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Short Communication

Evaluation of photodegradation efficiency on semiconductor immobilized clay photocatalyst by using probit model approximation

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ABSTRACT

Photodegradation process and mechanism is a relative new and eco-friendly process to recycle and reuse of water. Some investigation concerned with effort to increase photocatalyst activity by immobilizing semiconductor oxide such as ZnO in clay as solid support. It was related to that photodegradation was directed by adsorption mechanism. However sometimes the activity of a photocatalyst is not linearly correlated with adsorption mechanism. In this research evaluation on photoactivity of ZnO-hectorite (ZnO/CTMA/Hectorite) and TiO_2-montmorillonite based material using statistical approximation compared to the linear model is studied. The model is evaluated for photodegradation of phenol solution. Some beneficial results of the probit model are (i) the guarantee of activity prediction value in the range of 0–100% (ii) interaction of adsorption and photodegradation mechanism is well described.

1. Introduction

Photodegradation and adsorption technology are two of the several techniques commonly used in textile and other wastewater treatment in industry. Both techniques are basically based on the capability of porous material to reduce contaminant such as dye and toxic organic compounds. Due to its high specific surface area, some studies reported the potency of clay minerals as adsorbent and photocatalyst support for dye and organic compounds.[1–5] Dispersion of some semiconductor photocatalyst into clay minerals porous structure were reported as significant material for wastewater treatment in the advance oxidation process scheme. Some composite materials such as TiO_2-montmorillonite, ZnO-hectorite are the examples.[6–9] As stated in general concept, adsorption plays role in whole mechanism of photodegradation and therefore, the kinetic of adsorption affects the kinetic of photodegradation. Predicting kinetic of adsorption and photodegradation system in order to fit the activity of adsorbent or photocatalyst material between the laboratory scale of the experiment and industrial scale is required and the important thing.[9–12] Some statistical approaches and modellings based on several factors and observations data to construct a reliable model are widely used. As many reported by several kinetic studies, adsorption and photodegradation reaction of a target molecule from solution by an adsorbent

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commonly obey first order reaction as expressed by following eq. (1):

$$A_t = A_0 e^{-kt} \tag{1}$$

with A_t is concentration of compound or target molecule at time of t, A_0 is initial concentration and k is kinetic constant. Generally, in order to find a model, experiment was conducted by sampling at varied t. Therefore the value of k was obtained from regression equation as the transformation result of eq. (2).

$$\ln(A_t) = \ln(A_0) - kt \tag{2}$$

For the adsorption or photodegradation of a dye compound in solution, concentration of target molecule at varied time can be identified by measuring the absorbance of the solution. Considering that absorbance is in linear relationship with concentration eq. (3)

$$B_t = \alpha\lambda A_t \tag{3}$$

B_t is absorbance at the time of t, a is coefficient of molar extinction and l is the length of sample.

In which absorbance can be used as parameter to identify the rate of change.

Refer to some studies using statistical approach in catalytic activity modelling, both linear and non linear estimation to the efficiency of photodegradation process in relation with adsorption kinetic can be performed.[13–15] In the non *linear estimation* the nature of the relationship between some parameters affecting catalyst activity can be constructed by some approximations; for example the dependent variable to be a logarithmic function of the independent variable(s), an exponential function, a function of some complex ratio of independent measures, etc.[8–12] Some of these models are be fit with general kinetic approximation.[8,9,16–20] Another specific model, Probit model approximation was reported to adjustable as predicting the trend of chemical changes or catalytic condition.[20–22]

In this paper, the construction formula connecting the variable of concentration in kinetics equation of photodegradation and adsorption methods was performed. In advance, analysis to the photodegradation efficiency specifically for relationship study between target molecule concentration at treated condition refers to the initial concentration was evaluated. As new approach in kinetics modelling, two methods; linear regression and probit model are utilized. Aim of the study is to evaluate the fitness of the models in both process which are influencing each other.

1.1. *Probit model*

In the non linear models, for example function F (.) was defined to ensure its value between null and 1, $0 \leq F(z) \leq 1$ for any real number z and then it can be constructed a model:

$$\Pi(x) = F(\beta_0 + \beta_1 x_1 + \ldots + \beta x_k) = F(\beta_0 + x\beta) \tag{4}$$

As F (.) is the standard normal cumulative distribution function will be obtained probit models, which can be written as

$$F(z) = \Phi(z) \equiv \int_{-\infty}^{z} \phi(v)dv \tag{5}$$

where $\phi(z)$ is normal standard density,

$$\phi(z) = (2\pi)^{-1/2}\exp(-z^2/2) \tag{6}$$

In many applications, the main purpose of probit model is to explain the effect of x changes on the probability. In order to find the partial effect of the variable x is continuous on Π (x) can be obtained from the partial derivation of.

$$\frac{\partial \Pi(x)}{\partial x_j} = F(\beta_0 + x\beta)\beta_j \text{ dimana } f(z) \equiv \frac{dF}{dz}(z) \tag{7}$$

f (.) is density function and the effect of x_j on $\Pi(x)$ will have the same sign with the sign of βj because f (.) always is positive. Eq. (5), indicates the relative effect of any two values of the variable x does not depend on x. The ratio of the partial effect for x_j and x_k are β_j/β_k.

In special cases, if f (.) is symmetric at null point, the greater effect can be found at $(\beta_0 + \beta_1 x) = 0$.

If x_1 is a binary variable, then the partial effect of a change to a nul x_1 of the other conditions specified value of x, i.e

$$\begin{aligned}\text{Effect } x_1 =& F(\beta_0 + \beta_1 + \beta_2 x_2 + \ldots + \beta_k x_k) \\ & - F(\beta_0 + \beta_2 x_2 + \ldots + \beta_k x_k)\end{aligned} \tag{8}$$

this equation depends on another x_j. Model with interaction between the independent variables include discrete and continuous can be solved in the same way.

1.2. *Absorbance value on adsorption and photodegradation kinetics*

By using linear models can both set equal to the initial concentration A_0,

$$\ln(B_t^A) = \ln(B_0) - k_1 t \tag{9}$$

B_t^A is the value of absorbance at t-measured time by adsorption method. Linear model of photodegradation method is:

$$\ln(B_t^F) = \ln(B_0) - k_2 t \tag{10}$$

The difference of both eqs. (9) and (10) is

$$\Delta\ln(B_t) = -(k_2 - k_1)t \tag{11}$$

Therefore the constructed linear model is

$$\ln(B_t^{AF}) = \beta_0 + \beta t + \gamma t M \tag{12}$$

with M is null for adsorption and one for photodegradation. From eqs. (11) and (12) it can be stated the following equation:

$$\ln(B_t^F) = \ln(B_t^A) - (k_2 - k_1)t \tag{13}$$

Therefore we can conclude that the relationship between absorbance and photodegradation are not dependent on the initial concentration. Probit models for adsorption with the initial concentration A_0 is:

$$B_t^A = \Phi_1(B_0 + k_1 t) \Leftrightarrow \Phi_1^{-1}(B_t^A) = B_0 + k_1 t \tag{14}$$

and probit model to photodegradation with initial concentration A_0,

$$B_t^F = \Phi_2(B_0 + k_2 t) \Leftrightarrow \Phi_2^{-1}(B_t^F) = B_0 + k_2 t \tag{15}$$

The difference of both eqs. (14) and (15) is