Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of Membrane Science 265 (2005) 85–93

journal of MEMBRANE SCIENCE

www.elsevier.com/locate/memsci

Mechanistic interpretation of ionic azo dye flux decline through compacted Na-montmorillonite membrane

Peter G. Oduor[a,*], T.M. Whitworth[b]

[a] *Department of Geosciences, North Dakota State University, Fargo, ND 58103, USA*
[b] *Department of Geological and Petroleum Engineering, University of Missouri-Rolla, Rolla, MO 65409, USA*

Received 26 July 2004; received in revised form 25 April 2005; accepted 27 April 2005
Available online 4 June 2005

Abstract

The decrease in filtrate flux of ionic azo dyes through compacted Na-montmorillonite membrane can be adequately described by (i) analytical and empirically derived transport equations, (ii) solute rejection and intrinsic retention equations and (iii) X-ray diffraction. Experiments were performed using two ionic azo dyes, Orange G (7-hydroxy-8-phenlyazo-1,3-naphthalenedisulfonic acid disodium salt), a molecular biology reagent and brilliant yellow (C.I. 24890 direct yellow 4). Filtrate samples were collected using a static head setup consisting of a longitudinal flow acrylic cylinder cell through compacted Na-montmorillonite membrane. The results indicated that there was initial rapid flux reduction for the first 3 days due to surficial fouling owing to affinity of hydrophilic organic compounds rapidly getting attached to exchange sites at the dye–membrane interface before slowing down to a quasi-steady-state (5–7 days) and gradual gelation period (8–16 days) during steady-state. The ratio of flux reduction was approximately 3:5 for brilliant yellow to Orange G. The flux values were higher than mass transfer coefficients. Flux decline for the dyes followed an exponential decay described by $J \propto 1/t^n$, with $n = 0.9556$ for yellow dye and $n = 0.8923$ for Orange G. X-ray diffraction indicated that both the lower molecular weight Orange G ($452.4\,\mathrm{g\,mol^{-1}}$) and higher molecular weight brilliant yellow ($624.6\,\mathrm{g\,mol^{-1}}$) dyes are less preferentially retained within the basal spacing of Na-montmorillonite due to only a slight shift in the range 5.8–6° 2θ region. The results offer a preliminary study in the fate, transport and recyclability of these ionic azo dyes through smectitic membranes.

Keywords: Mass transfer; Diffusion coefficient; Concentration polarization; Ion exchange; Basal spacing

1. Introduction

Compacted montmorillonite has been shown to exhibit membrane properties [1–6]. Mass transfer coefficients can therefore be used to describe transport processes of organic macromolecules like azo dyes through a compacted montmorillonite membrane. Ionic azo dyes will completely or partly dissociate in aqueous solutions depending on amount of dye dissolved per unit volume of deionized water. These soluble dyes have been found to sometimes modify the cationic exchange capabilities of soils, subsoils, and aquifer materials [7–9]. Jackson and Landolt [10] pointed out that owing to the large molecular mass of most azo dyes, there might be moderate ion exchange onto compacted Na-montmorillonite thus modifying the permeability of Na-montmorillonite. Extensive adsorption due to ion exchange usually fouls the membrane. This fouling can significantly affect solute transport. Flux rate equations usually incorporate a fouling factor to cater for flux decline, mass transfer coefficient and membrane efficiency.

In general, the membrane efficiency or selectivity of a Na-montmorillonite membrane increases with a decrease in organic species concentration when fouling is minimal. Analytical models have been used to characterize flux decline vis-à-vis amount of fouling in relation to the solute flux of organic molecules through membranes but very few have incorporated transient variation of all pertinent parameters like mutual diffusion coefficients of solute and solvent, mem-

---

[*] Corresponding author. Tel.: +1 701 231 7145; fax: +1 701 231 7149.
E-mail addresses: Peter.Oduor@ndsu.edu (P.G. Oduor), mikew@umr.edu (T.M. Whitworth).

0376-7388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2005.04.038

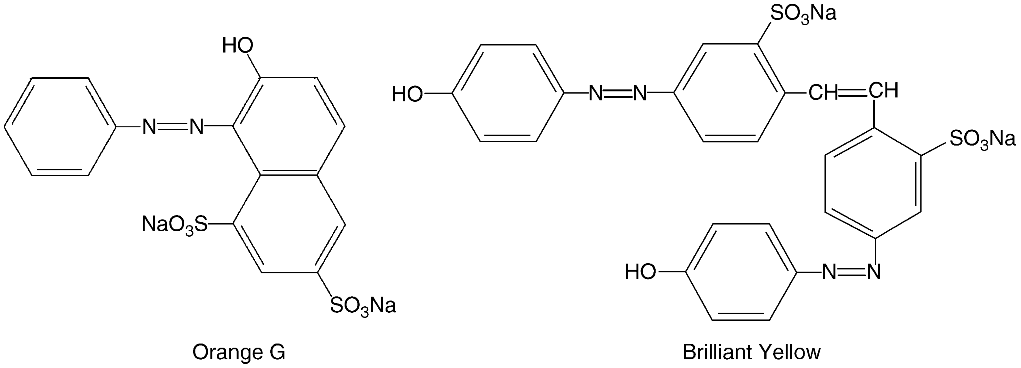

Fig. 1. Structures of organic dyes used in this study.

brane selectivity, flux decline and buildup of organic solutes adjacent to the membrane. Mulder [11] surmised that some rudimentary models describe flux decline as an exponential function of time. Other models have incorporated fouling and offered a qualitative explanation of organic contaminant fate and transport for specific organics [12].

The dyes used in this study were Orange G sodium salt, a reagent in molecular biology, $C_{16}H_{10}N_2Na_2OS_2$ (7-hydroxy-8-phenlyazo-1,3-naphthalenedisulfonic acid disodium salt) and mostly used as an internal standard for protein separation on SDS-capillary electrophoresis or a tracking dye in nucleic acid gel electrophoresis, and brilliant yellow $C_{26}H_{20}N_4O_8S_2$ (C.I. 24890 direct yellow 4) of molecular weight 624.56 g mol^{-1} (see molecular structures in Fig. 1). The purpose of this study was to form an initial assessment of specific ionic azo dye flux decline through compacted Na-montmorillonite, and characterize this phenomenon qualitatively and using a simple empirical transport equation.

2. Theory

Rejection of solute at the high-pressure side of the membrane increases concentration of the solute adjacent to the membrane (Fig. 2). Solute buildup adjacent to the membrane on the influent side (Fig. 2) is denoted by C_o, which is higher than the influent concentration, C_i. The influent concentration is usually regarded as invariant. After time t, the effluent concentration, C_e, increases until steady-state is attained, that is, when $C_e \approx C_i$. The distance $x = \Delta x$ is equivalent to membrane thickness in cm and the length $x = \delta$ corresponds to the distance where effect of polarization is diminished measured from the membrane surface on the influent side. A concentration gradient is generated which prevents migration of other molecules from the bulk feed side to the effluent side thus promoting a back diffusive flux, $J_d = -D\,\partial C/\partial x$ [4,11]. The solution flux (J_v, cm s^{-1}) exits through the membrane whereas, $J_s = C_x J_v$, where C_x is the concentration at a distance x from the membrane, and J_s is solute advected toward the membrane by hydraulic forces. Consider a mass balance within the boundary layer (Fig. 2), if the rejection of the solute is less than 100% such as is the case with imperfect membranes and considering the system as a closed one, i.e., solute-fixed or membrane-fixed frame of reference then [11]:

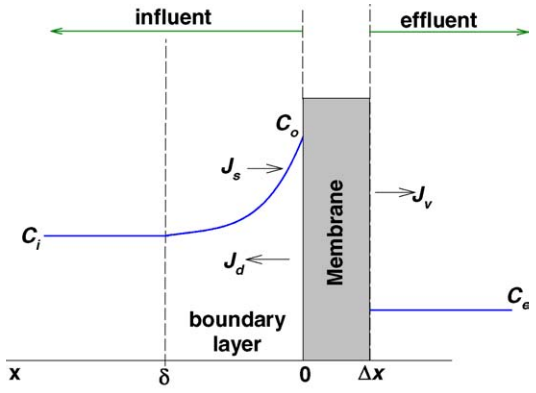

Fig. 2. Illustration of concentration profile.

$$C_x J_v + D\frac{dC}{dx} = C_e J_v. \tag{1}$$

If δ is the boundary layer thickness in cm, then applying the conditions, $C_x = C_o$ at $x = 0$ and $C_x = C_i$ at $x = \delta$, at steady-state, integration of Eq. (1) gives:

$$C_o - C_e = (C_i - C_e)\exp\left(\frac{J_v}{q}\right), \tag{2}$$

and $q = (D/\delta)$ where q is the mass transfer coefficient and D is the diffusion coefficient in cm^2 s^{-1}. Eq. (2) is known as the ‘film–model’ relationship. The dimensionless intrinsic retention R_{int} is given by [11]:

$$R_{int} = 1 - \frac{C_e}{C_o}. \tag{3}$$

The value of the intrinsic retention gives an approximate value of the efficiency of the membrane since it is related to the filtration coefficient. The filtration coefficient is also defined as the ratio of solute exiting the membrane as effluent (C_e) to that entering the membrane at the solute–membrane interface C_o, that is C_e/C_o, ranges from zero for ideal membranes to unity for porous media having no membrane prop-