TREATMENT OF MALACHITE GREEN IN AQUEOUS SOLUTION USING CHITOSAN/PECTIN/SiO_2 COMPOSITE

Tran Nguyen Phuong Lan[1*], Nguyen Le Hue Tran[1], Ly Kim Phung[1], Le Duc Duy[1], Nguyen Hong Nam[2], Tran Thi Minh Thu[3], Nguyen Trong Hong Phuc[1], Nguyen Minh Nhut[1]
[1]Can Tho University, [2]University of Science and Technology of Ha Noi – VAST, [3]Can Tho University of Technology

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ABSTRACT

The synthesis process of chitosan/pectin/SiO_2 composite (CPS) was performed under the following conditions: mass ratio of chitosan/pectin (CP):SiO_2=1:1.5 (g/g), mixing time of 0.5 h at room temperature. In this work, pectin was extracted from pomelo peel while rice husk ash was used for silica recovery. The obtained CPS were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Field emission scanning electron microscopy (FE-SEM). The typical functional groups of CP and SiO_2 are fully appeared in CPS. Malachite green (MG) was used in this work to evaluate the dye removal possibility of CPS at pH 7, a MG concentration of 60 mg/L, a MG dosage of 1 g/L, and an adsorption time of 30 min. The MG adsorption capacity and adsorption efficiency are 61.3 mg/g and 75.93%, respectively. The MG adsorption process is consistent with the Langmuir and Sips isotherm adsorption models, meaning the adsorption takes place homogeneously, monolayer, independently and is physical adsorption. Besides, the kinetics of the MG adsorption process follows the pseudo 2nd order kinetic model. As a result, the CPS is a potential composite for treating MG dye in an aqueous solution.

XỬ LÝ MALACHITE GREEN TRONG NƯỚC BẰNG VẬT LIỆU COMPOSITE CHITOSAN/PECTIN/SiO_2

Trần Nguyễn Phương Lan[1*], Nguyễn Lê Huế Trân[1], Lý Kim Phụng[1], Lê Đức Duy[1], Nguyễn Hồng Nam[2], Trần Thị Minh Thư[3], Nguyễn Trọng Hồng Phúc[1], Nguyễn Minh Nhựt[1]
[1]Trường Đại học Cần Thơ; [2]Trường Đại học Khoa học và Công nghệ Hà Nội - Viện Hàn Lâm Khoa học và Công nghệ Việt Nam, [3]Trường Đại học Kỹ thuật Công nghệ Cần Thơ

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TỪ KHÓA

Chitosan/pectin/SiO_2
Tro trấu
Vỏ bưởi
Malachite green
Hấp phụ

TÓM TẮT

Nghiên cứu này trình bày quy trình tổng hợp composite chitosan/pectin/SiO_2 (CPS) ở nhiệt độ phòng, với tỷ lệ khối lượng chitosan/pectin (CP):SiO_2 = 1:1.5 (g/g), thời gian khuấy trộn 0,5 giờ. Trong nghiên cứu này, pectin được trích ly từ vỏ bưởi và tro trấu được sử dụng để thu hồi SiO_2. Các CPS được đánh giá đặc trưng bằng phương pháp nhiễu xạ tia X (XRD), phổ biến đổi hồng ngoại Fourier (FTIR), và kính hiển vi quét điện tử (SEM). Các nhóm chức đặc trưng của pectin, chitosan và SiO_2 đều xuất hiện đầy đủ trong thành phần của CPS. Thí nghiệm hấp phụ xử lý malachite green (MG) được thực hiện ở pH 7, nồng độ MG 60 mg/L, khối lượng CPS 1 g/L, thời gian hấp phụ 30 phút. Dung lượng và hiệu suất hấp phụ MG lần lượt là 61,3 mg/g và 75,93%. Quá trình hấp phụ MG phù hợp với mô hình hấp phụ đẳng nhiệt Langmuir và Sips, sự hấp phụ diễn ra đồng nhất, đơn lớp, độc lập và là hấp phụ vật lý. Ngoài ra, động học của quá trình hấp phụ tuân theo mô hình động học giả kiến bậc hai. Vì vậy, CPS là vật liệu composite tiềm năng được ứng dụng để xử lý thuốc nhuộm MG trong môi trường nước.

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* Corresponding author. *Email: tnplan@ctu.edu.vn*

1. Introduction

Various kinds of dye and pigment are extensively developed globally because of their wide applications. Typically, more than 0.7 million ton of synthesized dyes are produced annually, about 200,000 tons of dye are released to environment [1]. Malachite green (MG), a cation organic dye can cause several harmful diseases such as jaundice, blood clots and gastrointestinal irritation [2]. In Vietnam, rice husk, generated through rice producing, is mainly used as an energy source via burning. Its by-product is rice husk ash (RHA), which is a rich source of SiO_2 [3]. Chitosan, a product of chitin deacetylation, is found in the shells of shrimp, crap, and etc. and applied in many fields such as biotechnology, agriculture, cosmetic, food processing, and wastewater treatment [4]. Pectin, a group of polysaccharides in the plant cell wall, is composed of covalent bonding of D-galacturonic acid units. The mesocarp of pomelo peel is accounted for about 30 wt.% of fruit, which is used as the feedstock for pectin recovery. Chitosan/pectin (CP) composite with pectin originated from pomelo peel and application for methylene blue removal was investigated with the adsorption efficiency and capacity of 63.54% and 6.345 mg/g, respectively at a weight ratio of C and P of 1:9 [5]. Additionally, a composite of chitosan/SiO_2 was used for adsorbing heavy metals like Cu(II), Cr(VI) and Pb(II) [4]. Using nano chitosan/SiO_2 for the CO_2 adsorption reported a maximum adsorption capacity of 4.39 mmol/g [6]. The adsorption mechanism was demonstrated by using the experiment between carbon micro-particles and turmeric solution [7]. The maximum adsorption efficiency of MG between 95.6% and 98.3% by using *Sargassum crassifolium* was performed at the optimal condition: pH 8.0, 25 °C, biomass dose of 2.0 g during 150 min [8]. This study aimed to synthesize a composite (CPS) including CP and SiO_2 and evaluate its adsorption capacity towards MG cation dye. To improve the efficiency of MG adsorption, the CPS synthesis parameters such as the weight ratio of CP and SiO_2, stirring temperature and time were investigated. The possible MG adsorption mechanism of CPS was predicted using the adsorption isotherm models (Langmuir, Freundlich and Sips) and pseudo first and second order adsorption kinetic models.

2. Materials and Methods

RHA used in this study was collected from Tra Noc Industrial Park, Can Tho city. Sodium hydroxide (96%), hydrochloric acid (36-38%), citric acid (99.5%), acetic acid (99.5%), ethanol (96%), potassium chloride (99%), and malachite green ($C_{23}H_{25}ClN_2$) were provided by from Xilong (China). Chitosan (medium molecular weight, with a degree of deacetylation of 87%). Pomelo peels were collected at a local market in Can Tho city.

2.1. Synthesis of CPS composite

The CP synthesis procedure was adopted from the previous study [5]. The pectin extraction was carried out with a pomelo peel:citric acid (0.14 M) amount of 1:20 g/mL at 95^{o}C for 60 min. The extraction yield was 18%. Moreover, the CP composite was generated at a weight ratio of chitosan to pectin of 9:1 at room temperature (RT). Chitosan solution was prepared by dissolving 0.1 g of chitosan in 10 mL 5% acetic acid solution, while 0.9 g of pectin was put into 90 g deionized water to obtain the pectin solution [5]. SiO_2 was extracted using RHA and 5 M NaOH at a ratio of 1:10 g/mL for 3 h at 90^{o}C [9]. The suspension was then filtrated to remove solid, the aqueous mainly contains sodium silicate. After that, 3 M HCl solution was added dropwise to previous solution at a ratio of 9:20 v/v at RT until white precipitate appeared. SiO_2 powder was obtained by filtration and washing of suspension to neutral pH and dried at 60^{o}C. The CPS synthesis was processed as follows: Slowly added a certain weight of SiO_2 into the pectin solution at RT and stirred at 500 rpm for 1 h to obtain solution 1. Chitosan solution was added to the above solution. The obtained solution was then neutralized using 1 M NaOH, CPS was collected after filtration, washing and drying at 60^{o}C. This work investigated synthesis

parameters including the weight ratio of CP:SiO_2 = 1:0.5 – 1:3 (g/g), stirring temperature from RT to 90°C, and time from 0.25 – 4 h.

2.2. Characterization of CPS composite

CPS were characterized using X-ray diffraction (XRD, Empyrean, PANalytical), Fourier transform infrared spectroscopy (FTIR, MIR/NIR Frontier, PerkinElmer), and Field emission scanning electron microscopy (FE-SEM, Hitachi S-4800).

2.3. Evaluation of MG removal using CPS composite

Point of zero charge of CPS (pH_{pzc}) was determined via the difference of pH values in which adsorption of H^+ and OH^- ions on the CPS surface in 24 h. Briefly, 0.1 g of CPS and 25 mL of 0.1 M KCl were prepared. The pH value of each solution was adjusted from 3 to 12 using 0.1 M KOH or 0.1 M HCl. All experiments in this work were triplicated. The MG adsorption process was performed as follows: adsorbent dose (0.5 - 4.0 g/L), MG concentration (10 - 100 mg/L), and adsorption time (15-1440 min). The MG concentrations before and after adsorption were determined using an Evolution 60S UV-Visible Spectrophotometer (Thermo, USA) at λ_{max}= 617 nm [10]. The adsorption capacity (AC) and efficiency (AE) were calculated as follows:

$$AC = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

$$AE = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

whereas C_o (mg/L) and C_t (mg/L) are initial concentration and concentration at time t, respectively, V (L) and m (g) are solution volume and adsorbent weight, respectively.

3. Results and discussion

3.1. Synthesis of CPS composite

3.1.1. Effect of weight ratio of CP and SiO_2

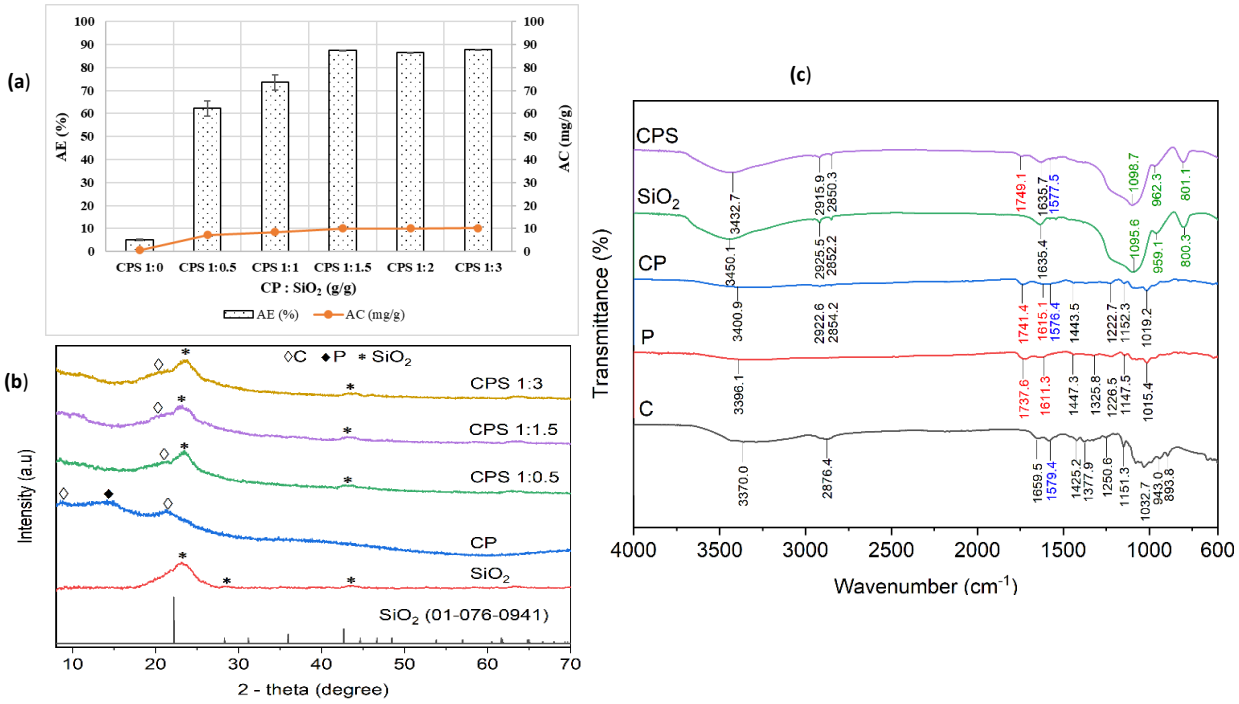

Figure 1. *Effect of weight ratio of CP and SiO_2 to MG adsorption (a); XRD pattern of CPS at different weight ratios (b); FTIR of pectin (P), chitosan (C), CP, SiO_2, CPS (c)*

Figure 1a reveals the MG adsorption process of CPS at a CP: SiO_2 weight ratio =1:0 to 1:3 g/g. The AE increases about 82.65% with the presence of SiO_2; thus, MG^+ cation could easily attach on the CPS surface via electrostatic interaction. The AE and AC remains unchanged at the weight ratio of 1:1.5 - 1:3.0 because the SiO_2 amount adhered on CPS is saturated. Thus, a suitable weight ratio of 1:1.5 g/g is selected for the next experiments.

The characteristic peak of SiO_2 found at $2\theta = 23.11^o$ and 43.6^o (Figure 1b) proves that amorphous phase of SiO_2 is the major phase in CPS following the standard card 01-076-0941 [11]. Chitosan and pectin in CP has amorphous phase and are identified at $2\theta = 9^o$ and 21^o (for chitosan) and 14^o (for pectin), respectively [12]. CPS obtained at various weight ratio of CP: SiO_2 has all of characteristic peaks of chitosan and SiO_2; however, the peak intensity of SiO_2 decreases and characteristic peak of pectin at $2\theta = 14^o$ disappears due to the shield of chitosan and SiO_2 in CPS. The presence of pectin, chitosan and SiO_2 in CPS are determined using FTIR (Figure 1c). The vibration of O-H and N-H at 3450.1-3370.0 cm^{-1} is overlapped, leading to difficult detection of N-H bonding. The bending vibration at 1579.4-1576.4 cm^{-1} belonged to N-H bonding in chitosan [13]. The presence of adsorption peaks at 1749.1-1737.6 cm^{-1} and 1615.1; 1611.3 cm^{-1} in pectin, CP and CPS, respectively is determined as C=O ($COOCH_3$) and C-O (COOH) in ester groups of pectin. Besides, C-H, -CH_3, C-O groups of ether, belong to polysaccharide, are identified at 2925.5-2850.3 cm^{-1}; 1447.3-1425.2 cm^{-1} and 1152.3-1147.5 cm^{-1} [14]. For SiO_2 identification, some peaks at 1095.6 cm^{-1} and 1098.7 cm^{-1} are the asymmetrical stretching vibration of Si-O-Si. Moreover, wavenumber of 959.1 and 962.3cm^{-1} are characteristics of stretching vibration of Si-OH while the symmetrical stretching vibration of Si-O is found at peaks of 800.3 and 801.1 cm^{-1} [15]. These above vibrations prove that CPS composite has been successfully synthesized with the full presence of pectin, chitosan and SiO_2.

3.1.2. Effect of stirring condition

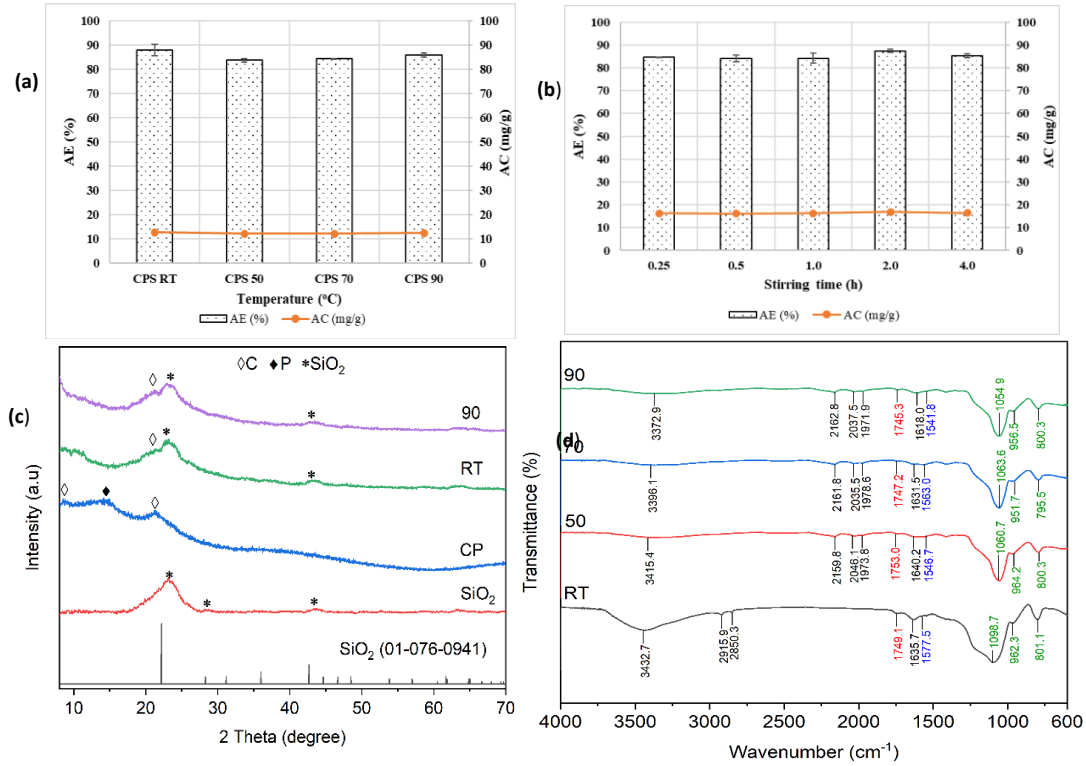

Figure 2. *Effect of stirring temperature (a) and time (b) on MG adsorption; XRD pattern of CPS at 90°C and RT, CP and SiO_2 (c); FTIR results of CPS at RT to 90°C (d)*

A stirring temperature change from RT to 90°C (Figure 2a) does not help enhance the MG adsorption of CPS. This indicates that temperature has no effect on the CPS synthesis. The effect of stirring time for CPS synthesis (0.25 - 4 h) on the AE and AC is shown in Figure 2b. As can be seen, prolonging stirring time does not change the MG adsorption efficiency and the presence of SiO_2 in CP improves the MG removal. The XRD pattern of CPS at different synthesis conditions in Figure 2 reveals the full characteristic peaks of SiO_2 and chitosan at $2\theta = 23.11^o$ and 21^o. However, the diffraction peak of pectin at $2\theta = 14^o$ disappears in the composite synthesized at 90 and that of RT due to the shield of chitosan and SiO_2 [12]. Hence, RT and 0.5 h are chosen in order to ensure the completion of CPS and save energy for the synthesis process. In addition, FTIR results (Figure 2d) at different stirring temperature exposes full characteristic groups of CPS. The appearance of 1753.0 – 1745.3 cm^{-1} is C=O bonding of pectin while the bending vibration of N-H group of chitosan is found at 1577.5-1541.8 cm^{-1}. Asymmetrical stretching vibration of Si-O-Si is identified at peaks of 1095.6 cm^{-1} and 1098.7 cm^{-1}. Stretching vibration of Si-OH and asymmetrical stretching vibration Si-O can be seen at 959.1-962.3cm^{-1} and 800.3-801.1 cm^{-1}, respectively. There is a difference of SiO_2 and CPS in SEM images (Figure 3). Many different shapes of SiO_2 are formed like spherical, irregular rods and microscopic scales, proving the major amorphous phase which agrees with the XRD result [8]; meanwhile, the CPS surface has large rough scales which are irregularly agglomerated. Besides, its surface also has less holes and canals confirming that the SiO_2 is covered by CP composite [16]. Figure 4 proposes a mechanism of CPS synthesis via the formation of hydrogen bond and electrostatic attraction between SiO_2, chitosan and pectin.

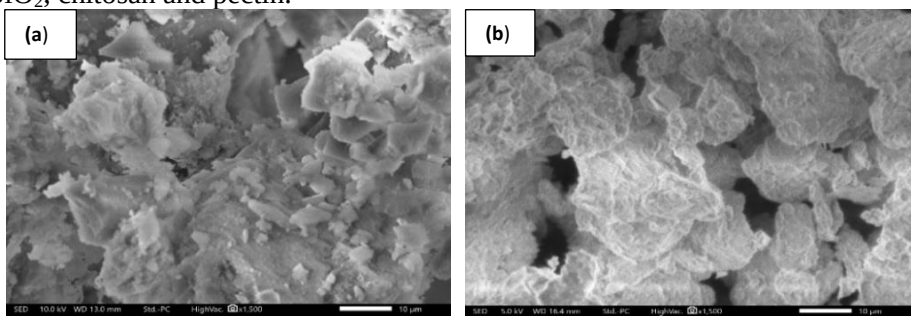

Figure 3. *SEM images of SiO_2 (a) and CPS (b)*

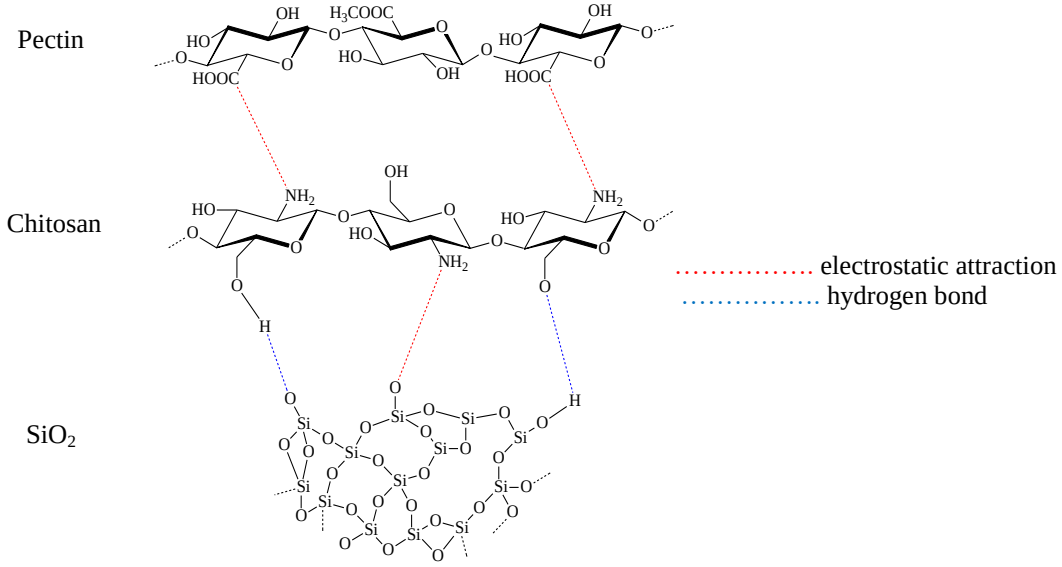

Figure 4. *The proposed mechanism of CPS formation*

3.2. Evaluation on MG adsorption capacity of CPS

The pH_{pzc} of CPS is 5.84 (Figure 5a). At pH>5.84, the CPS surface is negatively charged and versa; thus, MG adsorption favorably happens with pH>pH_{pzc}. The competition between H^+ ion and MG^+ cation occurs at acid environment, leading to an unfavorable adsorption process. For practical application, this work chooses adsorption condition at neutral pH because pH of dye effluent into the aquatic environment is mostly at 7-8. Firstly, the effect of adsorbent dose from 0.5 to 4.0 g/L (Figure 5b) on MG adsorption reports an increase of AE by 30.05% (62.84% - 92.89%) owing to more active sites of CPS at higher amount of adsorbent used. Particularly, at CPS dose from 0.5 to 3.0 g/L, the AE significantly increases between 62.84% and 91.82% and keeps unchanged at adsorbent loading of 3-4 g/L because the MG adsorption reaches equilibrium. In contrast, the AC decreases by 79.96 mg/g (98.09 – 18.13 mg/g) at adsorbent loading from 0.5 to 4 g/L. At low amount of adsorbent used, adsorption happens quickly, leading to easy diffusion of MG^+ on the CPS surface and vice versa. The adsorbent dose of 1 g/L is used for other experiments.

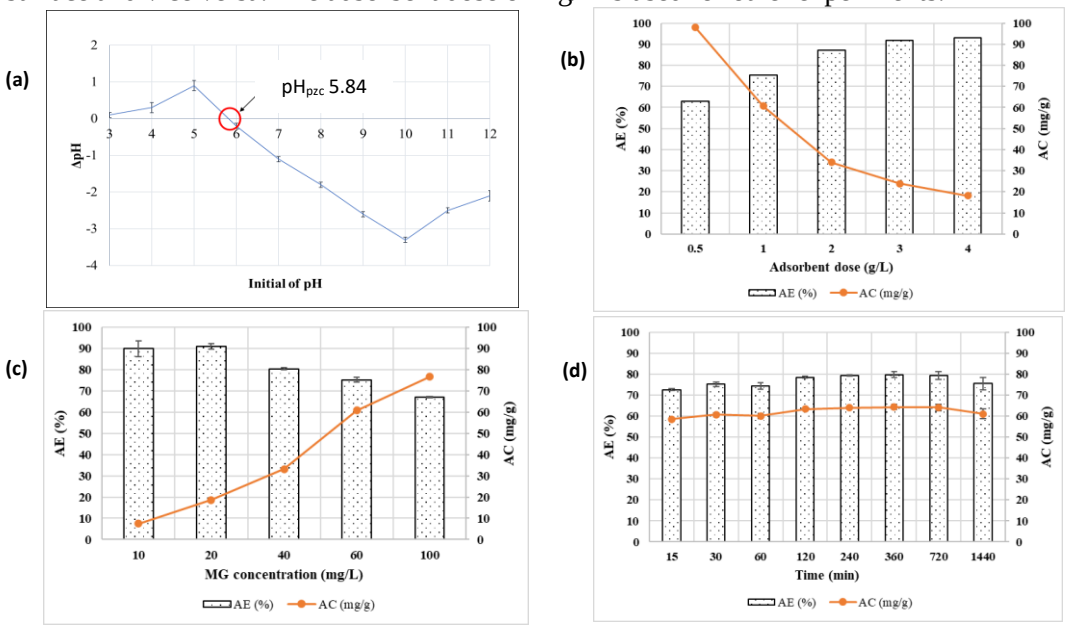

Figure 5. *Point of zero charge of CPS (a); effect of adsorbent dose (b), MG concentration (c) and time (d) on the removal of MG*

Figure 5c indicates a drop of AE from 89.79 to 67.02%, a rising of AC is recorded between 7.75 and 76.56 mg/g at MG concentration of 10-100 mg/L. At low concentration, the amount of MG^+ cation is relatively few in solution and the MG removal happens advantageously, bringing high AE and low AC. At higher concentration, the high AE and low AC are achieved. More MG^+ cation in solution help adsorbing on the CPS surface easily and more active sites of CPS are occupied; thus, the AC increases [17]. The adsorption time on CPS was varied from 15 to 1440 min and reached equilibrium within short time (Figure 5d). At 120 min, the AE and AC are 78.52% and 63.4 mg/g, respectively which are not much different compared to that of 30 min. At the longer adsorption time more than 120 min, the AE and AC kept unchanged. Hence, 30 min is a suitable time for the MG removal in this work. Correlation coefficients of Langmuir and Freundlich models are 0.998 and 0.994, respectively. Langmuir empirical constant from 0.724 to 0.969 means that the adsorption is favorable in the MG concentration between 10 and 100 mg/L. The Freundlich adsorption intensity n = 1.2 proves that the MG adsorption follows the physical process [7]. Depending on the R^2 in Table 1, the adsorption follows the Langmuir and Sips models. The mechanism of MG adsorption on CPS is homogeneous, monolayer, independent adsorption, without mutual interaction, meaning the adsorption and desorption processes have

equal rates when reaching equilibrium [3]. The MG adsorption fits to pseudo 2nd order kinetic model. The equilibrium of 2nd order kinetic model (q_e = 64.2 mg/g) and experimental AC (q_e = 60.71 mg/g) are nearly equal, proving that MG concentration strongly affects to the MG removal using CPS. The similar vibration ranges of CPS before and after adsorption indicate the presence of chitosan, pectin and SiO_2 (Figure 6). After adsorption, the intensification of vibrations in the lower range of 1010 cm^{-1} describes the electrostatic attraction between MG^+ and Si-OH group; the decrease of the vibration at 1700 cm^{-1} reveals the interaction of carboxyl group and MG^+ [18]. Broader vibrations in the range of 1400-1500 cm^{-1} are ascribed to -C-N group of dye [19].

Table 1. *Adsorption isotherm and kinetic models*

Models	Nonlinear equation	Value	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)	R^2 = 0.998 K_L = 0.0034 (L/mg) q_{max} = 276.48 (mg/g) 0.724 ≤R_L≤ 0.969	q_e and q_{max} (mg/g): equilibrium and maximum adsorption capacity; K_L (L/g): Langmuir empirical constant; R_L: Langmuir parameter
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$ (5)	R^2 = 0.994; n = 1.2 K_F = 1.58 (L/g)	K_F (L/g): Freundlich constant; n: the adsorption intensity
Sips	$q_e = \frac{Q_s \times a_s \times C_e^n}{1 + a_s \times C_e^n}$ (6)	R^2 = 0.997 Q_s = 270.9 (mg/g) a_s = 0.0035; n = 0.996	Q_S (mg/g): maximum adsorption capacity of Sips model; a_S: Sips isotherm model constant; n: adsorption intensity
Pseudo first order kinetic	$q_t = q_e \times (1 - e^{(-k_1 \times t)})$ (7)	R^2 = 0.910 k_1= 1.01 (1/min) q_e = 62.06 (mg/g)	q_e and q_t (mg/g): equilibrium adsorption capacity and adsorption capacity at t time; k_1 (1/min): pseudo first order rate constant; t (min): adsorption time
Pseudo second order kinetic	$q_t = \frac{q_e^2 \times k_2 \times t}{1 + q_e^2 \times k_2 \times t}$ (8)	R^2 = 0.951 k_2 = 0.007 (g/mg.min) q_e = 64.2 (mg/g)	k_2 (g/mg.min): pseudo second order rate constant; t (min): adsorption time

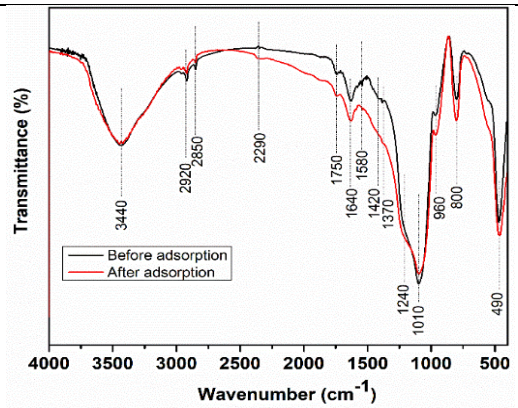

Figure 6. *FTIR results of CPS before and after adsorption*

4. Conclusion

CPS composite was successfully prepared at RT at a CP:SiO_2 weight ratio of 1:1.5 (g/g) within 0.5 h. The characteristic diffraction and vibration peaks of CPS were determined by XRD and FTIR, indicating the presence of pectin, chitosan, and SiO_2 in CPS. The CPS surface has large rough scales which are irregularly agglomerated, less holes and canals. MG is adsorbed on the CPS surface due to the presence of SiO_2 via the electrostatic attraction, with AE and AC of 75.93% and 61.3 mg/g, respectively at pH 7, adsorption dose of 1 g/L, MG concentration of 60 mg/L during 30 min. The adsorption process is consistent to Langmuir and Sips isotherm models and pseudo second order kinetic model. The adsorption process is homogeneous, monolayer, independent, without mutual interaction.

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