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Photodegradation Kinetics of Phenol and Methylene Blue Dye Present in Water Stream Over Immobilized Film TiO_2 Catalyst

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A photocatalytic reactor has been designed to study the kinetics of photocatalytic degradation of phenol and methylene blue dye present in water stream on immobilized TiO_2 catalyst. The principal part of the reactor consisted of a cylindrical pyrex glass tube whose outer surface was coated with the synthetic TiO_2 film catalyst prepared from sol-gel technique. An ultraviolet light lamp of 365 nm wavelength was set longitudinally in the center of the tube. The synthetic TiO_2 film formulation with the molar ratio of 1 titanium isopropoxide : 8 isopropanol : 1.1 H_2O : 3 acetyl acetone : 0.05 acetic acid was used to develop the immobilized TiO_2 film catalyst deposited over the glass support. The performance of the immobilized photocatalytic reactor was evaluated by studying the decomposition kinetics of phenol and methylene blue dye present in the aqueous stream. The kinetics of photocatalytic degradation of phenol and methylene blue obeyed first order heterogeneous equation. The kinetic parameters were evaluated from the kinetic data using the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model.

Keywords: Kinetics, methylene blue, phenol, photocatalytic reactor, *and* TiO_2 film catalyst.

INTRODUCTION

Heterogeneous photocatalytic degradation of organic pollutants has attracted much attention from scientists and engineers around the world. Up to now, the optimum design of the photocatalytic reactor is one of the most significant unresolved issues. Immobilized photocatalytic reactor has received considerable attention as an alternative for treating water polluted with hazardous organic chemicals. The process coupled with low-energy ultraviolet light with TiO_2 photocatalyst and its complete mineralization of toxic organic pollutants to carbon dioxide and water could overcome many of the drawbacks that exist for the traditional water treatment methods (Tchobanoglous and Burton 1991).

The catalyst particles in an immersion- or annular-type photoreactor have been resembled like slurry or fluidized bed reactors. However, the usage of suspensions requires the separation and recycling of the ultrafine catalyst from the treated liquid which are both usually inconvenient, time-consuming, and expensive (Shephard et al. 2002).

Thus, attention has recently turned to the immobilization of TiO_2 on solid carrier to eliminate the need for a follow-up clarifier for separation of catalyst particles (Okuya et al. 2002).

In the present research work, the main objective is to develop an effective TiO_2 film immobilization method using the simplest and yet promising sol-gel method and to immobilize it on a glass support material for the decomposition of phenol and methylene blue as model organic compounds. This glass material was further developed into an immobilized photocatalytic reactor that was free of separation and filtration limitations. The experimental kinetic data on photocatalytic degradation of phenol and methylene blue dye present in water stream were obtained under conditions that are relevant for the design of reactors.

EXPERIMENTAL

Synthesis of sol-gel derived TiO_2 thin film photocatalyst

A 340 ml of synthesized TiO_2 mixture via sol-gel route was prepared using 0.34 mol of titanium tetra-isopropoxide and 2.72 mol isopropanol was mixed under constant speed at room temperature. This mixture was stirred for 2 h to undergo a hydrolysis process for the formation of homogeneous solution. Then, 0.374 mol distilled water and 0.017 mol acetic acid were mixed and added drop wise to the above hydrolyzed mixture under constant stirring. Once the mixture became cloudy, 1.02 acetyl acetone was added to the mixture and left for continuous stirring for 30 min. The synthesis mixture was sealed and left for aging for at least 1 day before it could be used.

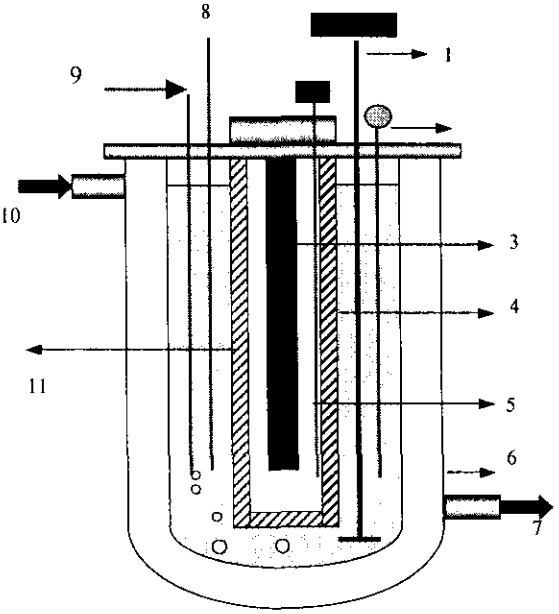
Dip-coating method was used to immobilize the synthesized TiO_2 mixture on the cleaned glass tube which was used as the support material. The TiO_2 coated glass tube was air dried for few minutes before putting into an oven at 120°C for 30 minutes, followed by calcination at 300°C to 700°C at 2°C/min for at least 1 h. The process from dipping to heat treatment was repeated in order to obtain a thicker, uniform photocatalyst layer on the glass surface.

Experimental set-up

A pyrex glass tube of diameter 3.5 cm and length 35 cm was used for TiO_2-catalyst supporting tube. The outer surface of the tube was coated with the sol-gel derived TiO_2 thin film by the method described earlier. A 365 nm ultraviolet lamp (Fisher, model UVL-28) was set longitudinally in the center of the tube. The experimental set up is shown in Figure 1. The system consists of a stainless steel jacketed reactor with height = 40 cm, outer diameter = 10 cm, and inner diameter = 6 cm, a water bath with circulation pump for temperature control in the reactor, a lamp-cooling device to cool the UV lamp, a stirrer with speed controller with digital display to ensure complete mixing in the tank, an air pump to provide oxygen which worked as an electron scavenger to prevent the recombination of electron-hole pairs, and a peristaltic pump with a reversible volume controller to pump the sample at a consistent volume for analysis.

Experimental procedure

The kinetic data were obtained by measuring the concentration of methylene blue (MB) and phenol initially at 5 min and followed by 30 min of interval time by withdrawing the samples. The reaction was carried out at different reaction



1: Stirrer
2: Sampling port
3: UV lamp
4: TiO_2 coated glass tube
5: Lamp cooling device
6: Jacketed reactor
7: Water circulation out
8 : Thermocouple
9 : Air Diffuser
10: Water circulation in
11: TiO_2 film

Figure 1. Schematic Diagram of Batch Photocatalytic Reactor (Cross-section View)

temperatures (30~50°C). The samples of dye were analyzed by means of UV-vis spectroscopy and phenol samples using HPLC. All experiments were conducted at initial concentration of phenol, C_{Po}= 1,000 μmol/liter and methylene blue, C_{MBo} = 40 μmol/litre, respectively, with the amount of TiO_2 photocatalyst film as W= 0.1g and treated solution volume, V= 1 liter unless stated elsewhere.

Analysis

The photocatalytic degradation of methylene blue of both initial and irradiated samples was determined by mean of UV-vis spectrophotometer analysis (Shimadzu UV-1601) through monitoring of color disappearance. A calibration curve of methylene blue solution absorbent was obtained at 660 nm wave length at different concentrations was prepared. The concentration of methylene blue at different reaction times was obtained by converting the absorbance of the sample to methylene blue concentration. High-performance liquid chromatograph (HPLC) was used to determine phenol concentration at different UV illuminating times. A column containing Inertsil 5μODS-2 (150 x 4.6 mm) was used in the sample analysis with eluent of 10mM KH_2PO_4 in 60% methyl cynide. The identification of phenol was based on retention time through a chromatography column. A calibration curve of phenol solution with area under the phenol peak at different concentrations was prepared. The concentration of phenol over a period of UV illumination time was obtained by converting the peak area of the samples to phenol concentration using calibration curve.

RESULTS AND DISCUSSION

The immobilized TiO_2 photocatalyst was used to obtain kinetic data for degradation of aqueous solution containing phenol and MB dye in the photoreactor. The aims were to analyze kinetic data and obtain kinetic parameters. Houas et al. (2001) reported the reaction mechanism for the photocatalytic degradation of methylene blue over TiO_2 catalyst based on the Langmuir-Hinshelwood Hougen-Watson (LHHW) mechanism where the reaction was treated as heterogeneous.

In the present study, the kinetic modeling and parameters evaluation of photocatalytic degradation of MB and phenol were evaluated based on the kinetic data obtained in a batch reactor.

Photodegradation of MB

The photodegradation of MB in the presence of UV light and oxygen occurred over the TiO_2 photocatalyst surface. The reaction is treated as a heterogeneous reaction. The reaction mechanism of MB degradation was based on the LHHW mechanism and consisted of three steps: *adsorption*, *surface reaction*, and *desorption*.

Adsorption

$$C_{16}H_{18}N_3SCl + S^* \longleftrightarrow C_{16}H_{18}N_3SCl \cdot S^* \quad (1)$$

$$O_2 + S^* \longleftrightarrow O_2 \cdot S^* \quad (2)$$

Surface reaction

$$\begin{aligned} & C_{16}H_{18}N_3SCl \cdot S^* + 25.5O_2 \cdot S^* \longleftrightarrow \\ & \quad 16CO_2 \cdot S^* + 6H_2O \cdot S^* + 3HNO_3 \cdot S^* \\ & \quad\quad + H_2SO_4 \cdot S^* + HCl \cdot S^* \end{aligned} \quad (3)$$

Desorption

$$CO_2 \cdot S^* \longleftrightarrow CO_2 + S^* \quad (4)$$

$$H_2O \cdot S^* \longrightarrow H_2O + S^* \quad (5)$$

$$HNO_3 \cdot S^* \longleftrightarrow HNO_3 + S^* \quad (6)$$

$$H_2SO_4 \cdot S^* \longleftrightarrow H_2SO_4 + S^* \quad (7)$$

$$HCl \cdot S^* \longleftrightarrow HCl + S^* \quad (8)$$

where: "S^*" represents the active site on the catalyst surface. The adsorption reaction was assumed to be rate controlling where methylene blue adsorbs on the catalyst surface. Houas et al. (2001) reported that the rate of photocatalytic degradation of methylene blue was first order to the methylene blue concentration. The concentration of oxygen was not included in the rate expression since it was present in excess compared to the concentration of methylene blue (C_{MBo} = 40 μmol/liter). The overall rate of reaction of photocatalytic degradation of methylene blue ($-r'_{MB}$) (mmol/liter.g.$_{cat}$) can be expressed as Eq. (9) as in Fogler (1999).

$$(-r'_{MB}) = \frac{k_A K_A C_{MB}}{1 + K_A C_{MB}} \tag{9}$$

where: k_A (μmol/liter.g.$_{cat}$) represents the adsorption reaction rate constant, K_A (liter/μmol) represents adsorption equilibrium constant, and C_{MB} (μmol/liter) represents the concentration of MB.

The rate of reaction, ($-r'_{MB}$) was calculated from the differential of concentration of MB with respect to reaction time, *t*, (dC_{MB}/dt). The experimental concentration profile of MB, C_{MB} was plotted against reaction time, *t* and was fitted using the appropriate polynomial function. The rate of reaction, ($-r'_{MB}$) (μmol/liter.min.g$_{cat}$) is defined as:

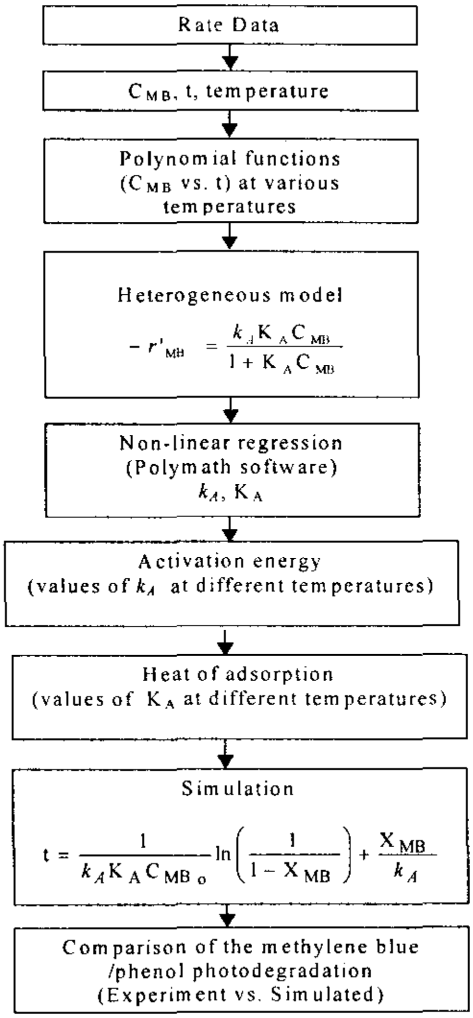


Figure 2. Flow Diagram of Kinetic Studies and Parameters Estimation

$$(-r'_{MB}) = -\frac{dC_{MB}}{dt} \tag{10}$$

Substituting Eq. (10) in Eq. (9) gives:

$$-\frac{dC_{MB}}{dt} = \frac{k_A K_A C_{MB}}{1 + K_A C_{MB}} \tag{11}$$

X_{MB}, conversion of methylene blue degraded and expressed as:

$$X_{MB} = \frac{C_{MBo} - C_{MB}}{C_{MBo}} \tag{12}$$

Substituting Eq. (12) into Eq. (11):

$$\frac{dX_{MB}}{dt} = \frac{k_A K_A C_{MBo}(1 - X_{MB})}{1 + K_A C_{MBo}(1 - X_{MB})} \tag{13}$$

Integrating Eq. (13) gives Eq. (14):

$$t = \frac{1}{k_A K_A C_{MBo}} \ln\left(\frac{1}{1 - X_{MB}}\right) + \frac{X_{MB}}{k_A} \tag{14}$$

The above equation can be used to calculate the value of X_{MB} once the adsorption rate constant k_A and adsorption equilibrium constant K_A are evaluated from the rate data. Figure 2 shows the flow diagram of the algorithm followed in the present study for the evaluation of rate parameters.

Kinetics and evaluation of rate parameters

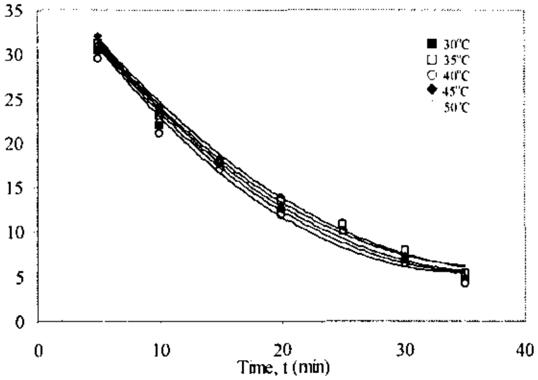


Figure 3. Concentration of Methylene Blue as a Function of Reaction Time at Different Temperatures

Table 1. Kinetic Data of Methylene Blue Dye and Phenol Degradation at Different Reaction Times and Temperatures

Temp (°C)	Concentration of methylene blue dye, C_{MB} (µmol/litre)								Concentration of phenol, C_p(µmol/litre)							
	Reaction time (min)								Reaction time (min)							
	0	5	10	15	20	25	30	35	0	30	60	90	120	150	180	240
30	40	32	24	18.2	14	11	7.9	5.49	1000	910	730	594	440	330	220	110
35	40	31.2	23.2	17.9	13.5	10.9	7.9	5.3	1000	900	720	586	430	326	217	109
40	40	31.1	23	17.5	13	10.1	7.3	4.8	1000	880	710	570	424	318	210	106
45	40	30.5	22	17.5	12.4	10	7	4.5	1000	865	690	550	412	310	206	103
50	40	29.5	21	17	12	10	6.5	4.2	1000	840	670	540	400	300	200	100

Table 2. Rate Parameters k_A and K_A Values at Different Temperatures for Degradation of Phenol and Methylene Blue Dye

Temp (°C)	Phenol		Methylene blue dye	
	k_A (µmol/min.litre.g_{cat})	K_A (litre/mol)	k_A (µmol/min.litre.g_{cat})	K_A (litre/mol)
30	5.5244	0.0059	3.3477	0.0023
35	5.9442	0.0054	3.6011	0.0020
40	6.3513	0.0047	4.1578	0.0018
45	7.3175	0.0041	4.4370	0.0017
50	8.4573	0.0038	4.8792	0.0015

In order to obtain the rate of reaction from experimental data, a series of experiments were carried out at methylene blue concentration, C_{MBo} = 40 µmol/liter at different reaction times and reaction temperatures. The reaction temperature was varied from 30 to 50°C in order to obtain the reaction rate constant, k_A for activation energy calculation. Table 1 shows the experimental data for MB photodegradation at different temperatures and reaction times. Figure 3 shows the MB concentration, C_{MB} against reaction time at different reaction temperatures. The experimental data were fitted with suitable polynomials obtained from the Microsoft Excel program to represent the trend of the concentration profile. A second order polynomials satisfactorily fitted the concentration profile at each temperature. The values of k_A and K_A were estimated using nonlinear least square regression with Polymath software (Fogler 1999). The nonlinear regression was based on the Levenberg-Marquardt algorithm for finding the values of parameters, which minimize the sum of squares of the errors as expressed by Eq. (15).

$$f = \sum_{i=1}^{n} \left[(r'_{MB})_{cal.} - (r'_{MB})_{exp.} \right]^2 \tag{15}$$

where: $(-r'_{MB})_{cal.}$ is the rate of reaction calculated by Polymath program, $(-r'_{MB})_{exp.}$ is the experimental rate of reaction and n is the number of experiments. The reaction rate constant, k_A and adsorption equilibrium constant, K_A values at different reaction temperatures are shown in Table 2. The activation energy was estimated based on Arrhenius law presented as Eq. (16).

$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{16}$$

where: k_A is the reaction rate constant, A is the pre-exponential factor, R is gas constant (8.314 J/mol.K), E is the activation energy, and T is the reaction temperature in degree Kelvin. The reaction rate constant, k_A was plotted against the reciprocal of reaction temperatures, (1/T). The activation energy was calculated from the slope of the Arrhenius plot and was found as 10.72 kJ/mol for MB photocatalytic degradation. The rate constant k_A is expressed as a function of temperature as:

$$k_A = 1912\exp\left(\frac{-10.72x10^3}{RT}\right) \tag{17}$$

The photocatalytic reaction does not require heating as it is initiated by photonic activation (Byrne et al. 1998). The true activation energy is very small or even zero. Thus, photocatalytic process is usually not temperature sensitive.

The observed degradation rates of 4-chlorophenol, phenol, benzoic acid increase with temperature. The overall apparent activation energies obtained from Arrhenius plots were 7.4, 8.6 and 9.1 kJ/mol for 4-chlorophenol, phenol, benzoic acid in TiO_2 suspensions, respectively. Obviously, these values were smaller than those ordinary thermal reactions, thus photocatalytic reaction is less temperature dependent (Chen and Ray 1999). Chen et al. (2000) reported activation energy range from 5 to 20 kJ/mol. These values are quite close to that for a hydroxyl radical reaction, suggesting that the photodegradation of most organic pollutants may be governed by hydroxyl radical reaction.

As a consequence, the optimum operating temperature is usually around 40°C, and there is no need to heat the system. As there is no need as such heating in photocatalytic process, the process is attractive in aqueous media, especially for photocatalytic water purification, since water has a high heat capacity.

The heat of adsorption was estimated from the slope of the plot of K_A against the reciprocal of temperature. The heat of adsorption in photocatalytic degradation MB was found as -16.91 kJ/mol (showing adsorption process is exothermic).

Photodegradation of phenol

Esplugas et al. (2002) reported the reaction mechanism for the photocatalytic degradation of phenol over TiO_2 catalyst based on the LHHW model where the reaction was treated as heterogeneous. In photocatalytic degradation of phenol over the TiO_2 photocatalyst surface, the mechanism is presented as adsorption, surface reaction, and desorption steps following the LHHW-type reaction mechanism (Fogler 1999).

Adsorption

$$C_6H_5OH + S^* \longleftrightarrow C_6H_5OH \cdot S^* \quad O_2 + S^* \longleftrightarrow O_2 \cdot S^* \tag{18}$$

Surface reaction

$$C_6H_5OH \cdot S^* + 7O_2 \cdot S^\circ \longleftrightarrow 6CO_2 \cdot S^* + 3H_2O \cdot S^* \tag{19}$$

Desorption

$$CO_2 \cdot S^* \longleftrightarrow CO_2 + S^* \tag{20}$$

$$H_2O \cdot S^* \longrightarrow H_2O + S^* \tag{21}$$

Esplugas et al. (2002) reported that the rate of photocatalytic degradation of phenol was first order to the concentration of phenol. Concentration of oxygen was not included in the rate expression since it was present in excess as compared to the concentration of phenol. Thus, the overall rate of reaction of photocatalytic degradation of phenol, ($-r'_p$) (μmol/liter.g.$_{cat}$) can be expressed as Eq. (22) based on adsorption of phenol controlling the reaction. Similar expression was also reported by Alemany et al. (1997) for the photocatalytic degradation of phenol.

$$(-r'_P) = \frac{k_A K_A C_P}{1 + K_A C_P} \tag{22}$$

where C_p *(mmol/liter)* is the phenol concentration. The rate of reaction, *($-r'_p$)* was calculated from the differential of phenol concentration with respect to the reaction time, *t*, *(dC_p/dt)*. The experimental concentration profile of phenol, C_P was plotted against reaction time, *t*, and was fitted using appropriate polynomial function.

The degradation of phenol was calculated from Eq. (23):

$$t = \frac{1}{k_A K_A C_{P_O}} \ln\left(\frac{1}{1 - X_P}\right) + \frac{X_P}{k_A} \qquad (23)$$

where X_p was the conversion of phenol degraded and C_{P_0} was the initial phenol concentration.

Kinetics and evaluation of rate parameters

In order to obtain the rate of reaction from experimental data, a series of experiments were carried out at phenol concentration, C_{P_0} = 1,000 mmol/liter at different reaction time and reaction temperatures. Reaction temperatures were varied from 30 to 50 °C in order to obtain the reaction rate constant, k_A for activation energy calculation. Table 1 presents the experimental data for phenol photocatalytic degradation at different temperature and reaction time.

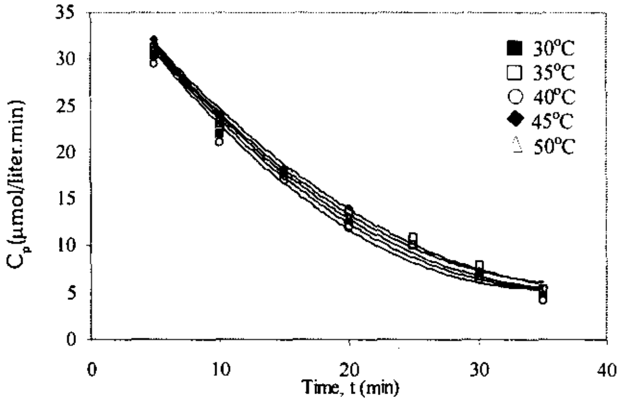


Figure 4: Concentration of Phenol as a Function of Reaction Time at Different Temperatures

Figure 4 shows phenol concentration, C_P against reaction time at different temperatures. The experimental data were fitted with suitable polynomials obtained from the Microsoft Excel program to represent the trend of the concentration profile. A second order polynomial satisfactorily fitted the concentration profile. The values of k_A and K_A were estimated using nonlinear least square regression with Polymath software. The nonlinear regression was based on the Levenberg-Marquardt algorithm for finding the parameters values, which minimize the sum of squares of the errors as expressed by Eq. (24):

$$f = \sum_{i=1}^{n} \left[(r'_P)_{cal.} - (r'_P)_{exp.} \right]^2 \qquad (24)$$

where, $(-r'_P)_{cal.}$ is the rate of reaction calculated by Polymath program, $(-r'_P)_{exp}$. is the experimental rate of reaction, and n is the number of experiments. The reaction rate constant, k_A and adsorption equilibrium constant, K_A values at the different reaction temperature are presented in Table 2. The activation energy of phenol photodegradation. was calculated from the slope of the Arrhenius plot and was found as 17.59 kJ/mol. The rate constant k_A of phenol degradation is expressed as a function of temperature is presented as:

$$k_A = 5792 \exp\left(\frac{-17.59x10^3}{RT}\right) \qquad (25)$$

The heat of adsorption was estimated from the slope of the plot of K_A against the reciprocal of temperature. The heat of adsorption in photocatalytic degradation phenol was found as −19.12 kJ/mol (showing adsorption process is exothermic).

Simulation of rate model

Simulation of rate model and prediction of MB degradation

The values of the rate parameters k_A and K_A obtained in the present study were used to simulate the MB degradation $(X_{MB})_{cal.}$ Eq. (14) was applied to calculate the MB degradation conversion using the rate parameters obtained. The mean error between the experimental data, $(X_{MB})_{exp}$ and calculated data, $(X_{MB})_{cal}$ of MB degradation was less than 0.03%. The standard deviation, s was in the range of 0.0794 to 0.1887 at different reaction temperatures and the 95% confidence was less

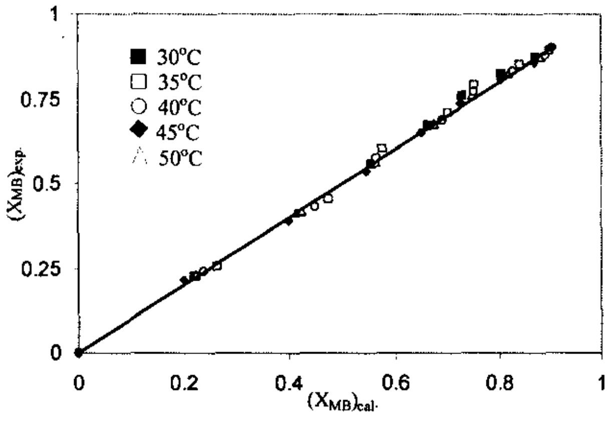


Figure 5. A Parity Plot of Experimental and Simulated Values of MB Degradation

than 0.2. The results show that the heterogeneous model was sufficient to predict the values of MB degradation, $(X_{MB})_{cal.}$ Thus, model expressed in Eq. (9) that treated the reaction as heterogeneous and first order to MB concentration can be used in the design of immobilized photocatalytic reactor for the removal of MB present in the water streams. A parity plot of experimental value of MB degradation, $(X_{MB})_{exp.}$ against simulated MB degradation, $(X_{MB})_{cal.}$ is shown in Figure 5.

Simulation of rate model and prediction of phenol degradation

Eq. (23) was applied to calculate the phenol degradation $(X_p)_{cal.}$ using the rate parameters k_A and K_A obtained. The mean error between the experimental values, $(X_p)_{exp.}$ and the calculated values, $(X_p)_{cal.}$ of phenol degradation was less than 2.5%. The standard deviation, s was in the range of 0.0167 to 0.0333 at different reaction temperatures and the 95% confidence was less than 0.25.

The results showed that the heterogeneous model was sufficient to predict the values of phenol degradation, $(X_p)_{cal}$. Thus, heterogeneous model expressed as Eq. (22) showing the reaction as first order to phenol concentration can be used in the design of immobilized photocatalytic reactor for the removal of phenol present in the water stream. A parity plot of experimental value of phenol degradation, $(X_p)_{exp.}$ against simulated phenol conversion, $(X_p)_{exp.}$ is shown in Figure 6.

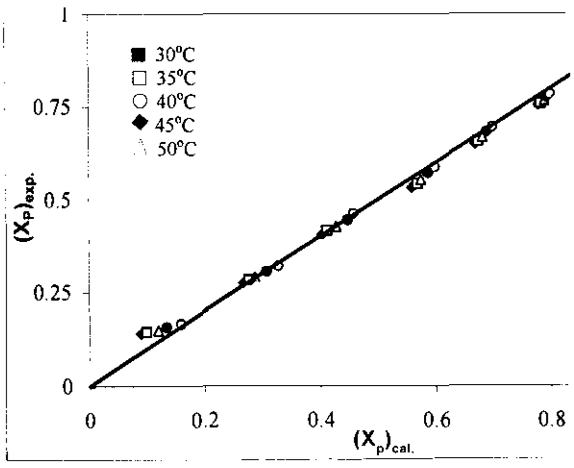


Figure 6. A Parity Plot of Experimental and Simulated Values of Phenol Degradation

CONCLUSIONS

Both photocatalytic degradation of methylene blue and phenol in the present study fitted with Langmuir-Hinshelwood-Hougen-Watson model showing the reaction as heterogeneous and first order to reactant concentration. The small value of activation energy (<20 kJ/mol) obtained from kinetic parameter, k_A at reaction temperature from 30 to 50 °C indicated the ambient temperature process of photocatalytic degradation of organic pollutant present in water streams. The immobilized photocatalytic reactor offers better option in the treatment of organic pollutant waste stream. The data generated in the present research study are useful for the design of photocatalytic reactor.

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