



Investigation of Decolouration Thermodynamics and Kinetics of Acid Brilliant Scarlet GB on Expanded Graphite Loaded with Titania

XIU-YAN PANG*, CHEN WEI and RUI-NIAN LIN

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, P.R. China

*Corresponding author: Fax: +86 312 5079525; E-mail: pxy833@163.com

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To study thermodynamic and kinetic characteristics of Acid Brilliant Scarlet GB decolouration on expanded graphite loaded with titania (EG), expanded graphite was prepared firstly with 50 mesh natural graphite as raw materials, potassium permanganate as oxidant, vitriol and tetra *n*-butyl titanate as intercalation compound. Then it was characterized with XRD and micromeritics instrument. The influence of decolouration time, adsorbate initial concentration, ionic strength and temperature on decolouration rate was detected. Based on pseudo first-order and second-order kinetic model, the decolouration model was discussed. Decolouration rate and activation energy were calculated. Studies show that decolouration rate of Acid Brilliant Scarlet GB on expanded graphite decrease with the increase of the adsorbate initial concentration and increase with the increase of ionic strength. The decolouration process can be well described by the pseudo second-order kinetic model. The decolouration equilibrium time and half decolouration time decrease with the increase of temperature and adsorption of expanded graphite is the main factor of decolouration.

Key Words: Expanded graphite loaded with titania, Acid brilliant scarlet GB, Adsorption, Photodegradation, Kinetics, Thermodynamics.

INTRODUCTION

Expanded graphite is obtained 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 dyes³⁻⁷. In the adsorption treatment of dyes with expanded graphite, Wang *et al.*^{3,8} pressed the worm-like particles into low-density plate of 0.1 g/cm, then the plate was used to treat dye waste-water from woolen mill. Pang *et al.*⁹ investigated the influencing factors in adsorption of dyes with expanded graphite 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 and temperature. The adsorption of basic fuchsine, 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 3B¹⁰ 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[•] free radical, 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 radiation¹¹. To recycle this catalyst after reaction, TiO₂ is often loaded by some kinds of carriers¹². The used carriers often have little adsorption capacity for pollutant, which would decrease the degradation capability of TiO₂.

Expanded graphite loaded with titania 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, expanded graphite is prepared and its degradation thermodynamics and kinetics for Acid Brilliant Scarlet GB is discussed. Results are compared

with the single adsorption of expanded graphite and photocatalysis of titania. Possible decolouration mechanism is discussed.

EXPERIMENTAL

Preparation of expanded graphite: Expanded graphite is prepared with potassium permanganate as oxidant, sulfuric acid and tetrabutyl titanate as intercalation reagent¹⁴. Reaction condition is controlled as: C : KMnO₄ : H₂SO₄ (diluted to 75 %): tetra *n*-butyl titanate = 1: 0.5 : 3.0 : 0.4 (mass ratio). The reaction lasts 1 h 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 h, the product is filtrated and then dried at 60 - 80 °C, expandable graphite is obtained. Expandable graphite is expanded at 900 °C for 10 s and then expanded graphite is obtained. To illustrate the existence of intercalation compound and its form, graphite, expandable graphite and expanded graphite 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 expanded graphite (c). Structural parameters of expanded graphite 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).

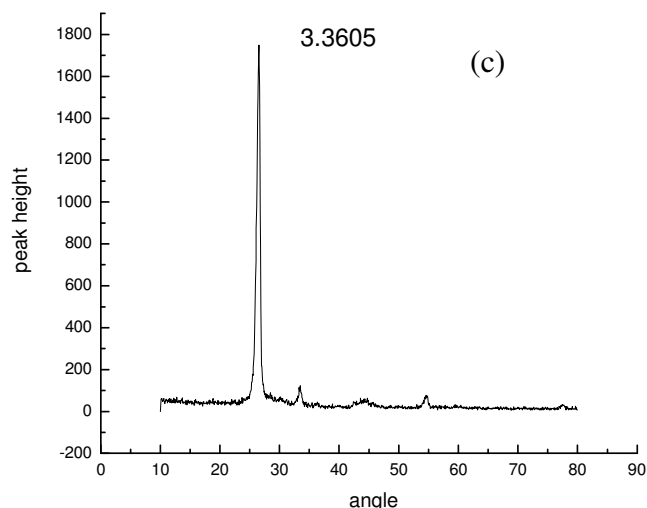
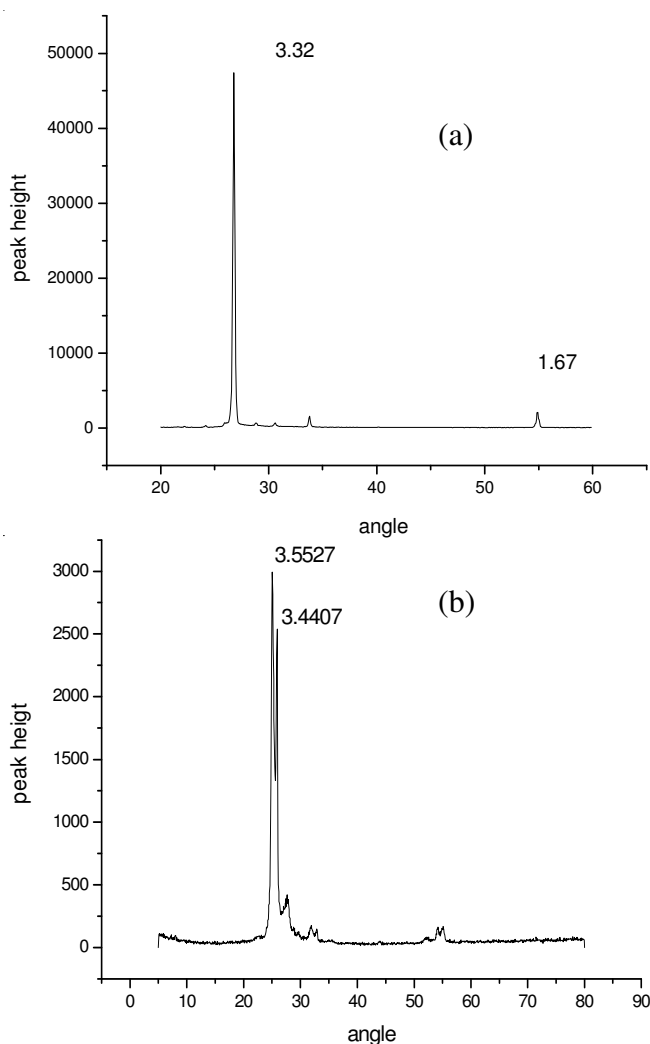


Fig. 1. XRD of (a) graphite; (b) expandable graphite and (c) expanded graphite

TABLE-1
STRUCTURAL PARAMETER OF EXPANDED GRAPHITE *

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

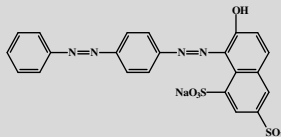
* -- Detection condition:

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

Adsorbate characteristics: Acid Brilliant Scarlet GB 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 Acid Brilliant Scarlet GB 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.

TABLE-2
CHEMICAL STRUCTURE AND MOLECULAR WEIGHT OF DYE USED IN EXPERIMENT

Dye	Structure	Molecular weight	λ_{\max} (nm)
Acid Brilliant Scarlet GB		556.49	512

Determination of decolouration rate: Batch decolouration experiments were carried in 250 mL beaker with the mass of expanded graphite to volume of dye solution was standardized at M/V = 0.05 g / 0.1 L = 0.5 g/L. Decolouration under different condition were compared. **Method I:** Decolouration was carried in dark with expanded graphite as adsorbent. **Method II:** Decolouration was carried under UV irradiation with expanded graphite as adsorbent. **Method III:** Decolouration

was carried under UV irradiation with no adsorbent. Absorbency of solution was detected at different time. Total decolouration rate, adsorption decolouration rate, UV photodegradation decolouration rate and UV revulsive titania photodegradation decolouration rate can be calculated according to equation (1).

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

D: Decolouration rate, %; A_0 : absorbency before decolouration; A_t : absorbency at moment t

Decolouration rate of dye in the influence of ionic strength: With concentration of Acid Brilliant Scarlet GB was set as 50 mg/L, ionic strength of the dye solutions was adjusted with NaCl and Na_2SO_4 in the rang of 0.0-1.0 mol/L. Then decolouration rate under different ionic strength were detected.

Decolouration rate of dye in the influence of pH: With concentration of Acid Brilliant Scarlet GB was set as 50 mg/L, pH of the dye solutions was adjusted with HCl or NaOH in the range of 2 to 10 and then detected with pHs-3C acidimeter (Weiye Instrument Company of Shanghai). The absorbencies under different pH were detected and then selected the pHs which do not effect absorbance of Acid Brilliant Scarlet GB at 512 nm to study the influence of pH on decolouration rate.

Decolouration kinetics experiment: In decolouration kinetics experiment, a series of desired dye concentration and fixed volume of 100 mL were placed in beaker where they were brought into contact with expanded graphite at 15, 25 and 35 °C, respectively. The mass of expanded graphite to volume of solution was standardized at $M/V = 0.0500 \text{ g} / 0.1 \text{ L} = 0.5000 \text{ g/L}$. Decolouration was carried under UV irradiation. Absorbency of dye solution corresponding to different decolouration time was analyzed until the absorbency kept as a constant and it was used to calculate the decolouration rate at different moment according to eqn. (1).

RESULTS AND DISCUSSION

Results of decolouration thermodynamics

Influence of adsorbate concentration and decolouring time on Decolouration rate: Fig. 2 shows decolouration rate is the function of decolouring time and Acid Brilliant Scarlet GB concentration. During the showed decolouring time, decolouration rate combined expanded graphite adsorption and titania photo-degradation increases with the increase of decolouring time and decreases with the increase of Acid Brilliant Scarlet GB concentration. The results illustrate decolouration is caused totally by expanded graphite adsorption and titania photo-degradation.

Influence of ionic strength on decolouration: To investigate the influence of ionic strength on decolouration rate of Acid Brilliant Scarlet GB, NaCl and Na_2SO_4 were used to adjust ionic strength in the range of 0.0-1.0 mol/L. The results corresponding to decolouring 10 h are showed in Fig. 3. It indicates that the presence of NaCl and Na_2SO_4 enhances decolouration of dyes. Absolute ionization of NaCl, Na_2SO_4 in solution makes them form negative and positive ions, there don't exist competitive adsorption of these ion with dye molecule. On the other hand, electrostatic interaction between

dye and adsorbent decreases with the increase in ionic strength probably because of the suppression of the electric double layer¹⁵ and hydrophobic attraction increases due to the salting-out effect. Over the range of 0.0-1.0 mol/L, the influence of Na_2SO_4 is more obvious than that of NaCl on decolouration rate.

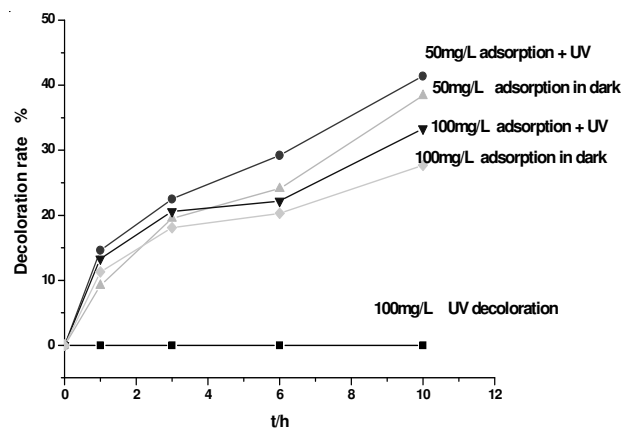


Fig. 2. Decolouration of Acid Brilliant Scarlet GB on expanded graphite

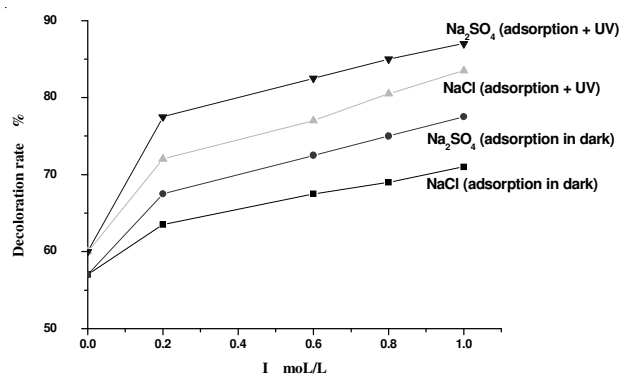


Fig. 3. Influence of ionic strength on decolouration rate

Influence of pH on dye absorbance: Ionic dyes upon dissolution release coloured dye anions/cations in solution and their absorbency changed along with the existence form, which was influenced by pH. So it is important to know how the pH affected absorbency (Fig. 4). pH adjustment led to changes of dye absorbency corresponding to the determined wavelength 512 nm. So the influence of pH on decolouration of Acid Brilliant Scarlet GB could not be carried on with absorbency method.

Results of decolouration kinetics

Influence of temperature and dye concentration on decolouration: Fig. 5 showed the decolouration rate is showed as a function of time and dye concentration. Decolouration rate decrease with the increase of Acid Brilliant Scarlet GB concentration and increase with decolouration time at a decreasing speed. It's about 24 h for the decolouration reach equilibrium. Under the same Acid Brilliant Scarlet GB initial concentration, the equilibrium decolouration rate decrease with the increase of decolouration temperature and the results might be caused by the increase of dye solubility in solution. In kinetic analysis, data corresponding to 8 h are used.

TABLE-3
COMPARISON OF DECOLOURATION 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 ($\%^{-1}\text{min}^{-1}$)	r
50	15	58.62	48.78 ± 1.04	0.11876 ± 0.00896	-0.98606	55.38 ± 0.0027	0.007 ± 0.142	0.96659
	25	56.62	39.97 ± 1.0623	0.15898 ± 0.01356	-0.98577	54.39 ± 0.00057	0.02539 ± 0.001815	0.99899
	35	53.49	22.67 ± 1.1829	0.36013 ± 0.03736	-0.97915	53.99 ± 0.00231	0.04348 ± 1.2236	0.9994
100	15	39.037	48.21 ± 1.262	0.28577 ± 0.04731	-0.9612	40.80 ± 0.0029	0.00167 ± 84.4166	0.9712
	25	35.086	36.91 ± 1.047	0.2215 ± 0.01025	-0.9929	36.37 ± 0.0013	0.0379 ± 0.9074	0.9976
	35	27.14	33.04 ± 1.0352	0.091 ± 0.00771	-0.9859	34.09 ± 0.00604	0.0125 ± 0.00313	0.9904
200	15	25.57	26.1235 ± 1.063	0.1927 ± 0.01367	-0.94011	23.01 ± 0.0016	0.0439 ± 3.7299	0.9804
	25	22.89	19.37 ± 1.098	0.4902 ± 0.02243	-0.9948	21.62 ± 0.00086	0.02586 ± 2.74175	0.9990
	35	16.47	11.05 ± 1.08829	0.3547 ± 0.02739	-0.9883	15.02 ± 0.00497	0.1436 ± 0.8489	0.996

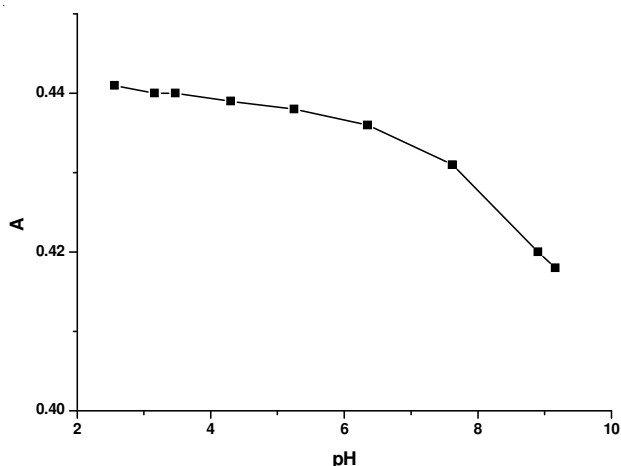


Fig. 4. Influence of pH on absorbance of Acid Brilliant Scarlet GB

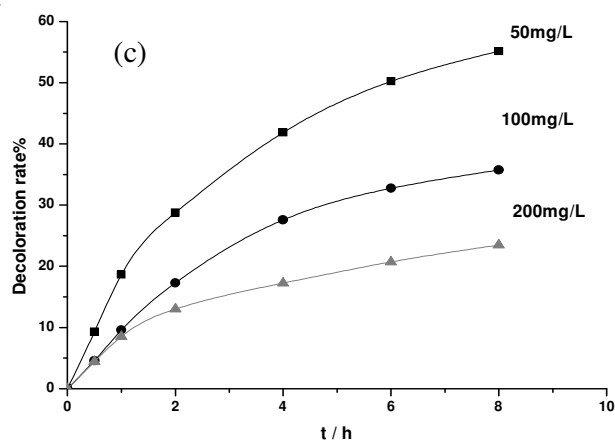
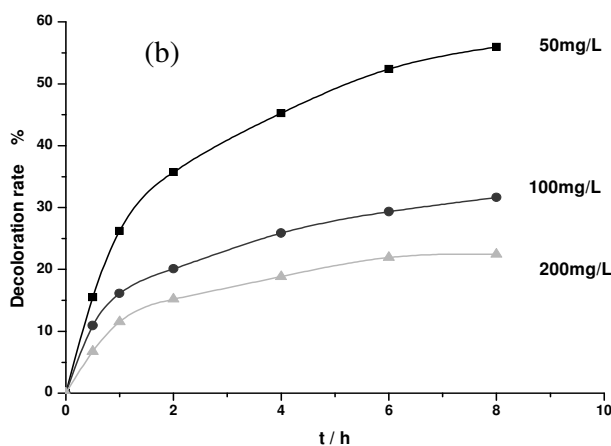
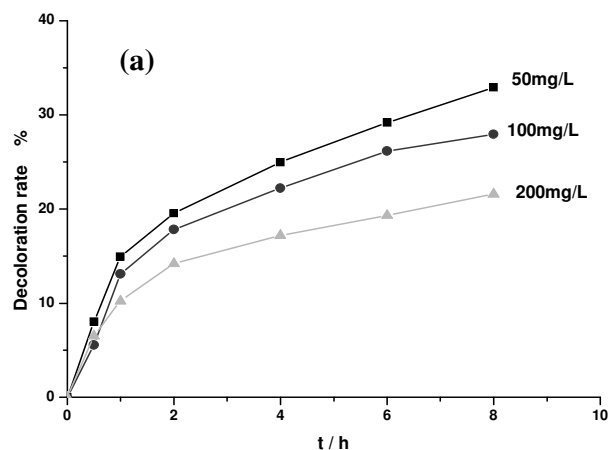


Fig. 5. Influence of initial Acid Brilliant Scarlet GB concentration and temperature on decolouration rate; (■) 50 mg/L, (●) 100 mg/L, (▲) 200 mg/L (a) 15 °C, (b) 25 °C, (c) 35 °C



Decolouration kinetic models: Both pseudo first- and second-order adsorption models were used to describe the decolouration kinetics data^{16,17}. In both models, all the steps of degradation such as external diffusion, internal diffusion and decolouration are lumped together, the overall decolouration 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).

$$\text{First-order model: } \ln(D_e - D) = \ln(D_e - k_t) \quad (2)$$

$$\text{Second-order model: } t/D = 1/(k D_e^2) + t/D_e \quad (3)$$

where, k , decolouration rate constant (min^{-1} for first-order decolouration, $\%^{-1}\cdot\text{min}^{-1}$ for second-order adsorption); t , decolouring time (min); D_e , equilibrium decolouration rate (%).

Since D reaches a plateau (D_e) at equilibrium, D values smaller than the $0.9 D_e$ were used for analysis. The plots of: $\ln(D_e - D)$ 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 $D_{e,cal}$ obtained from the intercepts is obviously inconsistent with the experimental data $D_{e,exp}$ 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 decolouration rate and half- decolouration times are estimated in Table-4 according to eqns. (4) and (5). Initial decolouration rate

decreases with the increase of Acid Brilliant Scarlet GB concentration and half-decolouration time is found to decrease with the increase in temperature.

$$u = kD_e^2 \quad (4)$$

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

where, u , initial decolouration rate, $\% \cdot \text{min}^{-1}$; $t_{1/2}$, half-degradation time, min.

C_0 (mg g^{-1})	Temperature ($^{\circ}\text{C}$)	u (min^{-1})	$t_{1/2}$ (h)	ΔH ($\text{kJ} \cdot \text{mol}^{-1}$)	r
50	15	19.984	0.1835	18.80	-0.997
	25	21.129	0.1547		
	35	24.2895	0.1356		
100	15	18.3856	0.2132	29.55	-0.9081
	25	26.3713	0.1982		
	35	39.3217	0.1713		
200	15	10.6967	0.2179	20.30	-0.9491
	25	11.1049	0.1998		
	35	23.6553	0.1671		

The second-order kinetic models constants listed in Table-3 were used to estimate decolouration activation energy using Arrhenius eqn. (6). The slope of plot of $\ln k$ versus $1/T$ is used to evaluate activation energy (E_a), which was found to be smaller than 40 kJ mol^{-1} (listed in Table - 4). The results illustrate the decolouration of expanded graphite for Acid Brilliant Scarlet GB is mainly physical interaction. To judge the single decolouration ability of expanded graphite adsorption and titania (loaded in expanded graphite) photo-degradation, comparison experiment was carried out. The results (Fig. 6) obviously proved that physical adsorption of expanded graphite is stronger than that titania photo-degradation.

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

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

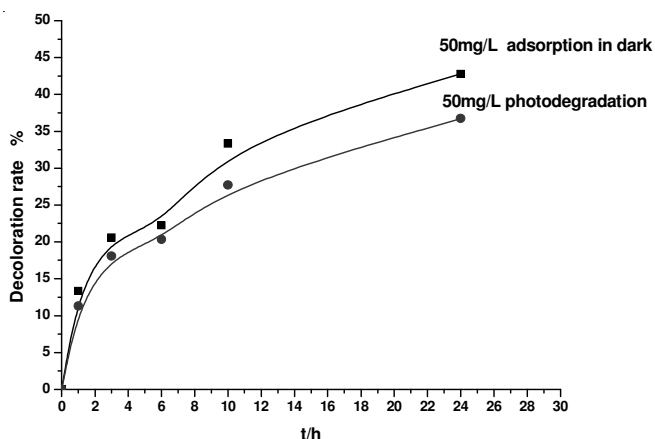


Fig. 6. Comparison of EG physical adsorption and Titania photodegradation

Analysis of possible decolouration mechanism: In order to analysis the possible decolouration mechanism of Acid Brilliant Scarlet GB under the expanded graphite adsorption and titania photodegradation, the absorption spectrum scanning among 190-900 nm were carried out before and after decolouring treatment. As shown in Fig. 7, no new resultant

occurs and the adsorbate is mineralized under the photo-degradation of titania. So the decolouration mechanism would be: Acid Brilliant Scarlet GB in solution and adsorbed on surface of expanded graphite can jointly be photodegradation by titania, mineralizing product are mainly CO_2 and H_2O , adsorption of expanded graphite can improve the decolouration effect.

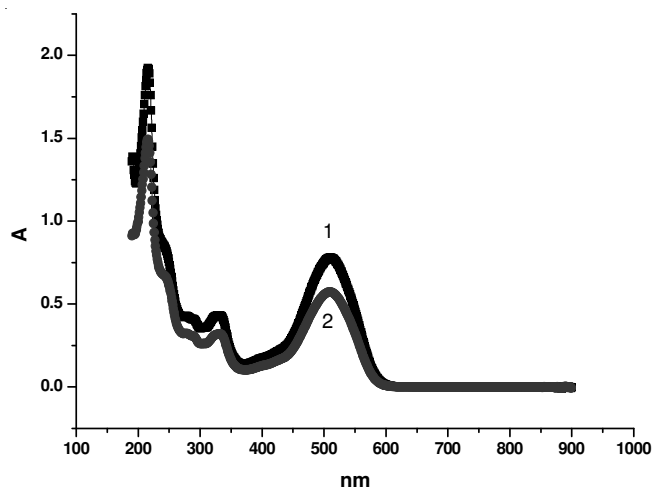


Fig. 7. Absorption spectrums of Acid Brilliant Scarlet GB; 1. before decolouration 2. after decolouration 12 h

Conclusion

This study has proved that expanded graphite possesses a higher decolouration ability for Acid Brilliant Scarlet GB than the single expanded graphite adsorption or titania photo-degradation. Decolouration process was influenced by initial dye concentration, decolouration time and ionic strength. Ionic strength plays an important role in decolouration, higher ion strength or the presence of salt ions can improve the treatment of dye. The decolouration kinetic of Acid Brilliant Scarlet GB can be well described by the pseudo second-order kinetic model. The half-decolouration time of Acid Brilliant Scarlet GB is found to decrease with the increase in temperature. Decolouration of Acid Brilliant Scarlet GB on expanded graphite holds small activation energy and physical adsorption plays main role in the adsorption and photodegradation process.

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