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Study on the discolored thermodynamics of dyes on expanded graphite loaded with Titania

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Abstract: One adsorbent of expanded graphite (EG) loaded with Titania is prepared with chemical oxidation method, and its expanded volume, XRD spectrum, pore structure is detected. This paper investigates its decoloration for dyes of Acid brilliant red-3B with azobenzene structure, Auramine lake yellow-O with biphenyl structure and Basic fuchsine with tritane structure. Influence of dye concentration, pH and ion strength on the decoloration rate is investigated. The thermodynamic study shows that dye concentration has no obvious influence on equilibrium time, but it can decrease the decoloration rate; higher ion strength or the presence of salts can improve decoloration; pH not only affect dye absorbency, but also affect decoloration of adsorbent for dyes; a proper adjustment of pH can improve decoloration. Contrastive degradation experiments testify EG loaded with Titania possess a higher decoloration rate for dyes than the single EG adsorption or Titania photo-degradation. Especially, EG adsorption for dyes is stronger than that of Titania photo-degradation.

Key words: Expanded graphite loaded with Titania, Dye, Adsorption thermodynamics, Decoloration, pH, Ion strength.

INTRODUCTION

Concerning decoloration of dye, the current methods are adsorption and chemical oxidation. About physical adsorption, porous solids are often used as adsorbents, such as activated carbon [1, 2], modified Al_2O_3 [3], anion exchange resin [4], active sludge [5, 6]. Expanded graphite (EG) is from graphite intercalation compounds (expandable graphite), and it possesses abundant porous structure with the size ranging from nanometer to micron scale [7]. Due to its excellent adsorption capacity for oil, research on the adsorption of oils is more popular [8, 9]. While its adsorption for dyes just gets under way [10, 11].

In chemical oxidation of dyes, nano-TiO_2 is the most commonly used photo-catalyst. Under ultraviolet radiation, TiO_2 has a strong ability to generate $OH\cdot$, which will ultimately enable complete oxidation of organic pollutants in water, and generates CO_2, H_2O, and other simple inorganic ions (such as NO_3^-, SO_4^{2-}, PO_4^{3-} and halogen, etc.). So far, more than 3000 kinds of refractory organic compounds have been found being degraded by TiO_2 under ultraviolet radiation [12]. In order to recycle this catalyst after reaction, TiO_2 is often loaded by some kinds of carriers [13]. The used carrier often has little adsorption capacity for pollutant, which would decrease the degradation capability of TiO_2.

EG loaded with Titania is a kind of adsorbent with porous structure and loading Titania [14, 15], it couples adsorption of EG and photo-catalysis of TiO_2 together. Preparation of EG and loading of TiO_2 can be finished together. In this experiment, EG loaded with Titania is prepared, and its degradation thermodynamics for dyes of Acid brilliant red 3B with azobenzene structure, Auramine lake yellow-O with biphenyl structure and Basic fuchsine with tritane structure is discussed. Results are compared with the single adsorption of EG and photo-catalysis of Titania.

MATERIALS AND METHODS

Preparation of EG Loaded with Titania

EG loaded with Titania was prepared with potassium permanganate as oxidant, sulfuric acid and tetrabutyl titanate as intercalation reagent [15]. Reaction condition was: C : $KMnO_4$: H_2SO_4 (diluted to 75%) : tetrabutyl titanate = 1: 0.5 : 3.0 : 0.4. Reaction lasted 60 min in 45 ℃ water bath, then product was transferred into beaker and washed with water until pH = 6.0-7.0 and washing water without color of potassium permanganate. After soaking in water for 2-3 hours, the product was filtrated and then dried at 60 ℃~80 ℃, expandable graphite was obtained. Expandable graphite was expanded at 900 ℃ for 10s, then EG loaded with Titania was obtained. To illustrate the existence of intercalation compound and its form, graphite, expandable graphite and EG were charactered with XRD (Y-2000 X-Ray powder diffraction instrument). As showed in Fig. 1, anatase TiO_2 is found in expandable graphite (b), and Titania is found in EG (c). Structural parameters of EG loaded with Titania were characterized by expanded volume, specific surface area and total pore volume. These data were detected with BET N_2 adsorption by Micromeritics Instrument Corporation TriStar II 3020 V1.02. Porosity characteristics of EG are showed as Table 1.

Adsorbates

Three kinds of dyes were selected as reference compounds. They were Acid brilliant red 3B with azobenzene structure, Auramine Lake yellow-O with biphenyl structure and Basic fuchsine with tritane structure. The dyes were supplied by Yuhua trade company, Tientsin, China. Molecular structures and molecular weight of these dyes are showed in Table 2.

Simulated dye wastewaters were prepared by dissolving the different dyes in distilled deionized water at various concentrations. Color measurements were made with T6 New Century UV spectrophotometry (Puxi Tongyong Instrument Limited Company of Beijing) operating in the visible range on absorbance mode.

Determination of Decoloration Rate

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

Decoloration rate =

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

A_o——absorbency before decoloration;

A_t ——absorbency at moment t

Decoloration Rate of Dyes in the Influence of Ion Strength and pH

NaCl and Na_2SO_4 were used to investigate their influence on decoloration rate and their concentration changeed from 0 to 50 g/L. Solution of acid brilliant red 3B and Auramine lake yellow-O were all set as 50 mg/L, and Basic fuchsine was set as 20 mg/L.

In the range of 2 to 12, pH of the dye solutions was adjusted by HCl or NaOH, then detected with pHS-3C acidimeter (Weiye Instrument Company of Shanghai). Absorbency under different pH was detected. Dye whose absorbency does not influenced by pH was chosen to study the influence of pH on decoloration rate.

RESULTS AND DISCUSSION

Decoloration Equilibrium Time

Fig.2 shows decoloration equilibrium time of dyes at 25℃, results are not affected by dyes concentration.

It is 24 hours for Acid brilliant red-3B in dark, 5 hours for Auramine lake yellow-O in dark and 12 hours for Basic fuchsin in dark.

Influence of Ion Strength on Decoloration

To investigate the influence of ion strength on decoloration rate of acid brilliant red-3B, auramine lake yellow-O and basic fuchsine, NaCl and Na_2SO_4 were used to adjust ion strength at a ranging of 0 ~ 50 g/L. The results are showed in Fig.3. It indicates that the presence of NaCl and Na_2SO_4 enhances decoloration 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 layer [1], and hydrophobic attraction increases due to the "salting-out" effect. Over a range of 10.0 g/L to 50.0 g/L, the influence of NaCl is more obvious than that of Na_2SO_4 on decoloration rate.

Compare of Adsorption and Titania UV Degradation

To judge the single decoloring ability of EG adsorption and Titania (loaded in EG) photo-degradation, comparison experiment was carried out. Total decoloration rate is defined as the summation of EG adsorption and Titania photo-degradation. Decoloration under Dark is defined as the only EG adsorption and the difference between total decoloration and adsorption decoloration is defined as the only photo-degradation of Titania. Result showed in Fig. 4 illustrates decoloration is caused totally by EG adsorption and Titania photo-degradation. Specially, the former is stronger than Titania photo-degradation.

Influence of pH on Decoloration Rate

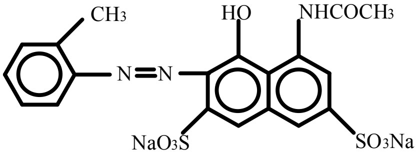
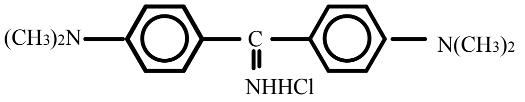
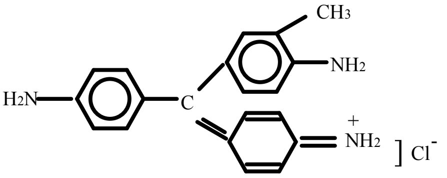
Ionic dyes upon dissolution release colored dye anions/cations in solution, and their absorbency changes along with the existence form, which is influenced by pH. So it is important to know how the pH affected absorbency and what the range of pH is before the study of pH on decoloration rate. Fig.5 indicates that acidity led to a change of absorbency under a certain wavelength. So pH studies can not be conducted on auramine lake yellow-O and basic fuchsine. As for acid brilliant red-3B, the change of pH from 2.0 to 9.0 has no noticeable impact on absorbency, and the influence of pH on decoloration rate was investigated. Fig.6 gives a degressive relationship between decoloration rate and pH. Decrease of H^+ enhances ionization of dye and reduces the amount of unionized molecules. The lipophilic nature of the adsorbent leads to the degressive adsorbance.

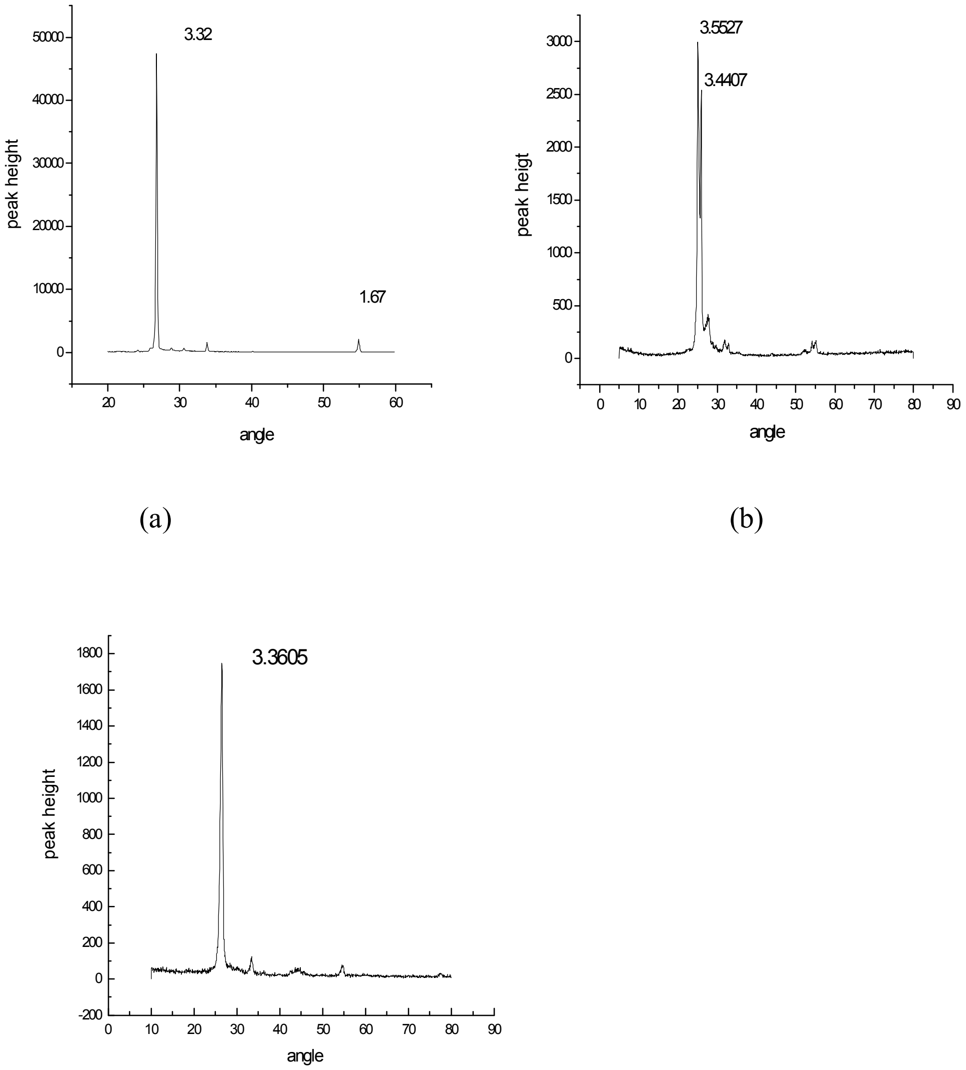
Table1: Structural Parameter of EG Loaded with Titania

Expanded volume (mL/ g)	Specific surface area (m^2/g)	Pore volume (cm^3/g)
320	20.3285	0.073891

a -- Detection condition:
Analysis adsorptive: N_2; 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 Dyes Used for Experiment

Dye	Structure	Molecular weight	λ_{max}(nm)
Acid brilliant red -3B		675.0	520
Auramine lake yellow O		318.5	430
Basic fuchsine		338.5	543

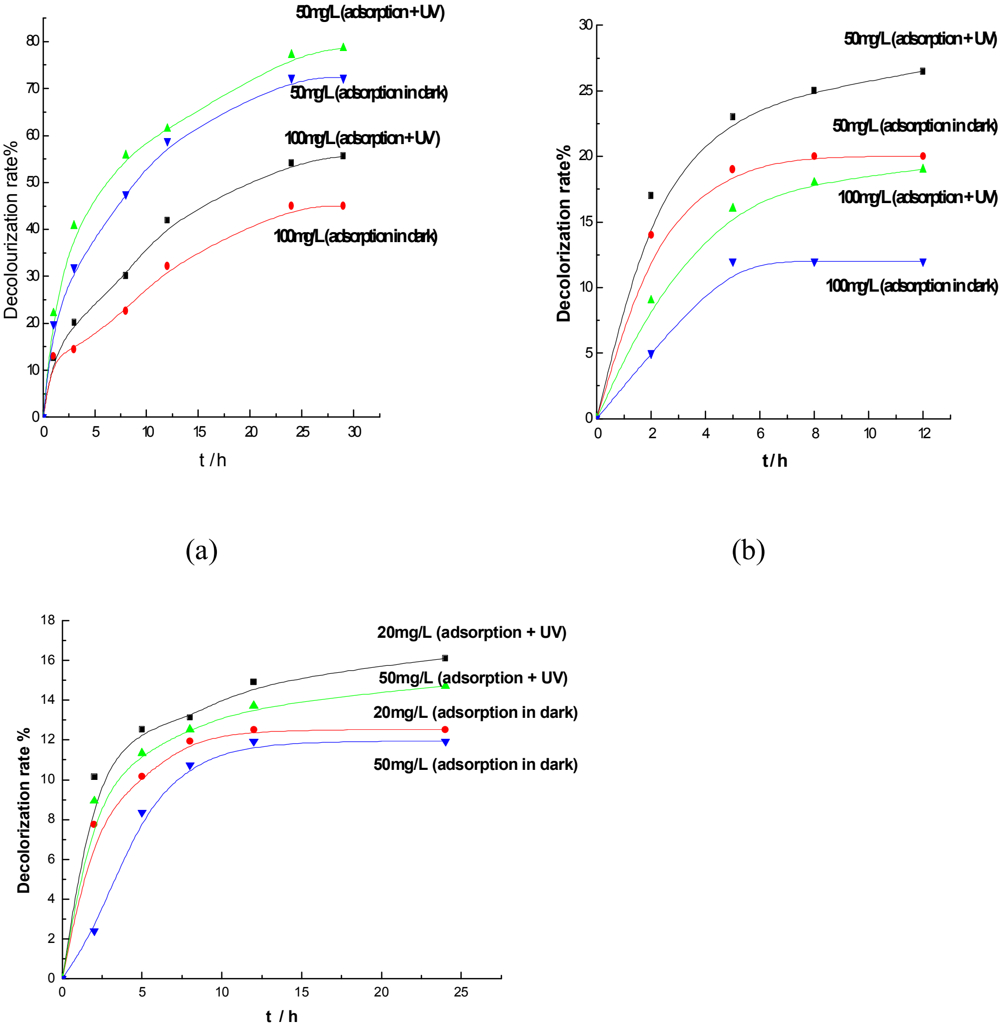


(a) (b)

(c)

Fig. 1: XRD of Graphite Expandable graphite and EG

(a) Graphite； (b) Expandable graphite ；(c) EG

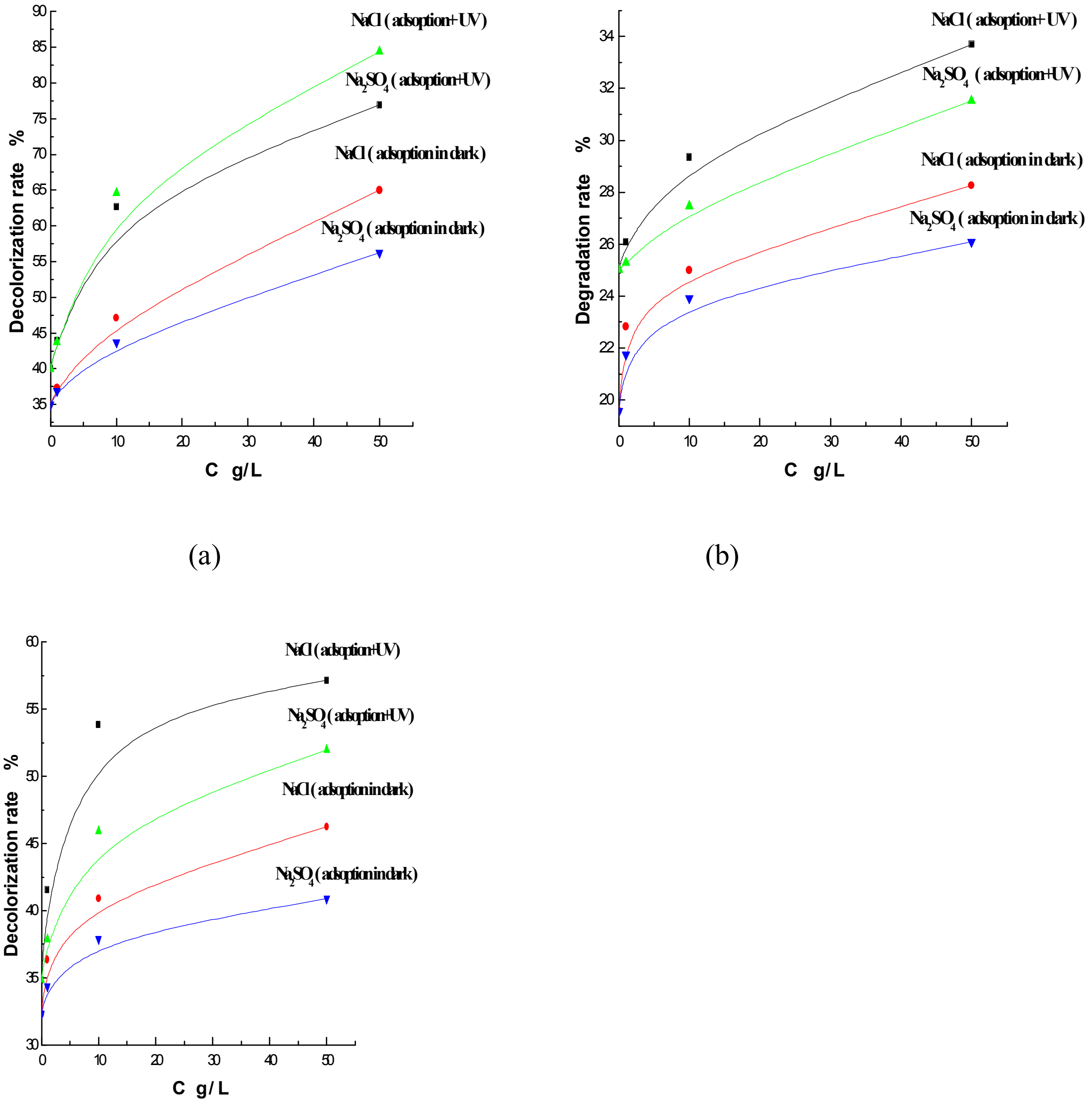


(a) (b)

(c)

Fig.2: Decoloration Equilibrium Time of Dyes

(a) Acid brilliant red-3B; (b) Auramine lake yellow-O; (c) Basic fuchsin



(a) (b)

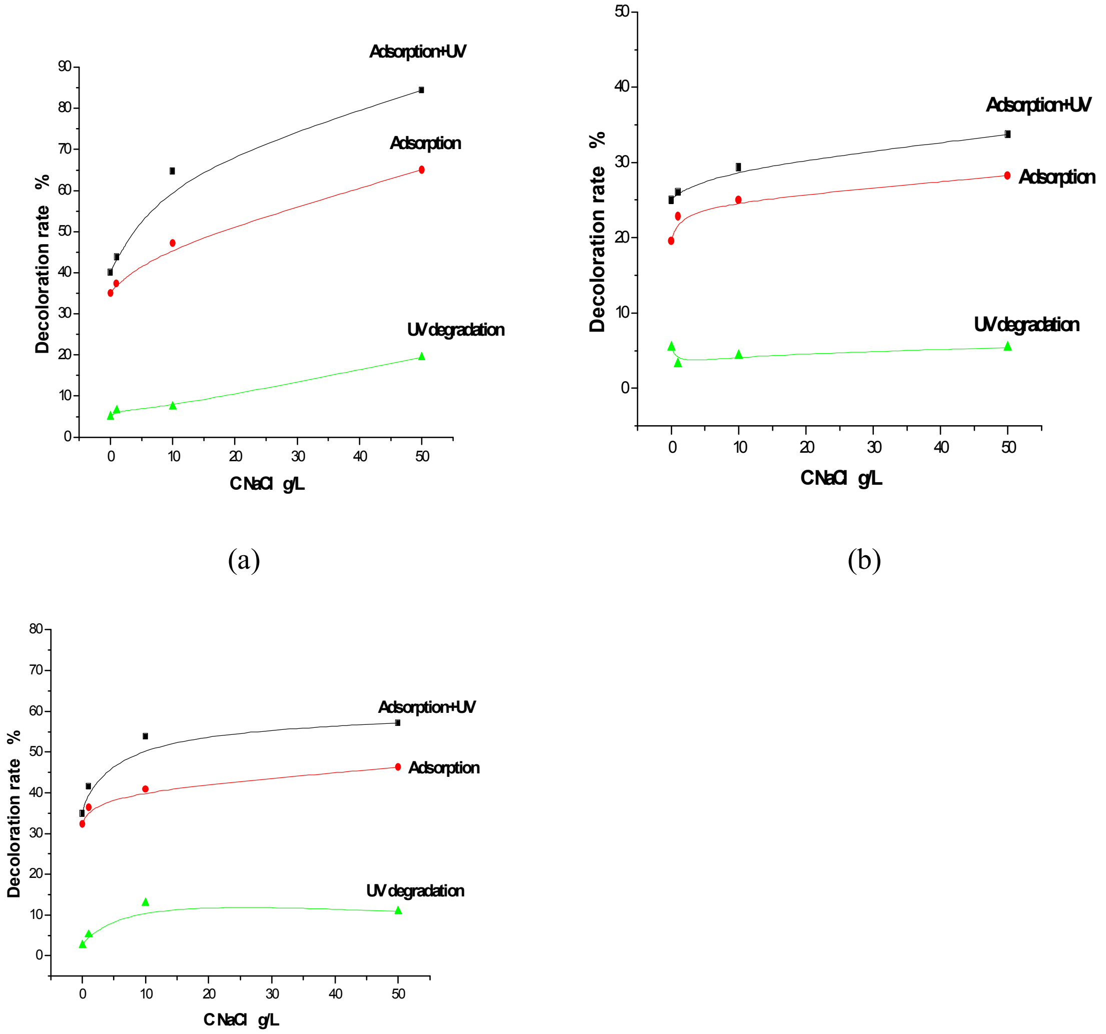
(c)

Fig. 3: Influence of Ion Strength on Decoloration Rate of EG Loaded with Titania

(a) Acid brilliant red-3B, 50mg/L, 24h ;

(b) Auramine lake yellow-O, 50mg/L, 5h;

(C) Basic fuchsine, 20mg/L, 12h

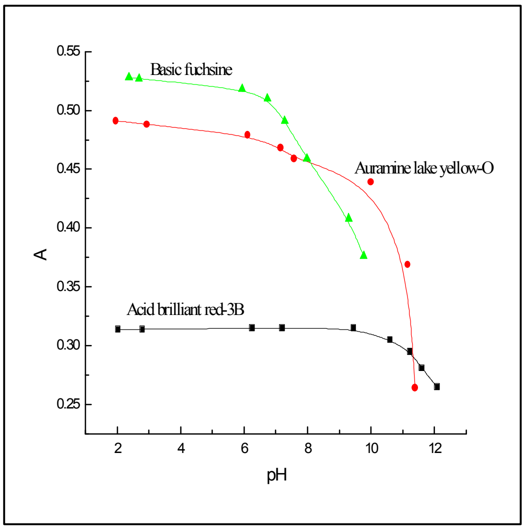


(a) (b)

(c)

Fig. 4: Comparison of EG Adsorption and Titania Photo-degradation

(a) Acid brilliant red-3B, 50mg/L, 24h ; (b) Auramine lake yellow-O, 50mg/L, 5h; (c) Basic fuchsine, 20mg/L, 12h



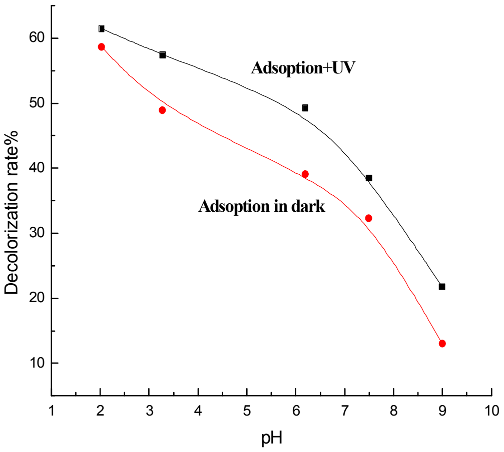


Fig.5: Influence of pH on Dye Absorbency Fig. 6: Influence of pH on Decoloration Rate of Acid brilliant red-3B

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