EFFECT OF OPERATIONAL PARAMETERS ON DEGRADATION OF JANUS GREEN B FROM AQUEOUS SOLUTION USING ZnO/ZHC/AC COMPOSITE

ẢNH HƯỞNG CỦA CÁC THÔNG SỐ LÀM VIỆC ĐẾN SỰ PHÂN HỦY JANUS GREEN B TRONG DUNG DỊCH NƯỚC SỬ DỤNG ZnO/ZHC/AC COMPOSIT

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ABSTRACT

This paper reports the synthesis of zinc oxide and zinc hydroxide carbonate loaded on activated carbon (ZnO/ZHC/AC composite) for degradation of Janus Green B (JGB). The ZnO/ZHC/AC sample was prepared by hydrothermal method with the presence of hexamethylene tetramine (HMTA) at the pH = 8.0 without calcination process. As-prepared sample was characterized by XRD, FE-SEM, BET and N_2 adsorption/desorption isotherms. In particularly, the effects of operational parameters such as dosage catalyst, initial dye concentration, initial pH and light irradiation were investigated in detail. In addition, the photodegradation rate of JGB on the catalyst was also evaluated by using the pseudo-first-order model.

***Keywords**: Photodegradation, Zinc Oxide, Zinc Hydroxide Carbonate, Activated Carbon, Janus Green B.*

TÓM TẮT

Bài báo này đưa ra cách tổng hợp kẽm oxit và kẽm hydoxit cacbonat mang trên than hoạt tính (ZnO/ZHC/AC composit) cho sự phân hủy Janus Green B (JGB) dưới sự chiếu xạ của tia UV. Mẫu ZnO/ZHC/AC được chuẩn bị bằng phương pháp thủy nhiệt với sự có mặt của hexametylen tetramin (HMTA) tại pH = 8,0 và không sử dụng quá trình nung. Mẫu tổng hợp được đặc trưng bởi XRD, FE-SEM, BET và đẳng nhiệt hấp phụ N_2. Đặc biệt, các ảnh hưởng của các thông số làm việc như lượng xúc tác, nồng độ ban đầu của chất màu, giá trị pH ban đầu và nguồn sáng được nghiên cứu một cách chi tiết. Bên cạnh đó, tốc độ quang phân hủy của JGB trên xúc tác cũng được đánh giá bằng việc sử dụng mô hình phản ứng bậc 1.

***Từ khóa:** Quang phân hủy, kẽm oxit, kẽm hydroxit cacbonat, than hoạt tính, Janus Green B.*

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1. INTRODUCTION

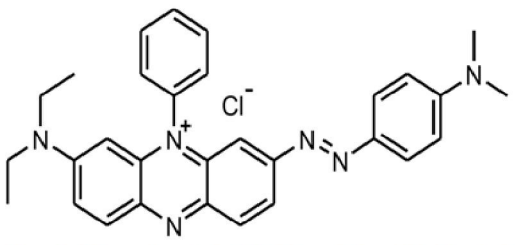
Effluents of textile and the dyeing industries cause seriously environmental pollution and health problems [1]. The toxic dyes must be mineralized before being released into environment. There are many methods for treatment of wastewater such as precipitation, coagulation, biological degradation, absorption and ion exchange but semiconductor photocatalysis is one of the most promising processes as compared to other conventional techniques [2].

As compared to the available semiconductor materials for catalytic application, ZnO has wider application because of its availability, stability, low cost, and wide band gap energy [3,4]. However, problems for the use of ZnO powders are difficulty in separating the powder from the solution after completing the reaction, aggregation of particles in suspension at high loading, and difficulty in application to continuous flow systems [5].

In the our previous report, the feasible adsorption of activated carbon (AC) and catalytic ability of ZnO/ZHC were completely studied [6]. It was reported that the photocatalytic activity of ZnO/ZHC/10AC (with 10 wt% of AC) was higher than that of ZnO/ZHC and the as-prepared sample exhibited a good cycling stability. In this study, in order to fully investigate the catalytic ability of this composite, the effects of reaction parameters such as dosage catalyst, initial dye concentration, initial pH, and light irradiation were investigated.

2. EXPERIMENTAL

2.1. Materials



Chemical formula : $C_{30}H_{31}N_6Cl$ **Mw : 511.06 g/mol**
C.I.number: 11050 **λ_{max} : 611 nm**
Nature : Cationic dye

Figure 1. The chemical structure and physical properties of JGB

Janus Green B (JGB) was purchased from Sigma-Aldrich, the chemical structure and some of the important physicochemical properties of JGB are presented in Figure 1. AC (char coal with powder 100-400 mesh) was obtained from Sigma-Aldrich. Zinc acetate ($Zn(CH_3COO)_2.2H_2O$, 99%), hexamethylene tetramine-HMTA ($C_6H_{12}N_4$, 99%) and liquid ammonia (NH_3, 28%) were obtained from China. All the chemicals were used without any purification and distilled water was used throughout the experiments.

2.2. Preparation of catalysts

ZnO/ZHC/AC composites were prepared by hydrothermal method. Typically, 2.19g zinc acetate and 0.7g HMTA were dissolved in 100mL of distilled water to form clear solution. Subsequently, the pH of solution was adjusted to 8.0 by using liquid ammonia under stirring. After 5 min of stirring, an amount of AC (10%) was added to above solution. The suspension was stirred vigorously for 5 min and then transferred into Teflon-lined autoclave and heated at 150°C for 24h. The collected solids were washed several times with distilled water and dried at 80°C for 24h. The grey obtained powders were donated as ZnO/ZHC/10AC corresponding to the AC weight percentage of 10 wt.%, respectively.

2.3. Characterization

The crystalline phase of samples was investigated by X-ray power diffraction. XRD patterns were obtained by using Bruker D8 Ax XRD-diffractometer (Germany) with Cu Kα irradiation (40kV, 40mA). The 2θ ranging from 10 to 80° was selected to analyse the crystal structure. The morphology of the samples was observed by field emission scanning electron microscopy (FE-SEM, JEOL-7600F). The textural properties were measured via N_2 adsorption/desorption isotherms using a micromeritics (Gemini VII analyzer). The specific surface area, pore volume and pore diameter were obtained by using the Brunauer-Emmett-Teller (BET) method.

2.4. Photocatalytic test

The photocatalytic performance of sample was carried out by degradation of JGB in water under UV irradiation. Typically, 50mg of catalyst were added to a beaker 250mL containing 100mL of JGB with certain concentration, solution pH was adjusted by H_2SO_4 0.1M and NaOH 0.1M. At given time intervals of 10 min, 2mL of sample was collected from the suspension and then filtered by a syringe filter (0.45µm PTFE membrane) to remove the catalyst. The dye concentration of the filtrate was analyzed by a UV-Vis spectrophotometer (Agilent 8453) at the maximum absorbance wavelength 611nm.

The degradation rate of JGB by the ZnO/ZHC/AC composite can be evaluated by using the pseudo-first-order model called Langmuir–Hinshelwood model as follow:

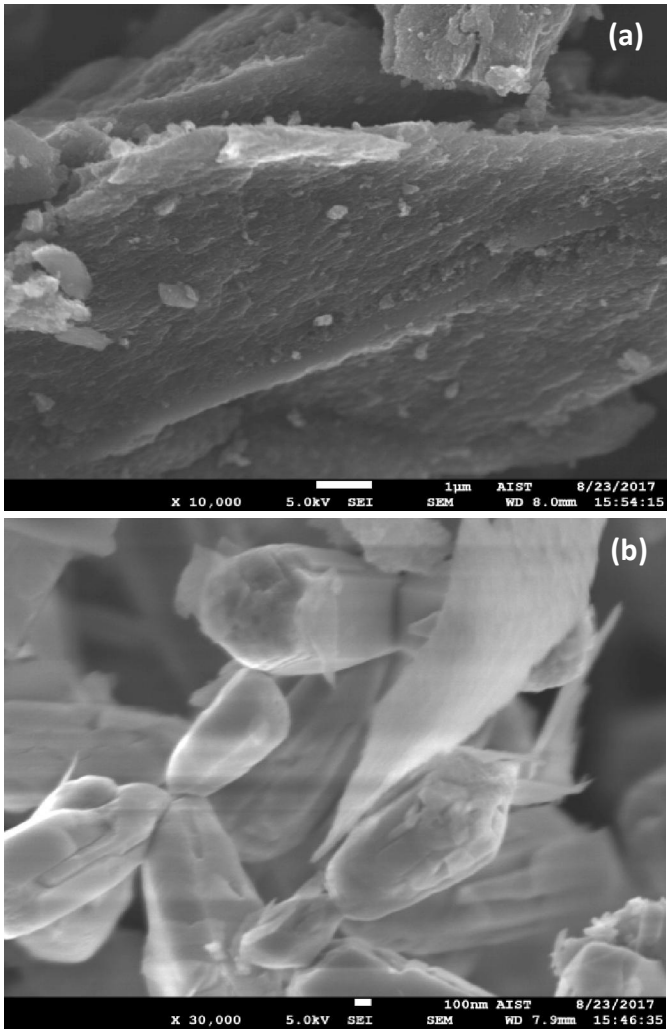
$$\ln\frac{C_0}{C_t} = kt \quad (1)$$

Where C_0 and C_t are the concentration of JGB at initial (t = 0) and time t (min), respectively. k is the pseudo first-order rate constant. The k value was calculated from the slope of the $\ln(C_0/C_t)$ – t plots.

3. RESULTS AND DISCUSSION

3.1. Characterization of samples

Characterizations of material are presented in Figure 2. As seen in Figures 2 (a) and (b), ZnO/ZHC with rod-like shape growth on the surface of AC, the growth directions of the nanorods appeared relatively random on nonplanar of AC. The bulk shape had average length of about 1µm and width of about 500nm. The N_2 adsorption/desorption isotherms of samples showed the hysteresis loops, in Figure 2(c), indicating the mesoporous materials. Some textural properties of material obtained by BET method were shown in Table 1. As seen in Figure 2(c), the peak at 2θ = 14° could be ascribed to activated carbon. For ZnO/ZHC/10AC composite, the peak of AC was disappeared and other peaks corresponding to ZnO/ZHC were observed.



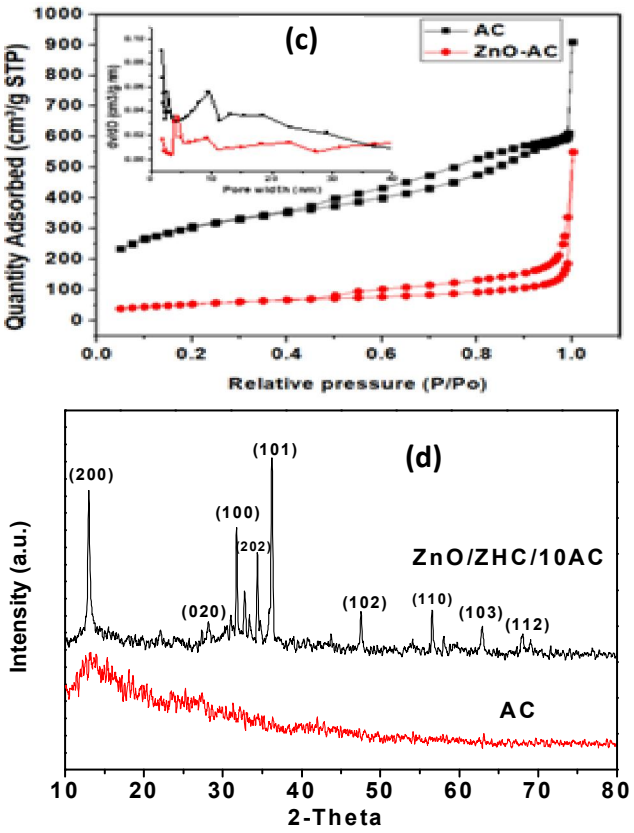


Figure 2. (a) and (b) SEM images of AC and ZnO/ZHC/10AC composite; (c) N_2 adsorption/desorption isotherms (inset: pore size distributions) of AC and ZnO/ZHC/10AC composite; (d) XRD patterns of AC and ZnO/ZHC/10AC composite.

3.2. Effect of operational parameters

3.2.1. Effect of dosage catalyst

Table 1. Textural properties of AC and ZnO/ZHC/10AC composite

Samples	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
AC	1062	1.06	3.58
ZnO/ZHC/10AC	191	0.29	6.29

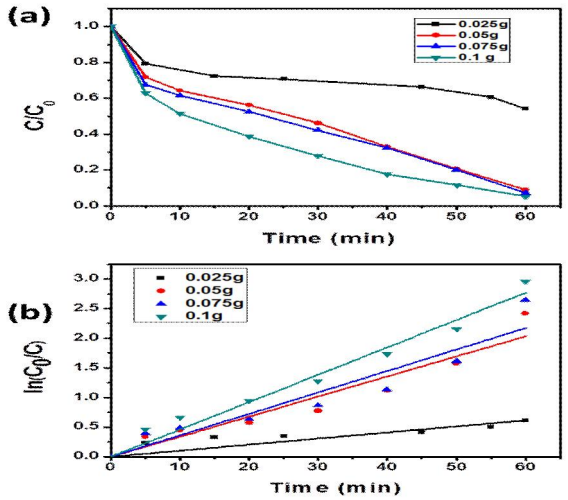


Figure 3. (a) Effect of ZnO/ZHC/10AC dosage on the degradation of JGB under UV-irradiation and (b) the kinetic curves

Effect of dosage catalyst on the degradation of dye is shown in Figure 3. The degradation rate for the mineralization of JGB was found to be faster at higher dosage catalyst [7]. The reaction rate (k) increased from 0.010 to 0.046min^{-1} with an increase in dosage catalyst from 0.025 to 0.1g, in table 1. However, the degradation efficiencies at dosage catalyst of 0.05, 0.075 and 0.1g were relatively similar to each other.

3.2.2. Effect of concentration dye

In order to examine the impact of various dye concentrations on the photocatalytic degradation, the experiments were conducted by varying the concentration of JGB from 5 to 20mg/L. While other conditions such as dosage catalyst, reaction temperature, and initial pH were remained at constant, 0.1g, 25°C and 6.5, respectively. As presented in Figure 4, the degradation efficiency of Janus Green B was significantly decreased with an increase in the initial concentration of Janus Green B. The degradation efficiency and reaction rate of the JGB aqueous solution at concentration of 5 mg/L and reaction time of 60 min were 99.87% and 0.409 min^{-1}, respectively. These values were sharply decreased to 60.72% and 0.16 min^{-1}, respectively, at concentration of 20mg/L, as seen in Table 3.

Table 2. Kinetic parameters for photodegradation of JGB at different dosages catalyst

Dosage catalyst	K (min^{-1})	R^2	Degradiation (%)
0.025 g	0.010	0.84	45.88
0.05 g	0.034	0.93	91.08
0.075 g	0.036	0.91	92.90
0.1 g	0.046	0.98	94.82

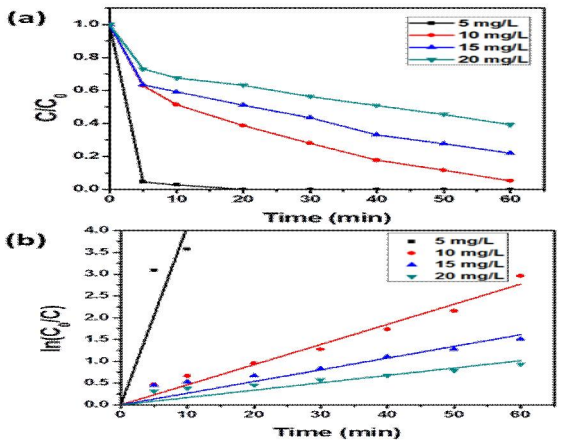


Figure 4. (a) Effect of initial dye concentration on the degradation of JGB and (b) the kinetic curves

Table 3. Kinetic parameters for photodegradation of JGB at different dye concentrations

Samples	K (min^{-1})	R^2	Degradation (%)
5 mg/L	0.409	0.83	99.87
10 mg/L	0.046	0.98	94.82
15 mg/L	0.026	0.93	77.95
20 mg/L	0.016	0.89	60.72

3.2.3. Effect of solution pH

The solution pH is an important parameter in photocatalytic degradation reactions for industrial applications. The effect of initial solution pH on degradation of JGB was investigated in the pH range of 3–11, at the 0.1g catalyst dosage, 10mg/L dye concentration, and reaction temperature of 25°C. The pH of the reaction solution was adjusted before light irradiation and it was not controlled during the reaction. The obtained results are presented in Figure 5. It was apparently found that the degradation of JGB significantly enhanced with increasing pH value. It has been reported that the pH of zero point charge for ZnO is approximately 9.0 (denoted as pH_{zpc}) [8]. At pH lower than the pH_{zpc} of the ZnO, the stable suspension forms because their net positive charge prevents agglomeration. Similar phenomenon was observed when pH is higher than the pH_{zpc} of ZnO, where ZnO particles are negatively charged on by adsorbing OH^- ions, led the increase in adsorption of Janus Green B molecules, a cation dye, on ZnO/ZHC/AC sample. Overall results indicated that the degradation of Janus Green B was significantly influenced by the solution pH. The alkaline condition was very beneficial to the photocatalytic oxidation of JGB dye. The reaction rate of JGB at different pH values are presented in Table 4.

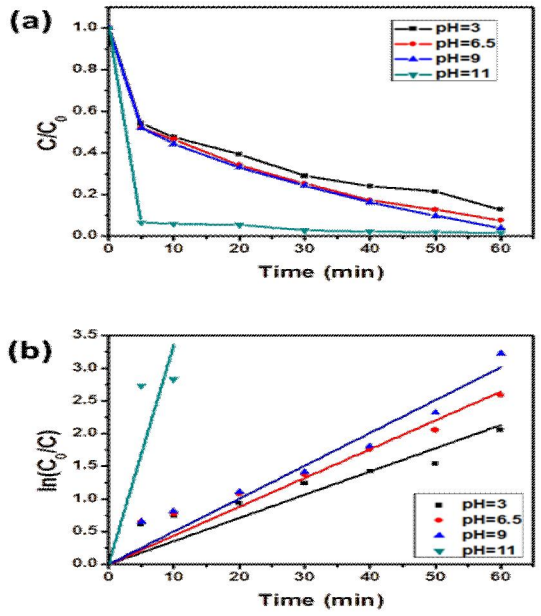


Figure 5. (a) Effect of initial pH on degradation of JGB and (b) the kinetic curves

Table 4. Kinetic parameters for photodegradation of JGB at different initial pH values

Samples	k (min^{-1})	R^2	Degradation (%)
pH =3.0	0.035	0.91	87.20
pH =6.5	0.044	0.96	92.44
pH =9.0	0.050	0.96	96.03
pH =11.0	0.336	0.75	98.25

3.2.4. Effect of irradiation of different light sources

Degradation of Janus Green B under different light sources has been shown in Figure 6. The degradation of JGB under tungsten lamp and none UV irradiation were relatively similar to each other. However, the degradation efficiency and reaction rate increased with UV irradiation, 94.02% and 0.119 min^{-1}, respectively. Particularly, these values slightly increased under solar light, indicating the huge potential application in industrial scale for degradation of dyes from wastewater by as-synthesized material [3,9].

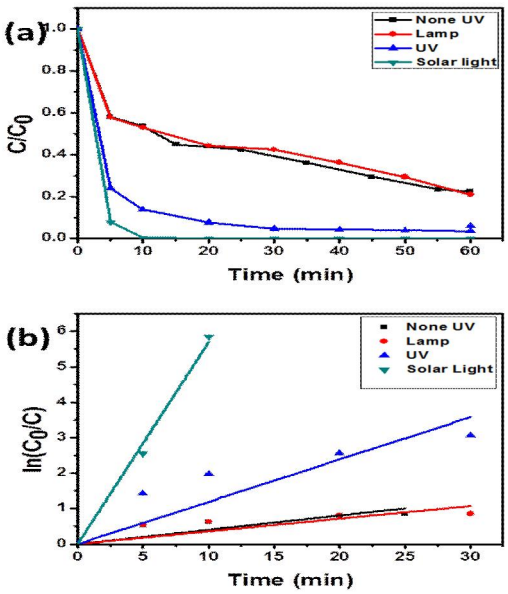


Figure 6. (a) Effect of irradiation of different light sources on degradation of JGB at reaction conditions: 0.1 g dosage catalyst, 10 mg/L initial concentration of JGB, initial pH of 6.5 and (b) the kinetic curves

Table 5. Kinetic parameters for photodegradation of JGB at different light sources

Samples	k (min^{-1})	R^2	Degradation (%)
None UV	0.040	0.785	77.64
Lamp	0.036	0.704	79.01
UV	0.119	0.825	94.02
Solar light	0.570	0.992	100

3.2.5. Potential degradation of toxic chemicals on ZnO/ZHC/10AC composite.

The photocatalytic activity of ZnO/ZHC/10AC composite with other toxic chemicals were investigated by using dyes such as Methylene Blue, Tartrazine, and a pharmaceutical product, Caffeine. The reaction conditions were remained at 0.1g dosage catalyst, 10mg/L initial concentration, initial pH of 6.5. The results are shown in Figure 7. It was easy to find that ZnO/ZHC/10AC could remove all chemicals. The degradation efficiency and reaction rate of caffeine were the lowest, 66.53% and 0.059 min^{-1}, respectively. Whereas, the highest values were observed for the methylene blue, 99.50% and 0.127 min^{-1}, respectively, as seen in Table 6.

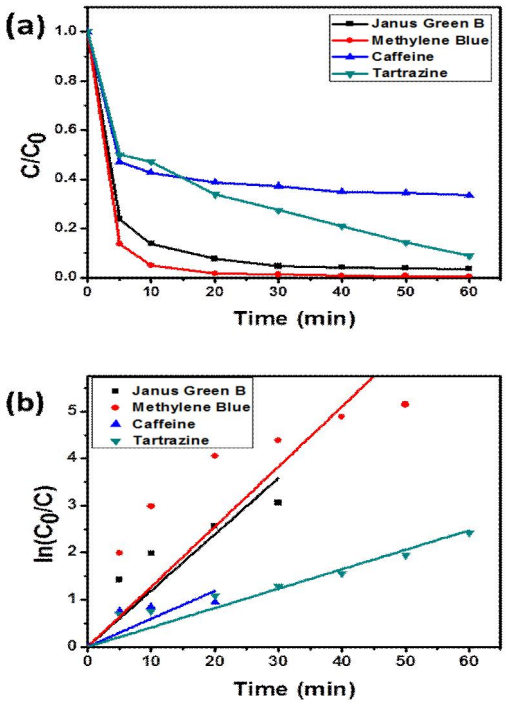


Figure 7. (a) Photodegradation of toxic chemicals in wastewater by ZnO/ZHC/10AC and (b) the kinetic curves

Table 6. Kinetic parameters for photodegradation of toxic chemicals

Toxic chemicals	K (min^{-1})	R^2	Degradation (%)
JGB	0.119	0.825	96.44
Methylene Blue	0.127	0.801	99.50
Caffeine	0.059	0.635	66.53
Tartrazine	0.041	0.937	91.10

4. CONCLUSION

In summary, ZnO/ZHC/10AC composite was synthesized by a hydrothermal method without calcination step. As-prepared sample showed ZnO/ZHC rod-like shape growth on the surface of AC. The photocatalytic activity of sample was evaluated by degradation of JGB under UV light. The optimal parameters obtained in this paper as following: 0.1g dosage catalyst, 5mg/L concentration of JGB, initial pH of 11.0. As-synthesized sample showed the huge potential application due to the removal ability of JGB under solar light with degradation efficiency of 100%. Also it showed the high degradation efficiencies and reaction rates for all of dyes and a pharmaceutical product that were used in this paper.

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