



## Preparation of expanded graphite loaded with zinc oxide and its decolorizing performance for dye

Xiuyan Pang, Ruinian Lin\*, Xin Su

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, (PEOPLE' REPUBLIC OF CHINA)

E-mail : pxy833@163.com

### ABSTRACT

Expanded graphite (EG) loaded with Zinc oxide (ZnO/EG) was prepared with 50 mesh natural graphite as raw materials,  $\text{KMnO}_4$  as the oxidant,  $\text{H}_2\text{SO}_4$  as intercalation reagent and  $\text{ZnSO}_4$  as the secondary intercalation agent. When mass ratio of  $\text{C}:\text{KMnO}_4:\text{H}_2\text{SO}_4(98\%):\text{ZnSO}_4\cdot\text{H}_2\text{O}$  is controlled as 1.0:0.35:5.0:0.4,  $\text{H}_2\text{SO}_4$  diluted to 80% before reaction; and the reaction lasts 40 min at  $30^\circ\text{C}$ , ZnO/EG with an expanded volume of  $420\text{ mL}\cdot\text{g}^{-1}$  is obtained when the graphite intercalation compound is expanded at  $950^\circ\text{C}$ . X-ray diffraction analysis shows that ZnO on ZnO/EG is in the form of hexagonal crystal system. Decolorization kinetics and thermodynamics of ZnO/EG for Auramine lake yellow O were investigated. Kinetic research results show the decolorization process can be described with the pseudo second-order kinetic model. Thermodynamics research results show the decolorization isotherm for Auramine lake yellow O is type I. Decolorization property of ZnO/EG under ultraviolet radiation is higher than either adsorption decolorization of EG or the ultraviolet radiation decolorization of ZnO. Increase of solution ionic strength is of benefit to improve the decolorization capacity of ZnO/EG. © 2014 Trade Science Inc. - INDIA

### KEYWORDS

Expanded graphite loaded  
with ZnO;  
 $\text{ZnSO}_4$ ;  
Photo catalysis;  
Decolorization.

### INTRODUCTION

Dye wastewater produced by textile, paper and printing factories has become one of the major sources of pollution, it requires pretreatment prior to disposal into receiving water body. Biochemical and physical-chemical methods are widely used, especially the combined physical/chemical methods<sup>[1-3]</sup>. Photo catalytic degradation of organic contaminants with semiconductor nano particles is an important method. The semiconductor photo catalysts mainly include metallic oxide and sulfide. Titanium dioxide ( $\text{TiO}_2$ ) is one of the most

practical photo catalytic catalysts due to its high oxidation and chemical stability.  $\text{TiO}_2$  can generate electron-hole pairs when it expose to ultraviolet (UV) light, and these electron-hole pairs can diffuse to  $\text{TiO}_2$  surface and induce the formation of highly energetic radicals and ions<sup>[4]</sup>, which can decompose organic compounds. However,  $\text{TiO}_2$  has the shortcoming of low quantum efficiency and lack of usage for visible light in practical application. Compared with  $\text{TiO}_2$ , ZnO belongs to direct band wide bandgap semiconductor, its energy gap is 3.37eV at room temperature, which is the same as the 3.2eV of  $\text{TiO}_2$ . It had been reported

that ZnO possesses higher quantum efficiency and photo catalysis efficiency<sup>[5]</sup>. It has been used as catalyst of decomposition of sec-butyl alcohol<sup>[6]</sup>, benzene<sup>[7,8]</sup> and dyes<sup>[9-11]</sup>. In the practical application of ZnO, it is often loaded with carrier in order to increase specific areas and easy to recycle or assemble as a fixed-bed reactor<sup>[6,7]</sup>.

Expanded graphite (EG) is a kind of eco-material; it is prepared from graphite intercalation compounds. Under oxidation, natural graphite layer can be opened; a number of organic and inorganic compounds, elements can insert, and remain in the graphite layers to form graphite intercalation compound called expansible graphite. EG is prepared with expandable graphite expanding at high temperature<sup>[12]</sup>. EG has a worm-like shape and network-like porous structure with dimensions ranging from several nanometer to hundreds micron<sup>[13]</sup>, and it has been testified that this absorbent possesses high adsorption capacity for organic materials, such as heavy oil<sup>[14]</sup> and dyes<sup>[15]</sup>. At the same time, EG is a kind of carrier based on its porous structure. It will increase photo-catalytic reaction rate due to the adsorption of EG. The reported supporting methods of catalysts on EG mainly include impregnation with expansible graphite<sup>[16]</sup> or EG<sup>[17]</sup> as carrier, and chemical oxidation of graphite with catalyst precursor as intercalation reagent<sup>[18]</sup>.

In view of the photo catalysis of ZnO and EG adsorption capability for organic contaminants, the purpose of this research is to prepared expanded graphite loaded with ZnO (ZnO/EG) composite through chemical oxidation intercalation of natural graphite with  $\text{KMnO}_4$  as oxidant,  $\text{H}_2\text{SO}_4$  as intercalation reagent and  $\text{ZnSO}_4$  as the secondary intercalation reagent. The prepared ZnO/EG is characterized with expanded volume, X-ray diffraction and scan electronic microscope to illuminate its existence form. Decolorization capability of ZnO/EG for dye Auramine lake yellow O with a diphenylmethane structure was investigated.

## EXPERIMENTAL

### Instruments and reagents

SX3-4-13 muffle furnace (Tientsin, precision of temperature  $\pm 0.1\% \sim 0.4\% ^\circ\text{C}$ ); Y-4Q X-ray diffractometer (XRD) (Dandong, China); TM3000 electron micro-

scope (Japan) were used in this experiment. T6 New Century UV spectrophotometer (Puxi Tongyong Instrument Limited Company of Beijing); UV light source: 20W, wave length 200-275nm.

Material graphite (C, 5092) was provided by Action Carbon CO. LTD, Baoding, China.  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{H}_2\text{SO}_4$  (98%),  $\text{KMnO}_4$  are all analytical reagents. Auramine lake yellow O was purchased from Tianjin Medical Corporation.

### Methods

#### Preparation of ZnO/EG

Under a definite reaction temperature, the quantified reactants are mixed in a 250mL beaker and stirred in the order of diluted  $\text{H}_2\text{SO}_4$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , material graphite C and  $\text{KMnO}_4$ . After reaction, the solid phase is washed with de-ionized water until pH of the waste water reaches to 6.0~7.0; after dipping in water for 2.0 h, filtrate and dry the samples at 60~80 $^\circ\text{C}$  for about 6.0 h, expansible graphite is obtained. Dosages of  $\text{KMnO}_4$ , 98%  $\text{H}_2\text{SO}_4$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , concentration of  $\text{H}_2\text{SO}_4$ , reaction temperature and reaction time are all optimized through single factor test. The feasible condition preparing expansible graphite is determined as: mass ratio of C: $\text{KMnO}_4$ : $\text{H}_2\text{SO}_4$ (98%): $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  is controlled as 1.0:0.35:5.0:0.4, the reaction lasts 40 min at 30 $^\circ\text{C}$ , and  $\text{H}_2\text{SO}_4$  is diluted to a mass concentration of 80%. Then the prepared expansible graphite expands at 950  $^\circ\text{C}$ , and ZnO/EG with an expanded volume of 420  $\text{mL} \cdot \text{g}^{-1}$  is obtained (expanded volume is the volume of 1.0 g expansible graphite after expansion at a definite oven temperature).

#### X-ray diffraction analysis (XRD)

XRD for graphite, expandable graphite and ZnO/EG are carried out employing Ni-filtered Cu K $\alpha$  radiation with 2 $\theta$  ranging from 10 $^\circ$  to 75 $^\circ$ . As shown in Figure 1, (a), the two peaks with the interplanar crystal spacing of 3.34  $\text{Å}$  and 1.67  $\text{Å}$  corresponding to diffraction angle of 26.6 $^\circ$ , 54.8 $^\circ$  are the characteristic spectrum of material graphite. While, as shown in Figure 1 (b) and (c), the characteristic peaks of expansible graphite and ZnO/EG composite transfer to a small angle of 26.3 $^\circ$  and 26.5 $^\circ$ , respectively. Each corresponds to a big interplanar crystal spacing of 3.39  $\text{Å}$  and 3.36  $\text{Å}$  due to intercalation in graphene planes. Material graphite

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is a crystal compound with graphene planes structure bonded by Van Der Waals force. Under the oxidation of  $\text{KMnO}_4$  and  $\text{H}_2\text{SO}_4$ , the plane repellency will increase due to the formation of carbon cations. Then the non-carbonaceous reactants can easily insert into the planes, leading to the increase of interplanar crystal spacing. In Figure 1 (b) of expansible graphite,  $18.9^\circ$ ,  $28.6^\circ$ ,  $35.4^\circ$ ,  $55.9^\circ$  are characteristic spectrums of  $\text{Zn}_3\text{O}(\text{SO}_4)_2$ ,  $\text{ZnSO}_4$ . While, in XRD spectrum of  $\text{ZnO}/\text{EG}$ ,  $31.7^\circ$ ,  $34.4^\circ$ ,  $36.2^\circ$ ,  $47.5^\circ$ ,  $56.4^\circ$ ,  $62.9^\circ$ ,  $67.9^\circ$  are characteristic spectrums of  $\text{ZnO}$  existing in the form of hexagonal system; and it illuminates  $\text{Zn}_3\text{O}(\text{SO}_4)_2$ ,  $\text{ZnSO}_4$  completely decompose and turn into  $\text{ZnO}$  at  $950^\circ\text{C}$ .

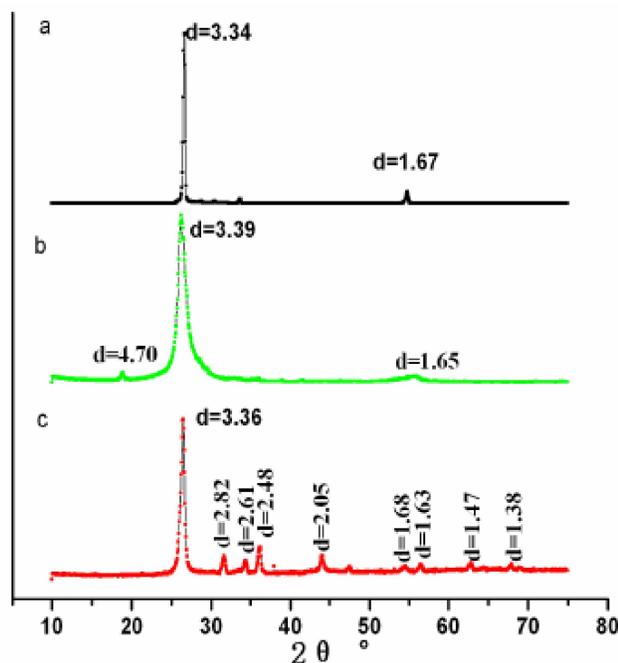


Figure 1 : XRD analysis of material graphite and products; (a) Material graphite; (b) expansible graphite; (c)  $\text{ZnO}/\text{EG}$

### Scan electronic microscopy (SEM) analysis of product

As shown in Figure 2, the  $\text{ZnO}/\text{EG}$  show as worms with many pores in different size, and  $\text{ZnO}$  white par-

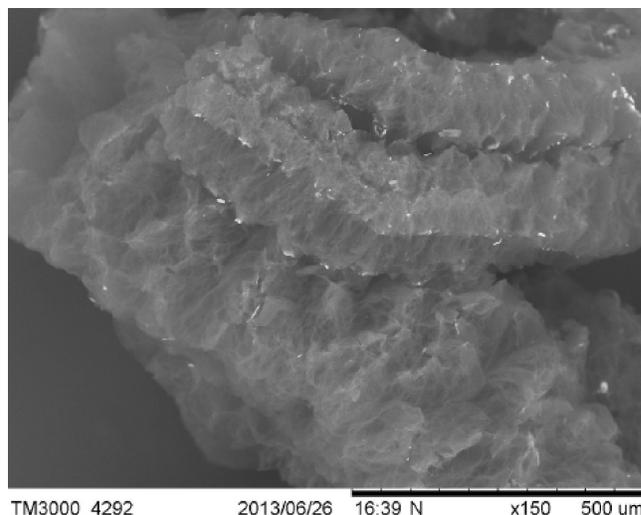


Figure 2 : SEM of  $\text{ZnO}/\text{EG}$

ticles adsorb on surface or pore canal. Therefore,  $\text{ZnO}$  can be loaded on the EG through chemical oxidation and intercalation of natural graphite with  $\text{ZnSO}_4$  as the secondary intercalation reagent, and then expanded at high temperature above  $950^\circ\text{C}$ . As testified in XRD analysis, the supported  $\text{ZnO}$  exists in the form of hexagonal system.

### Adsorbate characteristics

Dye of Auramine lake yellow O is selected as reference compound. Molecular structure, molecular weight and its quantitative determination method are shown in TABLE 1. Simulated dye wastewaters are prepared by dissolving Auramine Lake Yellow O in deionized water at various concentrations.

### Decoloration experiment

Batch decoloration experiments under a definite temperature, ionic strength and dye concentration are performed in 250 mL beaker with the mass of  $\text{ZnO}/\text{EG}$  to solution volume fixed at  $M/V=0.200\text{ g}/0.1\text{L}=2.000\text{ g}\cdot\text{L}^{-1}$ .  $\text{NaCl}$  and  $\text{Na}_2\text{SO}_4$  are used to adjust ionic strength of the solution. Decoloration experiments under different condition are compared. Method I: Decoloration is carried out in dark. Method II: Decoloration is carried

TABLE 1 : Auramine Lake Yellow O characteristics and quantitative determination method<sup>a</sup>

Structure	M g/mol	$\lambda_{\text{max}}$ nm	Quantitative equation
	318.5	430	$Y = -0.01235 + 0.04741X$

<sup>a</sup> X—mass concentration of solution  $\text{mg}\cdot\text{L}^{-1}$  Y—absorbency

out under UV irradiation (UV irradiation condition: power 20W, wave length 200-275nm, distance between illuminant and liquid level 15cm). Absorbency of solution is detected at different time. Total decoloration rate, adsorption decoloration rate, UV photo degradation decoloration rate are calculated according to equation (1). Removal amount of dye can be calculated according to equation (2).

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

$D$ , Decoloration rate, %;  $A_0$ , initial absorbency of dye solution;  $A_t$ , absorbency at moment  $t$ .

$$q = V (C_0 - C) / m \quad (2)$$

$C_0$ —initial concentration of dye,  $\text{mg}\cdot\text{L}^{-1}$ ,  $C$ —concentration of dye at moment  $t$ ,  $\text{mg}\cdot\text{L}^{-1}$ ,  $V$ —volume of solution, L,  $m$ —mass of ZnO/EG,  $q$ —removal amount of dye,  $\text{mg}\cdot\text{g}^{-1}$

## RESULTS AND DISCUSSION

### Influence of dye concentration on equilibrium time

With the initial dye concentration is controlled as  $50 \text{ mg}\cdot\text{L}^{-1}$  and  $400 \text{ mg}\cdot\text{L}^{-1}$ , respectively, the decoloration rate of ZnO/EG for Auramine Lake Yellow O are calculated using equation (1) according to change of absorbency. As shown in Figure 3, decoloration rate show as a function of time and dye concentration at  $20^\circ\text{C}$ . In the initial stage of decoloration, it occurs more rapidly at higher concentration, but decoloration need longer time to reach equilibrium, and decoloration rate increase with the increase of initial dye concentration.

### Decoloration kinetic models

In order to find a feasible model to match the kinetic data, both pseudo first-order and pseudo second-order models are used<sup>[19]</sup>. In both models, all the steps such as external diffusion, internal diffusion, adsorption and decoloration are lumped together, the overall decoloration rate is proportional to either the

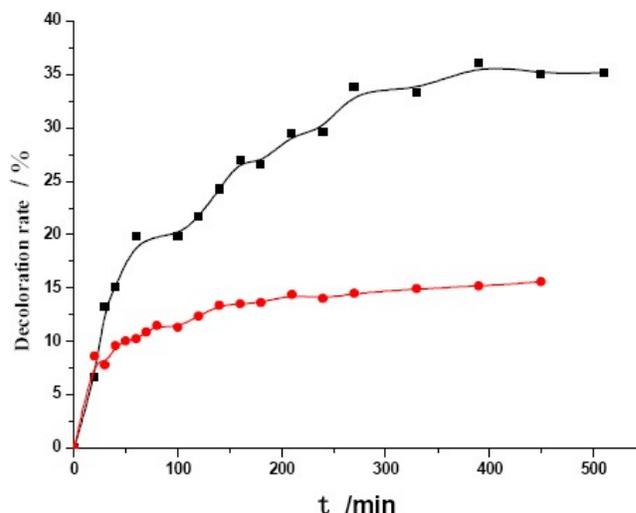


Figure 3 : Influence of initial Auramine Lake Yellow O concentration on decoloration rate; (●)  $50 \text{ mg}\cdot\text{L}^{-1}$  (■)  $400 \text{ mg}\cdot\text{L}^{-1}$

driving force (as in the pseudo first-order equation (3)) or the square of the driving force (as in the pseudo second-order equation (4)). Removal amount of dye at different moment are calculated according to equation (2).

$$\text{Pseudo first-order model, } \ln(q_e - q) = \ln q_e - kt \quad (3)$$

$$\text{Pseudo second-order model, } t/q = 1/(k q_e^2) + t/q_e \quad (4)$$

$k$ , decoloration rate constant ( $\text{h}^{-1}$  for pseudo first-order decoloration,  $\text{g}\cdot(\text{mg}\cdot\text{h})^{-1}$  for pseudo second-order adsorption);  $t$ , decoloration time (h);  $q_e$ , equilibrium removal amount ( $\text{mg}\cdot\text{g}^{-1}$ )

Since  $q$  reaches a plateau ( $q_e$ ),  $q$  values smaller than the  $0.9 q_e$  are used for analysis. The plots of  $\ln(q_e - q)$  versus  $t$  and  $t/q$  versus  $t$  are used to test the pseudo first- and pseudo second-order models, and the matching results are given in TABLE 2. According to the correlation coefficients, pseudo second-order model gives satisfactory fits. At the same time, the  $q_{e, \text{cal}}$  obtained from the intercepts is obviously consistent with the experimental data  $q_{e, \text{exp}}$  in the pseudo first-order model. Thus, the kinetic data can be described with the pseudo second-order model.

TABLE 2 : Comparison of decoloration kinetic models<sup>b</sup>

$C_0 \text{ mg}\cdot\text{L}^{-1}$	$q_{e, \text{exp}} \text{ mg}\cdot\text{g}^{-1}$	Pseudo first-order model			Pseudo second-order model		
		$q_{e, \text{cal}} \text{ mg}\cdot\text{g}^{-1}$	$k \text{ h}^{-1}$	$r$	$q_{e, \text{cal}} \text{ mg}\cdot\text{g}^{-1}$	$k \text{ g}\cdot(\text{mg}\cdot\text{h})^{-1}$	$r$
50	17.51	14.43	0.0096	-0.9943	18.28	0.000975	0.9942
400	31.36	18.66	0.0082	-0.9813	32.42	0.00112	0.9974

<sup>b</sup> Experiment temperature  $20^\circ\text{C}$

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### Results of decoloration thermodynamics

#### Influence of dye concentration on decoloration rate

At 20°C, decoloration experiments are performed under different condition of different initial dye concentration, decoloration under UV beam and decoloration in dark, the removal amount of Auramine Lake Yellow O is calculated according to equation (2), respectively. Total removal amount is the value of dye removed by ZnO/EG under UV beam; adsorption removal amount is the value of dye removed by ZnO/EG under dark; UV photo degradation removal amount of ZnO for dye is the difference between total removal amount and adsorption removal amount. With equilibrium concentration of dye as horizontal axis, and removal amount as vertical axis, the decoloration isotherms are drew as Figure 4. The results show that isotherms of no matter the total removal amount of ZnO/EG for dye under UV beam, or the adsorption removal amount of ZnO/EG for dye in dark, or UV photo degradation removal amount of ZnO for dye are all consistent with I type. The decoloration capability increases in the order of UV photo degradation decoloration of ZnO, adsorption decoloration of ZnO/EG in dark and decoloration of ZnO/EG under UV beam. The lower UV photo degradation decoloration of ZnO might be caused by the insufficient intercalation of  $ZnSO_4$ , and then caused a small number of ZnO supported on EG.

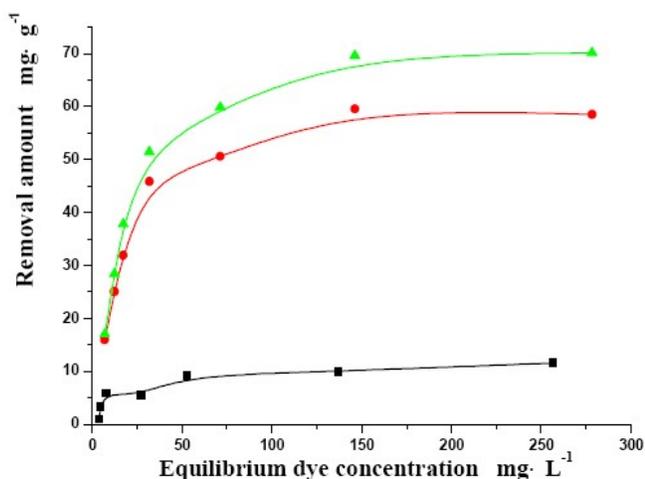


Figure 4 : Decoloration isotherms of dye on ZnO/EG under different condition; (▲) Total removal amount; (●) Adsorption removal amount; (■) UV photo degradation removal amount

#### Investigation of thermodynamic model and model parameters

To get feasible thermodynamic model and model parameters describing the decoloration of Auramine Lake Yellow O on ZnO/EG, Langmuir and Freundlich equations (5) and (6) are used to treat the thermodynamic data, and the results are shown in TABLE 3. As for the linearly dependent coefficient, Langmuir equation is more matching the thermodynamic data than Freundlich equation.

TABLE 3 : Langmuir and Freundlich isotherm constants at 20 °C

Langmuir model			Freundlich model		
$q_0$ mg·g <sup>-1</sup>	$A$ mg·L <sup>-1</sup>	$r$	$K_F$ mg·g <sup>-1</sup>	$n$	$r$
71.3	23.50	0.995	6.203	2.153	0.881

At the same time, the monolayer saturated adsorbance of 70.1 mg·g<sup>-1</sup> corresponding to Langmuir constant, is more consistent with the experimental result.

$$\text{Langmuir equation: } 1/q_e = 1/q_0 + A/(q_0 \times C_e) \quad (5)$$

$$\text{Freundlich equation: } \ln q_e = \ln K_F + (1/n) \ln C_e \quad (6)$$

$q_0$  Maximum adsorption amount of dye in forming complete monolayer coverage on ZnO/EG pore surface; mg/g;

$A$  Equilibrium concentration of dye corresponding to half saturation adsorbance; mg/mL

$K_F$  Freundlich equation constant;  $1/n$  adsorption intensity for Freundlich equation

#### Influence of ionic strength on decoloration

To investigate the influence of ionic strength on decoloration rate of Auramine Lake Yellow O, NaCl and  $Na_2SO_4$  are used to adjust ionic strength in the range of 0.0 ~ 0.5 mol/L. The results corresponding to decoloration 8.0 h are shown in Figure 5. It indicates that the presence of NaCl and  $Na_2SO_4$  enhances decoloration of ZnO/EG for dye under UV beam. These results might be caused by the decrease of effective dye concentration in solution, however an increase of adsorbance on ZnO/EG for the existence of NaCl and  $Na_2SO_4$ . Nevertheless, UV photo degradation decoloration of ZnO decrease with the increase of ionic

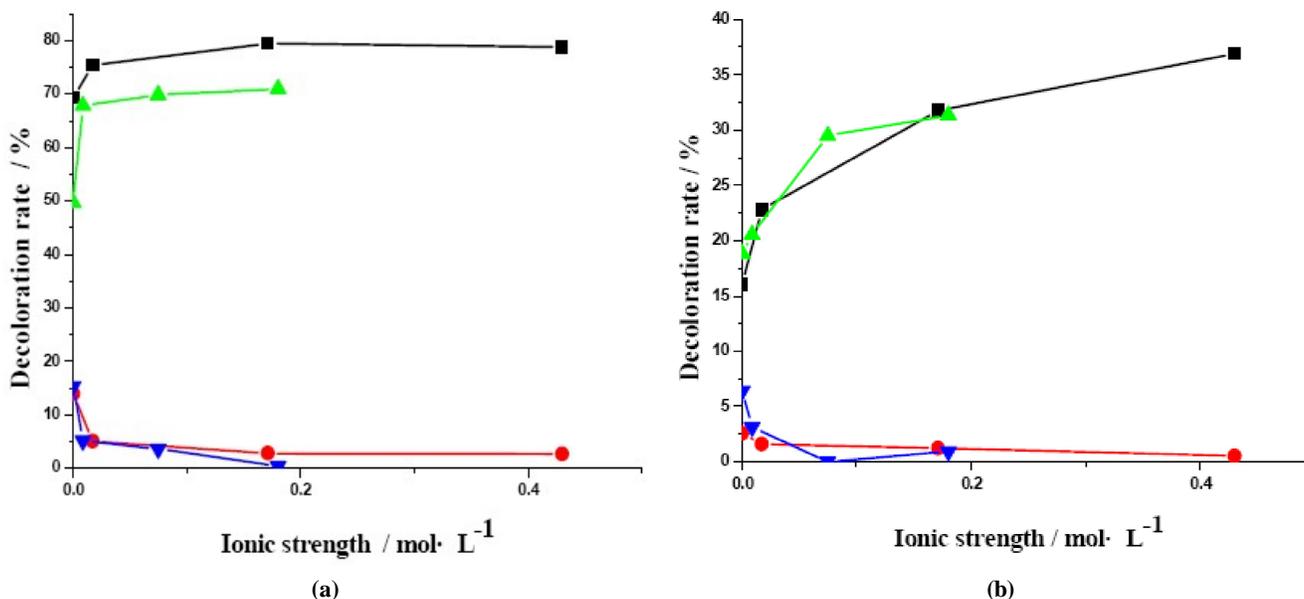


Figure 5 : Influence of ionic strength on decoloration capability of ZnO/EG; (a) Dye concentration 50 mg·L<sup>-1</sup> (b) Dye concentration 400 mg·L<sup>-1</sup>; (● ■) Influence of NaCl on decoloration rate (▲ ▼) Influence of Na<sub>2</sub>SO<sub>4</sub> on decoloration rate; (■ ▲) decoloration of ZnO/EG for dye under UV beam (● ▼) UV photo degradation decoloration of ZnO for dye

strength for the possible reason of increase of electron hole recombination and decrease of quantum efficiency<sup>[20]</sup>.

### Analysis of possible decoloration mechanism

In order to analysis the possible decoloration mechanism of ZnO/EG for Auramine Lake Yellow O, the absorption spectrum scanning in the wave length ranges of 190~900 nm is carried out with samples of prepared dye solution and dye solution decolorized with ZnO/EG under UV beam, respectively. As shown in Figure 6, no new resultant occurs in solution, Auramine

Lake Yellow O is completely mineralized under the UV photo degradation of ZnO<sup>[21]</sup>, or it is adsorbed on ZnO/EG surface, which cause an obvious decrease of solution absorbancy. So the decoloration mechanism would be: Auramine Lake Yellow O can be decolorized through adsorption and photo degradation of ZnO/EG; and a part of dyes are mineralized and turned into CO<sub>2</sub> and H<sub>2</sub>O, adsorption of EG can improve the decoloration effect.

## CONCLUSIONS

Researches on the preparation of ZnO/EG and its decoloration capability for Auramine Lake Yellow O has proved:

- (1) ZnO/EG can be prepared according to the mass ratio C:KMnO<sub>4</sub>:H<sub>2</sub>SO<sub>4</sub>(98%): ZnSO<sub>4</sub>·7H<sub>2</sub>O of 1.0:0.35:5.0:0.4, the reaction lasts 40 min at 30°C, and H<sub>2</sub>SO<sub>4</sub> is diluted to a mass concentration of 80%. The expansion product obtained at 950°C is ZnO/EG with an expanded volume of 420 mL·g<sup>-1</sup>.
- (2) ZnO/EG possesses a higher decoloration capability for Auramine Lake Yellow O than the single EG adsorption or ZnO photo degradation. Decoloration capability is influenced by initial dye concentration, decoloration time and ionic strength, and higher ionic strength can improve the decoloration

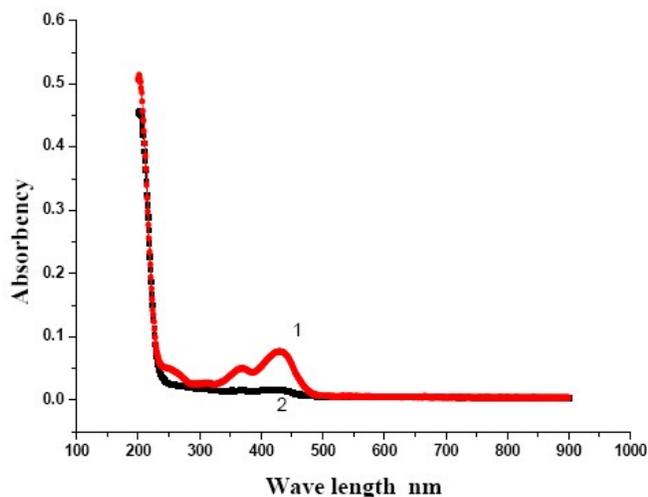


Figure 6 : Absorption spectrums of Auramine Lake Yellow O; 1. Before decoloration 2. Decoloration after 8h

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efficiency of dye.

- (3) Decoloration kinetic data of ZnO/EG for Auramine Lake Yellow O can be described by pseudo second-order model.
- (4) Decoloration isotherms of adsorption and photo degradation of ZnO/EG for Auramine Lake Yellow O, adsorption of EG, photo degradation of ZnO are all type I. Langmuir equation is more consistent with the thermodynamic data than Freundlich equation.

### ACKNOWLEDGEMENTS

This study was supported by Doctor Foundation of Hebei province Education Office (China, No.B2004402). We gratefully acknowledge their support during the study.

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