CONGO RED DYE REMOVAL FROM AQUEOUS SOLUTIONS BY ZnO NANOPARTICLES: KINETIC STUDY

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TÓM TẮT

NGHIÊN CỨU ĐỘNG HỌC QUÁ TRÌNH LOẠI BỎ CHẤT MÀU CONGO RED BẰNG VẬT LIỆU ZnO KÍCH THƯỚC NANO

Trong nghiên cứu này, chúng tôi tổng hợp vật liệu ZnO kích thước nano bằng phương pháp kết tủa. Vật liệu nano ZnO được đặc trưng bằng các phương pháp phân tích hóa lý XRD, FTIR, TEM, GTA. Kết quả cho thấy hạt ZnO có hình cầu, kích thước trung bình là 22-25 nm, diện tích bề mặt riêng là 9,7852 m^2/g. *Vật liệu nano ZnO được ứng dụng làm chất hấp phụ xử lý chất màu congo red trong dung dịch nước. Kết quả cho thấy dung lượng hấp phụ của vật liệu nano ZnO đối với chất màu congo red là 70,59 mg/g và quá trình hấp phụ tuân theo phương trình động học biểu kiến bậc 2. Từ đó có thể kết luận là vật liệu nano ZnO có tiềm năng ứng dụng làm chất hấp phụ để xử lý chất màu trong dung dịch nước.*
Keywords: *Zinc oxide, nanoparticles, congo red, kinetic*

1. INTRODUCTION

In the recent decates, wastewater treatment has attracted the attention of scientists due to health and environmental issues that pollutants can cause. One of the leading sources of water pollutions is without doubt industrial activities. Every day, huge amounts of industrial wastewater are discharged into water body, and this severely affects not only the health of all living forms but also the quality of the whole ecosystem. Particularly, wastewaters from textile, pharmaceutical, food, cosmetics, plastics, photographic, paper industries, etc. are releasing large quantities of organic dyes to environment. It was estimated that the world production of dyes in 1990s was 1,000,000 tons. For decades, it has rapidly increased with more than 100,000 types of commercial dyes. Approximately, the amount of 8-20% of the used dyes entered water environment. Numbers of them are toxic or carcinogenic substances that are resistant to environmental degradation [1]. Congo red dye, a benzidine-based anionic bisazo dye [1-napthalenesulfonic acid, 3,3-(4,4-biphenylene bis (azo) bis (4-amino-) disodium salt, is of great concern due to its high toxicity to human and its stability in the environment. Numbers of studies proved that congo red can servely affect human health as well as the environment [2,5].

Several methods have been proposed in order

to remove organic dyes from aqueous solutions such as adsorption, chemical coagulation, photocatalytic decomposition, biodegradation and advanced oxidation processes [3-5]. Compared to others, adsorption is considered as one the most popular methods with the advantages of being simple and cost-effective [5]. Recently, nano materials have been being widely applied as adsorbents in water treatment because of their high stability and good adsorption capacity. Among these, zinc oxide nanoparticles (ZnO) are of interest as they are environment-friendly, have low cost and good adsorption capacity.

There have been numerous published methods of ZnO nanomaterials synthesis including electrochemical precipitation, sol-gel method, microwave method, hydrothermal method, laser separation method and precipitation method. Of which the precipitation method is one of the most common that requires very simple operation and low cost. In this study, the aim was to synthesize ZnO nanoparticles by a simple and cost-effective precipitation method that allows to prepare the material in a large-scale. The material was thoroughly characterized and applied to remove congo red in aqueous solutions.

2. EXPERIMENTAL

2.1. Materials and method

All used chemicals including $Zn(NO_3)_2.6H_2O$, CH_3COOH, and NaOH were of analytical grade and used without further purification.

The amount of 6.224g of $Zn(NO_3)_2.6H_2O$ was added to 100 mL of distilled water. The mixture was stirred on magnetic stirrer at 400 rpm. The pH of the obtained solution was gradually adjusted to 10 using sodium hydroxide solution 0.1M. The mixture was additionally stirred for 2 hours at 80^0C. The white precipitate was collected by centrifugation at a rate of 6000 rpm (Hettich Mikro 22R Centrifuges), washed with distilled water, and dried at 80^0C overnight (24 hours).

2.2. Characterization methods

The thermal properties were studied by TGA (DSC131, Labsys TG/DSC1600, TMA, and Setaram, France) from ambient temperature to 900ºC with the increasing rate of 10ºC.The synthesized ZnO nanoparticles were characterized by X-ray diffraction (XRD, Bruker D8 advanced X-ray diffractometer) with Cu Kα radiation (λ = 1.54 Å) and the scan rate of 0.02 s− 1 from 20° to 70°. Morphology of ZnO nanoparticles was analyzed by a transmission electron microscope (TEM), JEOL JEM-1010.

The nitrogen adsorption-desorption isotherms of ZnO nanoparticles were recorded by the TriStar II 3020 nitrogen adsorption apparatus (Micromeritics Instruments, USA) at 77K. The pore size distribution and the BET specific surface area (SBET) of the material were determined by the Barrett–Joyner–Halenda (BJH) method.

2.3. Adsorption experiments

Desired congo red solutions were obtained by diluting the stock solution (1000 mg/L). Congo red concentrations of the solutions were confirmed by Agilent 8453 UV Vis-spectrophotometer at 497 nm before every adsorption experiment.

Batch experiments were carried out by mixing 0.01 g of the adsorbent with 40 mL of congo red solutions in 50mL-centrifuge tubes. The mixtures were ultrasonicated at 30ºC (Elmasonic S100H Ultrasonic Bath) and then centrifuged at 6000 rpm. Congo red concentrations of supernatants were measured.

In order to find the equilibrium time of the congo red adsorption by ZnO nanoparticles, the initial congo red concentration of 100 mg/L was applied. The supernatant was sampled at definite time intervals and measured for congo red concentration until negligible change in the congo red concentration was observed, signalling the equilibrium of the adsorption process. During the experiment, samples of supernatant were returned to the centrifuge tube after every measurement [7]. The adsorbed amount of congo red per unit of weight of ZnO nanoparticles, q_t (mg/L), was calculated from the mass balance equation:

$$q_t = \frac{(C_0 - C_t)V}{W}$$

where C_0 and C_t (mg/L) are initial congo red concentration and the congo red concentration after time t, respectively; V(L) is the volume of the solutions; and W(g) is the mass of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Characterization of ZnO nanoparticles

The thermogravimetric (TG) curve of ZnO nanoparticles was recorded (Figure 1). The TG curve of ZnO nanoparticles slightly went down as the temperature was increased from 25 to 800^{0}C. The mass loss of 2.08% corresponds to the loss of absorbed water. The process reaches to the maximum degradation rate at 270.34^{0}C. It can be concluded that there is no significant change in mass when increasing the temperature from room temperature to 800^{o}C or in other words, stable ZnO crystals were successfully synthesized. The result was confirmed by using X-ray diffraction analysis.

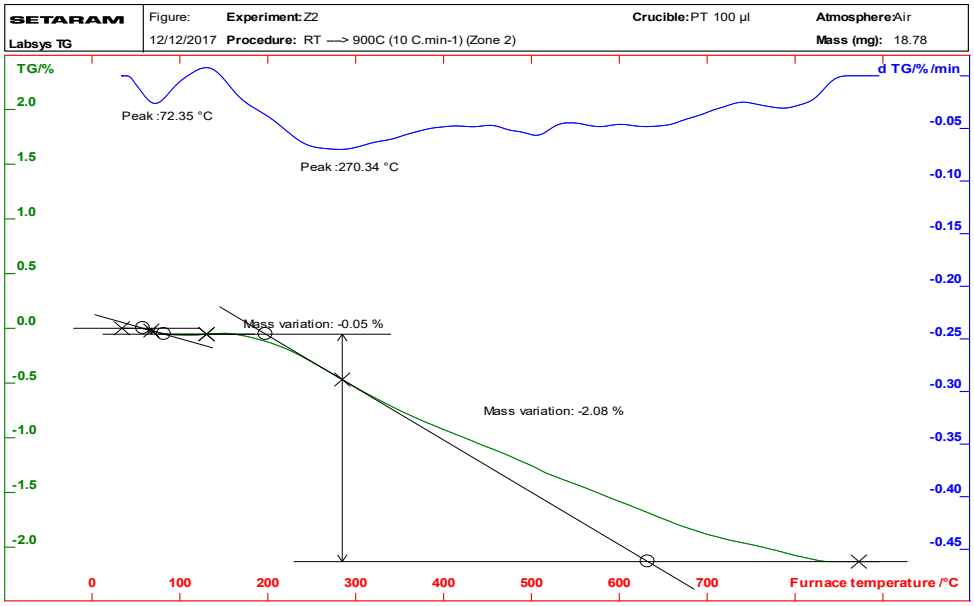

Figure 1. Thermo-gravimetric curves of ZnO nanoparticles

XRD patterns of ZnO nanoparticles are shown in Figure 2. The major peaks at scattering angles (2θ) of 31.8°, 34.4°, 36.2°, 47.5°, 56.6°, 62.8°, 66.3°, 68.1°, and 69.3° correspond to the lattice planes of (100), (002), (101), (102), (110), (103), (200), (112), and (201), respectively. These represent the wurtzite hexagonal phase of ZnO, confirming the formation of ZnO particles. The observed diffraction reflections are well-matched with the reported literature as well as standard JCPDS data card No. 36-1451 [6]. Other diffraction peaks referring to any impurities were not detected, suggesting that precipitated $Zn(OH)_2$ was completely decomposed to ZnO. The significant expansion of the peaks indicates that the crystal size of the obtained ZnO nanomaterials is small. The crystal size of ZnO nanoparticles was calculated from the broadening of diffraction peaks using Debye–Scherer formula : $D=k\lambda/\beta\cos\theta$, where D is crystal size, k is constant (0.94), λ= 0.154 nm represents the wavelength of X-ray radiation, β is the full width at half maximum of diffraction peaks (FWHM) in radian, and θ is the Bragg's angle [8]. The crystal size of the ZnO

nanoparticles was evaluated by measuring the FWHM of the most intense peak (101) because it has a relatively strong intensity and does not overlap with other diffraction peaks. Approximately, the average crystal size of ZnO nanoparticles is of 20 nm.

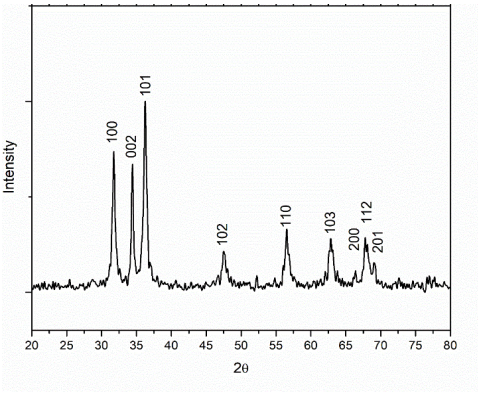

Figure 2: XRD patterns of ZnO particles

Figure 3 shows the TEM image of the ZnO nanoparticles. As can be seen, the particles appear in spherical shapes. As agglomeration was observed, the size of the particles was roughly estimated to be 20-30 nm. Nitrogen adsorption-desorption isotherms of ZnO nanoparticles are displayed in Figure 4. The material has type IV isotherm (IUPAC classification) [5]. Moreover, the very narrow hysteresis loop at moderate relative pressure indicates the present of mesopores in the structure of the ZnO nanoparticles. BET surface areas and average pore size of ZnO nanoparticles are 9.7852 (m^2/g) and 11.33 (nm), respectively (Table 1). The high total surface areas may help the material to be a promissing adsorbent.

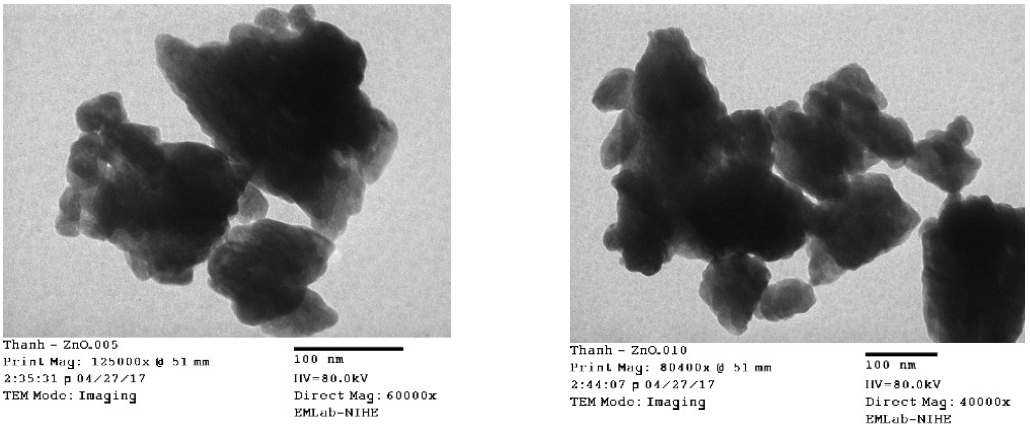

Figure 3: TEM image of the ZnO nanoparticles

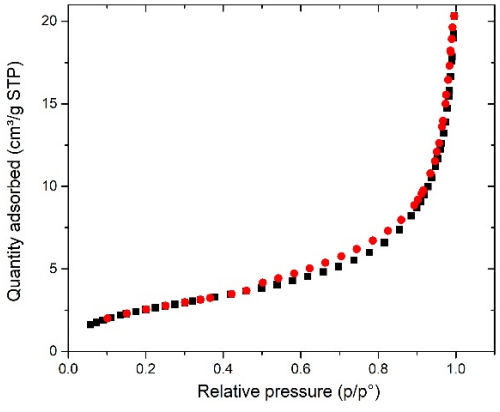

Figure 4. Nitrogen adsorption-desorption isotherms of ZnO nanoparticles

Table 1: BET surface areas, pore volume, and pore size in the ZnO nanoparticles

S_{BET} (m^2/g)[a]	Pore volume (cm^3/g)[b]	Average pore size (nm)[c]
9.7852	0.031169	11.3386

[a] BET surface area calculated from the linear part of the BET plot.

[b] BJH Adsorption cumulative volume of pores between 17.0 Å and 3000.0 Å diameter.

[c] Adsorption average pore diameter (4V/A by BET).

3.2. Adsorption kinetic

The relationship between adsorption capacity of ZnO nanoparticles and adsorption time is illustrated in Figure 5.

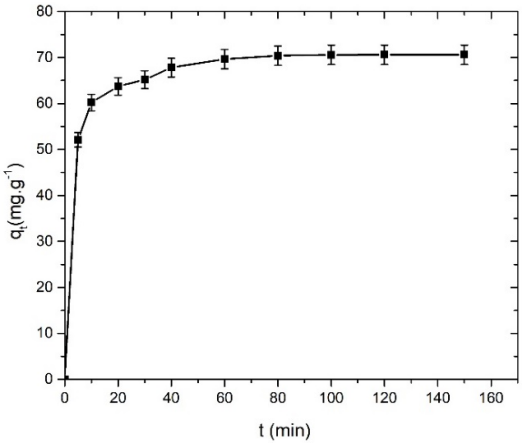

Figure 5. The relationship between adsorption capacity of congo red on ZnO nanoparticles and adsorption time (T=30^{0}C, volume: 40 mL; adsorbent dose: 0.01 g; initial congo red concentration: 100 mg/L)

The adsorption capacity sharply rises within the first 10 minutes and negligibly changes after 60 minutes. Initially, fast increase in dye adsorption may be due to availability of large number of free surface active sites onto ZnO nanoparticles for dye adsorption. After some time, the adsorption of dyes was slow and finally attained equilibrium. It may be due to the saturation of adsorbent surface and repulsive force build between dye molecules on adsorbent surface [5]. The two most common adsorption models including the pseudo-first order and pseudo-second order were applied to characterize the adsorption of congo red:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2{,}303}t$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

Where q_e and q_t (mg/g) are the amount of congo red adsorbed at equilibrium and at time t (minute); k_1(min^{-1}) and k_2(g.mg^{-1}.min^{-1}) are rate constants of the pseudo-first order and pseudo-second order. Results are showed in Figure 6 and Table 2. The values of k_1, and q_e were determined by plotting the log (q_e–q_t) versus t while the values of k_2 and q_e were obtained by plotting the t/q_t versus t. It is indicated that the adsorption of congo red by ZnO nanoparticles does not follow pseudo first order kinetics but the second order kinetics.

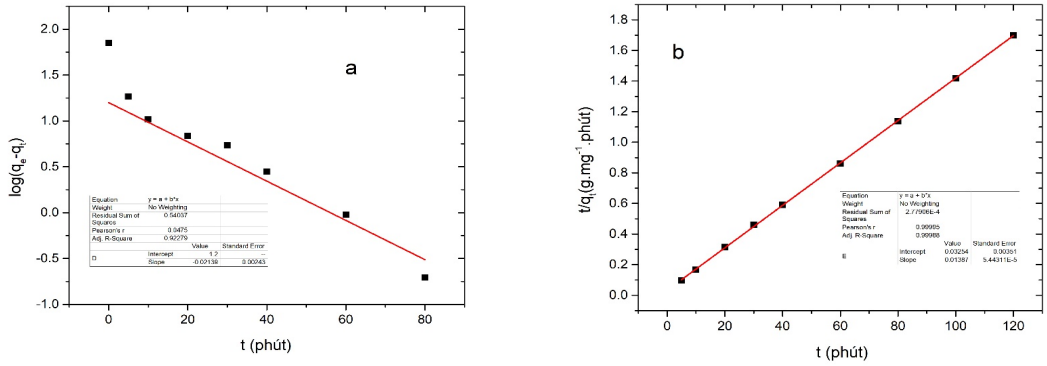

Figure 6: Pseudo-first-order kinetics (a) and pseudo-second-order kinetics (b) for congo red adsorption on the ZnO nanoparticles (T=30^{0}C, volume: 40 mL; adsorbent dose: 0.01 g; initial congo red concentration: 100 mg/L)

The regression coefficient of pseudo-second order (R^2 =0.999) is greater than that of the pseudo-first order (R^2 =0.922). The q_e (cal) value obtained from a plot between t/q_t versus t is closer to q_e (exp) value (Figure 6b, Table 2). The adsorption capacity of ZnO nanomaterials for congo red dye is calculated to be 70.59 mg/g.

Table 2: Pseudo-first-order and pseudo-second-order kinetic model constants

$q_{e\ (exp)}$	Pseudo-first-order model			Pseudo-second-order model		
	$q_{e\ (cal)}$	$k_1(min^{-1})$	R^2	$q_{e\ (cal)}$	$k_2(g.mg^{-1}.min^{-1})$	R^2
70.59	15.85	0.0493	0.922	72.09	0.0059	0.999

4. CONCLUSION

In this study, ZnO nanoparticles were successfully synthesized by precipitation method. The result of the X-ray diffraction method indicates that the ZnO nanoparticle has a wurtzite structure with the crystal size of 20 nm. Approximately, the size of spherical ZnO nanoparticles is 20-30 nm. ZnO nanomaterial was applied as adsorbent to remove congo red in aqueous solutions. The adsorption capacity of ZnO nanomaterials for congo red is 70.59 mg/g and the adsorption process follows pseudo-second-order kinetic model.

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REFERENCES

1. Hunger, K.(2003), *"Industrial Dyes: Chemistry, Properties, Applications",* Wiley-VCH, Weinheim.

2. Sanjay K. Sharma (2015), *"Green chemistry for dyes removal from wastewater: research trends and applications",* Scrivener Publishing, John Wiley & Sons.

3. R. M. Christie (2007), *"Environmental aspects of textile dyeing"*, Woodhead Publishing Limited.

4. Erol Alver, Mehmet Bulut, Ayşegül Ülkü Metin, Hakan Çiftçi (2017), *"One step effective removal of Congo Red in chitosan nanoparticles by encapsulation",* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy ,171: 132–138.

5. Nhu Thanh Nguyen, Ngoc Thinh Nguyen, Van Anh Nguyen (2020), "*In Situ Synthesis and Characterization of ZnO/Chitosan Nanocomposite as an Adsorbent for Removal of Congo Red from Aqueous Solution"*, Advances in Polymer Technology, Volume 2020, Article ID 3892694.

6. Joint Committee for Powder Diffraction Society (JCPDS), Powder Diffraction Database, Pattern: 36-1451.

7. Magdalena Blachnio, Tetyana M Budnyak, Anna Derylo- Marczewska, Adam W. Marczewski, and Valentin A. Tertykh (2018), *"Chitosan-silica hybrid composites for removal of sulfonated azo dyes from aqueous solutions"*, Langmuir, 34, 6, 2258-2273.

8. Navish Kataria, V.K. Garg (2017), "*Removal of Congo red and Brilliant green dyes from aqueous solution using flower shaped ZnO nanoparticles"*, Journal of Environmental Chemical Engineering 5 5420–5428.