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MASS-TRANSFER MODEL FOR HUMIC ACID REMOVAL BY ULTRAFILTRATION

Humic acid (HA) molecules present in the soil dissolve in the water and can be found also in the well water. They have different size, molecular weight and structure. It is important to remove these molecules because they build carcinogenic by-products when they react with disinfectants. Membrane filtration can be an effective method of removing humic acid from water. Earlier experiments have proved that ultrafiltration membranes are proper for this task. The aim of this study was to find a new formula which helps to design a well-water filtration. We needed to model the mass transfer during the membrane filtration and to calculate the mass-transfer coefficient. The calculations were carried out in two ways: by using the results of laboratory measurements and criterial equations and by using heat-transfer analogy. The results reveal that the values measured and calculated are in agreement, the heat-transfer analogy can be applied and the equations are useful for designing the membrane for drinking water treatment.

Keywords: *mass-transfer model, humic acid, membrane filtration, drinking water, natural organic matter, disinfection by-product*

NOMENCLATURE

J – flux [$dm^3/(m^2h)$],
J^* – critical flux [$dm^3/(m^2h)$],
Δp – transmembrane pressure difference [bar],
c_P – permeate concentration [mg/ dm^3],
c_G – gel layer concentration [mg/ dm^3],
c_B – bulk concentration [mg/ dm^3],
D – diffusion coefficient [m^2/s],
δ – thickness of boundary layer [m],
k – mass-transfer coefficient [m/s],
x – association coefficient [–],
M_s – molecular weight of solvent [kg/kmol],
V_0 – molecular volume of the diffusing material [$m^3/kmol$],
T – temperature [K],

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η – dynamic viscosity [Pas],
ν – kinematic viscosity [m^2/s],
ρ – density [kg/m^3],
d – inner diameter of hollow-fiber membrane [m],
v – velocity of solution [m/s],
Q_R – recirculation flow rate [m^3/s],
A – filter area of the membrane [m^2],
L – length of membrane [m].

1. INTRODUCTION

Humic substances (fulvic acid, humic acid, humin, etc.) dissolve in natural soil waters, because they are heterogeneous mixtures of degradation products from plant and animal residues [1]. The properties of humic substances depend on their origin, but usually a humic acid is the major component of natural organic matter (NOM) found also in surface and well water. It has been proved that in the course of traditional water treatment humic acids react with disinfectants, e.g. chlorine, to form trihalomethanes which in the drinking water are dangerous carcinogens [2].

Recently both researchers and industrial manufacturers face with an important and difficult task of removing humic acids because they form many kinds of chemical structures and all are sensitive to environmental impacts.

Literature data and laboratory-scale experiments [3]–[5] proved that the membrane filtration is an effective and economic tool for humic acid removal: chemicals are not used in the separation and the humus-rich by-product of the membrane filtration can be utilized in agriculture.

In this work, ultrafiltration was applied to remove humic acids from different natural well waters contaminated by humic acids and, for comparison, from model solutions. The filtration process was described by mass-transfer model. The model parameters were calculated for different membranes and for different patterns of fluid flow. In the case of laminar and turbulent flow, the Sherwood equation of mass transfer was used, while in the case of transient flow, a regime heat transfer analogy was applied [6], [7], [8].

2. MATERIALS AND METHODS

In our experiments, the following feeds were used:

- Rich in humic acids well water from Zenta (Serbia), Bekescsaba (Hungary) and Oroshaza (Hungary).
- Model solution of humic acid.
- Deionized water.

For humic acid removal two membranes were chosen on the basis of earlier experiment: PM1 and PM2 membranes (manufacturer: KOCH, membrane material: polysulfone of the molecular weight cut-offs of 1 and 2 kDa). The membrane modules were home-made from 15 hollow fiber, inside-out membranes each (length: 30 cm, inside diameter: 1 mm, active surface: 0.012 m^2) [4].

Humic acid content was determined based on the measurement of the UV absorbance at 254 nm [9], [10]. In earlier experiments, total organic carbon (TOC, mg/dm^3) and dissolved organic carbon (DOC, mg/dm^3) were also measured, but the modelling calculations were done on the basis of the absorbance measurements [3], [4].

3. MASS-TRANSFER MODEL

In our measurements, we have used cross-flow ultrafiltration through hollow-fibre membranes. In the concentration-polarization layer, molecular diffusion can be detected which drifts upstream the convective flow of the solvent. During filtration the gel layer (gel layer concentration c_G is constant) and the boundary layer (boundary layer concentration c_M) are developed (figure 1).

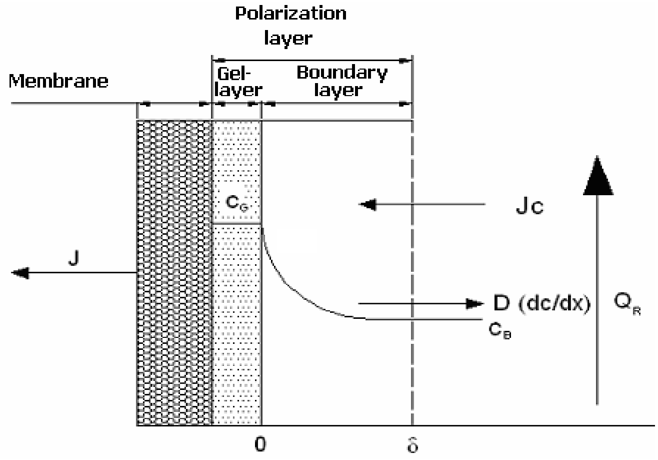

Fig. 1. The schematic diagram of the cross-flow filtration

In the case of a constant permeate flow, temperature and pressure values, the flux of component and the molecular diffusion are equivalent:

$$J \cdot (c - c_p) = D \cdot \frac{dc}{dx} . \tag{1}$$

The differential equation can be separated, so the mass-transfer model is the following (assuming that $c_G >> c_P$; $c_P \sim 0$)

$$J = \frac{D}{\delta} \ln \frac{c_G}{c_B}, \tag{2}$$

where J [$\mathrm{dm^3/(m^2 \cdot h)}$] is the flux, D is the diffusion coefficient [$\mathrm{m^2/s}$], δ [m] is the thickness of the boundary layer, c_G [$\mathrm{mg/dm^3}$] is the concentration of gel layer (it depends on the rejected macromolecules, and is independent of the membrane and the flow rates), c_B [$\mathrm{mg/dm^3}$] is the concentration of the bulk, $k = D/\delta$ is the mass-transfer coefficient [m/s].

Based on the geometric parameters of the membrane module (15 pieces of inside-out hollow-fibre membranes, inner diameter of 1 mm), the feed concentration and the flow relations, we are able to calculate the Sherwood number in the case of laminar flow, turbulent flow and transient flow regime.

4. RESULTS AND DISCUSSION

The aim of the modelling was to determine the mass-transfer coefficient (k). The calculations were carried out in two ways: by using the results of laboratory measurements and those from the criterial equations and by using heat-transfer analogy.

4.1. CALCULATION ON THE BASIS OF LABORATORY MEASUREMENTS

In the experiments, three different kinds of well water, model solution and deionized water were used for measuring the flux at different pressures and recirculation flow rates [4]. In order to calculate the mass-transfer coefficient (k) from equation (3), we need to determine the bulk (c_B) and gel layer (c_G) concentration and the critical flux (J^*):

$$J = k \cdot \ln \frac{c_G}{c_B}. \tag{3}$$

The critical fluxes were determined by measuring the flux of model solution and well water at different transmembrane pressures (Δp). In the case of pure water (deionized water), the flux is directly proportional to transmembrane pressure. Due to filtering of natural water or model solution the flux increase is reduced because of the concentration-polarization until the flux is constant. This flux has its critical value (J^*) at the critical transmembrane pressure (Δp^*), as is shown in figure 2.

The concentration of gel layer depends on the flow conditions and the feed but is independent of the membrane. The concentration of gel layer was determined by means of concentration experiments, which were carried out in the laminar and transient flow regimes. The results for PM1 membrane are shown in table 1.

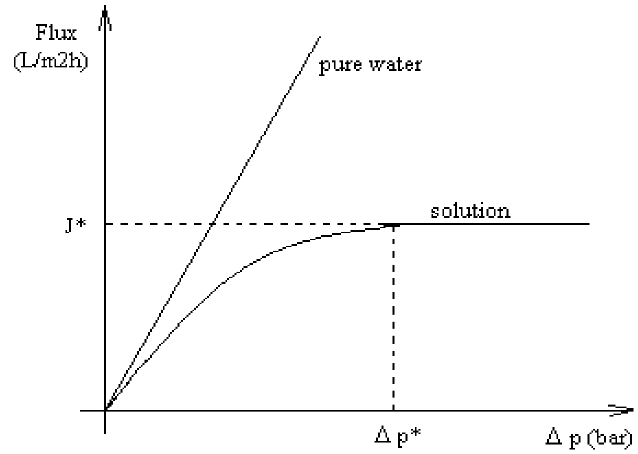

Fig. 2. The schematic diagram of flux in function of transmembrane pressure in the case of pure water and solutions

Table 1

Measured critical flux, concentration of gel layer, bulk concentration and calculated mass-transfer coefficient (model solution, well water: Zenta, Bekescsaba, Oroshaza)

Feed, PM1	J^* $dm^3/(m^2h)$ laminar	J^* $dm^3/(m^2h)$ transient	C_B mg/dm^3	C_G mg/dm^3	k m/s laminar	k m/s transient
Model solution	143.98	450.51	11.75	2440.6	**$7.47\cdot10^{-6}$**	**$2.34\cdot10^{-5}$**
Zenta	112.11	340.57	21.24	18033.7	**$4.60\cdot10^{-6}$**	**$1.40\cdot10^{-5}$**
Bekescsaba	186.61	241.31	11.34	54176.4	**$6.37\cdot10^{-6}$**	**$1.75\cdot10^{-5}$**
Oroshaza	113.47	306.67	22.84	44355.9	**$3.83\cdot10^{-6}$**	**$1.16\cdot10^{-5}$**

4.2. CALCULATION ON THE BASIS OF CRITERIAL EQUATIONS

In order to calculate the diffusion coefficient, the equation of Wilke–Chang was used [9]:

$$D = 2.66\cdot10^{-8}\cdot\frac{(x\cdot M_s)^{0.5}}{V_0^{0.6}}\cdot\frac{T}{\eta}, \tag{4}$$

where D is the diffusion coefficient (m^2/s), x stands for the assosiation coefficient of the solvent (for water $x = 2.6$), M_s is the molecular weight of the solvent (kg/kmol), V_0 – the molecular volume of the diffusing material at the boiling point (m^3/kmol), T – the temperature of the solution (K), η – the dynamic viscosity of the solvent (Pas).

The humic acid molecules can be very different, depending on their origin, e.g. on the surroundings etc, and it is a hard task to measure their exact molecular weight (size-exclusion chromatography, gel-filter chromatography can be used as approximate definition). Based on literature data it may be concluded that the approximate molecular weight of humic substances ranges between 1600 and 20000 g/mol [1], [2], [10], [11].

The dimensionless Schmidt number was calculated based on the physical data of the solvent:

$$Sc = \frac{\eta}{D \cdot \rho}, \tag{5}$$

where η is the dynamic viscosity of the solvent (Pas) and ρ is its density (kg/m^3).

The Reynolds number defines the hydrodynamic regime:

$$Re = \frac{d \cdot v \cdot \rho}{\eta}, \tag{6}$$

where d is the inner diameter of the hollow-fibre membrane (m), v – the velocity of the solution (m/s), ρ – the density of the solvent (water) (kg/m^3), and η – the dynamic viscosity of the solvent (Pas). The liquid velocity can be calculated from the recycle flow rate $v = Q_R / A$, where Q_R stands for the recirculation flow rate (m^3/s), A is the active surface of the membrane (m^2).

The aim of this study was to determine the mass-transfer coefficient k. Basic equations reported in literature [7] describe laminar and turbulent flow regimes:

- laminar

$$Sh = 1.62 \cdot (Re \cdot Sc \cdot d / L)^{0.33}, \tag{7}$$

- turbulent

$$Sh = 0.04 \cdot Re^{0.75} \cdot Sc^{0.33} = \frac{k \cdot d}{D}. \tag{8}$$

In the literature, no equation for the transient flow regime could be found, so heat transfer analogy was applied [8]. The invariants were determined on the basis of laboratory measurements:

$$Sh = 0.063 \cdot (Re^{2/3} - 125) \cdot Sc^{1/3} \cdot [1 + (d / L)^{2/3}]. \tag{9}$$

The mass-transfer coefficient can be calculated from the Sherwood number:

$$k = \frac{Sh \cdot D}{d}. \tag{10}$$

The values calculated are collected in tables 2, 3 and 4. From the results it can be seen that an increase in the Reynolds number (the flow velocity is high) brings about a decrease in the thickness of the concentration-polarization layer (δ), so the mass transfer coefficient ($k = D/\delta$) increases.

Table 2

Molecular weight, molecular volume, diffusion coefficient of the diffusing material and the calculated values of the Reynolds number

M g/mol	V_0 m^3/kmol	D m^2/s	Re Laminar	Transient	Turbulent
1600	1764.4	$1.66 \cdot 10^{-10}$	2353.6	4707.2	11768
5000	5502.1	$8.39 \cdot 10^{-11}$	2353.6	4707.2	11768
10000	11000.4	$5.54 \cdot 10^{-11}$	2353.6	4707.2	11768
15000	16506	$4.34 \cdot 10^{-11}$	2353.6	4707.2	11768
20000	22008	$3.65 \cdot 10^{-11}$	2353.6	4707.2	11768

Table 3

Schmidt and Sherwood numbers at different molecular weights of humic acid

M g/mol	Sc	Sh Laminar	Transient	Turbulent
1600	6024.10	59.69	177.37	798.82
5000	11918.95	74.77	222.34	1000.56
10000	18050.54	85.74	255.21	1147.43
15000	23041.47	92.94	276.66	1243.69
20000	27397.26	98.40	292.97	1316.83

Table 4

Coefficients of mass transfer calculated at different molecular weights and flow regimes

M g/mol	k (m/s)		
	$Re = 2353.6$ (laminar)	$Re = 4707$ (transient)	$Re = 11739$ (turbulent)
1600	$9.90 \cdot 10^{-6}$	$2.95 \cdot 10^{-5}$	$1.33 \cdot 10^{-4}$
5000	$6.27 \cdot 10^{-6}$	$1.87 \cdot 10^{-5}$	$8.39 \cdot 10^{-5}$
10000	$4.75 \cdot 10^{-6}$	$1.41 \cdot 10^{-5}$	$6.36 \cdot 10^{-5}$
15000	$4.03 \cdot 10^{-6}$	$1.20 \cdot 10^{-5}$	$5.40 \cdot 10^{-5}$
20000	$3.59 \cdot 10^{-6}$	$1.07 \cdot 10^{-5}$	$4.80 \cdot 10^{-5}$

5. CONCLUSIONS

From the mass-transfer model the following inferences can be drawn:

- The criterial equations for calculating the Sherwood number can be applied to laminar and turbulent flow regimes, the results are reliable.
- The new equation that is based on the heat-transfer analogy describes satisfactorily the transient flow regime, whose values are between the values characteristic of laminar and turbulent flows.
- The mass-transfer coefficients for model solutions and natural well waters determined from the laboratory measurements and from the criterial equations are in agreement. So the approximate molecular weight of other natural well waters can be estimated.

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