Photocatalytic degradation as Davidson–Cole relaxation in time domain*

C. L. Wang

School of Physics, Shandong University
Jinan 250100, P. R. China
wangcl@sdu.edu.cn

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Photocatalytic degradation processes of different materials are fitted with Mittag-Leffler function and incomplete gamma function, which are response functions for Cole–Cole relaxation and Davidson–Cole relaxation. The fitting results show that both functions can fit experimental data fairly well. The order of derivative in the kinetic differential equations can be either less, or greater than one. In the case of the order of derivative is greater than one, only incomplete gamma function is reasonable for describing the photocatalytic degradation. This work further confirms the existence of the universality in photocatalytic degradation kinetics.

Keywords: Universal relaxation law; photocatalytic degradation; Davidson–Cole relaxation.

1. Introduction

It has been demonstrated in the earlier paper¹ that there exists universality photocatalytic degradation process. The kinetics of the degradation can be well described by the response function of Cole–Cole relaxation. The corresponding differential equation is of noninteger order, i.e.,

$${}_0^C D_t^\alpha [C(t)] = -\tau^{-\alpha} C(t), \quad (1)$$

where $C(t)$ the concentration at time t , and ${}_0^C D_t^\alpha$ is α -order derivative under Caputo sense,

$${}_0^C D_t^\alpha [f(t)] = \frac{1}{\Gamma(1-\alpha)} \int_0^t \frac{1}{(t-x)^\alpha} \left[\frac{d}{dx} f(x) \right] dx \quad (2)$$

and τ is a characteristic degradation time. The solution of Eq. (1) is

$$C(t) = C_0 \cdot E_\alpha \left(-\left(\frac{t}{\tau} \right)^\alpha \right), \quad (3)$$

where E_α is called single parameter Mittag-Leffler function.² The validity has been proven rigorously recently,^{3,4} i.e., the response function of Cole–Cole relaxation is single parameter Mittag-Leffler function. This means that the photocatalytic degradation process follows the same differential equation as that for Cole–Cole relaxation, apart from the concentration $C(t)$ in Eqs. (1) and (3), which is replaced by polarization $P(t)$. The order of derivative α is found to be about 0.7 for the fitting photocatalytic degradation processes. The concentration $C(t)$ is a monotonic function of time in these degradation processes. In other words, the concentration, or Mittag-Leffler function decreases from a finite value to zero as the time approaches infinite in monotonic way. However, in case the

order of derivative is greater than one, Mittag-Leffler function is not a monotonic function, but oscillates around zero with increase of time. This is not reasonable in reality for the degradation process, since the concentration cannot be negative at any timescale. On the other hand, the response function of Davidson–Cole relaxation, which is the incomplete gamma function,⁴ decreases with time monotonically for any positive order of derivative. Therefore, in this paper, experimental data of several photocatalytic degradation processes are fitted with Mittag-Leffler function as well as incomplete gamma function for further revealing the universality of chemical reaction kinetics in the photocatalytic degradations.

2. Formula of Davidson–Cole Relaxation

The differential equation for a Davidson–Cole relaxation is⁴

$${}_C(D_t + \tau^{-1})^\gamma [C(t)] = -\tau^{-\gamma}, \quad (4)$$

where the derivative is defined as

$${}_C(D_t + \lambda)^\gamma [f(t)] \equiv \frac{d}{dt} (e_{1,1-\gamma}^{-\gamma}(t; -\lambda) * f(t)), \quad (5)$$

where Prabhakar function $e_{\alpha,\beta}^\gamma$ is used in the above expression, and its definition is

$$e_{\alpha,\beta}^\gamma(t; \lambda) \equiv t^{\beta-1} E_{\alpha,\beta}^\gamma(t^\alpha \lambda). \quad (6)$$

Here, $E_{\alpha,\beta}^\gamma$ is three-parameter Mittag-Leffler function.

The initial condition for Eq. (4) is

$$C(t)|_{t=0} = C_0. \quad (7)$$

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The solution of differential equation (4) with the above initial condition is

$$C(t) = C_0 \cdot \frac{\Gamma(\gamma, t/\tau)}{\Gamma(\gamma)}. \quad (8)$$

Here, $\Gamma(\gamma)$ is gamma function and $\Gamma(\gamma, t/\tau)$ is upper incomplete gamma function, which is defined as

$$\Gamma(\gamma, t) = \int_t^{\infty} x^{\gamma-1} e^{-x} dx. \quad (9)$$

The fitting method is similar to the earlier paper.¹ The experimental data are taken from published works.⁵⁻⁷ First example is the degradation of methyl orange (MO) using bismuth titanate particles synthesized by one-step hydrothermal process.⁵ The second fitting example is for visible light degradation of RhB (10 ppm) using three-dimensional

ordered macro-porous (3DOM)-SrTiO₃/Ag/AgPO₄ ternary composites.⁶ Third example is the photocatalytic degradation of RhB solution with Ag/AgCl/PrGO (PrGO is for photo-reduced graphene oxide) composites.⁷

3. Results and Discussions

Fitting results for the first example are shown in Fig. 1. The fitting parameters are listed in Table 1, the coefficient of determination R^2 are listed in the last column. Fitting curves with N-doped TiO₂ (N-TiO₂) are shown in Fig. 1(a), Bi₄Ti₃O₁₂ (BiT) nanospheres in Fig. 1(b), Bit nanoplates in Fig. 1(c) and BiT nanobelts in Fig. 1(d). The dotted-dashed lines denoted as “inc- Γ ” stand for incomplete gamma function. The dashed lines denoted as “M-L” stand for Mittag-Leffler function. It can be easily see from the curves in Fig. 1

Fig. 1. Fitting curves for photocatalytic degradation of MO using bismuth titanate particles. “Exp” for experimental data,⁵ dotted-dashed line “inc- Γ ” for incomplete gamma function, dashed line “M-L” for Mittag-Leffler function. (a) N-TiO₂, (b) BiT nanospheres, (c) BiT nanoplates and (d) BiT nanobelts.

Table 1. Fitting parameters for photocatalytic degradation of MO using bismuth titanate particles.⁵

Sample	M-L			Inc- Γ		
	α	τ (min)	$R^2\%$	γ	τ (min)	$R^2\%$
a	1.26	443.75	99.91	1.53	284.24	99.97
b	1.10	289.05	99.94	1.21	229.26	99.88
c	1.09	256.06	99.91	1.21	202.50	99.87
d	1.03	142.21	99.90	1.13	121.05	99.90

that all the experimental data can be fitted with both functions fairly well. The R^2 values in Table 1 suggest that the fitting with Mittag-Leffler function is marginally better than that with the incomplete gamma function. An interesting point is

that the order of derivative both α and γ is all greater than one. This means that only the response function of Davisson–Cole relaxation is reasonable in this case, as addressed at the end of the introduction section.

Fitting results for the second example are shown in Fig. 2, with fitting parameters in Table 2. Fitting curves with Ag_3PO_4 are shown in Fig. 2(a), with S30A70(300) (abbreviations are adopted from Ref. 6) in Fig. 2(b), S35A65(300) in Fig. 2(c), S40A60(300) in Fig. 2(d), S50A50(300) in Fig. 2(e), S60A40(300) in Fig. 2(f), S70A30(300) in Fig. 2(g) and $3\text{DOM-SrTiO}_3(300)$ in Fig. 2(h). It has to be pointed out that the experimental data used for the fitting are rescaled with the RhB concentration at the time of irradiation being on.

All the theoretical curves fit the experimental data fairly well in Fig. 2. There is almost no difference for the curves

Fig. 2. Fitting curves for photocatalytic degradation of RhB (10 ppm) using (3DOM)- $\text{SrTiO}_3/\text{Ag}/\text{AgPO}_4$ ternary composites.⁶ (a) Ag_3PO_4 , (b) $3\text{DOM-SrTiO}_3(300)$, (c) S30A70(300) , (d) S35A65(300) , (e) S40A60(300) , (f) S50A50(300) , (g) S60A70(300) and (h) S70A30(300) .

Fig. 2. (Continued)

Table 2. Fitting parameters for photocatalytic degradation of RhB using three-dimensional ordered macro-porous (3DOM)-SrTiO₃/Ag/AgPO₄ ternary composites.⁶

Sample	M-L			Inc-Γ		
	α	τ (min)	$R^2\%$	γ	τ (min)	$R^2\%$
a	1.20	11.62	99.60	1.47	7.47	99.82
b	1.42	63.25	97.43	1.51	50.55	97.48
c	1.12	5.48	99.88	1.45	3.46	99.74
d	1.02	2.41	99.91	1.22	1.92	99.96
e	1.17	5.98	99.81	1.69	3.16	99.72
f	1.21	7.49	99.46	1.60	4.30	98.81
g	1.27	9.48	99.62	1.67	5.35	99.01
h	1.15	10.38	99.28	1.26	7.95	98.97

from the two theoretical functions at small timescales. The difference appears at long timescale in several samples, for instance in Figs. 2(c) and 2(e)–2(h). The values of R^2 in Table 2 suggest that the fitting is very good with both Mittag–Leffler function and incomplete gamma function. A slight poor fitting can be found in Fig. 2(b), with R^2 around 0.97 for both theoretical models. This poor fitting comes from the reaction or kinetic process is far from finishing. Therefore, the parameters for Fig. 2(b) are not reliable in this sense. The most interesting feature is observed in Fig. 2(d). The characteristic time of this degradation is the shortest one. This means that this is a very good photocatalyst, since it has a very quick degradation process. Another crucial feature is that the order of derivative for Mittag–Leffler function is

Fig. 3. (Color online) Fitting curves for photocatalytic degradation of RhB using S35A65(300).⁶ (a) for RhB (20 ppm) and (b) for RhB (30 ppm). Red dotted line for zero concentration.

Table 3. Fitting parameters for photocatalytic degradation of different concentration RhB using S40A60(300).⁶

Sample	M-L			Inc- Γ		
	α	τ (min)	$R^2\%$	γ	τ (min)	$R^2\%$
a	1.22	6.34	99.10	2.50	2.22	99.31
b	1.22	10.18	99.52	2.79	3.19	99.19

greater than one. This means that Mittag-Leffler function is not reasonable, but an incomplete gamma function. In other words, only the response function of Davidson–Cole relaxation can be applied.

To further test the validity of these two functions, experimental data with long timescales are fitted and shown in Fig. 3, with the fitting parameters in Table 3. The experimental data are taken from Ref. 6 for catalyst S35A65(300), but with the very initial RhB concentration as 20 and 30 ppm, respectively. The dotted horizontal lines stand for zero RhB concentration. The values of R^2 in Table 3 are over 99% for fittings with both functions, but this does not suggest that they validate well. It is very obvious that the Mittag-Leffler function becomes negative in long timescale, since the order of derivative is greater than one. The incomplete gamma function model decreases to zero in a monotonic manner. This confirms that for the order of derivative being larger than

Fig. 4. Fitting curves for photocatalytic degradation of RhB solution with Ag/AgCl/PrGO composites.⁷ (a) Ag/AgBr, (b) Ag/AgBr-PrGO(0 h), (c) Ag/AgBr-PrGO(1 h), (d) Ag/AgBr-PrGO(2 h), (e) Ag/AgBr-PrGO(4 h), (f) Ag/AgBr-PrGO(8 h), (g) Ag/AgBr-PrGO(12 h) and (h) Ag/AgBr-PrGO(16 h).

(c)

(d)

(e)

(f)

(g)

(h)

Fig. 4. (Continued)

Table 4. Fitting parameters for photocatalytic degradation of RhB solution with Ag/AgCl/PrGO composites.⁷

Sample	M-L			Inc-Γ		
	α	τ (min)	$R^2\%$	γ	τ (min)	$R^2\%$
a	0.64	4.72	99.95	0.44	16.73	99.83
b	0.73	3.30	99.94	0.51	9.08	99.80
c	0.68	2.50	99.75	0.41	10.51	99.48
d	0.77	3.06	99.98	0.55	7.33	99.91
e	0.71	2.13	99.88	0.43	7.93	99.65
f	0.69	1.78	99.87	0.37	8.58	99.64
g	0.72	2.06	99.95	0.43	7.52	99.79
h	0.77	2.30	99.90	0.50	6.45	99.91

one, response function of Davidson–Cole relaxation is the valid one.

Fitting results for the third example are shown in Fig. 4, with fitting parameters in Table 4. The photocatalytic degradation process of this compound has been fitted with different kinetic models in the previous paper.¹ It has been found that the degradation process can be fitted with response function of Cole–Cole relaxation very well. Here, the degradation process is fitted with the response function of Davidson–Cole relaxation for comparison. The experimental data can be fitted with both models fairly well, as can be seen from curves in Fig. 4 and R^2 values in Table 4. The values of R^2 indicate that fitting with Mittag-Leffler function is marginally better than with incomplete gamma function. This means that both response function of Cole–Cole relaxation and Davidson–Cole relaxation can be well applied.

4. Conclusions

It is found in this work that the photocatalytic degradation can also be described by the response function of Davidson–Cole

relaxation, apart from the response function of Cole–Cole relaxation. The universality and fractional feature of chemical reaction kinetics at least in photocatalytic degradation is confirmed in this work.

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