

Study on the discolored thermodynamics and kinetics of Methyl Orange on Expanded graphite loaded with titania

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Abstract: To study thermodynamic and kinetic characteristics of Methyl Orange decoloration on Expanded graphite loaded with Titania (EG), EG was prepared firstly with 50 mesh natural graphite as raw materials, potassium permanganate as oxidant, vitriol and tetranbutyl titanate as intercalation compound. Then it was characted with XRD and Micromeritics Instrument. The influence of decoloration time, dye initial concentration, ionic strength and temperature on decoloration rate was detected. Based on pseudo first-order and second-order kinetic model, the decoloration model was discussed. Decoloration rate and activation energy were calculated. Studies show that decoloration rate of Methyl Orange on EG decrease with the increase of the adsorbate initial concentration and increase with the increase of ionic strength; the decoloration process can be well described by the pseudo second-order kinetic model; Decoloration equilibrium time and half decoloration time decrease with the increase of temperature, and adsorption of EG is the main factor of decoloration.

Key words: Expanded graphite loaded with Titania, Methyl Orange, Adsorption, Photodegradation, Kinetics, Thermodynamics.

INTRODUCTION

Expanded graphite is from graphite intercalation compounds. Under oxidation, the graphite layer can be opened, a number of organic and inorganic compounds, elements can be inserted, and remain in the graphite layers to form a graphite intercalation compounds (also known as expandable graphite). Expanded graphite is prepared with expandable graphite expanded at high temperature such as 900~1000 °C ^[1, 2]. Expanded

graphite possesses low density, high chemical stability under high or low temperature. The worm-like shape and network-like porous structure ranging from several nanometer to hundreds micron makes it as adsorbent of oils and dyes ^[3~ 7]. In the adsorption treatment of dyes with expanded graphite, Wang pressed the worm-like particles into low-density plate of 0.1g/cm³ ^[8], then the plate was used to treat dye waste-water from woolen mill. Pang etc. investigated the

influencing factors in adsorption of dyes with expanded graphite [9] and indicated that the adsorption capacity of expanded graphite is influenced by various factors, not only the expanded volume, primary concentration of dyes, contact time, but also the amount of the adsorbent, pH, ionic strength and temperature. The adsorption of Basic Fuchsin, Auramine Lake Yellow O and Acid Brilliant Red 3B on expanded graphite is a spontaneous process. Linear relationship was obtained between adsorption capacity and expanded graphite specific surface area. Higher ionic strength and proper pH values would improve adsorption capacity. Adsorption kinetics of expanded graphite for Acid Brilliant Red 3B [10] showed adsorption process has small activation energy, and it can be well described by the pseudo second-order kinetic model. Internal diffusion appears to be the rate-limiting step for the adsorption process.

In chemical oxidation of dyes, nano-TiO₂ is the most commonly used photo-catalyst. Under ultraviolet radiation, TiO₂ has a strong ability to generate OH·, which will ultimately enable complete oxidation of organic pollutants in water, and generates CO₂, H₂O, and other simple inorganic ions (such as NO₃⁻, SO₄²⁻, PO₄³⁻ and halogen, etc.). So far, more than 3000 kinds of refractory organic compounds have been found being degraded by TiO₂ under ultraviolet radiation [11]. To recycle this catalyst after reaction, TiO₂ is often loaded by some kinds of carriers [12]. The used carriers often have little adsorption capacity for pollutant, which would decrease the degradation capability of TiO₂.

Expanded graphite loaded with Titania (EG) is a kind of new adsorbent with porous structure and loading Titania [13, 14], it couples adsorption of expanded graphite and photo-catalysis of TiO₂ together. In this experiment, EG is prepared, and its degradation thermodynamics and kinetics for Methyl Orange is discussed. Results are compared with the single adsorption of expanded graphite and photo-catalysis of Titania. Possible decoloration mechanism is discussed.

MATERIALS AND METHODS

Natural graphite (C, 5092) was provided by Action Carbon CO. LTD, Baoding, China. H₂SO₄ (96%), KMnO₄, tetrabutyl titanate are all analytical reagents.

Preparation of EG

EG is prepared with potassium permanganate as oxidant, sulfuric acid and tetrabutyl titanate as intercalation reagent [14]. Reaction condition is controlled as: C : KMnO₄ : H₂SO₄ (diluted to 75%) : tetrabutyl titanate = 1: 0.5 : 3.0 : 0.4 (mass ratio). The reaction lasts 60 min in 45 °C water bath, then product is transferred into beaker and washed with water until pH = 6.0~7.0. After dipping in water for 2-3 hours, the product is filtrated and then dried at 60 ~ 80°C, expandable graphite is obtained. Expandable graphite is expanded at 900 °C for 10s, and then EG is obtained. To illustrate the existence of intercalation compound and its form, graphite, expandable graphite and EG are characterized with XRD (Y-2000 X-Ray powder diffraction instrument). As showed in **Fig. 1**, anatase TiO₂ is found in expandable graphite (b), and Titania is found in EG (c). As mentioned in reference [14], structural parameters of EG are characterized by expanded volume, surface area and total pore cubage. These data are detected with BET N₂ adsorption by Micromeritics Instrument Corporation TriStar II 3020 V1.02 (as listed in **Table 1.**)

Dye Characteristics

Methyl Orange with azobenzene structure was selected as reference compounds. Molecular structures and molecular weight of the dye was showed in **Table 2**. It was supplied by Yuhua trade company, Tientsin, China.

Simulated dye wastewater was prepared by dissolving the Methyl Orange in distilled deionized water at various concentrations. Absorbance value was recorded at the wavelength for maximum absorbance (λ_{max}) corresponding to dye as showed in **Table 2**.

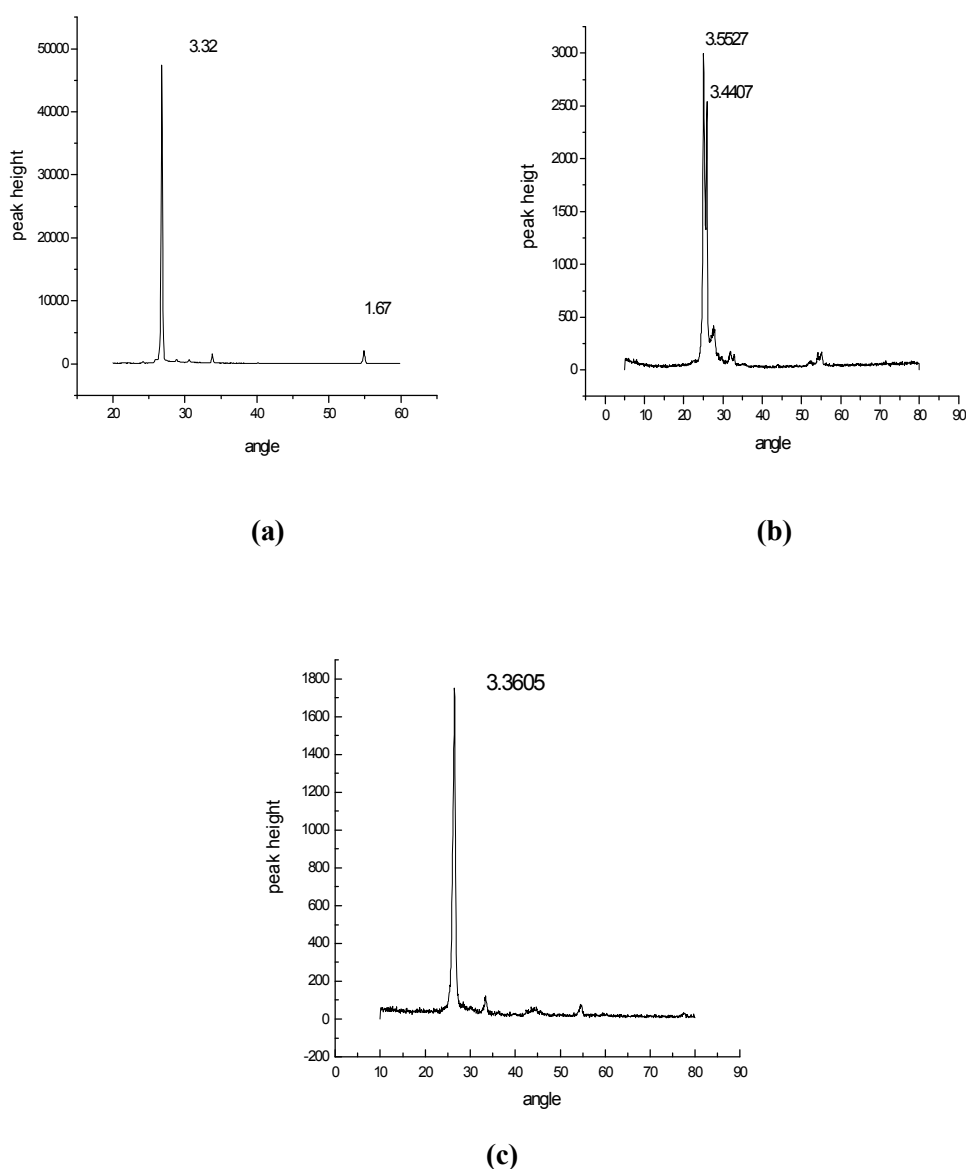


Fig. 1 XRD of Graphite, Expandable graphite and EG
(a) Graphite; (b) Expandable graphite ; (c) EG

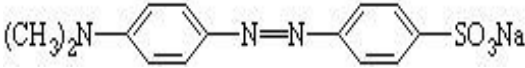
Table 1: Structural Parameter of EG *

Expanded volume (mL/ g)	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Adsorption average pore width 4V/A (nm)	Density (g/cm ⁻³)
320	20.3285	0.073891	14.65302	1.000

* -- Detection condition:

Analysis adsorptive: N₂; Sample mass: 0.1688 g; Equilibration interval: 10 s; Surface area or pore volume of pores between 1.7000 nm and 300.0000 nm diameter

Table 2: Chemical Structure and Molecular Weight of Methyl Orange

Dye	Structure	Molecular weight	$\lambda_{\max}(\text{nm})$
Methyl Orange		327.33	463

Determination of Decoloration Rate

Batch decoloration experiments were carried in 250 mL beaker with the mass of EG to volume of dye solution was standardized at $M/V=0.05 \text{ g} / 0.1 \text{ L}=0.5 \text{ g/L}$. Decoloration under different condition were compared. Method I: Decoloration was carried in dark with EG as adsorbent. Method II: Decoloration was carried under UV irradiation with EG as adsorbent. Method III: Decoloration was carried under UV irradiation with no adsorbent. Absorbency of solution was detected at different time. Total decoloration rate, adsorption decoloration rate, UV photodegradation decoloration rate and UV revulsive Titania photodegradation decoloration rate can be calculated according to equation (1).

$$D = (A_0 - A_t) / A_0 * 100\% \quad (1)$$

D : Decoloration rate, %; A_0 : absorbency before decoloration; A_t : absorbency at moment t

Decoloration Rate of Dye in the Influence of Ionic Strength

With concentration of Methyl Orange was set as 50 mg/L, ionic strength of the dye solutions was adjusted with NaCl and Na_2SO_4 in rang of 0.0 ~ 1.0 mol/L. Then decoloration rate under different ionic strength were detected.

Decoloration Kinetics Experiment

In decoloration kinetics experiment, a series of desired dye concentration and fixed volume of 100.0 mL were placed in beaker where they were brought into contact with EG at 15 °C, 25 °C and 35 °C, respectively. The mass of EG to volume of solution was standardized at $M/V=0.0500 \text{ g} / 0.1 \text{ L}=0.5000 \text{ g/L}$. Decoloration was carried under UV irradiation. Absorbency of dye solution corresponding to different

decoloration time was analysed until the absorbency kept as a constant, and it was used to calculate the decoloration rate at different moment according to equation (1).

RESULTS AND DISCUSSION

Results of Decoloration Thermodynamics

Influence of Dye Concentration and Decoloring Time on Decoloration rate

Fig. 2 shows decoloration rate is the function of decoloring time and Methyl Orange concentration. During the showed decoloring time, decoloration rate combined EG adsorption and Titania photo-degradation increases with the increase of decoloring time, and decreases with the increase of Methyl Orange concentration. The results illustrate decoloration is caused totally by EG adsorption and Titania photo-degradation.

Influence of Ionic Strength on Decoloration

To investigate the influence of ionic strength on decoloration rate of Methyl Orange, NaCl and Na_2SO_4 were used to adjust ionic strength in the range of 0.0 ~ 1.2 mol/L. The results corresponding to decoloring 24.0 h are showed in **Fig. 3**. It indicates that the presence of NaCl and Na_2SO_4 enhances decoloration of dyes. Electrostatic interaction between dye and Methyl Orange decreases with the increase in ionic strength probably because of the suppression of the electric double layer^[15], and hydrophobic attraction increases due to the “salting-out” effect. Over the range of 0.0 ~ 1.2 mol/L, the influence of NaCl is more obvious than that of Na_2SO_4 on decoloration rate.

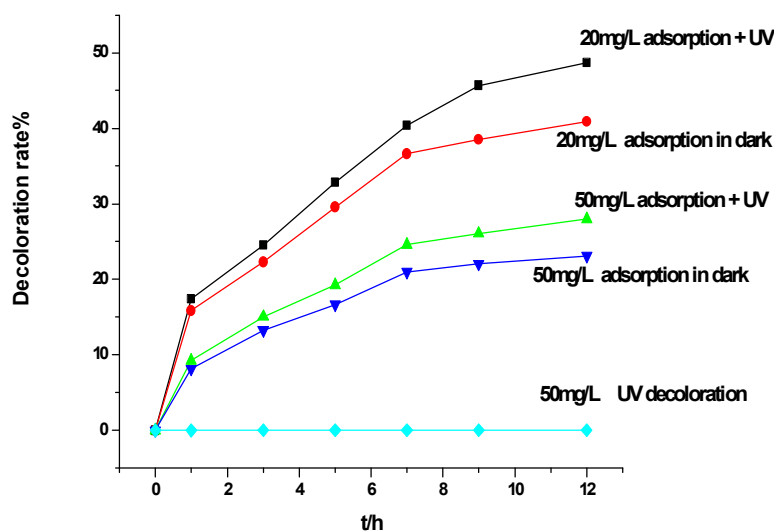


Fig. 2 Decoloration of Methyl Orange on EG

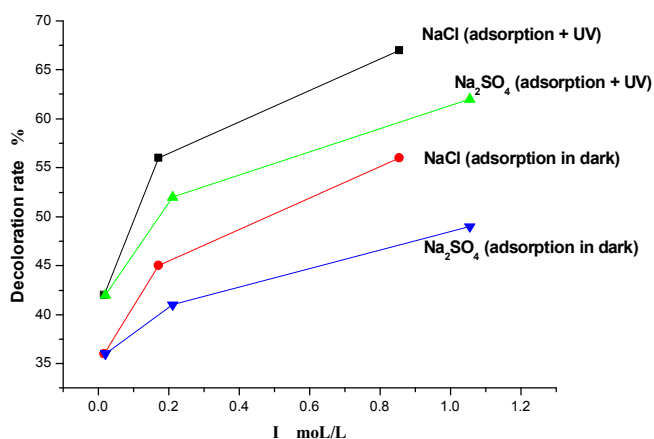


Fig. 3 Influence of Ionic Strength on Decoloration rate

Results of Decoloration Kinetics

Influence of Temperature and Dye Concentration on Decoloration

In **Fig. 4**, decoloration rate is showed as a function of time and dye concentration. Decoloration rate decrease with the increase of Methyl Orange concentration, and increase with decoloration time at a decreasing speed.

It's about 24.0 h for the decoloration reach equilibrium. Under the same Methyl Orange initial concentration, the equilibrium decoloration rate decrease with the increase of decoloration temperature, and the results might be caused by the increase of dye solubility in solution.

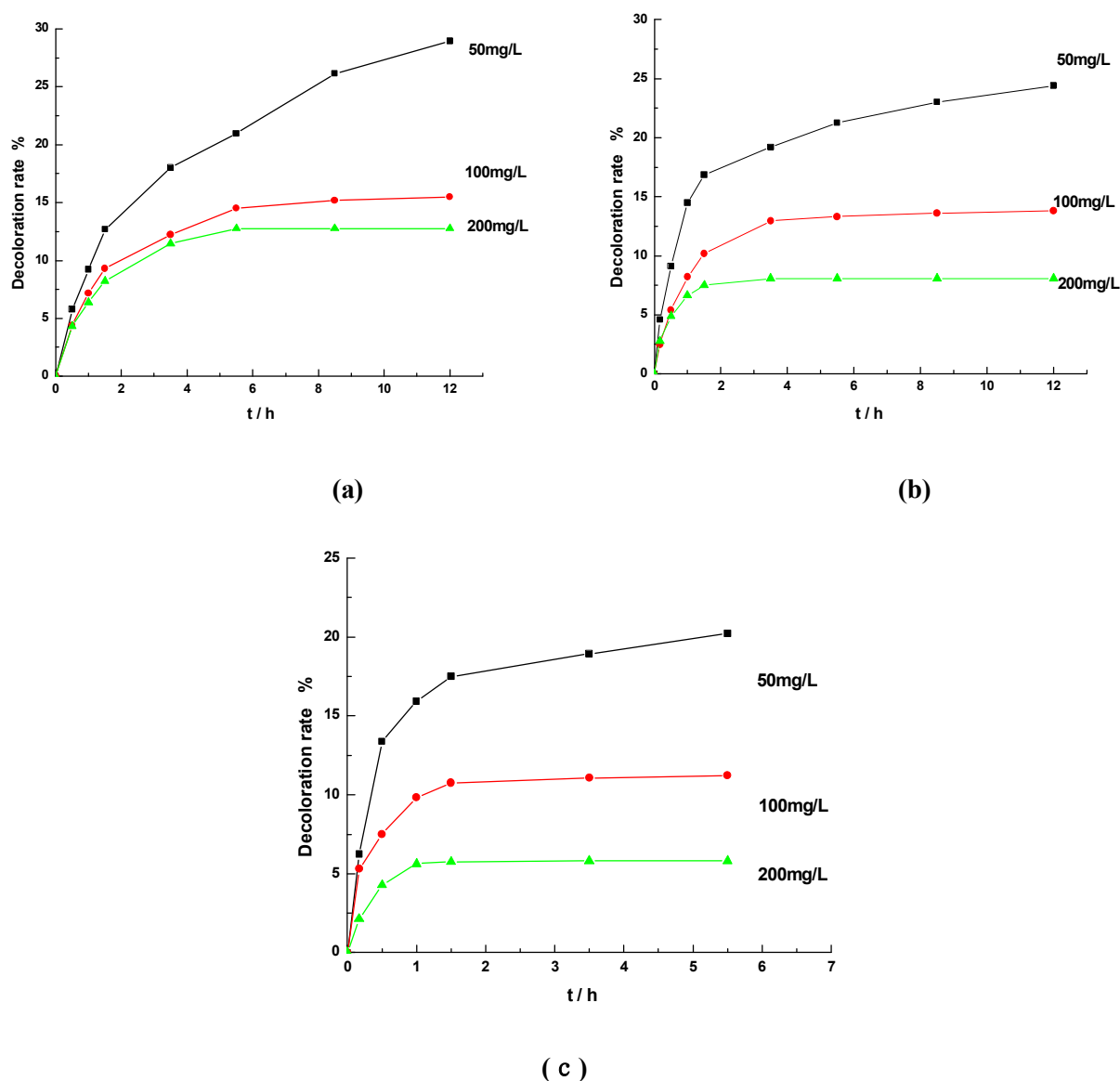


Fig. 4 Influence of Initial Methyl Orange Concentration and Temperature on Decoloration rate
 (■) 50mg/L, (●) 100mg/L, (▲) 200mg/L (a) 15 °C, (b) 25 °C, (c) 35 °C

Decoloration Kinetic Models

Both pseudo first- and second-order adsorption models were used to describe the decoloration kinetics data [16, 17]. In both models, all the steps of degradation such as external diffusion, internal diffusion, and decoloration are lumped together, the overall decoloration rate is proportional to either the driving force (as in the pseudo first-order equation) or the square of the driving force (as in the pseudo second-order equation).

First-order model: $\ln(De-D) = \ln De - kt$ (2)

Second-order model: $t/D = 1/(k De^2) + t/De$ (3)

k , decoloration rate constant (min^{-1} for first-order

decoloration, $\%^{-1} \cdot \text{min}^{-1}$ for second-order adsorption); t , decoloring time (min); De , equilibrium decoloration rate (%)

Since D reaches a plateau (De) at equilibrium, D values smaller than the $0.9 De$ were used for analysis. The plots of: $\ln(De-D)$ versus t and t/D versus t were used to test the first- and second-order models, and the fitting results are given in **Table 3**. According to the correlation coefficients, second-order model gives satisfactory fits. At the same time, the De_{cal} obtained from the intercepts is obviously inconsistent with the experimental data De_{exp} in the first-order model. In the

second-order model, the $D_{e,cal}$ agrees reasonably well with $D_{e,exp}$. Thus, the second-order model is more suitable to describe the degradation kinetics data.

Based on the second-order model, the initial decoloration rate and half- decoloration times are estimated in **Table 4** according to equation (4) and (5). Initial decoloration rate decreases with the increase of

Methyl Orange concentration, and half- decoloration time is found to decrease with the increase in temperature.

$$u=kD_e^2 \tag{4}$$

$$t_{1/2}=1/(kD_e) \tag{5}$$

u , initial decoloration rate, % • min⁻¹; $t_{1/2}$, half-degradation time, min.

Table 3: Comparison of Decoloration Kinetic Models

C_0 (mg/L)	Temperature (°C)	$D_{e,exp}$	First-order			Second-order		
			$D_{e,cal}$	k (min ⁻¹)	r	$D_{e,cal}$	k (% ⁻¹ •min ⁻¹)	r
50	15	28.95	26.64±1.06	0.0042±0.0002	-0.9913	28.44±0.02	0.00030±0.00002	0.9990
	25	24.40	23.07±1.042	0.013±0.0008	-0.9940	23.80±0.23	0.00098±0.00003	0.9990
	35	20.22	17.01±1.144	0.022±0.0027	-0.9884	20.79±0.001	0.0025±0.0010	0.9993
100	15	15.50	13.76±1.073	0.0075±0.0003	-0.9964	17.96±0.0011	0.00062±0.00003	0.9992
	25	13.82	12.76±1.071	0.013±0.0003	-0.9984	15.06±0.001	0.0014±0.0009	0.9992
	35	11.23	9.94±1.094	0.0336±0.0018	-0.9958	11.85±0.002	0.0064±0.0005	0.9992
200	15	12.77	12.31±1.024	0.0175±0.0003	-0.9996	13.48±1.34	0.0016±0.0018	0.9971
	25	8.08	7.85±1.049	0.0286±0.0010	-0.9973	7.91±0.016	0.0075±0.0007	0.9996
	35	5.80	6.93±1.143	0.0580±0.0029	-0.9951	5.66±0.008	0.0149±0.0007	0.9970

Table 4: Kinetic Parameters for the Second-order Model

C_0 (mg • L ⁻¹)	Temperature(°C)	u (min ⁻¹)	$t_{1/2}$ (min)	ΔH (kJ•mol ⁻¹)	r
50	15	0.214	116.611	37.42	-0.9924
	25	0.558	41.558		
	35	1.086	19.677		
100	15	0.201	89.425	31.54	-0.9804
	25	0.318	47.359		
	35	0.900	13.159		
200	15	0.346	42.087	28.03	-0.9911
	25	0.448	17.185		
	35	0.477	11.879		

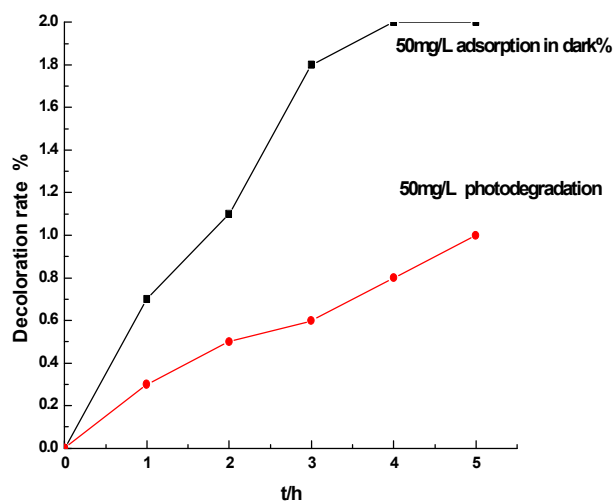


Fig. 5 Comparison of EG Physical Adsorption and Titania Photodegradation

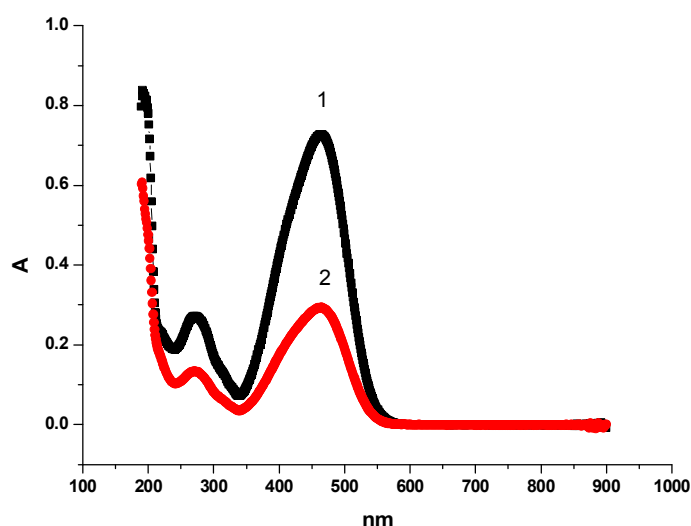


Fig. 6 Absorption Spectrums of Methyl Orange
1. Before decoloration 2. Decoloration 12h

The second-order kinetic models constants listed in Table 3 were used to estimate decoloration activation energy using Arrhenius equation (6). The slope of plot of $\ln k$ versus $1/T$ is used to evaluate E_a , which was found to be smaller than 40 kJ mol^{-1} (listed in Table 4). The results illustrate the decoloration of EG for Methyl Orange is mainly physical interaction. To judge the single decoloration ability of EG adsorption and Titania (loaded in EG) photo-degradation, comparison experiment was carried out. The results

(showed in Fig. 5) proved that physical adsorption of EG is stronger than that Titania photo-degradation.

$$\ln k = \ln A - E_a / (RT) \quad (6)$$

A , pre-exponential factor; E_a , activation energy of decoloration, $\text{kJ} \cdot \text{mol}^{-1}$

Analysis of Possible Decoloration Mechanism

In order to analysis the possible decoloration mechanism of Methyl Orange under the EG adsorption and Titania photodegradation, the absorption spectrum

scanning among 190~900 nm were carried out before and after decoloring treatment. As showed in Fig. 6, no new resultant was detected; the adsorbate is mineralized under the photodegradation of Titania. So the decoloration mechanism would be: Methyl Orange in solution and adsorbed on surface of EG can jointly be photodegradation by Titania, mineralizing product are mainly CO₂ and H₂O, adsorption of EG can improve the decoloration effect.

CONCLUSIONS

This study has proved that EG possesses a higher decoloration ability for than the single EG adsorption or Titania photo-degradation. Decoloration process was influenced by initial dye concentration, decoloration time and ionic strength. Ionic strength plays an important role in decoloration, higher ion

strength or the presence of salt ions can improve the treatment of dye. The decoloration kinetic of Methyl Orange can be well described by the pseudo second-order kinetic model. The half-decoloration time of Methyl Orange is found to decrease with the increase in temperature. Decoloration of Methyl Orange on EG holds small activation energy, and physical adsorption plays main role in the decoloration.

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