CuO/ZEOLITE COMPOSITE: EFFECT OF ALKALINE ENVIRONMENT ON PHYSICOCHEMICAL PROPERTIES AND THE ADSORPTION CAPACITY OF METHYLENE BLUE

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ABSTRACT

This study presented the effect of NaOH concentrations on the synthesis of CuO/zeolite X composite (CZX). From XRD result, the characteristic peaks of zeolite X (ZX) and CuO were found. The vibrations of the above components were also shown in the FTIR results. The morphology of composite was characterized by a fairly uniform dispersion of CuO rods onto the ZX surface. The MB adsorption efficiencies of ZX and CZX3 were 58.47% and 84.15%, respectively, indicating the improvement on the adsorption ability using CZX3. At pH 7, a composite dose of 0.5 g/L, a MB concentration of 50 mg/L and contact time of 30 min, the adsorption efficiency and capacity of CZX3 reached 80.33% and 95.42 mg/g, respectively. The MB adsorption process of CZX followed the Sips model (R^2 = 0.991) and pseudo-second-order kinetic (R^2 = 0.999). The composite can be reused through three cycles with a reduction in the efficiency lower than 10% compared to the fresh composite.

CuO/ZEOLITE COMPOSITE: ẢNH HƯỞNG CỦA MÔI TRƯỜNG KIỀM ĐẾN TÍNH CHẤT LÝ HOÁ VÀ KHẢ NĂNG HẤP PHỤ METHYLENE BLUE

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TỪ KHÓA

Composite CuO/zeolite
Tro trấu
Hấp phụ
Methylene blue
Mô hình đẳng nhiệt Sips

TÓM TẮT

Nghiên cứu này trình bày sự ảnh hưởng của các nồng độ NaOH đến quá trình tổng hợp vật liệu composite CuO/zeolite X (CZX). Từ kết quả XRD, các peak đặc trưng của zeolite X (ZX) và CuO được tìm thấy. Các dao động của các thành phần trên cũng được thể hiện ở kết quả FTIR. Hình thái của vật liệu CZX được đặc trưng bởi sự phân tán khá đồng đều của các thanh CuO có hình dạng thanh trên bề mặt ZX. Hiệu suất hấp phụ MB của ZX và CZX3 lần lượt là 58,47% và 84,15%, thể hiện sự cải thiện về khả năng hấp phụ của composite so với ZX. Tại pH 7, khối lượng vật liệu 0,5 g/L, nồng độ MB 50 mg/L và thời gian 30 phút, hiệu suất và dung lượng hấp phụ của CZX3 lần lượt là 80,33% và 95,42 mg/g. Quá trình hấp phụ MB của CZX3 tuân theo mô hình Sips (R^2 = 0,991) và động học giả định bậc 2 (R^2 = 0,999). Vật liệu có khả năng tái sử dụng qua 3 chu kỳ với hiệu suất giảm nhỏ hơn 10% so với vật liệu composite ban đầu.

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1. Introduction

The development of industrialization, especially textile industry, has led to detrimental effects on aquatic environment. Wastewater generated by textile manufacturing facilities contains various toxic dyes with the stable chemical structures, which adversely impact both ecological systems and human health [1], [2]. Methylene blue (MB), a cationic organic dye, is widely utilized in many multiple industries, including textiles, leather and paper [3]. Due to its extensive application, significant amounts of MB are discharged into wastewater. Hence, it is crucial to develop effective treatment methods to mitigate its environmental impact. Adsorption is considered as a suitable option for effluent treatment because of its popularity, high efficiency, low cost and ease of implement [4]. Besides, a critical factor influencing adsorption efficiency is the choice of absorbent. Numerous materials have been documented for their capacity to remove MB including silica [4], zeolite [2], activated carbon and CuO [5]. To enhance the adsorption efficiency, composite materials have been developed. Zeolite is a widely recognized as inorganic material characterized by its porous structure, superior ion-exchange capacity and diverse applications in the removal of pollutants from aquatic environments [6]. Concurrently, CuO exhibits a strong affinity for adsorbing organic dyes [5]. Consequently, the integration of zeolite and CuO is essential for improving the adsorption efficiency of MB. Although CuO/zeolite composite has been extensively developed [7], the influence of alkaline environment on the physicochemical properties of the composite remains insufficiently explored. Because of the ratio of Cu^{2+} and OH^- significantly affected on the formation and morphology of CuO [8], it is crucial to investigate various NaOH concentrations. The objective of this work is to synthesize the CuO/zeolite X composite (CZX) using NaOH concentrations from 0.25 to 1.5M. Moreover, the MB removal efficiency of CZX is evaluated at the different adsorption conditions, including CZX dose of 0.25-2.0 g/L, MB concentrations of 10–100 mg/L and the contact time from 15 to 1440 min. The adsorption mechanism of MB is further elucidated via the adsorption isotherm and kinetics models. Finally, the regeneration possibility of CZX will be determined.

2. Materials and Methods

2.1. Materials and chemicals

Chemicals used in this work including sodium hydroxide 96%, potassium hydroxide 90%, hydrochloric acid 36–38%, aluminum powder 97%, copper sulfate pentahydrate 99%, potassium chloride 99.5%, ammonium acetate 98%, methylene blue 98.5%. These chemicals were purchased from Xilong, China. Rice husk ash (RHA) was collected in Tra Noc Industrial Park, Cantho City, Vietnam.

2.2. Synthesis of CZX composite

This work synthesized zeolite X (ZX) from RHA which uses a previously published method at a molar ratio of SiO_2:Al_2O_3 of 4:1, 5M NaOH concentration, in 4 h and 90 ^oC without aging [6]. The synthesis procedure of CZX was conducted as follows: First, a solution of $CuSO_4$ is prepared by dissolving $CuSO_4.5H_2O$ in 100 mL of deionized water within a two-neck round-bottom flask. NaOH solutions at various concentrations (0.25-1.5 M) was then added dropwise to the above solution under the stirring speed of 300 rpm at 80 ^oC for 2 h. After that, the appropriate amount of ZX was introduced, and the suspension continued to be stirred at 300 rpm in 80 ^oC. After 5 h, the solid containing CZX was collected, filtered, washed till achieving a neutral pH and subsequently dried in an oven. CZX composites synthesized at various NaOH concentrations of 0.25, 0.5, 0.75, 1.0, and 1.5 M were labeled as CXZ1, CZX2, CZX3, CZX4 and CZX5, respectively.

2.3. Characterization of CZX composites

Following the synthesis process, the physicochemical properties of CZX were characterized using X-ray diffraction (XRD, Empyrean, PANalytical), Fourier transform infrared spectroscopy

(FTIR, Jasco FT-IR 4600) and scanning electron microscopy (SEM, JCM 7000, JEOL). The point of zero charge (pH_{pzc}) of CZX was also assessed by immersing 0.02 g of CZX in 20 mL of 0.1 M KCl solution at various pH levels (from 3 to 10) within 24 h. The pH of solutions was adjusted using 0.05 M HCl or 0.05 M KOH. After 24 h, the differences of pH between the initial and final solutions were measured to determine the pH_{pzc} of CZX.

2.4. Potential CV adsorption of CZX

The effect of various CZX doses between 0.25 and 2.0 g/L on the MB removal was investigated as follows: a specific amount of CZX and 25 mL of 50 mg/L MB solution at pH 7 are placed in a 100 mL Erlenmeyer flask and are shaken at 200 rpm. After 30 min, adsorbents were separated by centrifugation (Centrifuge Smart 15 Plus – Hanil, Korea) and the absorbance of solution was measured via a UV-vis spectrophotometer (Multiskan SkyHigh, Thermo Fisher Scientific) at the maximum wavelength of 664 nm. Additional adsorption parameters including MB concentrations (10 – 100 mg/L) and the contact time (15 – 1440 min) were similarly assessed to evaluate the effect of adsorbent doses. The adsorption efficiency (AE, %) and capacity (AC, mg/g) were calculated using equation (1) and equation (2).

$$\text{AE (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

$$\text{AC (mg/g)} = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

whereas C_o (mg/L) and C_t (mg/L) are the initial MB concentration and MB concentration at time t, respectively; V (L) is the MB volume used and m (g) is the weight of CZX.

The adsorption mechanism was proposed using the correlation between experimental and calculated data from the adsorption isotherm and kinetics models as shown in Table 1. This study used Langmuir model which was represented the assumptions of monolayer and homogeneous adsorption. The Freundlich model suggested the mechanisms of multilayer and heterogeneous adsorption while the Sips model better exhibited a realistic adsorption process because of the combined assumptions of Langmuir and Freundlich [9]. To support the adsorption mechanisms, kinetic models were also used, the agreement between the experimental data and the two kinetic models indicated whether the mechanism was mainly chemical or physical adsorption [10].

2.5. Regeneration of CZX composite

The regeneration of CZX composite was evaluated via the collection of adsorbents at the optimal adsorption condition. For the desorption process, CZX composites were rinsed with the solution of CH_3COONH_4 0.2 M at the ratio of solid and liquid = 1:2 (g : mL) during 30 min [1]. The obtained CZX was then dried until the constant weight and used for the next adsorption cycles.

3. Results and discussion

3.1. Properties of CZX composite

Figure 1a illustrated the synthesized materials including CZX1, CZX2, CZX3, CZX4 and CZX5. Reduction processes were incomplete due to low pH levels (at 4 and 5), resulting in the blue coloration of solutions corresponding to CZX1 and CZX2. It implied that lower NaOH concentrations of 0.25 M and 0.5 M were insufficient to reduce Cu^{2+} ions in the solution to CuO. Conversely, an increase in NaOH concentrations of 0.75 M (pH 8), 1.0 M (pH 10) and 1.5 M (pH 14) caused a color change from blue to black. The study aimed to successfully synthesized composites whose main components were CuO and zeolite, based on observations and pH values of the reaction system; thus, CZX3, CZX4 and CZX5 were selected for further characterization. XRD patterns of composites at NaOH concentrations of 0.75 to 1.5 M were compared to the standard cards of ZX and CuO [6], [7], as shown in Figure 1b. Consequently, the phase composition of CZX comprised both ZX and CuO. Some typical peaks of ZX were observed at

2θ: 6.17°; 10.05°; 11.79°; 15.46°; 18.46°; 20.11°; 23.21°; 26.60° and 30.98°, remaining consistent throughout the synthesis process. Moreover, peaks corresponding to CuO were detected at 2θ: 32.61°; 35.58°; 38.73°; 46.40°; 48.82°; 51.63°; 53.25°; 56.46°; and 58.27° in CZX3, CZX4 and CZX5. These findings confirmed the presence of both ZX and CuO in composites, indicating the success of the synthesis method. Figure 1c indicated the FTIR spectra of CZX3, CZX4 and CZX5 composites. The presence of water molecules both on the surface and within the composite structure, was evidenced by the vibrations of the OH groups observed at 3467 cm^{-1} and 1642 cm^{-1} [8]. The spectral region from 500 to 1000 cm^{-1} corresponded to the characteristic vibrations of the tetrahedral units within the ZX structure [1]. Moreover, the vibrations associated with CuO were detected at wavenumbers below 500 cm^{-1} [8]. The FTIR results confirmed that the presence of ZX and CuO within the composite. Interestingly, despite varying NaOH concentrations, the characteristic vibrations of composite were consistently maintained, with no significant differences observed.

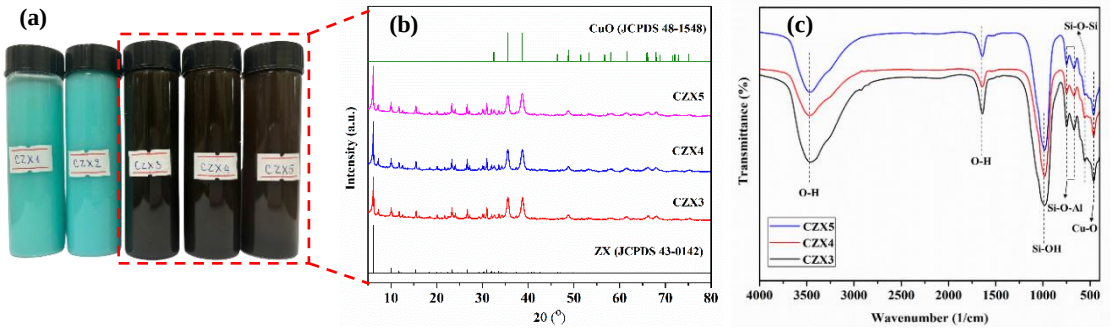

Figure 1. *(a) The obtained CZX composites at different NaOH concentrations; (b) XRD patterns and (c) FTIR spectra of CZX composites at different NaOH concentrations*

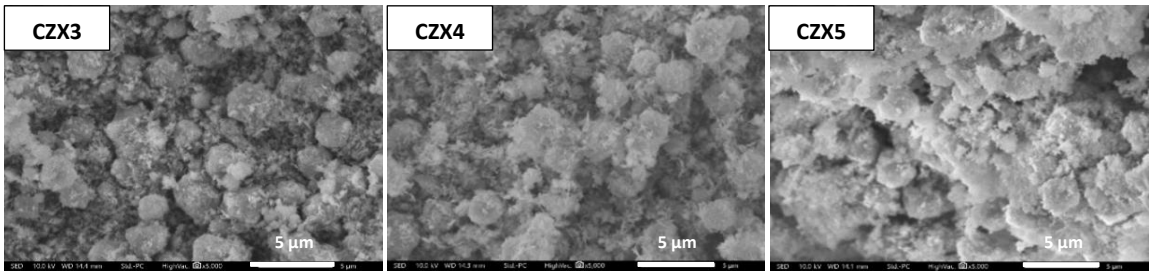

Figure 2. *SEM images of CZX composites at different NaOH concentrations*

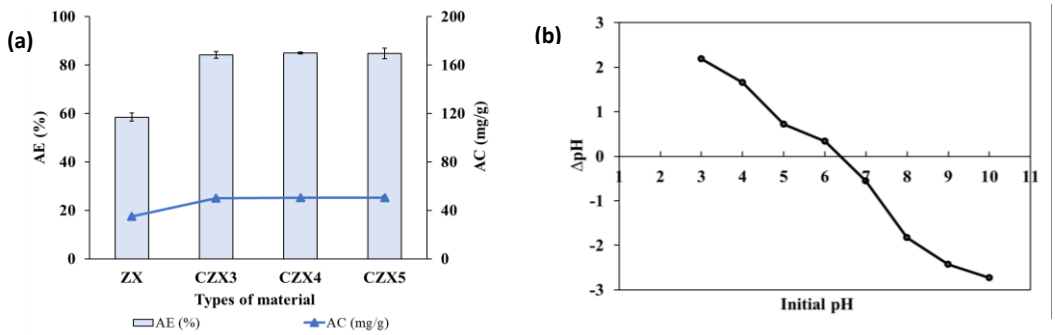

Figure 3. *(a) The potential CV adsorption of ZX and CZX composites and (b) pH_{pzc} of CZX3 composite*

The morphologies of CZX3, CZX4 and CZX5 were shown in Figure 2. The hexagonal structure of ZX exhibited numerous surface porosities, which played as sites for the random adherence of CuO crystals [7]. At an optimal NaOH concentration of 0.75 M, CuO was uniformly distributed on the surface of ZX. However, the CuO agglomeration areas were created

on the ZX surface when increasing the NaOH concentration to 1.0 M. Further increasing the NaOH concentration to 2.0 M led to the formation of CuO arrays that overlapped the entire surface of ZX. Similar morphologies of CuO crystal have been also reported in previous studies [8]. The effectiveness of MB removal using ZX and CZX composites was evaluated under specific adsorption conditions such as pH 7, a dose of 1 g/L, a MB concentration of 50 mg/L within 30 min (Figure 3a). AEs increased from 58.4 to 84.15% and ACs also rose about 1.5 times (between 34.73 and 49.98 mg/g) using CZX3 instead of ZX. At higher NaOH concentrations, insignificant differences in AEs and ACs were observed. The combination of CuO and zeolite created more adsorption sites than single-phase zeolite, improving the AE and AC. Raising the NaOH concentration did not show significant changes in properties and MB adsorption capacity of the composite. Thus, CZX3 was chosen as the optimal composite for the further adsorption studies. The pH_{pzc} of CZX3 was determined to be 6.38 (Figure 3b), indicating that at pH value above 6.38, CZX3 acquired a negative charge, and conversely, it possessed a positive charge below this threshold. Hence, the MB adsorption process was conducted at pH 7.

3.2. The adsorption study of MB removal using CZX

The adsorbent dose is a crucial parameter influencing adsorption ability. In this work, the adsorbent doses varied from 0.25 to 2.0 g/L (Figure 4a). AEs increased between 72.68 and 91.80% while ACs dropped by 84.21% (from 172.67 to 27.26 mg/g). Higher adsorbent doses resulted in higher AEs due to improved interactions between adsorption sites and MB^+ ions within the system [5]. Conversely, a lower adsorbent dose of 0.25 g/L caused a reduction in AEs. At lower adsorbent loadings (between 0.25 and 0.5 g/L), the MB molecules tended to occupy available adsorption sites, leading a reduction in the effective excess of adsorption sites [2]. The decreasing tendency of ACs was due to the excess of adsorption sites. In an adsorption system with high dosage, many empty sites cause a waste of adsorbent [2]. This produced the high ACs of 172.67 mg/g and 95.42 mg/g, respectively. To optimize the correlation between ACs and AEs and minimize the waste of adsorbent, a CZX3 dose of 0.5 g/L was selected for subsequent experiments.

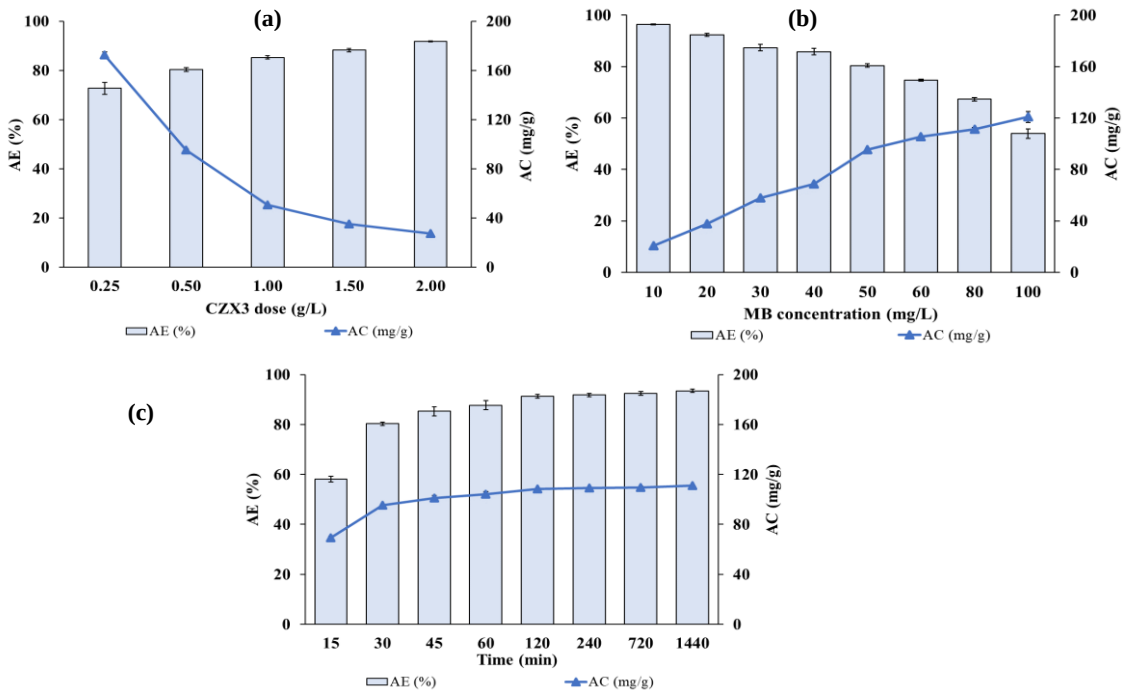

Figure 4. *The MB adsorption of CZX3 composite at various conditions: (a) adsorbent doses; (b) MB concentrations and (c) contact time*

The effect of MB concentrations on the MB removal using CZX3 was also found in Figure 4b. At lower MB concentrations (10–20 mg/L), AEs exceeded 90% after 30 min. However, at higher MB concentrations, AEs dramatically declined from 87.35 to 53.91% due to the saturation of adsorption sites caused by an excess of MB molecules in the solution [1], [5]. Within the MB concentration range from 10–100 mg/L, ACs increased six-fold from 20.63 to 120.74 mg/g. This increase was attributed to the full occupation of adsorption sites by MB molecules, leading elevated ACs at high MB concentrations [11]. Consequently, the optimal conditions were observed at an MB concentration of 50 mg/L, yielding an AE of 80.33% and an AC of 95.42 mg/g. The variations in ACs and AEs at various contact time from 15 to 1440 min was described in Figure 4c. At 15 min, both AEs and ACs significantly increased and achieved at 58.20% and 69.13 mg/g, respectively. After 30 min, the AE and AC rose by 22.13% and 27.55%, respectively and ultimately reached equilibrium at 120 min. The MB removal using CZX3 was effectively conducted under conditions of 0.5 g/L CZX3 dose, a MB concentration of 50 mg/L over 30 min.

3.3. Adsorption isotherm and kinetics models

The experimental and calculated data for the isotherm and kinetics models were summarized in Table 1. The correlation coefficients (R^2) indicated that the Sips model (R^2 = 0.991) provides a better fit than the Langmuir model (R^2 = 0.985) and the Freundlich model (R^2 = 0.941). Based on these R^2 values, the MB adsorption of XCZ3 was the closest to the Sips model, which suggested a maximum AC of 130.84 mg/g. The highest R^2 of Sips model implied that the removal of MB happens via both monolayer and multilayer adsorption mechanisms [9]. The adsorption intensity n = 0.76 from Sips model indicated that the monolayer adsorption predominates in the MB adsorption mechanism of CZX3. Furthermore, the adsorption process also took place on a uniform surface with independent adsorption sites, showing no interaction between them [1]. The Freundlich model also partially contributed to the MB adsorption mechanism, suggesting the presence of heterogeneous surfaces and interactions among adsorption sites [10]. The adsorption intensity of 0.76 observed in this study indicated a favorable adsorption process [9].

Table 1. *Parameters of adsorption isotherm and kinetics models*

Isotherm models			
Model	**Nonlinear equation**	**Parameter**	**Meaning**
Langmuir	$q_e = \frac{q_{max} \times K_L \times C_e}{1 + K_L \times C_e}$ (3) $R_L = \frac{1}{1 + K_L \times C_e}$ (4)	K_L = 0.22 L/mg q_{max} = 130.84 mg/g $0.08 \le R_L \le 0.92$ R^2 = 0.985	q_e and q_{max}: equilibrium and maximum ACs; K_L: the Langmuir empirical constant; R_L: Langmuir parameter
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$ (5)	K_F = 40.14 L/g n = 3.23; R^2 = 0.941	K_F: Freundlich constant; n: the adsoprtion intensity
Sips	$q_e = \frac{q_s \times a_s \times C_e^n}{1 + a_s \times C_e^n}$ (6)	q_S = 148.62 mg/g a_S = 0.24; n = 0.76 R^2 = 0.991	q_S: the maximum adsorption capacity of Sips model; a_S: the Sips isotherm model constant; n: the adsorption intensity
Kinetics models			
Model	**Nonlinear equation**	**Parameter**	**Meaning**
Pseudo first order (PFO)	$q_t = q_e \times \left(1 - e^{(-k_1 \times t)}\right)$(7)	k_1 = 0.068 1/min q_e = 105.09 mg/g R^2 = 0.929	q_e and q_t: equilibrium adsorption capacity and adsorption capacity at time t; k_1: PFO rate constant; t (min): adsorption time
Pseudo second order (PSO)	$q_t = \frac{q_e^2 \times k_2 \times t}{1 + q_e^2 \times k_2 \times t}$ (8)	k_2 = 0.001 g/mg.min q_e = 113.79 mg/g R^2 = 0.999	k_2: PSO rate constant; t: the adsorption time

The R^2 values of PFO and PSO models demonstrated a strong correlation between experimental and calculated data, with the PSO exhibiting a higher R^2 value. The equilibrium AC predicted by the PSO model was 113.79 mg/g, which was close to the experimental AC (about 111 mg/g at 1440 min), whereas the calculated AC from the PFO model was 105.09 mg/g. Moreover, the adsorption followed the PSO model suggested that charge sharing occurs between CZX3 and MB molecules, highlighting the electrostatic interaction between them [10]. The relative low PSO rate constant k_2 further reflected a rapid adsorption process of CZX3 toward MB. Because k_2 was inversely proportional to AC, suggesting that the adsorption process reached the equilibrium faster [2]. As a result, the MB adsorption process of CZX3 was characterized as a combination of both monolayer and multilayer adsorption, with electrostatic interactions serving as the predominant mechanism facilitating the effective adsorption of MB^+ cation onto the negatively charged surface of CZX3.

3.4. The regeneration of CZX

After recycling CZX3 using a 0.2 M CH_3COONH_4, AEs of MB were reported in Figure 5a. CH_3COONH_4 was selected as a desorbing agent because NH_4^+ ions could compete with MB^+ ions. The main adsorption mechanism was the electrostatic interaction of negatively charged sites on the composite and the MB^+. Thus, MB^+ adsorbed CZX was agitated in NH_4^+ solution, MB^+ molecules tended to diffuse from the composite surface back to the solution due to the competitive adsorption of NH_4^+, partially desorbing MB molecules on the composite surface [1]. At the second and third cycles, AEs decreased by 4.65% and 7.65%, compared to that of first cycle. This reduction can be predicted that the desorption process was incomplete, leaving some inactive adsorption sites. After three regeneration cycles, AEs dropped by about 10%, indicating the potential for CZX to be reused in the removal of organic dyes from aqueous solutions.

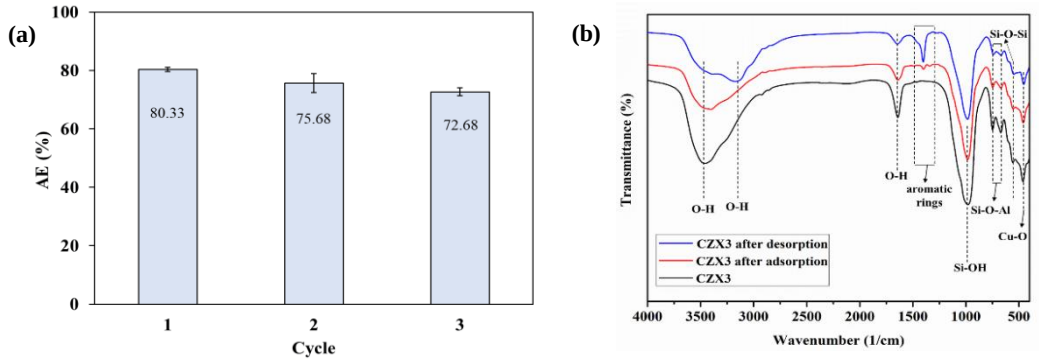

Figure 5. *(a) Potential regeneration of CZX3 composite,*
(b) FTIR spectra of fresh CZX3, adsorbed CZX3 and desorbed CZX3

Table 2. *Comparison of the MB adsorption between CZX3 and previous materials*

Adsorbents	Adsorption condition	$^*q_{max}$ (mg/g)	References
Zeolite	pH 7; 0.5 g/L dosage; MB concentration of 50 mg/L; 180 min	27.05	[12]
Zeolite ZSM-5	pH 7; 0.5 g/L dosage; MB concentration of 50 mg/L; 180 min	105.82	[11]
Zeolite A	pH 7; 0.781 g/L dosage; MB concentration of 10 mg/L; 179.82 min	44.35	[13]
Zeolite X	pH 8; 1.7 g/L dosage; MB concentration of 15 mg/L; 30 min	16.67	[2]
CuO/silica	pH 7; 0.5 g/L dosage; MB concentration of 36 mg/L; 20 min	87.80	[4]
CuO/activated carbon	pH 7; 0.1 g/L dosage; MB concentration of 10 mg/L; 30 min	54.73	[5]
CuO/activated carbon	pH 6; 1.2 g/L dosage; MB concentration of 30 mg/L; 60 min	141.73	[14]
CZX3	pH 7; 0.5 g/L dosage; MB concentration of 50 mg/L; 30 min	130.84	This work

$^*q_{max}$: the maximum AC followed the Langmuir model

The MB adsorption and desorption processes were further examined through FTIR analysis, as shown in Figure 5b. The characteristic vibrations of the CZX3 composite almost retained, indicating the stability of the composite after undergoing both adsorption and desorption. However, shifts in the vibrations were observed compared to the fresh CZX3, with several new peaks from 1300–1500 cm^{-1} range, confirming the presence of aromatic rings associated with MB [1]. This finding demonstrated that the CZX3 composite effectively adsorbs MB while still maintaining its structural integrity. Table 2 summarized the potential for MB removal using CZX3 in comparison to other adsorbents. Numerous types of zeolites have exhibited the maximum ACs from 16.67 to 105.82 mg/g [2], [9], [12]. Additionally, composites including CuO along with silica or activated carbon also had the large ACs with varying adsorbent doses between 0.1 and 0.5 g/L [4], [5]. The highest AC of obtained CZX composite in this study was 130.84 mg/g at an adsorbent dose of 0.5 g/L, indicating its promising potential for addressing dye pollution.

4. Conclusion

This work successfully synthesized the CZX composite and assessed the effect of NaOH concentrations on its physicochemical properties via XRD, FTIR and SEM techniques. The CZX3 composite revealed a superior AE of MB attributable to the synergistic interaction between CuO and ZX. The AE and AC achieved at 80.33% and 95.42 mg/g, respectively at pH 7, a CZX3 dose of 0.5 g/L, a MB concentration of 50 mg/L within 30 min. The MB adsorption mechanism of CZX3 composite was characterized by a combination of monolayer adsorption and predominant electrostatic interactions. Furthermore, the CZX3 composite was successfully regenerated, achieving an AC of 72.67% in the third cycle.

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