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Mathematical modelling of an annular photocatalytic reactor for methylene blue degradation under UV light irradiation using rGO-ZnO hybrid

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ABSTRACT

The application of heterogeneous photocatalysis in industrial scale has been hindered by a lack of simple mathematical models that can be easily applied to reactor design and scale-up. This work intends to use a simple mathematical model for predicting methylene blue (MB) degradation in a slurry-annular photocatalytic reactor using zinc oxide (ZnO) hybridized with reduced graphene oxide (rGO)-ZnO composite. The mathematical model presented may be used as a tool to design, scale-up, and optimize annular photocatalytic reactors for water and wastewater treatment. A mathematical model for the photocatalytic degradation of MB with rGO-ZnO under UV light irradiation was developed. This model was achieved by combination of Langmuir–Hinshelwood kinetics and Lambert–Beer law. The accuracy of developed model was checked for predicting MB degradation in other operation conditions such as different photocatalyst dosage and initial MB concentration. On the basis of these results, the accuracy of the model was tested under different experimental conditions, resulting able to be predictive in different operating conditions. Prog. Color Colorants Coat. 10 (2017), 173-180© Institute for Color Science and Technology.

1. Introduction

Many pollutants, such as heavy metals, dyes, and pharmaceuticals are discharged into the water cycle from various industries. In particular, a serious problem associated with toxic, mutagenic or carcinogenic nature of dyes has led to the need for the development of alternative processes for their destruction in water [1–9]. Among the various types of advanced oxidation processes (AOP), heterogeneous photocatalysis has been shown to be highly effective in the degradation and mineralization of a wide variety of priority pollutants in water and wastewater [10, 11]. More recently, utilization of zinc oxide (ZnO) as a photocatalysis has shown some advantages over widely used titania (TiO_2) over organic dye photodegradation [12, 13]. However, some serious drawbacks associated with using barely ZnO including photocorrosion [14] and fast charge recombination [15] could widely restrict the application of ZnO. To address these problems, hybridization of ZnO with graphene as a new member of carbonaceous material, has become the focus of intense [16]. Apart from anti-photocorrosion and anti-recombination effect, the graphene could also improve the absorptivity of the hybrid material as

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*Corresponding author: mahmoodi@icrc.ac.ir consequence of π-π staking interaction [17, 18].

In this context, ZnO-decorated graphene as an efficient hybrid photocatalyst for organic dye degradation has been thoroughly investigated using bench-scale photoreactor [17–24]. However, the application of photocatalysis using graphene-hybridized ZnO for water and wastewater treatment on an industrial scale requires the development of simple mathematical models that can be readily applied to reactor design on the basis of pilot data [25]. Current models are either too simplistic or too rigorous to fulfill the requirements for photocatalytic reactor design, scale-up, and optimization [26]. These models are linked to complex analysis of the radiation field in the photoreactor which requires modeling of the fluid dynamics and the reaction kinetics. As a consequence of very demanding numerical solutions for solving integro-differential equations, these models become highly difficult to be applied into large-scale photocatalytic reactors [26]. Hence, finding easier models which could be simply applied to scale-up and design purposes with a reliable prediction of the performances of photocatalytic reactors is of great importance.

The first step in building our predictive model is to calculate the kinetic of photocatalytic reaction occurring in an annular reactor by Langmuir–Hinshelwood (LH) model which is a regular method for describing organic dye degradation [27]. The second step is to describe and model radiation transport within the reactor by using Lambert–Beer type model. The final step is to combine LH model with Lambert–Beer to predict degradation of MB.

In this study, a simple linear mathematical model was utilized for a slurry, annular, photocatalytic reactor. The overall photoreactor model was validated with the experimental results of photocatalytic degradation of MB under a number of different experimental conditions. MB was selected as the model organic dye due to its widespread use worldwide in photodegradation experiment which enables us with a good reference for comparison our results with other researchers [28]. In this regard, this paper is organized as follows. After a brief presentation of the experimental investigations, a linear mathematical model is presented to predict the process of degradation MB. Thereafter, our degradation experiments are continued to evaluate the prediction ability of model under different conditions. The ZnO and reduced graphene oxide (rGO)-ZnO composite were synthesized in our laboratory.

2. Experimental

2.1. Materials

All chemicals used in this study were of analytical grade, purchased from Merck, and used as received without further purification. Diluted NaOH and H_2SO_4 solution was used to adjust the pH value at desired level for all photocatalytic experiments where it needed. All aqueous solutions were prepared using doubly distilled water.

2.2. Photocatalytic experiments

The pollutant selected for the photocatalytic oxidation experiment is basic dye, MB from azo dye family. UV-C (9 W, Philips, Poland) was used as an irradiation source which was placed in the center of batch mode immersion type photoreactor with 500 mL volume. In this system, an aquarium air pump was used to assure the saturation of dissolved oxygen. In a typical photodegrading process, a 500 mL suspension containing desired dosage of catalyst and 20 mgL^{-1} of MB was prepared. Before UV irradiation, this solution was stirred for 60 min in the darkness to establish the adsorption-desorption equilibrium between the surface of the catalyst and dye molecules. Thereafter, the UV lamp was turned on for another three hours. At certain time intervals, a 5 mL of sample solution was extracted and its supernatant's absorbance after centrifugation was measured at the maximum absorbance of dye at wavelength of 664 nm corresponding to main characteristic peak of MB by the means of spectrophotometer (UV–Vis spectrophotometer Perkin-Elmer Lambda 25). A standard calibration curve was obtained for different MB concentration, and allowed to convert absorbance to concentration (mgL^{-1}) units.

3. Results and Discussion

3.1. Preliminary experiments

Preliminary experiments were carried out in order to evaluate the ability of as-prepared material towards adsorption and photocatalysis of MB. In this regard, photocatalytic experiment was conducted under same condition for both ZnO and rGO-ZnO composite, and UV-Visible spectra temporal change at different time intervals are shown in Figure 1. After 60 min of dark experiment, the rGO-ZnO composite exhibits higher adsorption ability as compared to the bare ZnO, indicating that the incorporation of graphene sheets has enhanced the adsorption ability of the composite (Figure 1). To avoid the adsorption effect, all photocatalytic experiments were performed after a 60 min physical adsorption period under dark conditions. In the photocatalysis step, UV–Visible spectra of MB solution recording as a function of time in the presence of ZnO and the composite under UV irradiation decreases gradually with increasing the irradiation time, indicating diminishing the color of solution. Furthermore, the decrease of main characteristic peak (664 nm) indicates that chromophore of the dye is the most active site for oxidation attack. When rGO is introduced into pure ZnO, the dramatically enhanced photocatalytic degradation of MB was observed, mainly due to the hindrance of electron-hole pair recombination and great adsorption ability [29].

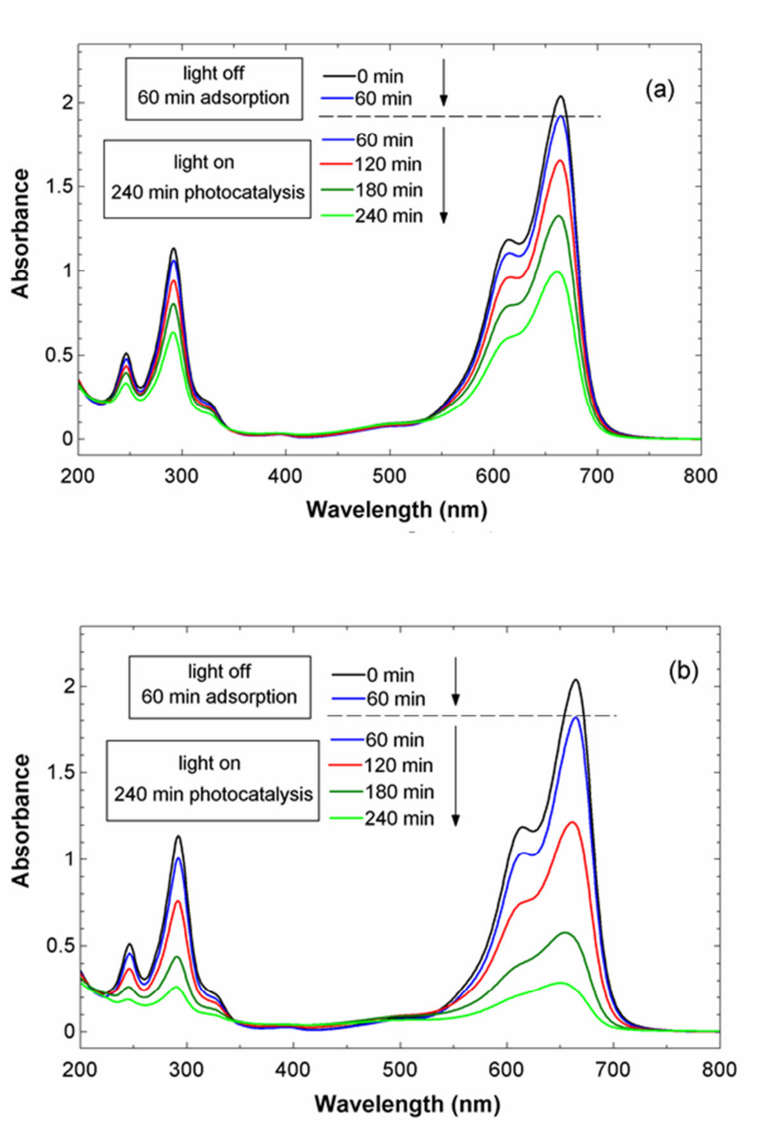

Figure 1: UV-Visible spectra temporal change of MB at different time intervals for (a) ZnO and (b) rGO-ZnO composite. Adsorption time of 60 min, photocatalyst dosage of 0.02 gL^{-1}, initial dye concentration of 20 mgL^{-1}, pH 5, and irradiation time of 240.

3.2. Mathematical modeling

3.2.1.Adsorption of MB under dark condition

The Langmuir isotherm model considers monolayer coverage on a homogeneous surface without taking into account the interaction between adsorbed molecules and uniform energies of adsorption onto the surface [28]. Its non-linear mathematical form is written as below (equation 1) [29]:

$$q_e = \frac{b \times C_e \times q_m}{1 + b \times C_e} \quad (1)$$

where C_e (mg L^{-1}) is the amount of MB adsorbed at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity of rGO-ZnO (mg g^{-1}), and b is the Langmuir constant (L mg^{-1}).

The Langmuir isotherm constants and coefficient of determination are given in Figure 2. As can be seen, the equilibrium data are well described by Langmuir isotherm model, with b constant of 0.020 L mg^{-1}.

3.2.2. Photocatalysis of MB under UV irradiation

The MB mass balance during catalytic oxidation can be written as below (equation 2):

$$V \times \frac{dC(t)}{dt} = r(C, I) \times W \quad (2)$$

where V is the solution volume (L), C(t) is the MB concentration at time t (mg L^{-1}), r is the reaction rate (g L^{-1} min^{-1}), W is the catalyst amount (g), I is the light intensity reaching the photocatalyst surface (mW cm^{-2}).

The kinetic expressions employed in the model are (equation 3-5),

$$-r = K_1 \times f_c \times g_1 \quad (3)$$

$$f_c = \frac{b \times C}{1 + b \times C} \quad (4)$$

$$g_1 = \frac{\alpha \times I}{1 + \alpha \times I} \quad (5)$$

where K_1 is the kinetic constant (mg g^{-1} min^{-1}) and α is the light absorption coefficient (cm^2 mW^{-1}).

Equation 4 is analogous to the LH rate law used in other studies [27]. Equation 5 relates reaction rate to photonic flux [30]. This equation presents a simple approach for the design of photocatalytic reactors by considering the photon as an immaterial reactants. In this expression, only a fraction of light intensity (α) reaching the photocatalyst particle is adsorbed.

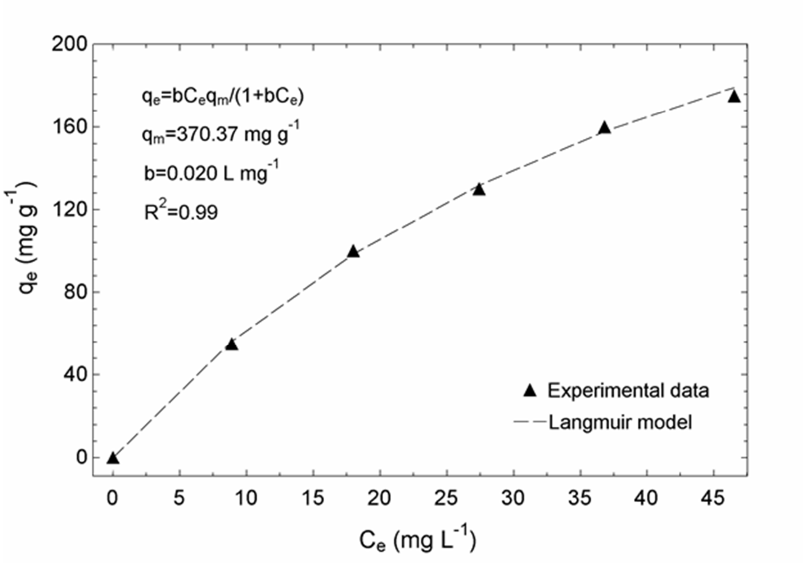

Figure 2: Langmuir isotherm model for MB adsorption by rGO-ZnO (rGO-ZnO dosage=0.01 g/500 mL, pH=5).

Furthermore, it is of great importance to take into account that the accessibility of active sites increases by increasing the photocatalyst dosage. On the other hand, increasing the catalyst concentration has a negative impact on light distance penetration in the suspension due to screening effect [31]. Equation 6 considers this screening effect by using a first order correlation similar to Lambert–Beer law, for the effective light energy received by the rGO-ZnO particles. This suggests that only a part of the light intensity entering the reactor will reach the photocatalyst particles.

$$I = I_0 \times e^{-K_I[w]} \qquad (6)$$

where K_I is the specific extinction coefficient per catalyst mass unit (L mg^{-1}); I_0 is the light intensity reaches the reactor surface (mW cm^{-2}); [w] is the catalysts dosage (mg L^{-1}).

By using equation 3 and 6, MB mass balance can be written as equation 7:

$$V \times \frac{dC(t)}{dt} = -K_1 \times \frac{b \times C(t)}{1+b \times C(t)} \times \frac{\alpha \times I_0 \times e^{-K_I \times [w]}}{1+\alpha \times I_0 \times e^{-K_I \times [w]}} \times W \qquad (7)$$

Eq. (7) was solved by the Eulero iterative method with the initial condition of $C(0)=C_{initial}$. Primary goal of the simulation by mathematical model is to identify the constants K_1, α, and K_I by fitting experimental data reported in Figure 3 as a function of irradiation time. The fitting procedure was realized by minimizing the sum of the squared deviations while changing these aforementioned constants. As can be seen in the inset of Figure 3, this approach results in obtaining the value of K_1: 23.16 (mg g^{-1} min^{-1}), α: 0.22 (cm^2 mW^{-1}) and K_I: 0.00000525 (L mg^{-1}).

After obtaining the model parameters, another series of experiments were conducted with different initial MB concentration ranging from 5 to 20 mg L^{-1} in order to evaluate the ability of the model to predict the experimental data. The resulting data are shown in Figure 4. In this series of experiments, the incident light intensity (I_0) and rGO-ZnO dosage are kept constant equal to 0.02 g L^{-1} and 32 mW cm^{-2}, respectively. The experimental results indicated that photocatalytic activity decreases by increasing the initial MB concentration. This could be due to the reduction in the path length of photo entering to the suspension. Besides, as the concentration increases, the availability of more organic molecules presented into solution require generation more hydroxyl radicals which is not occurred at fixed amount of photocatalyst [32, 33]. Moreover, the calculated values in all cases are in good agreement with the experimental data, as reported in Figure 4. The model also is capable of correctly predicting the experimental data in the higher MB concentration (20 mg L^{-1}).

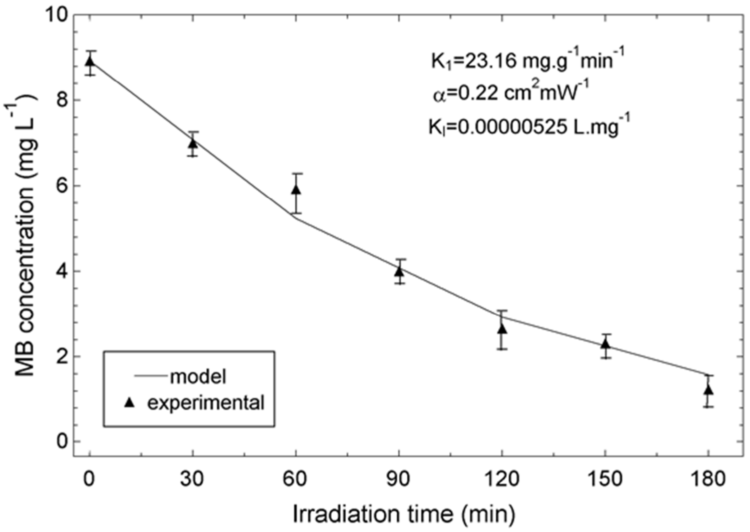

Figure 3: Comparison of calculated and experimental data in order to find the model constant (rGO-ZnO dosage=0.01 g/500 mL, pH=5, incident light intensity=32 mW cm^{-2}).

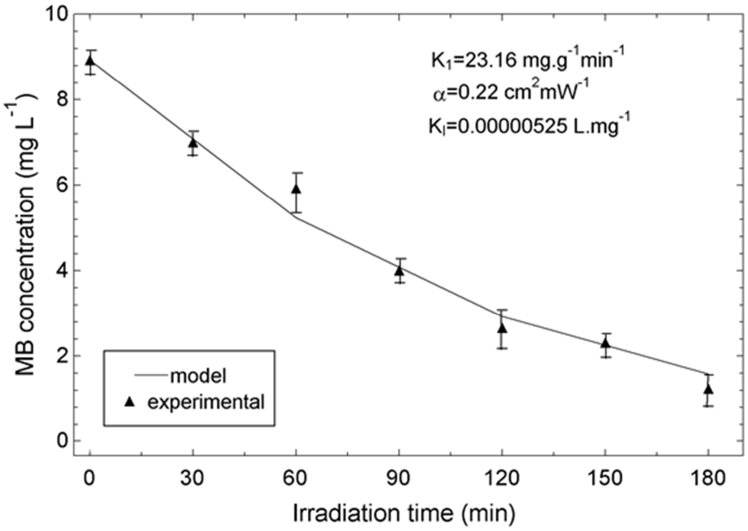

Figure 4: Experimental and predicted data as a function of MB initial concentration (rGO-ZnO dosage=0.01 g/500 mL, pH=5, incident light intensity=32 mW cm^{-2}).

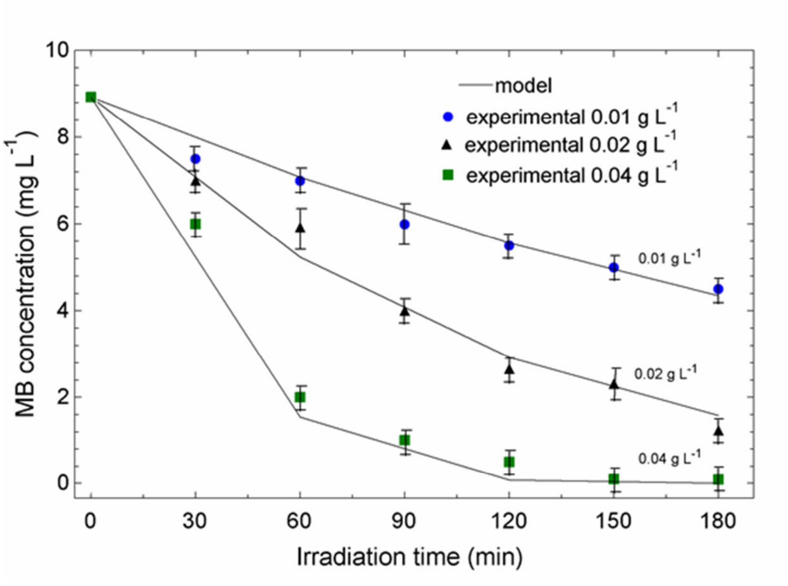

Figure 5: Experimental and predicted data as a function of rGO-ZnO composite dosage (MB initial concentration=10 mg L^{-1}, pH=5, incident light intensity=32 mW cm^{-2}).

The effect of varying the dosage of rGO-ZnO composite from 0.01 to 0.04 gL^{-1} on the MB degradation was carried out at fixed initial MB concentration of 10 mgL^{-1}, pH=5, and incident light intensity of 32 mW cm^{-2}. The results (Figure 5) reveal that the photocatalytic activity increases by the photocatalyst dosage. This enhancement could be due to the availability of extra active surface area for both adsorption and photocatalysis processes [34–36]. Finally, the experimental results of MB degradation were also satisfactorily predicted in this case by the model developed in this study.

4. Conclusions

In this paper, Graphene-hybridized ZnO composite was used in a suspended mode batch photoreactor for the photocatalytic degradation of methylene blue (MB). A mathematical model for the photocatalytic degradation of methylene blue (MB) with rGO-ZnO under UV light irradiation was developed. This model was achieved by a combination of Langmuir–Hinshelwood kinetics and Lambert–Beer law. The accuracy of the developed model was investigated for predicting MB degradation at different operation conditions such as different photocatalyst dosages and initial MB concentration. On the basis of these results, the accuracy of the model was tested under different experimental conditions, resulting able to be predictive in different operating conditions.

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