric acid, were all AR-grade chemicals. The spouted bed vessel consisted of a plexi-glass cylindrical column of 16 cm in diameter and 26 cm height.

The cylindrical column was supported by a truncated cone of 10 cm height and an inclined angle of $37^\circ 46''$. The truncated cone was provided with an inlet section of 2.5 cm diameter. Ion exchange resins were supported in the vessel by a sintered gla metal ion: Ni^{+2} and Pb^{+2} , initial concentration ss (G2) gas distributor placed at the end of inlet section. Air at different flow rates was introduced from the inlet section through the sintered glass to the spouted bed vessel thought a nozzle of 1 cm diameter. The flow rate of inlet air was regulated by a ball valve and measured by a calibrated rotameter. A non-return valve was fixed in the inlet nozzle to prevent back flow. A ball valve was fixed in a side pipe for drainage.

Method

Solutions of nickel and lead ions of different concentrations were prepared to be used throughout all experiments. Fresh resins were prepared before runs by immersion in 6% HCl, stirring for 15 minutes and washing with distilled water many times until pH 5.5 was reached, and finally resins were dried by air. Two liters of freshly prepared solution of heavy metal ion (Ni^{2+} or Pb^{2+}) of known initial concentration were placed in contact with 40 gm of dried resin in the spouted bed.

Physical form	Amber spherical beads
Matrix	Styrene divinylbenzene copolymer
Functional group	Sulfonate
Ionic form as shipped	Na ⁺
Total exchange capacity	≥ 2.00 eq/l (Na ⁺ form)
Moisture holding capacity	43 to 47% (Na ⁺ form)
Shipping weight	850 g/l
Specific gravity	1.26 to 1.30 (Na ⁺ form)
Uniformity coefficient	≤ 1.2
Harmonic mean size	620 ± 50µm
Fines content	< 0.300 mm : 0.1% max
Maximum reversible swelling	Na ⁺ → H ⁺ : 10

Table 1: Properties of macro-porous AMBERJET 1200 Na resin.

Air flow rate was adjusted by a ball valve as required. Kinetics of the ion exchange reaction was followed by withdrawing 5ml sample from the vessel every 3 mins; the samples were analyzed for the remaining heavy metal ion using atomic absorption spectrophotometer (AA 6650 - Shimadzu) made in Japan.

All experiments were carried out at $25 \pm 2^\circ\text{C}$. Density and viscosity of the solutions used were measured using a density bottle and an Ostwald viscometer respectively. The diffusivities of both Ni^{+2} and Pb^{+2} ions in solution have been calculated from Stokes – Einstein correlation [15]

$$\frac{D\mu}{T} = \text{Constant.}$$

The physical properties of nickel and lead ions solutions respectively measured at $25 \pm 2^\circ\text{C}$ are shown in (Tables 2 and 3) respectively.

Results and Discussion

The Pseudo-first order kinetic model

The Pseudo-first order kinetic equation for solid-liquid ion exchange system is based on the following differential material balance on the present batch reactor with respect to the ion to be removed

$$-V_s \frac{dC}{dt} = kAC \quad (1)$$

This upon integration yields:

$$\text{At } t=0, C=C_0$$

$$\text{And at } t=t, C_t=C$$

$$\ln \frac{C_0}{C} = \frac{kA}{V_s} t \quad (2)$$

Where: C_0 =initial concentrations of heavy metal ions; C =concentrations of heavy metal ion at time t ; V_s =volume of the solution; t =time; k =first order rate constant; A =surface area of resin. A typical plot of $\ln (C_0/C)$ versus time at different gas velocities for ion exchange of Ni^{+2} and Pb^{+2} respectively. It is well obvious that the present data fit well the pseudo first-order kinetic model.

It also indicates that the diffusion controlled nature of the ion exchange reaction, since as the gas velocity increases the rate of the reaction increases. From the slope of that plot (kA/V_s), volumetric mass transfer coefficient (kA) or K can be determined under different conditions. The effect of superficial air velocity on the volumetric mass transfer coefficient at different concentrations for Ni^{+2} and Pb^{+2} respectively. It is observed that the volumetric mass transfer coefficient K increases with increasing superficial air velocities. The volumetric mass transfer coefficient can be related to air superficial velocity according to the following equations: For Ni^{+2}

$$K\alpha V_g^{0.36} \quad (3)$$

Concentration (ppm)	ρ (g/cm ³)	μ (gm/cm.s)	D (cm ² /s)	$Sc = \mu/(\rho^*D)$
800	1.004	9.1109×10^{-3}	2.8865×10^{-5}	314.3765
1000	1.008	9.1658×10^{-3}	2.8692×10^{-5}	316.9171
1250	1.012	9.2563×10^{-3}	2.8412×10^{-5}	321.9283

Table 2: Physical properties of Ni^{2+} solutions used at $25 \pm 2^\circ\text{C}$.

Concentration (ppm)	ρ (g/cm ³)	μ (gm/cm.s)	D (cm ² /s)	$Sc = \mu/(\rho^*D)$
800	1.009	9.1820×10^{-3}	1.9811×10^{-5}	459.5098
1000	1.010	9.2305×10^{-3}	1.9707×10^{-5}	463.5752
1250	1.014	9.3177×10^{-3}	1.9522×10^{-5}	470.7417

Table 3: Physical properties of Pb^{2+} solutions used at $25 \pm 2^\circ\text{C}$.

For Pb^{+2}

$$K\alpha V_g^{0.28} \quad (4)$$

To explain the increase of K with the increase of superficial air velocity, it should be mentioned that with the increase of air velocity, the flow pattern within the vessel changed from stable spouting as indicated into jet spouting. The increase in K during stable spouting regime can be explained in terms of that as air velocity increases, both particles - circulation rate and particle cross rate at the bottom increase [16]. Where particle circulation rate expresses the total mass flow of particle at a given longitudinal position in the spout and particle cross flow expresses the solid flow from the annular zone into the spout zone through the interface. Thus a vigorous mixing can be achieved by increasing air velocity, which results in good mass transfer rate.

The increase in K during jet spouting regime can be explained by the fact that the upraising air stream induces radial as well as axial momentum which causes decrease in the thickness of diffusion boundary layer surrounding each particle [17].

It is worth mentioning that the power of V_g (0.28-0.36) obtained in the present work is less than the value obtained from theoretical Levich expression (0.5) [18], for diffusion controlled reaction. The deviation of the present result from the theoretical expression may be ascribed to the presence of mixed controlled reaction, i.e. the ion exchange of both Ni^{+2} and Pb^{+2} is controlled by both film diffusion and intra-particle diffusion. The lower power of V_g in case of Pb^{+2} compared to Ni^{+2} may be ascribed to that in case of Pb^{+2} , the contribution of intra-particle diffusion in the overall rate is of greater extent than in case of Ni^{+2} .

It would be of interest to compare the present results with the result obtained with other authors. (Table 4) shows the velocity exponent obtained by different authors who studied the effect of gas sparging on the rate of mass transfer [10,19]. It is obvious that the powers of V_g obtained by other authors are in fair agreement with the values obtained in the present study.

It may be concluded that the effect of spouting in mass transfer rate is equivalent and may be superior to gas sparging, as, it is well known that the total pressure drop across a spouted bed is always less than the pressure drop which would arise if the same material were fluidized [13]. The effect of initial metal ions concentration expressed as Sc on the volumetric mass transfer coefficient for Ni^{+2} and Pb^{+2} respectively. It is well remarkable that Sc has two opposite effects on K : i) As Sc increases from 314.38 to 316.92, K increases; which can be explained in terms of that the increase in metal ion concentration increases the driving force for mass transfer and thus enhances film diffusion [8]. ii) As Sc increases from 316.92 to 321.93, K decreases; which may be attributed to that at high metal ion concentration, the solution viscosity increases, and diffusivity of Ni^{+2} decreases according to Stock's Einstein law [15].

In addition the activity of Ni^{+2} decreases because of the inter ionic attraction which becomes more pronounced at high electrolyte

concentration [20]. It is well observed that the initial Pb^{+2} concentration expressed as Sc has a negligible effect on K , the slight dependence of K on initial Pb^{+2} concentration may be ascribed to that the intra-particle diffusion is the predominant rate controlling step in case of Pb^{+2} ion exchange.

It is well known that at high concentrations intra-particle diffusion step predominates [8]. Comparison between % removals of Ni^{+2} and Pb^{+2} at the same superficial air velocity and initial ion concentration. It is well clear that for the same air velocity and initial concentration the % removal of Pb^{+2} is higher than the % removal of Ni^{+2} in other words the affinity of Amberjet resin (1200 Na) for Pb^{+2} is higher than of Ni^{+2} as. It has been found by Pehlivan et al. [21] that the selectivity of SO₃H group of the strong cation resin increases with increasing atomic number, valance, and degree of ionization of the exchanged metals, thus selectivity increased in the series: $Pb^{+2} > Cd^{+2} > Cu^{+2} > Zn^{+2} > Ni^{+2}$

Mass transfer data correlation

In view of the complex hydrodynamic conditions of the present work, dimensional analysis was used to correlate the present data. For gas spouting the first order rate constant can be related to the other variables by the dimensionless equation:

$$J_D = a_1 (Re * Fr)^\alpha \quad (5)$$

Where : J_D is the mass transfer factor $(K/A_n * V_g) * (\mu / \rho D)^{0.66}$, Re is the Reynolds number $(\rho d_b V_g / \mu)$, Fr : Froude number $(V_g^2 / g d_b)$, a_1 and α are constants show that the present mass transfer data fit the following overall correlations: For Ni^{+2} : $314.38 < Sc < 321.93$ and $230.63 < Re * Fr < 50210.24$

$$J_D = 49 (Re * Fr)^{-0.215} \quad (6)$$

With the average deviation=15.5 % For Pb^{+2} : $459.51 < Sc < 470.74$ and $229.54 < Re * Fr < 50052.67$

$$J_D = 117.71 (Re * Fr)^{-0.2404} \quad (7)$$

With the average deviation=6.88 %.

Conclusion

The performance of a batch conical air spouted bed for the removal of heavy metal ions by ion exchange has been investigated. The kinetics of ion exchange has been studied under different conditions such as heavy metal type, initial concentration of heavy metal and air superficial velocities. The rate of ion exchange was expressed by the volumetric mass transfer coefficient (K).

The following conclusions have been withdrawn:

1. As the air velocity increases the volumetric mass transfer coefficient increases for both type of heavy metals ions
2. The initial concentration of nickel ions (expressed as Sc) has two opposing effects on the volumetric mass transfer, they are: As Sc increases from 314.38 to 316.92, K increases; which can be explained in terms of that the increase in metal ion concentration increases the driving force for mass transfer and thus enhances film diffusion. As Sc increases from 316.92 to 321.93, K decreases; which may be attributed to that at high metal ion concentration, the solution viscosity increases, and diffusivity of Ni^{+2} decreases according to Stock's Einstein law, and the activity of Ni^{+2} decreases because of the inter-ionic attraction which becomes more pronounced at high electrolyte concentration. While the initial concentration of lead has a negligible effect on volumetric mass transfer coefficient.

Author	Experimental method	n
Bohm et al.	Mass transfer	0.250
Noseir et al.	Mass transfer	0.242
Sharma et al.	Mass transfer	0.290
Fair et al.	Mass transfer	0.220
Zewail	Ion exchange of Ni^{+2}	0.58
Zewail	Ion exchange of Cd^{+2}	0.25

Table 4: Effect of the superficial gas velocity on the mass transfer ($K\alpha V_g^n$).

3. The present mass transfer data have been correlated in terms of J_D , Re and Fr to allow for the design and operation of industrial scale conical air spouted bed used to conduct diffusion controlled reactions or mixed controlled reactions.

4. Further studies should be conducted in future to study the effect of column geometry such as cone angle, gas inlet diameter and operating parameters such as particle diameter and stagnant bed height on the ion exchange kinetics.

Nomenclature

Symbols

Symbol	Description	Unit
A	Surface area of Resin	cm^2
a_1	Constant	-
C	Concentration of heavy metal at time (t)	ppm
C_o	Initial concentration of heavy metal	ppm
D	Diffusion Coefficient	cm^2/s
d_b	Bubble diameter	cm
g	Acceleration Gravity Time	cm/s^2
k	First order rate constant	cm/s
K	Volumetric mass transfer coefficient Mass transfer factor	cm^3/s
t	Time	s
T	Temperature	$^{\circ}\text{C}$
V_g	superficial air velocity	cm/s
V_s	Volume of solution	L

Greek symbols

Symbol	Description	Unit
α	Constant	-
ρ	Solution Density	gm/cm^3
μ	Solution density	$\text{gm}/\text{cm.s}$

Dimensionless group

Symbol	Description	Unit
F_r	Froude Number	-
J_D	Mass transfer factor	-
R_e	Reynolds Number	-
S_c	Schmidt Number	-

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