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Photochemical Heterogeneous Catalytic Reaction at Recirculated Reactor System

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Abstract—A study was undertaken to examine the possibility of combining a batch-recirculated photoreactor with a ceramic membrane filter for heterogeneous photocatalysis applications. D-cargo red GS (GS) was used as the test substrate and titanium dioxide was used as photocatalyst for this study. The dark adsorption of GS on the TiO_2 particle surface was also analyzed. The adsorption trends of GS at various initial concentrations followed the Langmuir isotherm trend. The GS were decolorized from 20% to 70% by the dark adsorption with various concentrations. The photodegradation of GS after the dark adsorption showed the behavior of Langmuir-Hinshelwood model. The variation of recirculation flow rate did not much influence photocatalysis. Variation tendencies of GS concentration were almost similar after about 90 minutes illumination in spite of the flow rate change. The values of k (apparent first order rate constant) also varied with increase of the recirculation flow rate, but there were no observable significant differences between them.

Key words: Titanium Dioxide, Azo Dye, Waste Water, Recirculation, Suspended Reactor

INTRODUCTION

The toxicity and mass production of dyes leads to the necessity of treatment. The major difficulty in treating textile wastewater containing dyes is the ineffectiveness of biological processes [Tang and An, 1995]. Physical processes, such as coagulation and adsorption, merely transfer the pollutants from wastewater to other media and cause secondary pollution. Heterogeneous photocatalysis, based largely on the use of TiO_2 as a photocatalyst, has proven to be an effective method for treatment of environmental pollutants [Chai et al., 2000; Blake, 1993; Lee and Lee, 1998; Rajeshwar, 1995; Rajeshwar and Ibanez, 1997]. So in recent years, due to the non-toxic insoluble, inexpensive, and highly reactive nature of TiO_2 under UV irradiation, TiO_2 photocatalytic degradation technique has been used to oxidize wastewater containing dyes and has attracted much attention [Fox and Dulay, 1993]. Matthews investigated the photocatalytic oxidation of methylene blue, rhodamine B and methyl orange using supported TiO_2 on sand, and the results showed that TiO_2/UV process is effective in totally mineralizing these compounds [Matthews, 1989, 1991]. Also, Sopajaree et al. investigated the TiO_2/UV reactor-membrane ultrafiltration (UF) system, and they proved that TiO_2 recirculation system is a possible candidate for dye wastewater treatment [Sopajaree et al., 1999]. Davids and Grainer used TiO_2/UV for the treatment of municipal wastewater containing dyes, and it was found that COD can be reduced while removing the color from the sewage [Davids and Grainer, 1994]. Chen and Chou showed that in the process of photobleaching methyl orange, the dye can be decolorized after 40 min of reaction [Chen and Chou, 1993].

Most of the studies related to such photoreaction have been carried out using suspensions of powered TiO_2 in the polluted solution. In recent studies, it may have been hard to use catalyst suspensions in a slurry photoreactor because of the filtration problems linked to the small size of titanium oxide. This led to a large attempt to immobilize the catalysts on supports including ceramic [Sunada and Heller, 1998], fiber glass [Shifu et al., 1996], glass quartz and stainless steel [Fernandez et al., 1995], activated carbon [Takeda et al., 1998] etc. However, these efforts have not produced materials which meet all demands of photocatalytic activity. Importantly, the photocatalytic efficiency of immobilized TiO_2 is often lower than the suspended particles [Matthews, 1990].

Though, there have been many problems, the catalyst slurry suspension systems do have attractive features: for example, higher photocatalyst surface area, lower susceptibility to surface poisoning/passivation effects etc. Although this process step is obviated by the use of an immobilized photocatalyst film, a slurry suspension photoreactor system is a hopeful development of technology for water-borne pollutants.

Attempts to find a suitable recirculation process for TiO_2 should take into account several factors. The most important factor is the adsorptive ability and the method of separating the photocatalyst particles from the treated water stream and recycling them into the photoreactor [Sopajaree et al., 1999]. Ceramic candle filters were used to remove flyash from the syngas produced at the coal gasification process. The particle removal efficiency of the filters was higher than 99.5%.

As one of the attempts, the present study was an investigation of the effect of heterogeneous photocatalysis and of a recirculation on dye wastewater. Also, the powder separation effect of ceramic candle filter and its suitability to combine photoreactor system was investigated.

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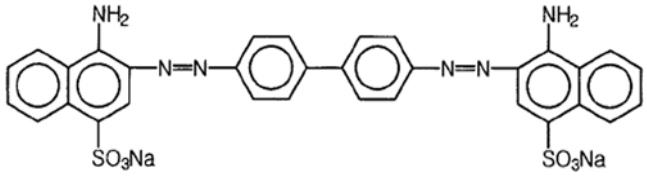

Fig. 1. The structure of azo dye(D-cargo red GS) in experiment.

EXPERIMENTAL

1. Materials

Direct dyes are widely used in the fabric and shoe industries. Most of the direct dyes are azo dyes that are characterized by nitrogen to nitrogen double bonds (-N=N-). They contain at least one, and up to four, azo groups usually attached to two radicals of which at least one but usually both are aromatic groups. Recently, it was found that they have carcinogenic properties. So, azo dyes were legally provided for as an important environmental pollutant. D-cargo red GS (GS), one of the azo dyes, was used as the test pollutant in this study. The structure of GS is shown in Fig. 1. It has the shape of red colored powder and is soluble in water.

Titanium dioxide as photocatalyst was P-25 (Degussa). The photocatalyst (TiO_2) is a nonporous 70 : 30% anatase-to-rutile mixture with a BET surface area of 55±15 m^2g^{-1} and crystallite sizes of 30 nm in 0.1 mm diameter aggregates. To minimize effects of impurities, P-25 in this experiment was dried in a dry oven at 100 °C over 12 hours. GS were provided for various concentrations of GS solutions with suspended TiO_2 powder.

2. 'Dark' Adsorption

The adsorption of GS on the TiO_2 particle surface was studied by equilibrating GS solutions with the TiO_2 slurry in the dark. Studies for the dark adsorption were separated into two parts. The first part was to evaluate the adsorption property of TiO_2 powder in a batch reactor to compare it with that of immobilized TiO_2 on any support. The second was to evaluate adsorption property of TiO_2 in the recirculated reaction system. In the former, the extent of equilibrium adsorption of the azo dye (GS) was evaluated from Co-C: which is represents the decrease of pollutant concentration in 1 liter aliquots of solution, after equilibrium has been reached through slow stirring for about 1 hour at pH 7.0 with 1 g of TiO_2. The latter was the same, but recirculation was carried out in the reaction system. The equilibrium concentrations (C_{eq}) of pollutant (GS) remaining in the aqueous phase were measured by UV/Visible spectrophotometer (Perkin Elmer model Lamdabio 20, 457 nm) on aliquots of the suspensions of small amount after syringe-filtration through the Micro filtering system (MFS, 0.45 micron).

3. TiO_2 Recirculating Photochemical Reactor

GS photodegradation by UV-irradiation was investigated for variation of GS concentration with time. The experimental variables for this study were initial GS concentration, recirculation flow rates and residence times (RT) of the GS-TiO_2 suspension in the reactor vessel. The measurement method and equipment are the same as those of the dark reaction.

Fig. 2 contains a schematic diagram of the recirculated TiO_2/UV photoreactor-filter system. This system consists of three main parts: a reaction vessel, a ceramic filter and a reservoir. The reaction vessel

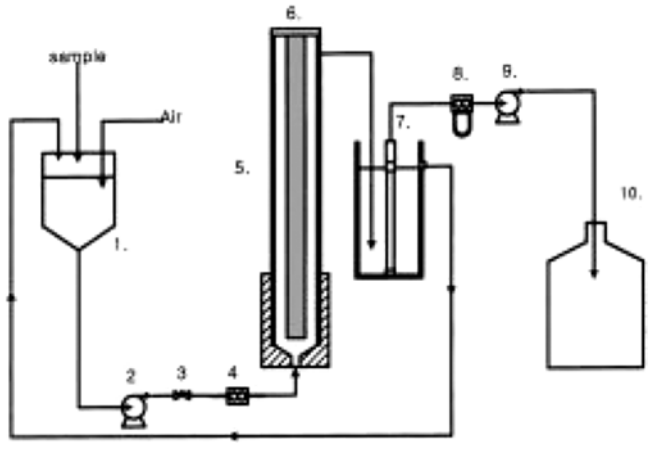

Fig. 2. Schematic diagram of the slurry recirculated photoreactor-filter system.

1. Reservoir	6. UV lamp
2. Pump	7. Ceramic filter
3. Valve	8. Pressure gauge
4. Flow meter	9. Pump
5. Reactor vessel	10. Tank

is a vertical annulus tube with the inner diameter of 25 mm and the outer diameter of 70 mm. Its inner tube material was quartz (2 mm thickness) and its outer tube material was acryl (5 mm thickness). The top and bottom parts of the vessel were safely guarded by MC nylon frames. The top frame protected the inner tube and the bottom frame protected the outer tube and the sample entry. The sample was gathered in the exit of the top part of the vessel. The vessel had a volume of 2.5 liters and a height of 90 cm. The ultraviolet (UV) light source to provide illumination in the photoreactor was placed in the inner quartz tube. Illumination was provided by a UV-lamp (Phillips, TUV36WTS, 39 W, UV-C). The reservoir volume was 8 liter. The reservoir containing the TiO_2 suspension was provided with air of an air diffuser to prevent sedimentation of TiO_2 particles. To circulate the solution in the system, a variable speed metering pump (LG-PF-064M) was used.

RESULTS AND DISCUSSION

1. 'Dark' Adsorption of GS on TiO_2

Fig. 3 illustrates the results obtained from measurements of the equilibrium extent of adsorption of GS onto TiO_2 as a function of time and the initial concentration of GS. This was carried out in a batch reactor. The TiO_2 dose was kept constant at 1 g/liter. Dark adsorption means that the pollutant (GS) was adsorbed at TiO_2 surface under no UV illumination condition. Adsorption equilibrium was achieved after 20 minutes.

The result shows that the adsorption isotherm for each concentration agrees directly with the Langmuir adsorption isotherm. This is encountered in chemisorption where the asymptotic approach to a limiting quantity from Fig. 3 indicates that all of the surface sites are occupied. Consequently, it is possible to show that the data which were representative of three different concentrations of GS are consistent with monolayer-limited adsorption of these into a surface solution monolayer under the influence of competition between solvent and solute species for adsorption sites at the solid/solution in-

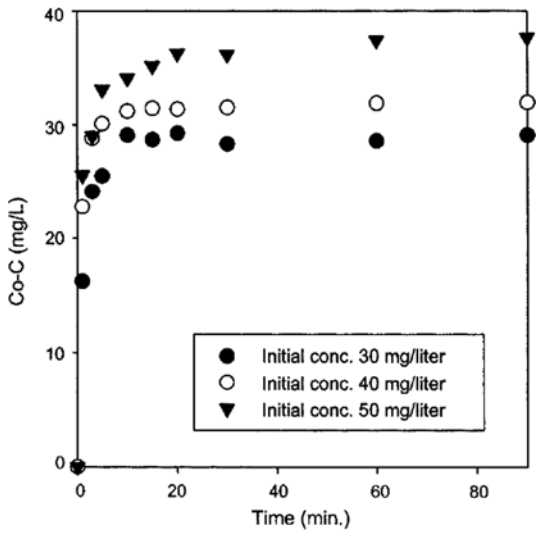

Fig. 3. Adsorption isotherms of GS with time (TiO_2 : 1 g/liter).

terfacial monolayer. This result nearly accords with that of a previous research [Sopajaree et al., 1999]. Numerous investigators have reported that the rates of photodegradation of chemical compounds on semiconductor surfaces follow the classical Langmuir-Hinshelwood expression and that the sorption of substrates to the semiconductor surfaces often follows Langmuir sorption isotherms. By the analysis of Langmuir adsorption isotherm model, these data can be analyzed in Eq. (1):

$$\frac{1}{q} = \frac{1}{q_o} + \frac{K}{q_o}\frac{1}{C} \quad (1)$$

where q is the adsorbed GS concentration (mg/liter), C is the initial GS concentration (mg/liter) in solution, q_o is a empirical constant (mg/liter) related to the adsorption affinity and K is a empirical constant (mg/liter) related to the saturation coverage. By plotting 1/q versus 1/C, the slope is K/q_o and the intercept is $1/q_o$.

Fig. 4 shows such a plot for the data in Fig. 3. From linear regression analysis, q_o and K can be determined to be 54.05 mg/liter and 25.74 mg/liter, respectively. These results may be compared with those obtained by a previous author [Sopajaree et al., 1999] for a batch recirculation photoreactor in which methylene blue (MB) and Degussa (P-25) TiO_2 particles were used as the test substrate and photocatalyst, respectively. In this study, values for q_o and K were 23.09 mg/liter and 6.17 mg/liter, respectively. The higher values observed for these parameters in our study mean that adsorption activity of GS to TiO_2 is higher than that of MB.

Though the results from Fig. 3 were fit in this analysis, the deviation of adsorption isotherm was observed in the higher concentration. The adsorption isotherm tends to decrease with the increase of the initial concentration. At high concentrations of GS, the adsorption amount of GS onto TiO_2 was small comparatively. It seems that an adsorption amount at high concentrations does not affect the overall photochemical reaction compared to that of the UV-illumination.

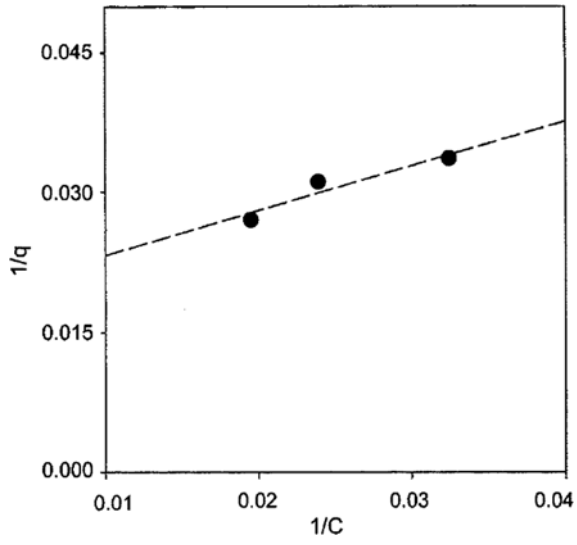

Fig. 4. Reciprocal plot of 1/q versus 1/C [Eq. (1)].

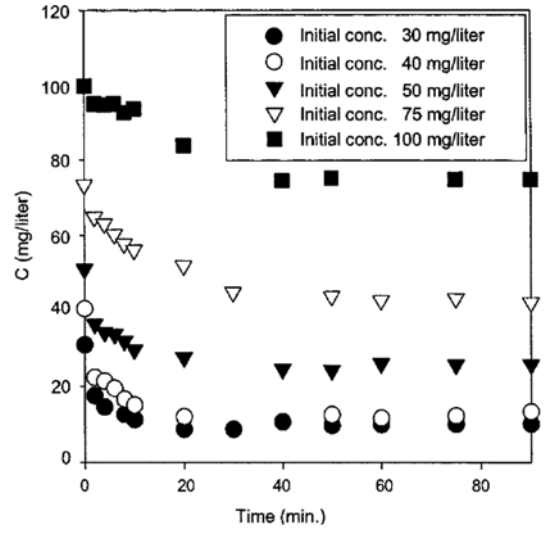

Fig. 5. Variations of GS concentration with time (TiO_2 : 1 g/liter).

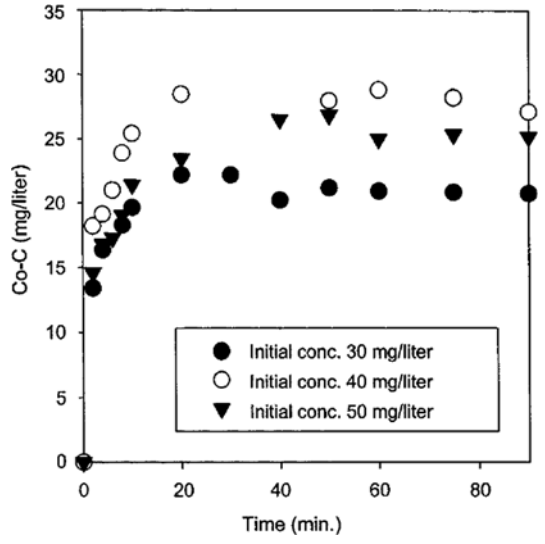

Fig. 6. Adsorption isotherms of GS with time (TiO_2 : 1 g/liter, 0.25 liter/min).

2. 'Dark' Adsorption Before Photocatalytic Reaction

GS solutions were pre-equilibrated in the dark prior to start of the photocatalytic reaction. The result for variations of GS concentrations with adsorption is shown on Fig. 5. Almost all attained the adsorption equilibrium after about 20 minutes. Fig. 6 shows the amount of GS adsorptions onto TiO_2 for lower concentrations from 30 mg/liter to 50 mg/liter. They also followed the Langmuir isotherm trend. Adsorption equilibriums of each initial concentrations are about 25±5 mg/liter. Regression analysis for all concentration ranges is shown on Fig. 7. By the Langmuir adsorption isotherm model presented earlier, q_o and K value can be determined to 31.01 mg/liter and 3.50 mg/liter respectively.

3. Photocatalytic Reaction of GS in the Recirculation Reactor

The result of photochemical reaction of GS in the recirculation reactor with recirculation flow-rate and time was shown in Fig. 8. GS solution was pre-equilibrated in the dark for about 20 minutes prior to start of the photocatalytic reaction. TiO_2 catalyst was added before pre-equilibration. Recirculation flow rates were varied 0.25, 0.5, 0.75 and 1.0 liter/min. Flow rate can be converted to residence time and that points to 10, 5, 3.33 and 2.5 minutes, respectively.

Sopajaree et al. suggested that under the low concentrations of pollutant (~10 mg/liter or lower), the Langmuir-Hinshelwood model [Rajeshwar, 1995, 1997] predicts simple first order kinetics behavior.

$$\frac{1}{R_o} \cong \frac{1}{R_S} + \frac{K}{R_S}\frac{1}{C_o} \tag{2}$$

where R_o is the initial reaction rate, R_s is the saturation rate, C_o is the initial pollutant concentration and K is the empirical parameter which can be obtained from Eq. (1). Following this assumption, semilog plots of C/C_o against time should be linear, the slopes of which would yield estimates of k. Thus, the apparent first-order rate constant, k (1/min) can be used as a comparative measure to assess the influence of the various experimental variables on the overall reaction rate.

The results of photochemical reaction of GS in the recirculation reactor with the various initial GS concentration after the dark adsorption are shown on Fig. 9. The variation of recirculation flow rate was an influence in the beginning of UV-illumination. For the extremes of recirculation the reactor system approaches a mixed flow reactor [Levenspiel, 1999]. However, the effects of recirculation flow rate diminish with time. After 1 hour of illumination, GS concentration was almost same in spite of the flow rate change. Removal efficiencies over 95% were reached within in the lower concentrations. Those of higher concentrations of GS needed about 120 minutes.

The reciprocal of K is the adsorption coefficient of TiO_2 for GS. Following this assumption, the parameter K/R_S in the Langmuir-Hishelwood equation can be yielded from the slope of $1/R_o$ against $1/C_o$. So, a reciprocal plot would yield K and R_S from the slope and intercept, respectively. Fig. 10 shows the reciprocal plot for those data. Regression analysis yielded values of K and R_S of 2.87 mg/

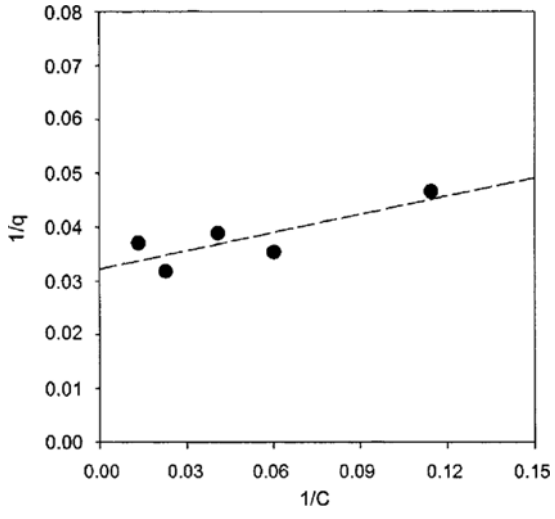

Fig. 7. Reciprocal plot of 1/q versus 1/C from adsorption of recirculation reactor.

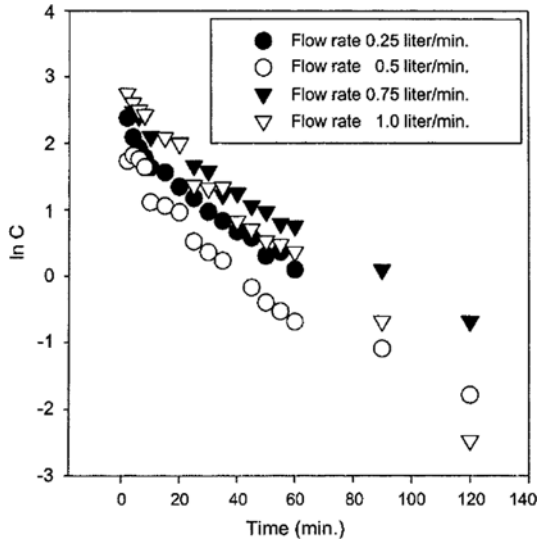

Fig. 8. Variations of GS concentration with time and recirculation flow rate (GS: 100 ppm, TiO_2 : 1 g/liter).

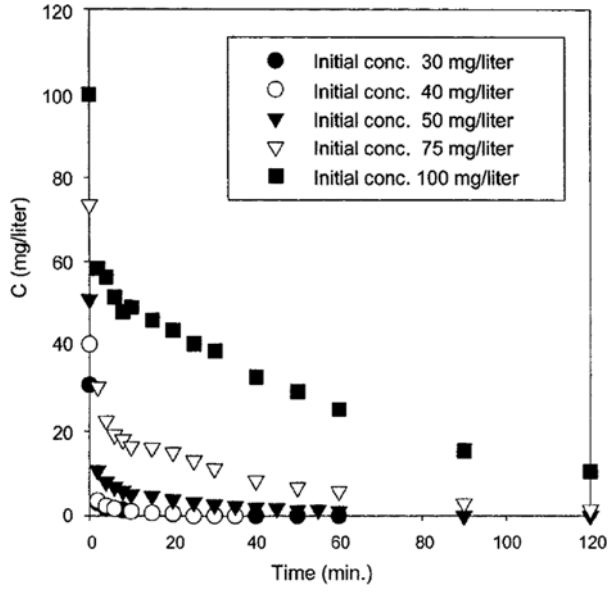

Fig. 9. Variations of GS concentration with time and initial GS concentration (0.25 liter/min, TiO_2 : 1 g/liter).

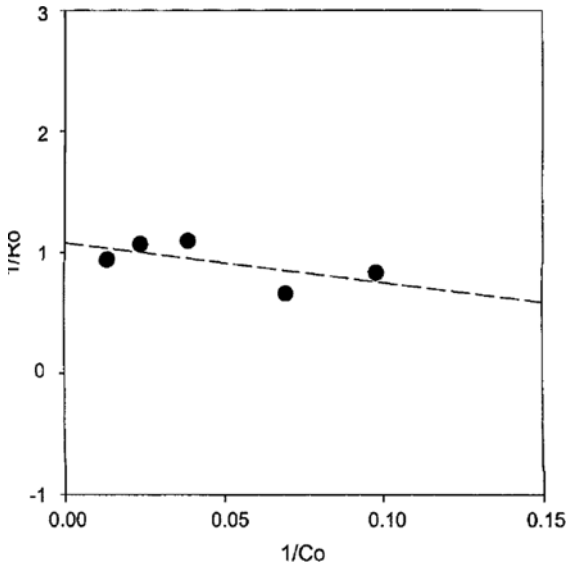

Fig. 10. Reciprocal plot of $1/R_o$ against $1/C_o$ (R_o: Initial rate, C_o: Initial concentration of GS).

liter and 0.0175 mg/liter.

In this case, semilog plots are also shown to underline the extent of adherence to the first-order kinetics limiting condition. Also, these experiments reveal that the recirculation flow rate has a weak influence on the reaction rate. Semilog plots of C against time should be linear as equation $\ln C = \ln C_o + k_r$, the slopes of which would yield estimates of k. Thus the apparent first-order rate constant, k (1/min) can be used as a comparative measure to assess the influence of the various experimental variables on the overall reaction rate. The photochemical reaction rate increases with increase of the GS concentration. The apparent first-order rate constant, k is calculated from the data obtained in Figs. 8 and 9. The values of k vary from 0.01 to 0.1 (1/min) with the operating condition.

It is interesting to note that the K values are different in the dark and light conditions of the TiO_2/GS interface, the K value being lower in the latter case. This reflects the fact that the adsorption tendency of GS was enhanced by irradiation of the photocatalyst surface. It seems that the force of attraction, which is caused by electron and hole, enhances the adsorption.

CONCLUSION

In this study, the effect of heterogeneous photocatalysis for dye wastewater treatment was investigated.

1. The trends of dark adsorption in a batch reactor were identical to those of Langmuir isotherms. From linear regression analysis for the Langmuir isotherm, q_o, saturation coverage constant, and K, adsorption affinity, can be determined to be 54.05 mg/liter and 25.74 mg/liter for lower concentrations below 50 mg/liter in the batch reactor.

2. In the photoreactor, GS solutions that were pre-equilibrated in the dark prior to start of the photocatalytic reaction followed the Langmuir isotherm. The GS were decolorized from 20% to 70% by the dark adsorption at various concentrations. Consequently, the GS photocatalytic degradation was affected by the adsorption. The q_o and K values for the concentration range from 30 mg/liter to 100 mg/liter were 31.01 mg/liter and 3.50 mg/liter, respectively.

3. The photodegradation of GS after the dark adsorption showed the behavior of Langmuir-Hinshelwood model. First order rate constants k were revealed variously from 0.01 to 0.1 (1/min) the operating conditions. The adsorption affinity value, K, was higher than that of the dark adsorption. It seemed that the attractive force caused by electron and hole enhanced the adsorption. Decomposition efficiencies of GS by photocatalytic degradation achieved 95% within 90 minutes in the lower concentrations. Those of higher concentrations of GS needed about 120 minutes.

4. The tendencies of GS concentration were very similar after about 90 minutes illumination in spite of the flow rate change. The values of k also varied with increase of the recirculation flow rate, but there were no observable significant differences between them.

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