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Short communication

Constrain in solving Langmuir–Hinshelwood kinetic expression for the photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst

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Abstract

Langmuir–Hinshelwood (L–H) and first-order expressions are the most widely used expressions to explain the kinetics of heterogeneous catalytic system. Previously lot of researchers approximated the L–H kinetic expression to first-order expression just to easily obtain the parameters involved in the L–H expression. However, it is inappropriate to alter a kinetic model, which is having definite assumptions behind it without any validation. This study reports the constrain in approximating the L–H kinetic expression to first-order kinetic expression using the experimental kinetic data of photocatalytic degradation of Auramine O aqueous solution in the presence of ZnO catalyst. Further, the present investigation showed that it is not appropriate to approximate the Langmuir–Hinshelwood kinetics to first-order kinetics. In addition, a second-order kinetic model is proposed and is found to well represent the experimental data of Auramine O degradation by ZnO catalyst for the range of initial dye concentration studied.

Keywords: Auramine O; Photocatalytic degradation; First-order kinetics; Langmuir–Hinshelwood kinetics; Parameter estimation

1. Introduction

The heterogeneous photocatalytic processes are proved to be one of the successful processes in treating the dye bearing wastewaters [1–3]. The chemical reactions catalyzed by heterogeneous catalysts can be due to various complex steps such as physical adsorption, reaction at catalyst surface followed by dye degradation upon illumination, formation of additional by-products such as halides, metals, inorganic acids, organic aldehydes and organic acids, etc. [4]. The various complex steps involved in the degradation process make difficult to determine the way the different variables affect the photocatalytic degradation rate. However, irrespective of the complex steps, intermediate product formations, the entire process can be globally represented using the simple kinetic expressions.

The most widely used kinetic expressions to represent the photocatalytic process are the first-order and the Langmuir–Hinshelwood kinetics. Langmuir–Hinshelwood kinetics have been reported for the heterogeneous catalytic degradation of several dye aqueous solutions [1,5–8]. The Langmuir–Hinshelwood kinetics was also used for modeling the degradation kinetics of toluene from air [9]. Pseudo-first-order kinetics have also been widely reported by several researchers for heterogeneous catalytic dye degradation systems [2,10,11]. Power law kinetics and fractional order kinetics have been reported for the photocatalytic oxidation of Acid Orange 7 by TiO_2 colloids immobilized on a flat substrate [12].

Previously several researchers explained the dye degradation systems by approximating the Langmuir–Hinshelwood kinetics to first-order kinetics [10,13–17]. However, it may

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be inappropriate to approximate Langmuir–Hinshelwood (L–H) kinetic expression just to easily estimate the parameters involved in the L–H expression. Thus, in the present investigation the experimental kinetic data of photocatalytic degradation of Auramine O by ZnO catalyst were fitted to the Langmuir–Hinshelwood kinetics without approximating it to first-order kinetic expression. The predicted photocatalytic degradation kinetics from L–H kinetic expression is compared with predicted kinetics from pseudo-first-order kinetic expression. In addition, the experimental kinetic data were also fitted to the second-order model and the best-fit kinetic model was selected based on the coefficient of determination, r^2 value.

2. Experimental

The multilamp photochemical reactor [HML-COMPACT-LP-MP88, HEBER scientific, India] used in the present study has a reaction chamber with 12 UV lamps (8 W mercury lamps of 365 nm). Only eight numbers of UV lamps were used for irradiation in the present study. Four numbers of DC cooling fans were provided at the bottom of the reaction chamber to minimize the heat generated inside the reaction chamber. The temperature of liquid was maintained at a constant value of 32 ± 0.2 °C. A built-in 1 L capacity magnetic stirrer of max 1200 RPM was provided at the bottom.

The dye Auramine O was supplied by CDH Chemicals, Mumbai, India. Stock dye solution was prepared by dissolving 1 g of Auramine O in 1 L of distilled water. All working solutions of desired initial dye concentration were prepared from the stock solutions.

Experiments were carried out with 1 L of dye solution of concentrations ranging from 80 to 200 mg/L. One gram of catalyst was added to the dye solution and the suspension was stirred in dark for 30 min to ensure equilibrium adsorption of Auramine O onto the surface of ZnO catalyst. After irradiation, 2 mL of samples were withdrawn at regular intervals of 5 min for 30 min. The concentrations of the dye solutions were measured using the UV spectrophotometer.

3. Results and discussions

The photocatalytic degradation processes following the first-order, second-order and Langmuir–Hinshelwood kinetics are given by Eqs. (1), (2) and (3), respectively:

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = k_1 C \tag{1}$$

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = k_2 C^2 \tag{2}$$

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kKC}{1+KC} \tag{3}$$

where r is the rate of dye degradation, min^{-1} mg/L; C is the concentration at any time, mg/L; k_1 is the first-order rate constant, min^{-1}; k and K are the limiting rate constants of reaction at maximum coverage under the given experimental conditions and equilibrium constant for adsorption of Auramine O onto ZnO particles.

Integrating Eqs. (1) and (2) with respect to the limits $C = C_{\mathrm{ads}}$ at time $t = 0$ and $C = C$ at any time t, the non-linearized form of first-order expression can be obtained as:

$$C = C_{\mathrm{ads}} \exp^{-k_1 t} \tag{4}$$

$$C = \frac{C_{\mathrm{ads}}}{K_2 C_{\mathrm{ads}} t + 1} \tag{5}$$

where C_{ads} is concentration of solution at equilibrium after the completion of dark experiments, mg/L. Similarly integrating Eq. (3) with respect to limits $C = C_{\mathrm{ads}}$ at time $t = 0$ and $C = C$ at any time t, the linearized Langmuir–Hinshelwood expression can be given as:

$$\ln\frac{C}{C_{\mathrm{ads}}} + K(C_{\mathrm{ads}} - C) = -kKt \tag{6}$$

Eq. (6) contains unknown parameter, K, in the X-axis. Thus a trial and error procedure was developed using *solver* add-in, Microsoft's spread sheet, Microsoft Excel to solve Eq. (6). However, most of the time the trial and error procedure failed to predict the constant K in Eq. (6) due to solver stuck. The solver stuck was expected due to the difficulty in assuming the initial value for K. Thus the Langmuir–Hinshelwood expression was solved directly using the relation between the reaction rate, r, and $kKC/(1+KC)$ as in Eq. (3).

Figs. 1–3 show the experimental kinetic data and predicted kinetics by first-order, second-order and Langmuir–Hinshelwood kinetics by non-linear method. For non-linear method a trial and error procedure which is applicable to computer operation was used to estimate the parameters involved in the first-order, second-order and Langmuir–Hinshelwood

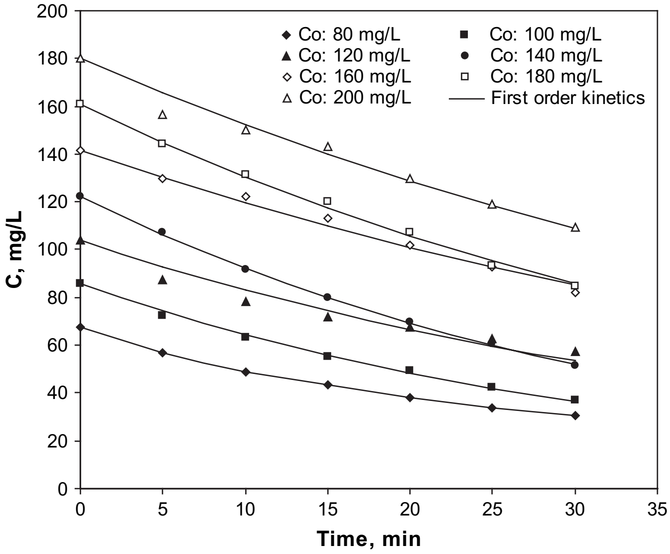

Fig. 1. Experimental data and first-order kinetics for photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst.

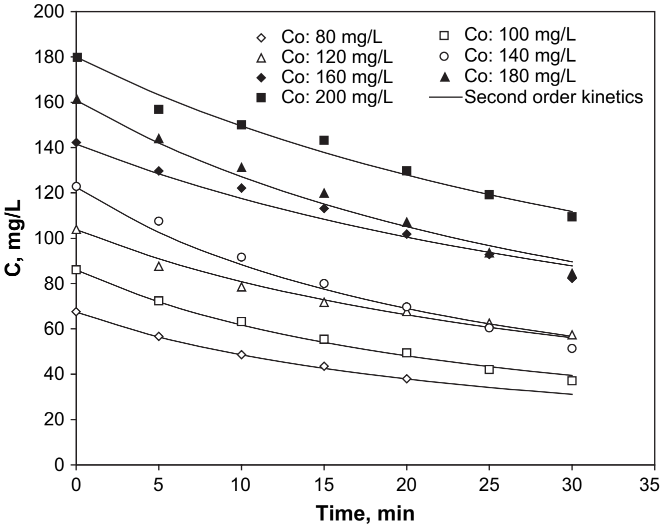

Fig. 2. Experimental data and second-order kinetics for photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst.

kinetic expressions. In non-linear method the respective coefficient of determination between experimental data and the predicted kinetics was maximized using the solver add-in with Microsoft's spread sheet, Microsoft Excel. The predicted kinetic constants are shown in Table 1. From Table 1, it is observed that first-order kinetics doesn't provide good fit to the experimental data at all initial dye concentrations. The reasonably higher r^2 value for second-order kinetics for the range of initial dye concentrations studied (Table 1) suggests that second-order kinetic expression can be used to better represent the kinetics of Auramine O degradation by ZnO catalyst. The lower r^2 values for Langmuir–Hinshelwood kinetics when compared to first-order kinetics suggest that it is inappropriate to represent the kinetics of photocatalysis of Auramine O by ZnO.

Previously several researchers approximated Langmuir–Hinshelwood kinetics to first-order by assuming the term $KC \ll 1$. Thus the Langmuir–Hinshelwood kinetic expression can be written as:

$$-r = \frac{\mathrm{d}C}{\mathrm{d}t} = kKC = K'C \tag{7}$$

where $K' = kK$. From Eq. (7) it is clear that the rate approximates to first-order kinetics upon assuming the term $KC \ll 1$. However, from Table 1, it was observed that the predicted K' from the Langmuir–Hinshelwood kinetics and the k value from the first-order kinetics were different. Thus both the models produced different outcomes for the same experimental kinetic data. Thus it is not an appropriate method to approximate the Langmuir–Hinshelwood kinetic expression to a first-order kinetic expression as reported in literatures while studying the kinetics of heterogeneous catalytic systems.

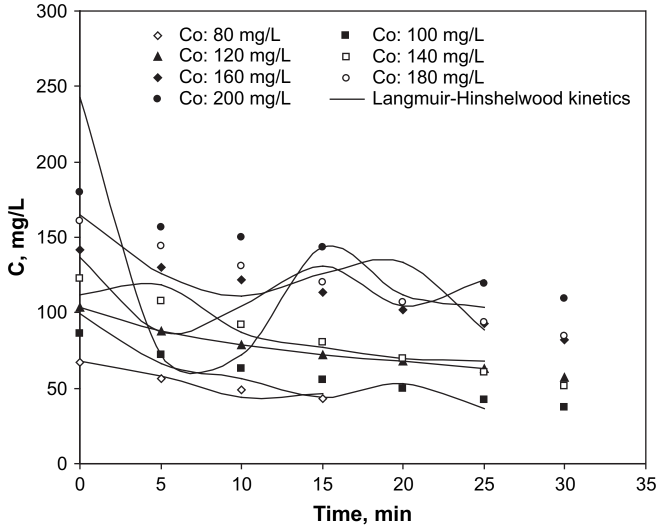

Fig. 3. Experimental data and Langmuir–Hinshelwood kinetics for photocatalytic degradation of Auramine O aqueous solutions by ZnO catalyst.

In literatures, in addition to Eq. (3), two more forms of the Langmuir–Hinshelwood expressions were reported to predict the kinetic parameters involved in the L–H expression, which are given by [5,6,18–20]:

$$-r = \frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kKC_e}{1+KC_e} \tag{8}$$

$$-r = \frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kKC_0}{1+KC_0} \tag{9}$$

where C_e (mg/L) and C_0 (mg/L) represent the amount of solute adsorbed onto the catalyst surface at equilibrium in dark atmosphere and the initial solute concentration, respectively. Though Eqs. (8) and (9) have been previously reported for many systems, it is inappropriate to get a kinetic parameter from these expressions. In a kinetic expression, the dependent variable should be a function of time, but in Eq. (2), there is no dependent variable related to time. The rate of reaction can be defined as the change in concentration with respect to time and is proportional to the concentration and is a function of initial dye concentration. But according to Eq. (8), the rate of reaction is not a function of initial solute concentration, C_e, or proportional to concentration at any time, t, instead it is equivalent to a constant value of "$kKC_e/1+KC_e$". In the case of Eq. (9), the rate of reaction is not a function of initial solute concentration, C_0, instead it is equivalent to a constant value of "kKC_01+KC_0". Further from Eqs. (8) and (9), it was observed that the right-hand side of these two expressions is fully a constant whereas in the left-hand side, the rate of reaction, r, gets varied with respect to time. For any system, it is not possible to correlate a variable with a constant. Thus it is not possible to get the L–H parameters from Eqs. (8) and (9). The better way to obtain the Langmuir–Hinshelwood kinetic parameters is from Eq. (3) without approximating it to first-order kinetics.

4. Conclusions

The present study shows the constrain in using the L–H kinetic expression to predict the kinetics of photocatalytic degradation systems. The kinetics of Auramine O degradation

Table 1
Kinetic constants predicted by non-linear method for photocatalytic degradation of Auramine O aqueous solution by ZnO Catalyst

C_0 (mg/L)	k_1 (min^{-1})	r^2	k_2	r^2	k	K	r^2
40	33.01279	0.797372	0.000576	0.998385	2.069495	0.007518	0.959361
60	35.51558	0.939268	4.57E-04	0.99235	394.9999	6.94E−05	0.895211
80	40.09657	0.802218	0.000273	0.985861	400	5.76E−05	0.60866
100	36.96502	0.967244	0.000316	0.978588	410	6.48E−05	0.960844
120	50.06056	0.718403	0.000144	0.965729	446.1506	3.85E−05	0.805286
140	47.40049	0.886865	0.000165	0.978929	446.3216	4.53E−05	0.914666
160	45.4773	0.70093	0.000113	0.978112	446.3207	4.21E−05	0.545688

by ZnO under illumination was found to be well represented by the newly proposed second-order kinetic model. Further, the present investigation showed that it is inappropriate to approximate Langmuir–Hinshelwood kinetics to first-order kinetic expression using the experimental kinetic data of photocatalytic degradation of Auramine O aqueous solution in presence of ZnO catalyst. The predicted kinetics by first-order and Langmuir–Hinshelwood expressions produced completely different outcomes suggesting that both these models were completely different. Solving the Langmuir–Hinshelwood kinetics without approximating it to first-order kinetics is the more appropriate way of obtaining the parameters involved in the Langmuir–Hinshelwood expression.

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