Degradation of emerging pollutants by photocatalysis: Radiation modeling and kinetics in packed-bed reactors.

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Evaluation of internal and external mass transfer limitations in the photocatalytic reactors

The assumptions of negligible mass transfer limitations in the cylindrical (CR) and annular (AR) reactors are based on the following calculations:

Internal mass transfer:

The internal mass transfer resistance was evaluated by means of the Thiele modulus according to the following equation:

$$\phi = t_{TiO2}\sqrt{\frac{k}{D_e}} \tag{1}$$

where t_{TiO2} is the thickness of the film, k an apparent first order kinetic rate constant and D_e the effective diffusion coefficient. Considering the information reported in the literature of D_e for organic compounds in a porous TiO_2 film, a value of 1.0×10^{-10} m²/s was adopted [1,2]. k was obtained from experimental data and H was determined from SEM images. The values of ϕ obtained for the different thicknesses of TiO_2 film employed in both reactors are shown in the following table:

Cylindrical reactor			Annular reactor		
t_{TiO2} (μm)	k (1/s)	ϕ	t_{TiO2} (μm)	k (1/s)	ϕ
0.27	1.44×10^{-5}	$1.02\ 10^{-4}$	0.27	2.33×10^{-4}	4.12×10^{-4}
0.44	1.87×10^{-5}	$1.90\ 10^{-4}$	3.24	1.86×10^{-4}	8.14×10^{-3}

The low values obtained of the Thiele modulus ϕ ($\phi \ll 1$) support the assumption of negligible internal mass transfer resistance.

External mass transfer:

External mass transfer resistance can be quantitatively evaluated by comparing the apparent global reaction rate $\langle r_{CA}\rangle_{V_R}$ and the mass transfer rate as follows [3]:

$$f_e = \frac{\langle r_{AC}\rangle_{V_R} d_p}{k_L C} \tag{2}$$

where d_p is the characteristic size of the packing material, k_L is the mass transfer coefficient in the liquid phase and C is the concentration of the chemical compound in the fluid. If $f_e < 0.05$, the external resistance can be considered negligible.

For fixed bed reactors, k_L can be estimated according to [4]:

$$k_L \left(\frac{\rho}{\mu g}\right)^{1/3} = 0.021(ad_p)^{-0.49} Re^{0.49} Sc^{-0.50}$$

(3)

where ρ is the density of water, μ is the dynamic viscosity of water, g is the acceleration of gravity, a is the surface area of the packing material, and Re and Sc are the Reynolds and Schmidt numbers, respectively. Re and Sc numbers were calculated as:

$$Re = \frac{\rho u_0 d_p}{\mu}$$

(4)

$$Sc = \frac{\mu}{\rho D_m}$$

(5)

where u_0 is the superficial velocity and D_m is the molecular diffusion coefficient.

The values of the parameters employed in the calculations are shown in the following table:

Parameter	Value
ρ	1000 kg/m³
u_0	0.013 m/s (CR)- 0.0047 m/s (AR)
d_p	5×10^{-3} m
μ	8.9×10^{-4} kg/m s
D_m	1×10^{-9} m²/s
a	901 m² /m³ (CR) -661 m²/m³ (AR)

From these calculations, the k_L obtained was 5.66×10^{-5} m/s for CR and 4.01×10^{-5} m/s for AR.

Finally, the values of f_e estimated in the CR for 100% of irradiation level were 0.024 and 0.026 for $t_{TiO_2} = 0.27$ μm and $t_{TiO_2} = 0.44$ μm, respectively. In the AR, under total irradiation, the f_e estimated were 0.031 and 0.048 for $t_{TiO_2} = 0.27$ μm and $t_{TiO_2} = 3.24$ μm, respectively.

Thus, as the calculated values of f_e were always less than 0.05, we can safely assume that external mass transfer limitations are negligible under these experimental conditions.

References
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