

Photodegradation mechanism of two dyes: the influence of adsorption behavior on the novel TiO₂ particles

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Abstract: The relationship between adsorption behavior and photocatalytic mechanism of the two dyes was investigated. Adsorption isotherms showed that the adsorption of cationic pink FG was Langmuir type behavior, while the reactive brilliant red k-2G was Freundlich type behavior. The increasing pH favored the adsorption of FG but have little effect on the photodegradation. The increasing pH favored the adsorption and the photodegradation of k-2G. The presence of scavenger of h_{vb}^+ and $OH\cdot$ radical potassium iodide inhibited the degradation of k-2G, free radicals scavenger tetranitromethane inhibited the photodegradation of FG. These results indicated that the photodegradation of FG mainly via free radicals in solution, and the photodegradation of k-2G was mainly on the catalysts surface or near the interface of solid and solution by react with h_{vb}^+ and surface-bound $OH\cdot$. The different effect of SO_4^{2-} , HCO_3^- on the adsorption and photodegradation of two dyes confirmed these results.

Keywords: photodegradation mechanism; adsorption behavior; dye

Introduction

The application of photodegradation of dye pollutants has been extensively developed and many of organic dyes were decomposed to mineral products. The TiO₂ photocatalyst is excited by UV light to produce conduction band electrons (e_{cb}^-) and valence band holes (h_{vb}^+), which are capable of initiating photocatalytic reaction (Poulios, 1999).

Generally, three different mechanisms are considered to explain the different performance among the heterogeneous photocatalysis process. One suggests that the oxidation organic compounds are initiated by the free radicals (including $OH\cdot$) in the solution, which are mainly induced by the photogenerated hole-electron pairs. The other proposal states that the organic compound has to be firstly adsorbed on the catalyst surface and then reacts with photogenerated hole-electron pairs or surface-bound $OH\cdot$ to form the final products. The third proposal involving both surface reaction via holes/surface-bound $OH\cdot$ and solution reaction via free radicals (Thomas, 2001). There are much debate as to whether photoreactions occur on the surface of TiO₂ involve reaction with h_{vb}^+ or surface-bound $OH\cdot$ or in the solution with free radicals. The photocatalytic degradation of two dyes, which have different structures, cationic pink FG and reactive brilliant red k-2G have been studied in this work. The experiments were carried out in a fluidized reactor with TiO₂ particles (G01). The initial concentration, pH, e_{cb}^- , h_{vb}^+ and $OH\cdot$ scavengers, SO_4^{2-} , HCO_3^- were investigated to illustrated the influence of adsorption behavior on the photodegradation mechanisms of the two dyes, the results are useful to control and to improve the performance of the photodegradation.

1 Materials and methods

1.1 Materials

The catalysts used in this work are TiO₂ particles G01 (1.0—1.5 mm in diameter, made in Co. HSD, Beijing). The BET surface area of G01 is 194.4 m²/g, density 900 kg/m³, the X-ray diffraction analysis showed that it is mainly anatase. The isoelectric point of G01 is pH 6.12. Potassium iodide was used as holes scavenger, tetranitromethane (TNM) as free radicals scavenger. NaHCO₃, Na₂SO₄ are analytical grade. The fluidized-bed reactor (FBR), which has an annulus structure, was designed and operated. An 18 W low-pressure mercury lamp (main wavelength is 254 nm, made in Co. ELR, Beijing) surrounded by a 0.005 m thick quartz glass tube shell was placed at the center of the reactor. Between the shell and the internal wall of the reactor contains 20 g of G01 particles. The catalysts were maintained in suspension by air purging (10 L/min), the bed height is about 50 cm. 2 L dye solution with certain concentration was feed into the reactor every batch experiment.

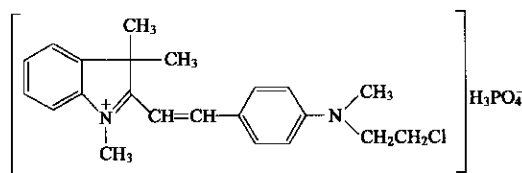


Fig. 1 Structure of cationic pink FG

1.2 Analytical methods

The reaction process was monitored by total organic carbon (TOC) analyzer (model Apollo 9000 Dohrmann, USA). The color removal of the solution was determined by measuring solution absorbance at the optimal analytical wavelength using a spectrophotometer (HITACHI U-3010).

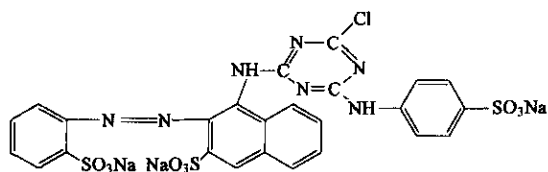


Fig. 2 Structure of reactive brilliant red k-2G

The pH of the solution was adjusted with HCl or NaOH as required, and determined with pH meter (Orion 828). G01 were characterized by X-ray powder diffraction (Model D/Max-RC). BET surface area was determined using N₂/BET method (ASAP Model 2000). The light intensity of the UV lamp was measured with luminometer (model UV-C, made in Photo. Ins. Factory, Beijing).

2 Results and discussion

2.1 Adsorption isotherms of the two dyes

All adsorption isotherms were obtained at 20 ± 2 °C in a temperature-controlled shaker under dark conditions, the equilibrium adsorption experiments were performed with 50 ml dye solution and 0.5 g G01 suspensions under unadjusted pH in the 90 ml Pyrex glass vessel. Fig. 3 shows the adsorption isotherm of FG, the curve of FG demonstrates the Langmuir type behavior, and the curve of k-2G (Fig. 4) demonstrates the Freundlich type behavior. The k-2G has a relatively stronger adsorption on G01 than FG. The equilibrium adsorption amount of k-2G and FG on G01 is about 30% and below 10%, respectively. The isoelectric point of G01 is pH 6.12, the surface of G01 is positively charged under pH < 6.12, and negatively charged in the range of pH > 6.12. Based on the adsorption isotherms, the chemical structure of the two dyes, and the catalysts surface properties, it is suggested that the adsorption mode of k-2G is adsorbed to TiO₂ particles surface through sulfonate group, FG is adsorbed to the TiO₂ particles surface through the positively charged penta-heterocycle N group (Hu, 2001).

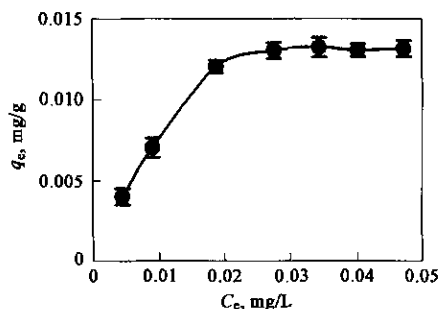


Fig. 3 Langmuir isotherm for FG, 10 g/L catalyst, pH = 5.48

2.2 Effect of initial concentration

The adsorption study has demonstrated that over 90% equilibrium adsorption amount of two dyes on G01 surface was achieved within 30 min. The photodegradation experiments (as well as in the following sections) under UV irradiation (254 nm, 86 μE/(s·m²)) were carried out after 30 min dark adsorption process in the fluidized-bed reactor. The color removal of two dyes is lower than 5% under irradiation in the absence of G01. We consider the photolysis of two

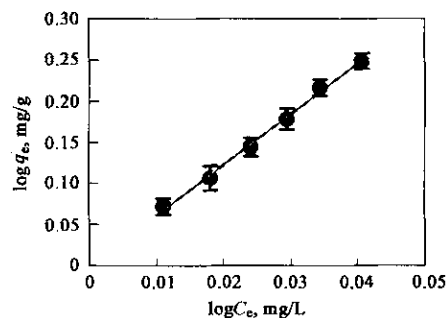


Fig. 4 Freundlich isotherm for k-2G, 10 g/L catalyst, pH = 5.28

dyes is neglectable, and the decrease of concentration was attributed to photodegradation by TiO₂ photocatalysis. The decolorize rate was measured to determine the photoreaction efficiency. The experiments data indicated that the photodegradation of k-2G and FG in fluidized-bed reactor are follow apparent first kinetic order, and the initial rate constants are given by (Poulios, 1999):

$$k = \alpha C_0^n, \quad (7)$$

where k is the photodecolorize rate constant, C_0 is the initial concentration of FG, and n is the kinetic partial order. Logarithmize the above equation yields the following equation:

$$\log k = \log \alpha + n \log C_0. \quad (8)$$

From the experiments data of FG yield n equal to -0.835, α equal to 0.0159, $\log k = -1.798 - 0.835 \log C_0$, so the constants decrease with the increasing of C_0 . This result agrees with the curve we obtained shown in Fig. 5. It can be observed that the photodecolorize rate constant of FG inverse proportional to the initial concentration. The amount of equilibrium adsorption (q_e) reached to a saturation value with the increasing of the initial concentration according to the Langmuir type behavior. If the photodegradation of FG mainly occurred on catalysts surface, the increased adsorption with the initial concentration in a certain range favored the surface-absorbed molecules to capture the $h\nu^+$ and surface-bound OH·, the k should firstly increase with the initial concentration then gradually decrease due to the increased light attenuation effects at higher dye concentration (Martin, 1995). The results of FG have different trends, it implied that the photocatalysis reaction of FG dominantly occurred in solution rather than in the catalysts surface. On the other hand, the adsorption behavior of k-2G is following Freundlich model, the relationship between $\log C_e$ and $\log q_e$ is linearity according to Freundlich adsorption equation $\log q_e = \log K + \frac{1}{n}$

+ $\log C_e$, $\frac{1}{n}$ is the slope, $\log K$ is the intercept. The

experiments data of k-2G yield $\frac{1}{n}$ equal to 0.9749, $\log K$ equal to 0.7448, $\log q_e = 0.7448 + 0.9749 \log C_e$. The high value of the $\frac{1}{n}$ indicated the high solution concentration of k-2G favor the adsorption on catalysts surface. The results show that at first the adsorption and photodecolorize rate constants increased with the dye concentration increasing. However, at higher dye concentration the light attenuation effects inhibited the reaction. The relationship between adsorption and

photodegradation indicated that photodegradation of k-2G is mainly surface reaction.

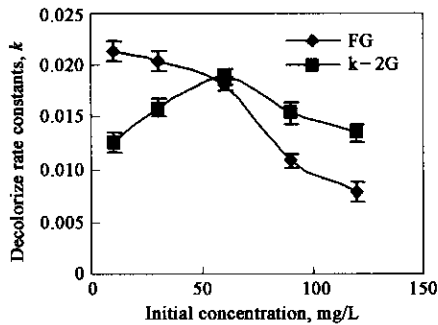


Fig. 5 The initial concentration of two dyes versus the decolorize rate constants

2.3 Effect of pH

A series of experiments were performed at different initial pH values to test the effect of pH on the photodegradation of two dyes. The absorbance of k-2G and FG were tested by spectrometer to ensure that no significant λ_{\max} shifting was observed at different pH. The initial concentration of the two dyes is 50 mg/L.

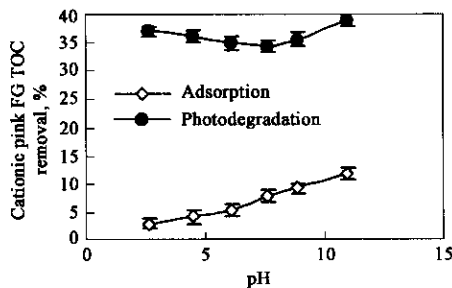


Fig. 6 Effect of pH on the adsorption and TOC removal of FG

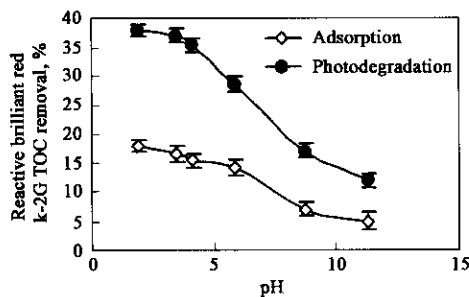


Fig. 7 Effect of pH on the adsorption and TOC removal of k-2G

The adsorption of FG is favorable in basic solution because its cationic property. The adsorption of FG rises with the increasing pH, but the TOC removal of FG for all the pH values are nearly the same as shown in Fig. 6. The curve shows no relationship to the initial amount of dye adsorption indicated that the reaction of FG is occur in solution rather than on catalysts surface. Finally, above pH 8.9 an increase in the TOC removal has been observed, the phenomena may be explained by the excess of OH^- anions favored the photogeneration of OH^\bullet radicals. Additionally, at sufficiently higher pH values the formation of oxidizing species such as the oxide radical anion $\text{O}^{\bullet -}$, could also be responsible for the enhancement (Poulios, 1999).

It is shown in Fig. 7 that the adsorption of k-2G on G01 surface and TOC removal of k-2G decreasing with the increasing pH. As pH increases, the more negatively charged catalysts would induce the electrostatic repulsion between the dye anion and catalysts surface, which is unfavorable to k-2G adsorption. These results indicated that k-2G adsorbed on the TiO_2 surface is an important step, the oxidation begins with the adsorption process of k-2G molecules, h_{ν}^+ and surface-bounded OH^\bullet decompose the adsorbed dye to final products.

2.4 The effect of KI and tetranitromethane (TNM)

Information about the photocatalytic reaction mechanism may be provided by determining the influence of hole or radical scavengers on the photodegradation efficiency of the two dyes. Iodide ion (Γ^-) is a scavenger reacts with h_{ν}^+ and surface-bounded OH^\bullet , reducing the number of oxidizing species available on the TiO_2 surface for reaction with dyes (Martin, 1995). Free radicals in the solution may arise from adsorbed OH^\bullet , which diffuse away from the catalysts surface or by reduction of H_2O_2 formed from a reaction involving the superoxide anion radicals. There is evidence that diffusion of surface-bound OH^\bullet is minimal. The powerful oxidizing agent tetranitromethane (TNM) was used to remove electrons and other reductants from solution. TNM will eliminate the species responsible for the formation of free radicals since TNM is not strongly adsorbed to the catalysts surface (Mao, 1991). The presence of Γ^- increased the TOC removal of FG (Fig. 8), the enhancement could be attributed to Γ^- scavenged the h_{ν}^+ prevented the h_{ν}^+/e_{cb}^- recombination. TOC removal of k-2G decreased in the presence of Γ^- , since Γ^- scavenged the h_{ν}^+ and surface-bounded OH^\bullet on catalysts surface reduced the number of reactive species available for photodegradation the adsorbed k-2G molecules. In addition, Γ^- competed the adsorptive sites on the G01 surface with k-2G, results in the efficiency decrease of k-2G photodegradation. These results confirmed the assumption that the photocatalytic reaction of FG mainly occurred with free radicals in solution, while the reaction of k-2G via h_{ν}^+ and surface-bounded OH^\bullet radicals on TiO_2 surface or near the interface of solid and solution.

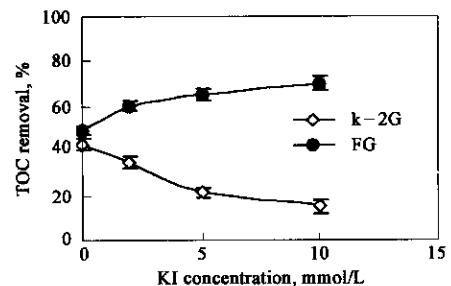


Fig. 8 Effect of hole scavenger KI on the photodegradation of two dyes at pH = 5.42

The photodegradation of FG was significantly inhibited in the presence of TNM (Fig. 9) confirmed that the photodegradation of FG is mainly via free radicals oxidation. On the other hand, there is minor adsorption of TNM on the catalysts surface, the presence of TNM have little effect on the photodegradation of k-2G confirmed the supposition that the surface-bound OH^\bullet and h_{ν}^+ react with adsorbed molecules

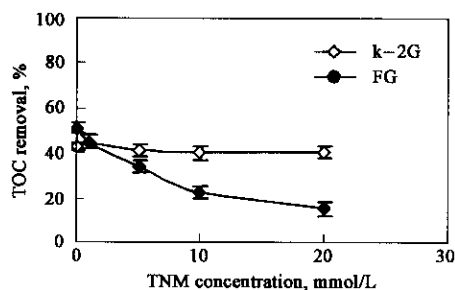


Fig. 9 Effect of free radicals scavenger TNM on the photodegradation of two dyes at pH = 5.21

on the catalyst surface decomposed the k-2G.

2.5 Effect SO₄²⁻, HCO₃⁻ on photodegradation of the two dyes

Both sulfate (SO₄²⁻) and bicarbonate (HCO₃⁻) were presented in the textile industry wastewater, several research groups have reported the inhibition in photocatalysis by these anions (John, 1996). The influence of SO₄²⁻, HCO₃⁻ on the degradation of FG and k-2G were studied here. The initial concentration of the two dyes is 50 mg/L. Dark adsorption experiments indicated that the presence of SO₄²⁻ decreased the equilibrium adsorption amount of k-2G from 28% to 2% consequently to inhibited the photodegradation of k-2G (Fig. 9). This result confirmed the h_ν⁺ and surface-bounded OH· radical reaction mechanism. The presence of SO₄²⁻ has minor effect on the adsorption and photodegradation of FG confirmed the free radicals reaction mechanism.

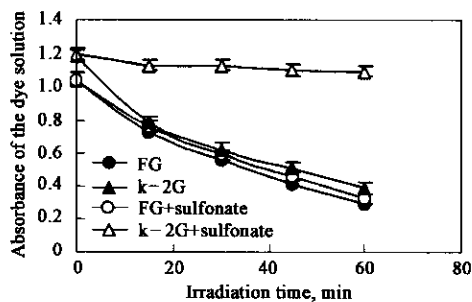
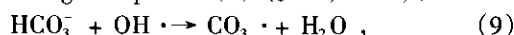


Fig. 10 Effect of SO₄²⁻ (3 mmol/L) on the photodegradation of two dyes

HCO₃⁻ has minor effect on the adsorption of the two dyes on GO1 surface. HCO₃⁻ is a known OH· radical scavenger according to Equation (9) (John, 1996):



HCO₃⁻ inhibited the photodegradation of FG, but have little effect on k-2G shown as Fig. 10. The results confirmed the assumption of the photodegradation mechanism of the two dyes again.

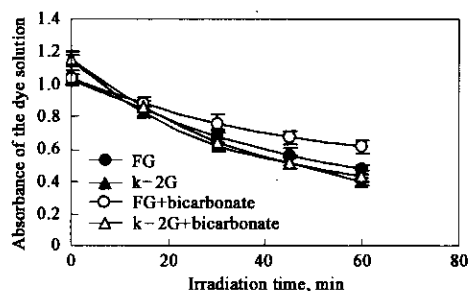


Fig. 11 Effect of HCO₃⁻ (3 mmol/L) on the photodegradation of two dyes

3 Conclusions

It has been shown that the different adsorption behavior of the two dyes results in different photodegradation mechanisms. This conclusion could be helpful to kinetic studies and to found optimal conditions of photodegradation in the fluidized reactor. The adsorption of FG follow Langmuir model, high initial concentration, free radicals scavengers inhibited the photodegradation of FG. The k-2G adsorption is Freundlich type behavior, higher initial concentration, acidic solution favorable to the photodegradation of k-2G, the h_ν⁺ and surface-bounded OH· radicals scavenger and the ions which competed the surface active sites with k-2G inhibited the photodegradation of k-2G.

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