Chemical Engineering Journal 150 (2009) 114–121

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption of cations on nanofiltration membrane: Separation mechanism, isotherm confirmation and thermodynamic analysis

S.S. Madaeni*, E. Salehi

Membrane Research Center, Chemical Engineering Department, Razi University, Tagh Bostan, Kermanshah 67149, Iran

ARTICLE INFO

Article history:
Received 24 September 2008
Received in revised form
24 November 2008
Accepted 3 December 2008

Keywords:
Membrane
Adsorption
Isotherm
Thermodynamic
Separation mechanism

ABSTRACT

In this research, the adsorption mechanism of the saturated brine cations (Fe^{2+}, Mg^{2+} and Ca^{2+}) on the negatively charged PVD membrane was investigated. The separation mechanism of the cations was cake deposition on the membrane surface due to adsorption. This was justified on the basis of Hermia blocking laws and surface cake analysis. Three equilibrium adsorption isotherms, Langmuir, Freundlich and Redlich–Peterson were fitted to the quasi-equilibrium adsorption data which were calculated using experimental flux and rejection. The Freundlich and Redlich–Peterson isotherms were found to well represent the measured sorption data on the basis of the acceptable coefficients of determination (r^2). An increase in temperature and pressure enhances the adsorption characteristics of the cations. However there are some limitations for pressure increment. For all cations, the significant thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated, compared and explained on the basis of charge density and hydration radius. The results indicate that the adsorption of cations on the nanofiltration membrane is endothermic and spontaneous due to positive ΔH° and negative ΔG°. The optimum temperature and pressure for sorption of the cations on PVD membrane were determined as 40 °C and 10 bar, respectively.

1. Introduction

The ability of nanofiltration membranes for processing salty solutions is partially based on the presence of chemical functional groups carrying positive or negative charges. This is an interesting technique in many aspects [1,2]. The fouling mechanism of the charged nanofiltration membrane is represented by sieving and electrostatic properties of the membrane [3]. In some cases, the membrane surface charge attracts the solution counter ions and the electrostatic interactions lead to considerable adsorption of particles on the membrane.

The adsorption mechanism and thermodynamic analysis in the field of membrane processes have recently obtained more attention. Mathematical models for adsorption of proteins on affinity membranes were presented using the equilibrium adsorption isotherms [4,5]. These models consider convection, diffusion and adsorption kinetics described by the Langmuir or Freundlich isotherms. The adsorption of papain on the nylon membranes was interpreted with pseudo-second-order kinetic models like Freundlich adsorption isotherm [6]. The adsorption-transport mechanisms of sulfate and chloride anions through PVD membrane were interpreted by the current authors [7] using both Langmuir and Freundlich isotherms. The thermodynamic analysis of adsorption indicates the feasibility and spontaneity of the adsorption process. This has been performed in previous studies [5,6]. A precise identification of the thermodynamic parameters such as ΔG°, ΔH° and ΔS° for adsorption leads to optimization of operating conditions such as temperature and pressure for removing the impurities from the solutions. However intensive membrane fouling due to high adsorption potential is a major limitation. Flux may be diminished to a critical value due to high adsorption on the membrane surface.

There is a strong motivation for finding a technique that allows in situ measurement of the adsorption properties of the membranes [8]. For interpretation of the sorption from binary or ternary metal solutions both mono-component and multi-component isotherms were employed. The results show the mono-component models are easy to use and successfully predict metal ions sorption from the multi-metal systems [9,10].

In the current study separation mechanism, isotherms and thermodynamic analysis for adsorption of metal cations on the negatively charged nanofiltration PVD membrane were investigated. Two-parameter equilibrium adsorption isotherms, Langmuir and Freundlich and a three-parameter isotherm, Redlich–Peterson were employed to fit the sorption data at three pressures of 8, 10 and 15 bar and three temperatures of 20, 30 and 40 °C. The effects of temperature and pressure on adsorption mechanism of cations were determined. The thermodynamic parameters of cation adsorption on the membrane were calculated and compared.

---

* Corresponding author. Tel.: +98 912 2045410; fax: +98 831 4274542.
E-mail address: smadaeni@yahoo.com (S.S. Madaeni).

1385-8947/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2008.12.005

2. An overview of adsorption isotherms

2.1. The Langmuir model

The Langmuir adsorption isotherm [11] is the most widely used for adsorption of a pollutant from a liquid solution given the following hypothesis:

- The adsorbed layer is one molecule thick (monolayer adsorption).
- Adsorption occurs at homogeneous sites within the adsorbent.
- Adsorptional energy is constant and does not depend on the degree of occupation of an adsorbent's active centers.
- All sites are identical and energetically equivalent.
- The adsorbent is structurally homogeneous.
- There is no interaction between molecules adsorbed on neighboring sites.

The Langmuir equation is represented as:

$$q = q_s \frac{kc}{1+kc} \qquad (1)$$

where q is equilibrium adsorbed amount per dry adsorbent mass (mg/g), q_s is the final adsorbed amount (mg/g), c is the adsorbate equilibrium concentration in solution (mg/l) and k is a constant reflecting the affinity of the membrane for the metal ions.

2.2. The Freundlich model

The empirical Freundlich isotherm [9,12] is used to describe the multilayer adsorption with interaction between molecules, on a heterogeneous sorbent surface. This isotherm can be expressed as:

$$q = kc^m \qquad (2)$$

where q is sorption at equilibrium (mg/g), c is the residual ion concentration at equilibrium (mg/l), k is the relative sorption capacity and m is an indicator of sorption intensity or surface heterogeneity. The value of m indicates the degree of non-linearity between solution concentration and adsorbed phase as follows: if m is equal to unity, the adsorption is linear; if the value is below unity, this implies that the adsorption process is chemical and the surface is relatively homogeneous; if the value is above unity, adsorption is a physical process and the sorbent is relatively heterogeneous. In recent case, the sorption favorability and the adsorption site's homogeneity increased, approaching m-value to unit.

2.3. The Redlich–Peterson model

Redlich–Peterson [12] is a three-parameter empirical equation which may be used to represent adsorption equilibria over a wide concentration range and can be applied either in homogeneous or heterogeneous systems. This isotherm is represented by

$$q = \frac{kc}{1+bc^m} \qquad (3)$$

where k and b are isotherm constants and m is an exponent which indicates the non-linearity of the adsorption systems. Eq. (3) is simplified to the Freundlich isotherm at high adsorbed concentration and to the Langmuir isotherm when $m = 1$.

3. Materials and methods

3.1. Feed

Saturated brine was used as the feed. This solution was obtained from Cholor-Alkali Unit in Emam Khominei Seaport Petrochemical Plant (Iran). The pH of the solution was in the range of 8.5–9. The concentrations of various solutes available in the solution are presented in Table 1. Physical properties of the ions in the feed are depicted in Table 2 [13,14].

Table 1
The concentrations of different solutes in the feed.

Solute	Concentration
NaCl	290 g/l
SO_4^{2-}	8.0 g/l
Mg^{2+}	9.2 mg/l
Ca^{2+}	8.2 mg/l
Fe^{2+}	0.8 mg/l

Table 2
Physical properties of the ions in the feed [13,14].

Ion	Ionic radius (nm)	Hydration radius (nm)	Hydration enthalpy (kJ/mol)
Na^+	0.095	0.365	418
Cl^-	0.181	0.347	338
SO_4^{2-}	0.23	0.38	1138
Mg^{2+}	0.065	0.429	1923
Ca^{2+}	0.1	0.349	1653
Fe^{2+}	0.055	0.435	1981

3.2. Analysis

Concentrations of Na^+, Fe^{2+}, Ca^{2+} and Mg^{2+} were determined by Atomic Absorption Spectrophotometry (AA-6300 Shimadzu). SO_4^{2-} and Cl^- analysis were performed using Ionic Chromatography (761 Compact IC, Metrohm).

3.3. Membrane

PVD (hydranuatics) polymeric membrane was employed for experiments. Characteristics of the membrane are presented in Table 3 [7,14].

3.4. Experimental set-up

Fig. 1 depicts the schematic of the experimental set-up. In the experimental trails, the cross-flow batch concentration process method was selected. It means that permeate flow was taken out of the loop and retentate flow was completely returned to the tank. For this purpose a high-pressure pump was employed. On the other hand, pipelines and fittings including the cell, which holds the membrane, must be able to tolerate high pressure. Characteristics of the pump were: $Q_{max} = 480$ l/h, $P_{max} = 80$ bar, $T_{max} = 50\,^\circ$C. Excluding some parts of the line that were stainless steel, other parts were high-pressure hoses. The system consisted of a valve to control the applied pressure by the pump and a by-pass valve. These valves were used to control the flow and the pressure. The cell consisted of two cubic parts and was made of a specific alloy. A membrane with the area of 0.0023 m^2 was sandwiched between two parts. There were two ducts connected to two hoses. One of these hoses was the feed inlet and the other was retentate out let. The rectangular

Table 3
Characteristics of PVD membrane [7,14].

Membrane	PVD
Skin material	Polyethylene terphetelete
Support material	Bis(phenol A polysulfone)
Surface characteristic	Smooth
Support characteristic	Coarse fiber
Membrane structure	Two layer
Mass per sheet (g)	0.76
Thickness (μm)	150