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REMOVAL OF NATURAL ORGANIC MATTER FROM POTABLE WATER USING PHOTO-CATALYTIC MEMBRANE REACTOR

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The application of photo-catalysis combined with membrane filtration for the oxidation of humic acid substances (HA) which is one of the major natural organic matters (NOMs) is discussed in this paper. Theoretical model shows a potential advantage of photo-catalytic filtration under low flux conditions. Cross-flow filtration is applied for HA removal using a TiO_2 membrane under UV conditions. An increase of the flux through the membrane was observed by applying UV light.

keywords: Natural organic matter (NOM), humic acid, membrane filtration, photocatalyst, potable water

1. INTRODUCTION

Natural organic matter (NOM) is a major cause of colour and odour in potable water. Moreover, the combination of NOM and chlorine, a common additive in potable water, has been pointed out to be a source of possible formation of carcinogens [1,2].

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While more than 90% of NOM can be removed by membrane filtration or by coagulation, removing small concentrations of NOM, especially small to medium size, with reasonable cost and efficiency is a challenging task.

Photo-catalytic oxidation has a potential as a process to remove small to medium sized NOM. Table 1 shows examples of photo-catalytic oxidation of humic acid (HA), which is one of the major components of surface water and often represented as NOM.

Table 1. HA decomposition by photo-catalysis

Feed	HA conc. (mg/L)	TiO_2 conc. (g/L)	pH	Degradation rate constant (10^{-2} min^{-1})	$t_{1/2}$ (min)	ref.
HA from river	50	0.25	6.5 ± 0.5	0.83	84	[3]
HA salt from Aldrich	50	0.25	6.5 ± 0.5	1.60	43	[3]
HA (Aldrich) in sea water with air flow	40	1	4.5	2.6		[4]
HA (Aldrich) in sea water with oxygen flow	40	1	4.5	4.1		[4]

Photo-catalysts are often applied in powder form dispersed in water [5,6]. In such a case an extra task to separate the photo-catalyst from the treated water is required. Powdered catalyst may not be preferred in the application of potable water treatment, as remaining photo-catalysts can be a health concern.

Photo-catalysts immobilized on/in substrates offer an alternative to powders. Various materials, such as polymers, inorganic materials, are used as supports [7,8]. The configuration of immobilized photo-catalytic system can be classified into either flow-over reactors [9–11] or flow-through (filtration) reactors [12] as show in Figure 1. A higher photo-catalytic surface area per volume of the reactor combined with sufficient light supply to the catalysts will reduce the module size in both cases.

Flow-through reactor is a configuration where NOM removal can be achieved not only by the photo-oxidation properties but also by the sieving properties of the photo-catalytic substrates. Fouling is reported as one of the major difficulties in membrane filtration with NOM containing solutions [13]. The application of photo-catalytic oxidation may clean the membrane surface and avoid fouling during the filtration. Photo-catalytic oxidation may be enhanced by additional chemicals in some cases [14]. Membrane contactor has been an alternative configuration that opens for an efficient addition of helping agents to the reaction field [15].

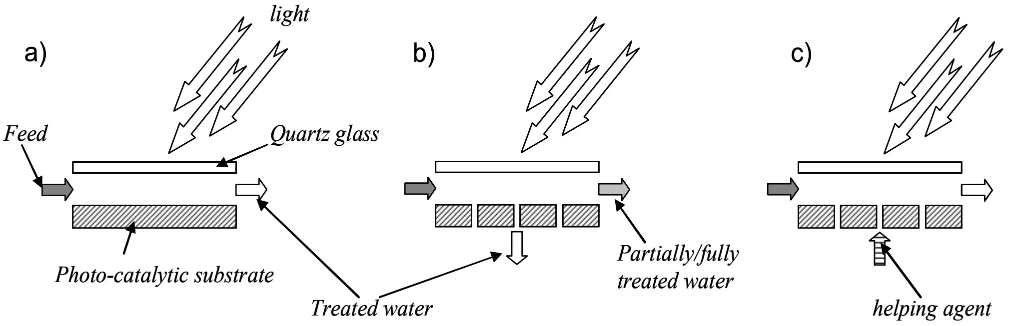


Fig. 1. Various photo-catalytic reactor configurations:

a) Flow-over reactor: water flows over a photo-catalytic substrate and organics in the water are oxidized during the contact with the substrate
b) Membrane filtration combined with photo-catalysis: The photo-catalytic substrate is porous and water permeates through it due to overpressure on the feed side. Organics in water are oxidized not only by flowing over the photo-catalytic substrate but also by permeating through it. Organics are also removed by the sieving property of the substrate. The concentration of organics in the retentate may decrease depending on the operating conditions.
c) Membrane contactor combined with photo-catalysis: Water flows over the photo-catalytic substrate. Helping agents, such as oxidants, can be supplied from the other side of the membrane.

In this study, application of a photo-catalytic membrane filtration to HA removal is studied. The operating conditions for a possible removal of HA are estimated based on theoretical models. Cross flow filtration with TiO_2 membrane is performed under UV to remove HA.

1.1..Models

1.1.1 Membrane filtration

Kedem-Katchalsky described the membrane transport as follows [16]:

$$J_v = L_P(\Delta P - o \cdot \Delta\pi)$$

$$J_S = P(C_2 - C_3) + (1-\sigma)C_a J_V$$

In the case of pure water permeation, the equation above is simplified to:

$$J_v = L_P \Delta P$$

In this model, the membrane performance is represented by three parameters: L_p, o and P. These parameters are independent on the operating conditions, while flux through the membrane and the ability to remove the solute from the solution changes with e.g. an increasing pressure at the feed side.

The pore model relates the membrane morphology to the permeation and the separation properties of the membrane [17]. Cylindrical pores and spherical molecules are assumed in this model:

$$L_P = (r_P^2 / 8\mu)(\mathrm{A}_k / \Delta x)$$

$$o = 1 - S_F \left\{1 + (16 + 9) q^2\right\}$$

$$P = D \cdot S_D (\mathrm{A}_k / \Delta x)$$

where,

$$q = \frac{r_s}{r_p}$$

$$S_F = (1-q)^2 \left\{2 - (1-q)^2\right\}$$

$$S_D = (1-q)^2$$

If solute is either partially or fully rejected during membrane filtration, the concentration of the solute at the membrane surface becomes higher than its concentration in the bulk at the feed side. This phenomenon is called concentration polarization.

Concentration polarization can be estimated by taking the material balance in the boundary layer [18]:

$$J_v C - D \tfrac{dC}{dx} = J_v C_3$$

Under the boundary conditions ($x = 0$: $C = C_b$, $x = \delta$; $C = C_m$), the equation above becomes:

$$\frac{C_2 - C_3}{C_1 - C_3} = \exp \frac{J_v}{k}$$

The mass transfer coefficient, k, in the boundary layer can be estimated from the flow conditions:

$$S_h \equiv \frac{dk}{D}$$

Sherwood number (Sh) is described as follows in case of a turbulent flow [19]:

$$S_h = 0.023 R_e^{0.875} S_c^{0.25}$$

where;

$$R_e \equiv \frac{\rho d u}{\mu} \text{ and } S_c \equiv \frac{\mu}{\rho D}$$

For typical operating conditions such as 4000<Re<10000, the mass transfer coefficient will vary in the range of 2 to 5 (10^{-6} m s^{-1}). In this study, k value is estimated to be 3.5 (10^{-6} m s^{-1}).

The size of HA (r_s) is assumed to be 5.4 nm by using the diffusivity value reported [20] and by applying the Stokes equation: $r_s = \frac{\kappa T}{6\pi\mu D}$. Note that the size distribution of HA is not taken into account in this study.

Target application is potable water treatment, which solution contains very low HA concentration, such as <1 mg/l. The Van't Hoff equation is applied to estimate the osmotic pressure in the estimation.

1.1.2. Photo-catalytic oxidation combined with membrane filtration

The following assumptions are made to examine the possible operating conditions for photo-catalytic membrane filtration:

- The membrane has sieving abilities at the surface
- Oxidation of non-sieved organics occurs during the permeation through the photo-catalytic layer
- The photo-catalytic layer has cylindrical pores with thickness of 10μm where light source can penetrate through and photo-catalysis does not affect the water permeation through the membrane

Photo-catalysis is often described by the first order equation: $\ln \frac{C_t}{C_0} = -Kt$. Contact time, t, is estimated as a function of the inverse of flux through the membrane: $t = \frac{A_k \cdot \Delta x}{J_V}$.

2. EXPERIMENTAL

Photo-catalytic membranes were prepared by depositing commercial photo-catalysts

(ST-01, Ishihara Sangyo LTD) on porous α-alumina disks (Keranor Ø 38 mm). 25 μg/l of sodium HA salt (Sigma Aldrich) was used as feed solution. Three black light lamps (8W, main wave length: 350nm) were combined and used as light source. All the experiments were performed at room temperature. Concentration change of HA solutions during the treatment was measured by UV-vis analysis (Shimadzu, UV-1800).

Membrane filtration tests were performed under cross-flow filtration conditions with a flow rate of 1 l/min. Both pure water flux and HA solution flux through the membrane were measured. The measurements were performed at increasing pressure. After reaching the maximum pressure, the pressure was reduced to the minimum value. The flux was measured several times to confirm the steady state.

3. RESULTS AND DISCUSSION

3.1. Membrane filtration combined with photo-catalysis

Figure 2 shows the maximum possible removal of HA with a variety of ratios between the membrane pore size and HA size. The estimated pore size based on the average HA size is also included in the figure. When the membrane pore size is smaller than the size of HA, HA will not permeate through the membrane and a 100% removal

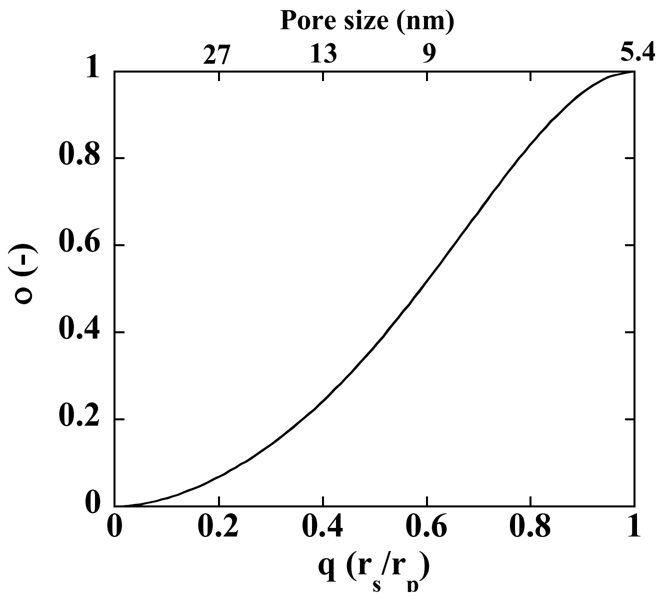
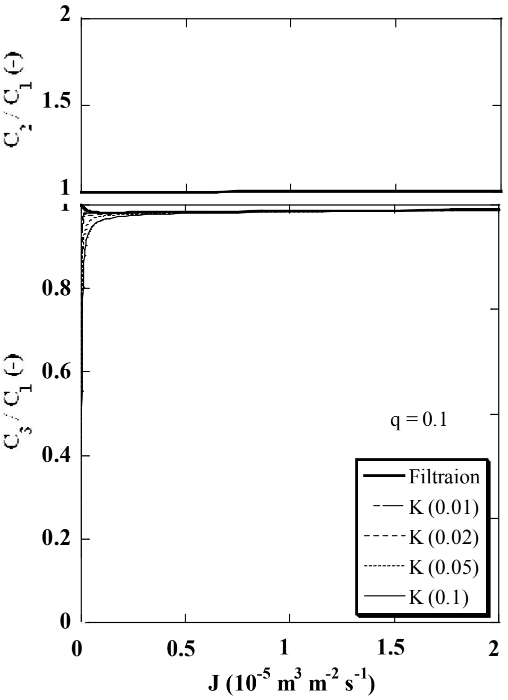
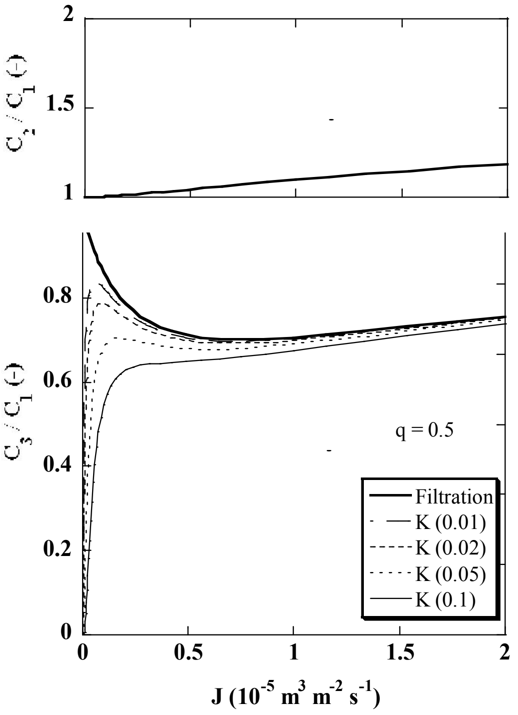


Fig. 2. Potential of HA removal as a function of the membrane pore size





(o = 1 in the figure) will be achieved. On the contrary, the degree of removal will depend on the pore size of the membrane with pore size larger than the size of HA. For example, 50% of HA can potentially be removed with a membrane having pores 170% larger than the size of HA.

Oxidation of HA during the permeation through membrane is one potential application of photo-catalysis combined filtration. Figure 3 illustrates the HA concentration decrease after passing through the membrane. The change is shown as the ratio of concentration in the permeate solution (C_3) and in the feed solution (C_1). Both conventional membrane filtration and photo-catalysis combined filtration with various kinetic constants are illustrated in Figure 3. Kinetic constants are varied from k= 0.01 to 0.1, are of similar order as the value for HA oxidation reported in Table 1. Figure shows membranes with three different pore sizes.

HA concentration in the permeated solution is high under low flux through membrane and becomes lower when increasing the flux that will be achieved by applying higher pressure. This tendency is observed as the contribution of permeation by diffusion becomes smaller with increasing volume fluxes, as

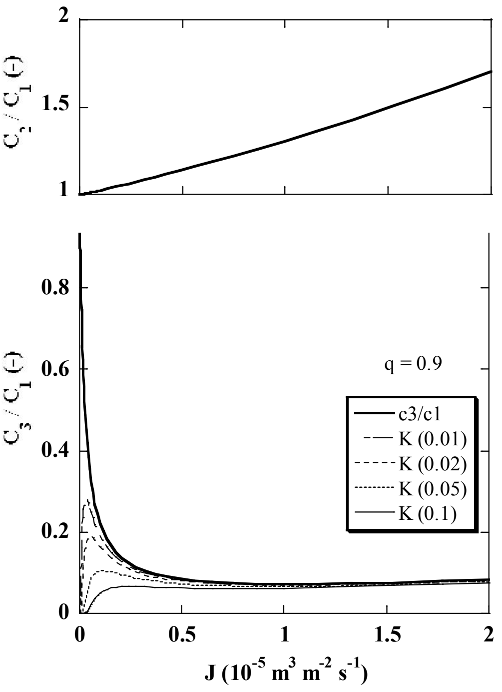


Fig. 3. HA concentration as a function of flux through membrane

results from the Kedem-Katchalsky equation. The concentration polarization (C_2/C_1) becomes higher with increasing flux and with increasing sieving property. When about 90% of the HA is removed by filtration ($C_3/C_1<0.1$), the concentration of HA at the membrane surface can be more than 1.5 times higher than the concentration in the bulk feed. An increase of the HA concentration may enhance the adsorption of HA onto the membrane and might cause a permeation resistance layer. The combination of photo-catalysis with membrane filtration can reduce the HA concentration in the permeated solution.The contribution of photo-catalytic oxidation varies with the operating conditions and the membrane pore size. This contribution becomes significant at low membrane fluxes, hence when the contact time between HA and photo-catalyst is long at low flux conditions. With kinetic constant K>0.05, the photo-catalytic filtration can prevent the increase of HA concentration in the feed due to the contribution of the diffusion. Low flux condition requires low pressure at the feed side that can reduce housing and operation costs. Photo-catalytic membrane filtration may be an alternative for small scale treatment.

On the contrary, the influence of photo-oxidation is almost negligible at high fluxes, e.g.> 1×10^{-5} $m^3/m^2/s$ (>0.9 m^3/m^2/day). Under such conditions, the HA removal is mainly determined by the membrane pore size.

Even though the kinetic constant is 5 to 10 times faster than assumed, it is not enough to treat large volume flux solution.

Another potential advantage of combining photo-catalysis and membrane filtration is the self-cleaning ability of the membrane surface during filtration [21]. Figure 4 shows HA removal property and flux as a function of the overpressure between the feed side and the permeate side. The flux in HA filtration at 0.2 bar overpressure was almost the same as pure water flux, suggesting that fouling is negligible under these conditions. Flux in HA filtration becomes smaller than in the case of pure water flux at overpressures higher than 0.4 bar. The decrease suggests a formation of a permeation resistance layer. After reaching the maximum pressure, the differential pressure was reduced back to 0.2 bar. The flux was smaller compared to the starting value as shown with closed keys in the figure. The flux measured by reducing the pressure shows a linear change with the pressure difference, suggesting a stable permeation resistance. Fouling caused by HA seems irreversible. The membrane surface after filtration was red due to the adsorbed HA, which was difficult to remove by standard washing with water. Although, the feed contains very dilute HA and operation conditions were in low flux conditions, HA fouling is much stronger than the ability to oxidise HA by photo-catalysis under black lamps. Stronger light sources may improve the self-cleaning and reduce the fouling effect but it may increase the operation cost.

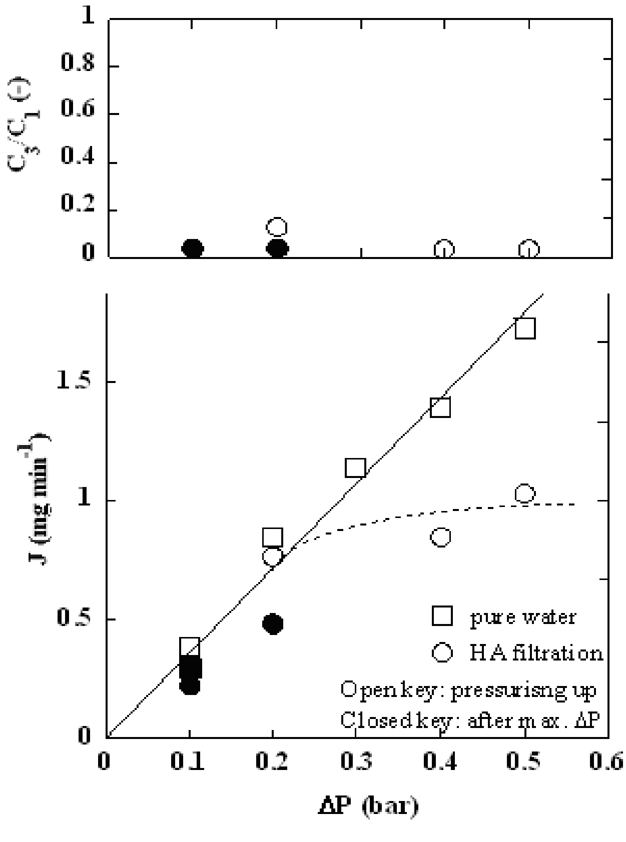


Fig. 4. HA cross-flow filtration under UV light

The photo-catalyst had some influence on the flux. Figure 5 shows the change of flux through the membrane under a stable operating pressure. The flux increased to about 120% almost instantly after applying UV light on the membrane surface. The increase in flux may be due to a change of the surface properties, such as becoming more hydrophilic. The flux did not change in dark after UV radiation for about 30 min.

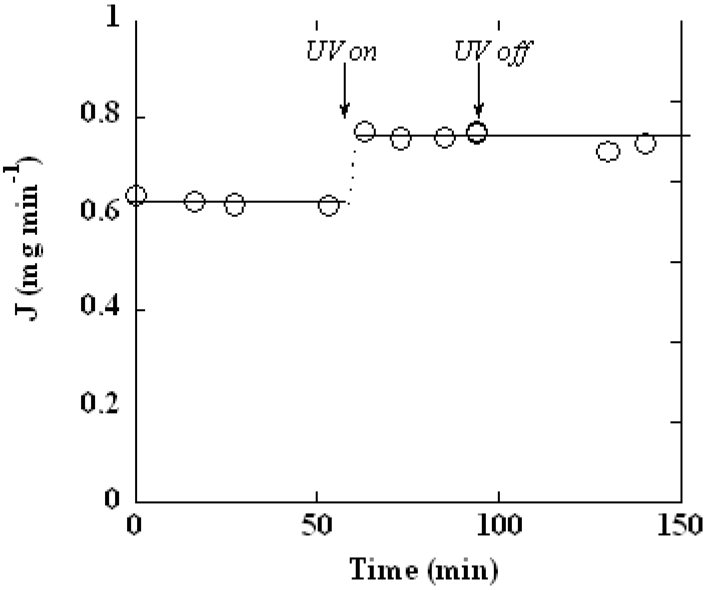


Fig. 5. Flux through the membrane in dark conditions and under UV light exposure (the pressure difference across the membrane (ΔP) was maintained at 0.2 bar)

4. CONCLUSION

Combining photo-catalysis with membrane filtration has a potential to improve the HA removal rate under low flux (low pressure) conditions such as $< 0.2 \times 10^{-5}$ m^3 m^{-2} s^{-1}. Photo-catalysis has not significant influence on the HA removal with membranes having a flux larger than 1×10^{-5} m^3 m^{-2} s^{-1}. Photo-catalytic oxidation needs to be improved to eliminate fouling caused by HA during filtration. Photo-catalytic surface increases the flux through the membrane by applying UV light.

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NOMENCLATURE

J_v [m^3 $m^{-2} \cdot s^{-1}$]: Volume flux through the membrane
J_s [mol $m^{-2} \cdot s^{-1}$]: solute flux through membrane
ΔP [Pa]: Pressure difference across the membrane
$\Delta\pi$ [Pa]: Osmotic pressure difference across the membrane
C_a [mol m^{-3}]: Average solution concentration

C_1 [mol m^{-3}]: Solution concentration in the feed
C_2 [mol m^{-3}]: Solution concentration over the membrane at feed side
C_3 [mol m^{-3}]: Solution concentration in the permeate
L_p [$m \cdot s^{-1} \cdot Pa^{-1}$]: Pure water permeability
o [-]: Reflection coefficient
P [$m \cdot s^{-1}$]: Solute permeability
r_p [m]: Pore size of the membrane
r_s [m]: Solute size
A_k [-]: Pore opening ratio
Δx [m]: Thickness of the membrane
μ [Ps s]: Viscosity of water
ρ [kg m^{-3}]: Density of water
k [m s^{-1}]: Mass transfer coefficient
Re [-]: Reynolds number
Sc [-]: Schmidt number
Sh [-]: Sherwood Number
D [$m^2 \cdot s^{-1}$]: Diffusion coefficient
K [s^{-1}]: Rate constant
t [s]: Contact time