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Study the effects of reaction parameter on degradation of janus green B by using nano zinc oxide loaded on activated carbon

ABSTRACT

In this study, zinc oxide nano particles loaded on activated carbon (ZnO/AC) has been successfully prepared for degradation of Janus Green B (JGB) under low UV light intensity. The activated carbon (AC) was synthesized from rice husk by two steps calcination at 800 ℃, ZnO/AC was synthesized by hydrothermal method with the assistant of HMTA. As-prepared sample was characterized by XRD, FE-SEM, N2 adsorption/desorption. The effects of operational parameters on the photo-degradation reaction progress, including catalyst dosage, initial dye concentration, initial pH value and the addition of inorganic anions were investigated in detail. In addition, the photodegradation rate of JGB on composite was evaluated by using the pseudo-first-order model.

Introduction

Urbanization and heavy industrialization caused our environment polluted seriously. It is a global menace to man's health and the magnitude of it is increasing day by day. Especially, wastewater released from dyeing industries is one of the main pollution sources. Up to now the environmental remediation technologies, including adsorption, biological oxidation, chemical oxidation, and incineration, have been used to treat all types of organic and toxic wastewater [1]; therein one of the typical environmental remediation methods is chemical degradation.

In chemical degradation methods, semiconductor photocatalysis has emerged as one of the most promising processes for waste water treatment as compared to other conventional techniques [2].

As one of the most important semiconductor photocatalysts, ZnO has attracted considerable interest because of its high photosensitivity and stability [3]. However, the use of ZnO powders has many difficult problems such as 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 [4]. Fortunately, these disadvantages of ZnO are avoidable through the process of surface modification and this can be achieved by coating ZnO particles by support materials like activated carbon and silica.

Rice husk is a by-product of the rice milling process, which is the outer covering of the rice grain, most of the rice husk is usually either dumped or burned in open spaces, thus causing damage to the land and environmental pollution. Much efforts have been made to utilize the rice husk including as an alternative fuel for energy production, production of activated carbon (AC) and as a raw material for manufacture of industrial chemicals based on silica and silicon compounds [5]. In there, AC has porous structure, high surface area and low cost so it is considered a great material for catalyst and adsorption of metal ions and organic molecules in both gas and aqueous phases.

Considering the study on degradation of dyes in aqueous solution, the ZnO/AC was prepared successfully by hydrothermal method using rice husk as an activated carbon source. The batch reaction was conducted to study the degradation of JGB on catalyst. The effects of catalyst dosage initial dye concentration, initial pH value and the addition of inorganic anions were investigated in detail.

Experimental

2.1. Materials

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. Rice husk was obtained from Thai Binh province. Zinc acetate ($Zn(CH_3COO)_2.2H_2O$, 99%), hexamethylene tetramine-HMTA ($C_6H_{12}N_4$, 99%), sodium hydroxide (NaOH, 99.5 %) 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.
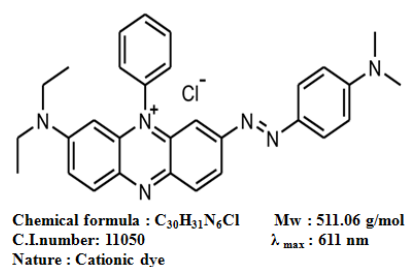

Chemical formula : $C_{30}H_{31}N_6Cl$ Mw : 511.06 g/mol
C.I.number: 11050 λ_{max} : 611 nm
Nature : Cationic dye

Figure 1. The chemical structure and physical properties of JGB [6].

2.2. Preparation of activated carbon from rice husk

The preparation of activated carbon is presented in Figure 2. Rice husk obtained from Thai Binh was washed with distilled water to remove soil and dust and then dried at 100 °C for 24h. The dry rice husk was carbonized at 400 °C for 2h at a heating rate of 5° C/min to produce charcoal. Subsequently, charcoal was crushed by pestle and mortar, the charcoal power was then impregnated with NaOH 4M at weight ratio NaOH:charcoal of 1:1. The mixture was dried at 100 °C for 24h. The obtained powder was calcined in a furnace under N_2 flow by 2 steps: (1) temperature increased from room temperature to 400 °C at 8°C/min and remained temperature for 1h; (2) the temperature increased from 400 °C to 800 °C at 10 °C/min and remained temperature for 2h. After cooling, the samples was washed with distilled water until pH reached neutral, then dried at 100 °C for 24h. Finally, the activated carbon was obtained and used for further studied.
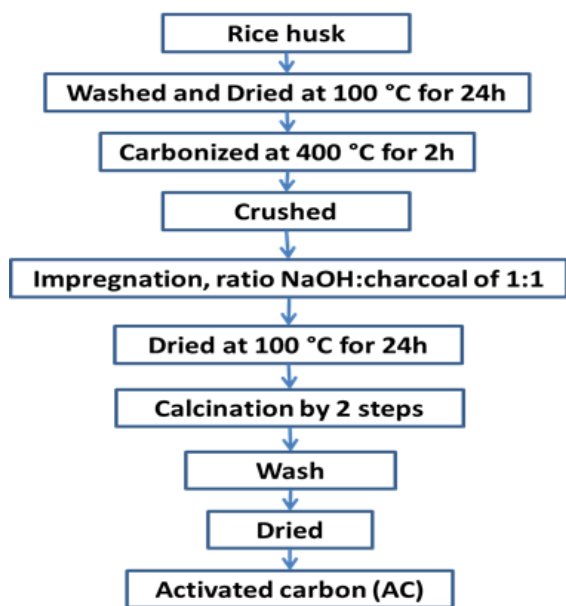
Figure 2. Preparation procedure of activated carbon

2.3. Preparation of ZnO/AC

ZnO/AC composite was prepared by hydrothermal method. Typically, 2.19 g zinc acetate and 0.7 g HMTA were dissolved in 100 mL 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 wt.%) was added to above solution. The suspension was stirred vigorously for 5 min and then transfered into teflon-lined autoclave and heated at 150 °C for 24h. The collected solids were washed several times with distilled water, dried at 80 °C for 24 h to obtained back powder, this sample, before calcination, was denoted as ZnO/ZHC/AC. Finally, the powder was calcined in N_2 at 400 °C for 2 hours. The obtained grey powder was denoted as ZnO/AC. For comparison, pure ZnO was prepared by the same procedure to ZnO/AC without adding the AC into the synthesis process.

2.4. 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, 40 mA). 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.

2.5. Photocatalytic test

The photodegradation of JGB on catalyst was carried out by batch test. Typically, 50 mg of catalyst was added into a 250 mL glass beaker containing 100 mL of JGB 10 mg/L. At given time intervals of 10 min, 2 mL of samples were withdrawn from the suspension and then filtered by a syringe filter (0.45 μm 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 611 nm.

$$\text{Degradation efficiency (\%)} = \frac{C_D - C_t}{C_D} \cdot 100\% \quad (1)$$

The photodegradation rate of JGB on catalysts can be evaluated by using the pseudo-first-order model as follow:

$$\ln \frac{C_0}{C_t} = kt \quad (2)$$

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.

Results and discussion

3.1. Characterization of samples

Characterizations of materials are presented in Figure 3. Figure 3 (a), AC was observed with the different shapes and had a rough surface. In the sample before calcination, ZnO/ZHC with rod-like shape growth on the surface of AC, the growth directions of the nanorods appeared relatively random on none-planar substrates. The bulk shape had average length and width of approximately 1 μm and 500 nm, respectively, in Figure 3(b). As seen in Figure 3(c), ZnO had the similar sharp to pure ZnO and it highly dispersed on surface of AC. The ZnO particles size was in range of 20-30 nm. These results revealed that the sharp of ZnO after calcination was different from that before calcination. For the ZnO/ZHC/AC sample, the peaks of ZnO were also observed in XRD result. In addition, the lattice plans (200) observed could be ascribed to zinc hydroxide carbonate (ZHC)

(JCPDS 19–1458) [7, 8]. The sample after calcinations at 400°C for 2h (ZnO/AC) included both diffraction peaks of AC and ZnO, and no other impurity peaks were observed. Some textural properties of material obtained by BET method were shown in Table 1.

Table 1. Textural properties of AC, ZnO, ZnO/ZHC/AC and ZnO/AC composites.

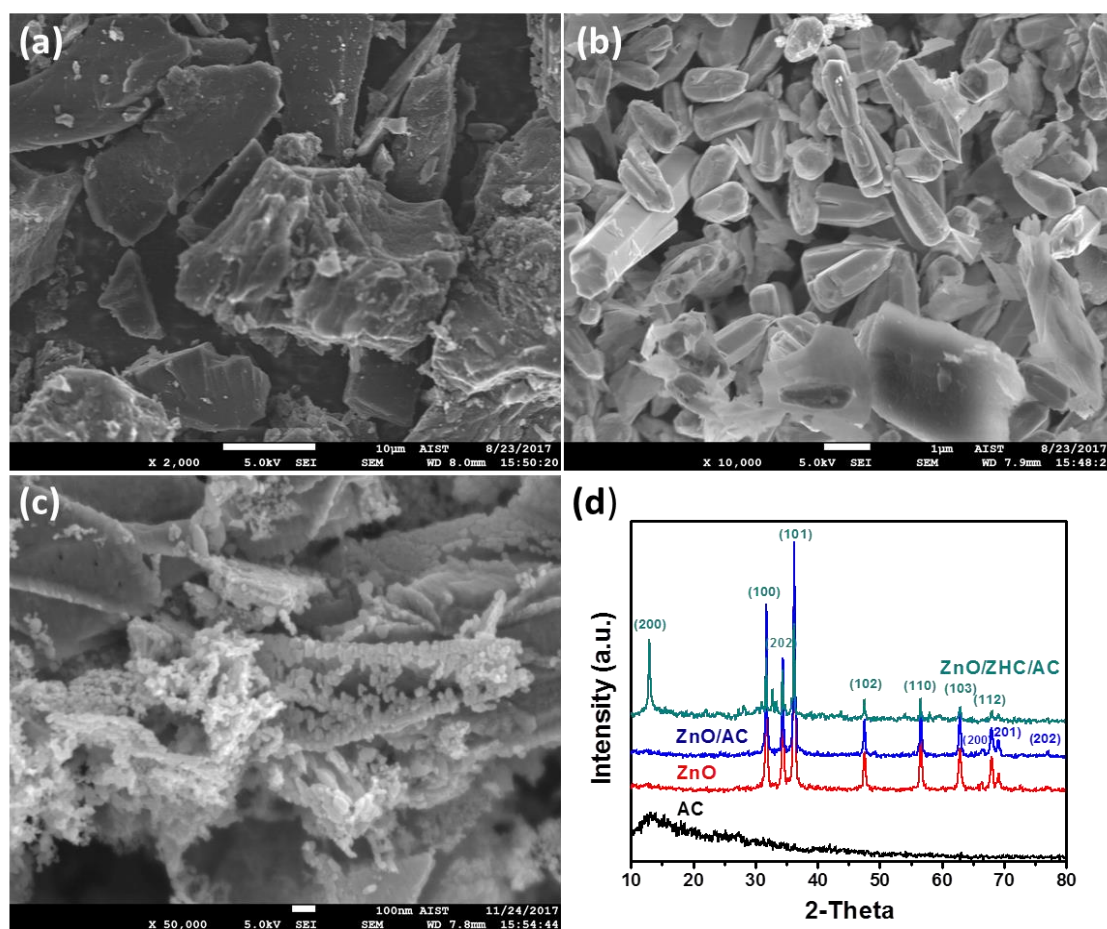| Samples	S_{BET} (m²/g)	Pore volume (cm³/g)	Average pore size (nm)
AC	1062	1.06	3.58
ZnO	24	0.28	47.9
ZnO/ZHC/AC	191	0.29	6.29
ZnO/AC	251	0.41	10.24

Figure 3. (a), (b) and (c) SEM images of AC, ZnO/ZHC/AC and ZnO/AC; (d) XRD patterns of AC, ZnO, ZnO/ZHC/AC and ZnO/AC composites.

3.2. Effect of reaction parameters

3.2.1. Effect of dosage catalyst

Effect of dosage catalyst on the degradation of dye is shown in Figure 4. In initial 35 min, the degradation rate and degradation efficiency of JGB increased when dosage catalyst increased from 0.025 to 0.1 g. However, the degradation efficiency was observed to be slightly degreased for dosage catalyst of 0.1 g after 35 min. The reaction rate in 60 min were 0.050, 0.083, 0.109 and 0.080 min^{-1} for 0.025, 0.05, 0.075 and 0.1 g dosage of ZnO/AC respectively, . The degradation of JGB reached 100% for dosage catalyst of 0.075 g, as seen in Table 2.

The effect of catalyst dosage on degradation process can be explained by the following reasons: the increasing catalyst dosage results in an increase in the number of active sites that are available at the surface of catalyst, so the density of catalyst particles in the area of illumination is improved. However, when surpassing the limit value because the suspension is increased, the short wave tail photons are not able to enter the reaction mixture and a decrease in UV light penetration as a result of increased scattering effect [9], the degradation efficiency decreased.
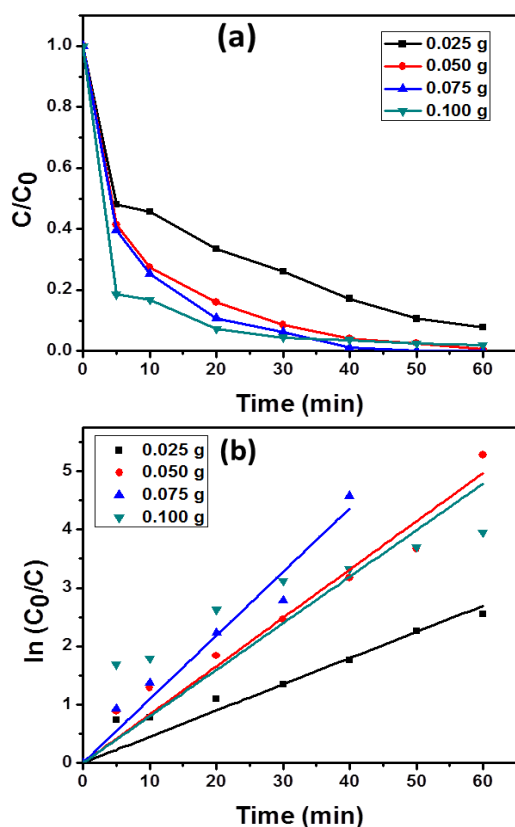
kinetic curves.

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

Dosage catalyst	k (min^{-1})	R^2	Degradation efficiency (%)
0.025 g	0.050	0.95	92.17
0.050 g	0.083	0.97	99.49
0.075 g	0.109	0.97	100.0
0.100 g	0.080	0.83	98.08

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 20 mg/L. While other condition, dosage catalyst, reaction temperature, and initial pH were remained at constant, 0.05 g, 25 °C and 6.0, respectively. The result is presented in Figure 5. It was found that the JGB was strongly degraded with high degradation rate at JGB concentration of 5 mg/L. The increase in JGB concentration leaded the decrease in degradation efficiency. The degradation efficiency for concentration of 5, 10, 15 and 20 mg/L were 100, 99.49, 88.23 and 83.40 %, respectively, in 60 min of reaction. The degradation rate also was decreased when concentration of JGB increased. The k values were calculated and listed in Table 3.

This effect can be interpreted by the following reasons: When increases of JGB concentration, the photons get intercepted before they can reach the catalyst surface, so the generation of •OH and •O_2^- radical decreases, meaning photodegradation efficiency of JGB solution decreases and a large number of JGB molecules along with the intermediates generated may compete for the constant total active sites available for adsorption at a fixed concentration of ZnO/AC [10]. Additionally, with increase in the initial dye concentration, the solution becomes more intensely coloured and the path length of photons entering into the solution decreases [11], thus the absorption of photos by the catalysts decreases, and consequently the degradation rate is reduced.

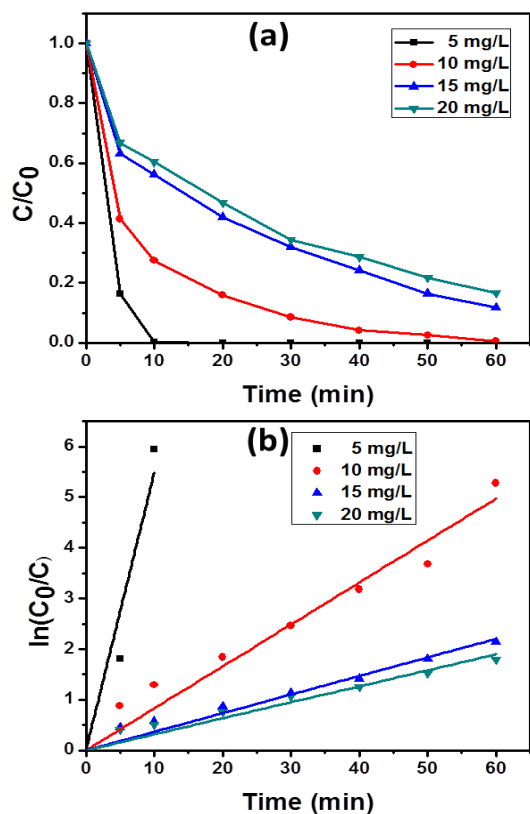**Figure 4.** (a) Effect of ZnO/AC dosage on the degradation of JGB under UV-irradiation and (b) the

Figure 5. (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 efficiency (%)
5 mg/L	0.548	0.92	100.0
10 mg/L	0.083	0.97	99.49
15 mg/L	0.037	0.97	88.23
20 mg/L	0.032	0.97	83.40

3.2.3. Effect of solution pH

One of the most important parameters in photocatalytic degradation reaction is the solution pH, thus the effect of initial solution pH to remove dye was examined and the result is presented in Figure 5. The effect of initial solution pH on degradation of JGB was investigated in the pH range of 3–12, at the 0.05 g catalyst dosage, 10 mg/L dye concentration, and reaction temperature of 25 ℃. The pH of the reaction solution was adjusted before light irradiation and it was not controlled during the reaction. The obtained results indicated that the degradation of Janus Green B was significantly influenced by the solution pH. The

degradation percentages for the different initial pH values were presented in Table 4. The alkaline condition, pH value was larger than 11, was very beneficial to the photocatalytic oxidation of Janus Green B dye. The reaction rate of JGB at different pH values are presented in Table 4.
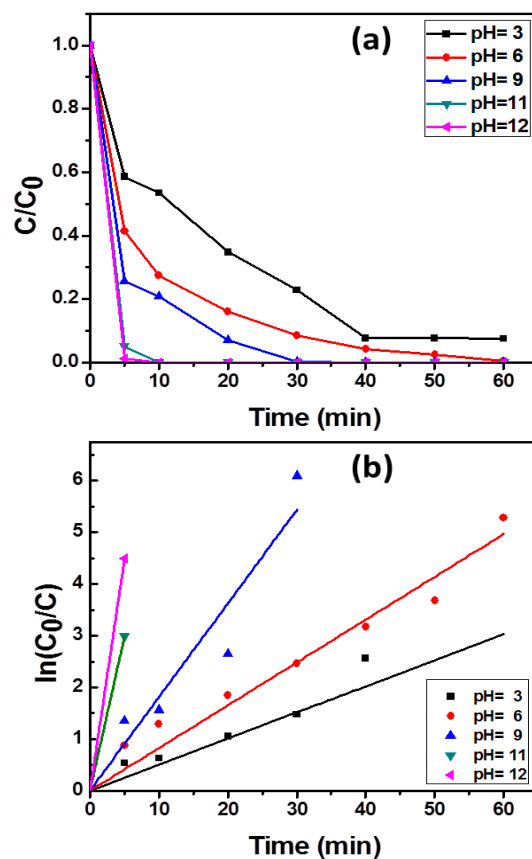

Figure 6. (a) Effect of initial pH on degradation of JGB and (b) the kinetic curves.

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

Samples	k (min^{-1})	R^2	Degradation efficiency (%)
pH= 3	0.051	0.95	92.56
pH= 6	0.083	0.97	99.49
pH= 9	0.181	0.92	100.0
pH=11	0.598	1.00	100.0
pH=12	0.899	1.00	100.0

3.2.4. Effect of inorganic anions on photocatalytic degradation of JGB dye
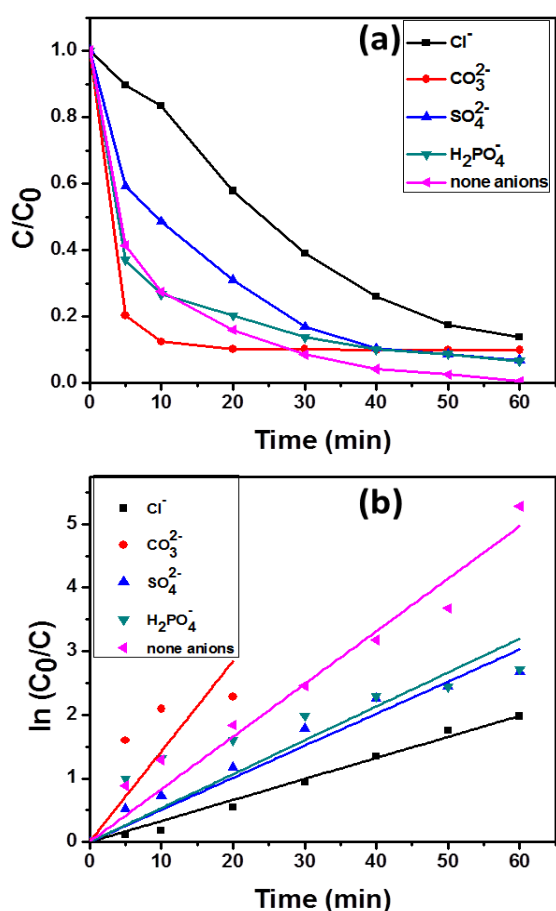
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Figure 7. (a) Effect of inorganic anions on photocatalytic degradation of JGB at reaction conditions: 0.05 g dosage catalyst, 10 mg/L initial concentration of JGB, initial pH of 6.0, 2 g/L concentration of anion and (b) the kinetic curves.

Wastewater from dyeing industry usually contains either organic contaminants or abundant inorganic anions such as sulfate and carbonate [12]. Thus, it is necessary to investigate the impact of these ions on the photocatalytic process. The influence of added inorganic anions on the removal of JGB dye was studied at 0.2 g/L concentration and displayed in Figure 7. It can be found that all of added inorganic anions had an inhibition effect on the photocatalytic process and lowered the photocatalytic degradation rate of JGB dye. At the presence of $H_2PO_4^-$, SO_4^{2-}, CO_3^{2-} and Cl^- the degradation efficiency decreased from 99.49 to 93.40, 93.11, 90.17 and 86.19%, respectively, as seen Table 5. Since the common cation of all the added inorganic anions (Na^+) is inert; hence, only anions are involved in the retardation effect. The degradation efficient of JGB was inhibited may be due to a competitive adsorption of these anions and the target organic substance at the surface of catalyst,

leading to blockage of the active sites at the surface of photocatalyst and these inorganic anions cover the ZnO surface, which prevents the exposure of the JGB molecule to ZnO. Additionally, these negatively charged inorganic anions can react with holes (h^+) and hydroxyl radicals (•OH) to produce less-reactive species due to their lower oxidation potentials, and those inorganic anions behaved similar to h^+ and •OH scavengers, which is a great impediment to the progress of the reaction.

Table 5. Kinetic parameters for photodegradation of JGB.

Samples	k (min^{-1})	R^2	Degradation (%)
none anions	0.083	0.97	99.49
Cl^-	0.033	0.99	86.19
CO_3^{2-}	0.142	0.69	90.17
SO_4^{2-}	0.050	0.96	93.11
$H_2PO_4^-$	0.053	0.85	93.40

Conclusion

In summary, the ZnO/AC catalyst was successful prepared from rice husk for photodegradation of JGB from aqueous solution. The JGB solution with a concentration of 10 mg/L and initial pH = 12 was degraded up to 100.0 % at dosage catalyst of 0.05 g within 60 min under UV irradiation. Alkaline condition was beneficial to the degradation of JGB solution. The presence of inorganic ions significantly caused the inhibiting degradation of JGB. These results gave an opening and promising application of this material in wastewater treatment.

Acknowledgments

References

[1] Moussavi G, Mahmoudi M. Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles. Journal of Hazardous Materials 2009;168:806-12.

[2] Kuriakose S, Choudhary V, Satpati B, Mohapatra S. Facile synthesis of Ag-ZnO hybrid nanospindles

for highly efficient photocatalytic degradation of methyl orange2014.

[3] Jia Z-g, Peng K-k, Li Y-h, Zhu R-s. Preparation and photocatalytic performance of porous ZnO microrods loaded with Ag. Transactions of Nonferrous Metals Society of China 2012;22:873-8.

[4] Sobana N, Muruganandam M, Swaminathan M. Characterization of AC–ZnO catalyst and its photocatalytic activity on 4-acetylphenol degradation. Catalysis Communications 2008;9:262-8.

[5] Kumar A, Mohanta K, Kumar D, Parkash O. Properties and industrial applications of rice husk: A review2011.

[6] Vu Van Tu, Phan Thi Yen, Nguyen Anh Vu, Tran Thi Thuy, Tuan VA. A Facile Precipitation Method to Synthesize Submicrometer-Size MgO for Removing Janus Green B from Aqueous Solution. Tạp chí Khoa học và Công nghệ 2016;115:6.

[7] Miao Y, Zhang H, Yuan S, Jiao Z, Zhu X. Preparation of flower-like ZnO architectures assembled with nanosheets for enhanced photocatalytic activity. Journal of Colloid and Interface Science 2016;462:9-18.

[8] Lei A, Qu B, Zhou W, Wang Y, Zhang Q, Zou B. Facile synthesis and enhanced photocatalytic activity of hierarchical porous ZnO microspheres. Materials Letters 2012;66:72-5.

[9] Zyoud A, Zu'bi A, Helal M, Park D, Campet G, Hilal H. Optimizing photo-mineralization of aqueous methyl orange by nano-ZnO catalyst under simulated natural conditions2015.

[10] Behnajady MA, Modirshahla N, Hamzavi R. Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst. Journal of Hazardous Materials 2006;133:226-32.

[11] Krishnakumar B, Swaminathan M. Solar photocatalytic degradation of Naphthol Blue Black. Desalination and Water Treatment 2013;51:6572-9.

[12] Guillard C, Puzenat E, Lachheb H, Houas A, Herrmann J-M. Why inorganic salts decrease the TiO2 photocatalytic efficiency2005.