Facile Preparation of Self-Assembled Chitosan-Based POSS-CNTs-CS Composite as Highly Efficient Dye Absorbent for Wastewater Treatment

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ABSTRACT: In this work, a new nanocomposite based on octa-amino polyhedral oligomeric silsesquioxanes (POSS), carbon nanotubes (CNTs), and chitosan (CS) was synthesized and used for wastewater treatment. The properties and morphologies of the prepared composite were analyzed by X-ray diffraction, scanning electron microscopy, transmission electron microscope, thermogravimetric, and atomic force microscopy. The results showed that POSS, CNTs, and CS formed a stable composite through intermolecular forces, and the modification of CS by POSS and CNTs improved its stability. In addition, the obtained composite showed good adsorption performance for the degradation of methyl orange and Congo red dyes. The pseudo-first-order model and pseudo-second-order model were used to analyze the adsorption data, and the results showed that the adsorption process conforms to the kinetic model. Moreover, the maximum adsorption capacity of the composite to methyl orange and Congo red reached 63.23 and 314.97 mg/g, respectively. This work provides new ideas for the preparation of self-assembled multi-composite and their potential applications in wastewater treatment.

1. INTRODUCTION

Synthetic dyes are widely used as colorants in textile, papermaking, leather, gasoline, pharmaceutical, and food industries, which produce a large amount of dye wastewater. Moreover, most organic dyes have aromatic molecular structure, stable physicochemical properties, and are difficult to degrade. The pollution of surface water and groundwater by synthetic dyes has always been an environmental problem that has plagued humans.1 At present, the common methods for treating dye wastewater include adsorption, catalytic degradation, and membrane separation.2 The catalytic degradation process is relatively complicated, and it is easy to produce a large amount of organic toxic and harmful substances. The secondary treatment greatly increases the cost. However, the amount of wastewater treated by membrane separation technology is small and the cost is relatively high. The adsorption process can not only treat a large amount of wastewater without producing by-products but also has low cost. Therefore, adsorption is a widely used technology in the treatment of dye wastewater.3−8

Polyhedral oligomeric silsesquioxane (POSS) is an organic/inorganic hybrid molecule with a cage structure. Unlike traditional nano fillers such as montmorillonite and silica, POSS has a regular cage structure, nanoscale and good compatibility with polymers. The preparation of POSS and polymer is simple, and can form a true molecular level compound with the polymer, improve the thermal stability,5,10 mechanical strength,11−13 oxidation resistance, anti-aging,14 and other properties of the polymer. Nanohybrid materials have very important academic significance and practical application value.15−17

Since the discovery and synthesis of carbon nanotubes (CNTs), many related works have been reported in the removal of organic and inorganic pollutants,18−24 and many explorations have been made in commercial applications. CNTs have stable properties, high temperature resistance, and a large specific surface area. Different functional groups on the surface can be grafted with other molecules to form different composites. At the same time, CNTs also have certain adsorption properties,1,25,26 which can be used in wastewater treatment. Chitosan (CS) is a biopolymer discovered in recent years, which has good physical and chemical and biological properties.27 It is widely used in food, papermaking, printing and dyeing,28 environmental protection, textiles, water treatment,29,30 medical treatment,31,32 and heavy metal recycling. CS is a positively charged polyelectrolyte in solution, which has strong adsorption and excellent stability to organic solvents, and it is convenient for secondary processing. CS molecules have amine groups and hydroxyl functional groups,

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which is easy to combine with other molecules through intermolecular forces to form composite.\textsuperscript{11,22,34} Gu et al. prepared a chitosan–ignosulfonate composite by chemical modification, and it shows good adsorption performance for Congo red and Rhodamine B.\textsuperscript{35} Demarchi et al. synthesized O-carboxymethylchitosan-N-lauryl/c-Fe\textsubscript{2}O\textsubscript{3} magnetic nanoparticles, which exhibit potential adsorption performance for RR198 and other possible anionic reactive dyes.\textsuperscript{36}

In this study, the composite based on POSS, CNTs, and CS was successfully synthesized. POSS and CS were grafted onto carboxylated CNTs by intermolecular forces, and the reaction mechanism was shown in Figure 1. In addition, compared with the CS molecules, the thermal stability and the adsorption capacity of the obtained composite were greatly improved. The current work provides new clues for the preparation of CS and POSS multi-composite and their potential applications in dye adsorption.

2. RESULTS AND DISCUSSION

Figure 2a shows the scanning electron microscopy (SEM) image of the synthesized POSS. It can be found that the particles of POSS have an obvious agglomeration, which may be caused by the intermolecular interaction between the amine group and the hydroxyl group at the end of POSS. To evaluate the morphologies of POSS, atomic force microscopy (AFM) image of the POSS dissolved in methanol was obtained. From Figure 2b,c, it can be seen that the prepared POSS particles size are approximately 1.133 nm with the height of 1.235 nm, and the large particles observed in the picture may be due to the agglomeration of POSS particles.

As shown in Figure 3a, the microscopic morphology of the POSS-CNTs-CS composite can be characterized by the transmission electron microscope (TEM). It can be clearly seen that the filamentous CNTs were grafted onto the CS. The functional groups of the synthesized POSS and the prepared POSS-CNTs-CS nanocomposite were analyzed by FT-IR, as shown in Figure 3b. In the spectrum of POSS, the peaks appeared at 3443 cm\textsuperscript{−1} correspond to the stretching vibration of N–H and C–H, and the peaks at 1050–1121 cm\textsuperscript{−1} correspond to stretching vibration of the POSS cage Si–O–Si structure. From the CS spectrum, there are some adsorption peaks appeared at 1597 cm\textsuperscript{−1} (–NH\textsubscript{2} bending), 1158 cm\textsuperscript{−1} (asymmetric stretching of the C–O–C bridge) and 1089 cm\textsuperscript{−1} (skeletal vibration involving the C–O stretching), 3417 cm\textsuperscript{−1} (wide peak of O–H stretching overlapped with N–H stretching), 2923 cm\textsuperscript{−1} (C–H stretching), and 1371 cm\textsuperscript{−1} (asymmetric C–H bending of CH\textsubscript{2} groups). The peaks of CNTs from 1550–1730 cm\textsuperscript{−1} can be assigned to the carboxyl groups. As for the prepared POSS-CNTs-CS composite, the peak at 1050 cm\textsuperscript{−1} is due to the Si–O–Si vibration of POSS, and the absorption peak appeared at 1415 cm\textsuperscript{−1} correspond to the stretching vibration of –CH\textsubscript{2}. In addition, the peak at 1539

Figure 1. (a) Molecular structure of POSS and (b) schematic illustration of the synthesis of POSS-CNTs-CS composite.

Figure 2. (a) SEM image and (b, c) AFM images of POSS particles.

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cm$^{-1}$ is the bending vibration of N–H and the stretching vibration of C–N of the amide bond (formed by the binding of amino group in POSS or CS with the carboxyl group in CNTs). The absorption peak at 1646 cm$^{-1}$ corresponds to the stretching vibration of −OH and O–C–O (the ester group formed by the combination of the hydroxyl group in CS and the carboxyl group in CNTs), while the peak at 3450 cm$^{-1}$ can be attributed to the vibration of −OH, C–H, and other groups. Due to the large amount of CS in the composite, the characteristic peaks of CNTs and POSS groups are relatively weak on the spectral of the POSS-CNTs-CS composite.

X-ray diffraction (XRD) patterns of the samples are shown in Figure 4a. The diffraction peak of POSS-NH$_2$ appeared at 2$\theta$ values of 6.52 and 22.23°, the broadness of the peak present in most POSS hybrids can be attributed to the hybrid formation in the presence of POSS inorganic segments. The characteristic peaks of CS appeared at 11.2 and 20.3°. As for the X-ray diffraction curve, a sharp characteristic peak appeared at 2$\theta = 26.05$°. In addition, the characteristic peaks of the POSS-CNTs-CS composite are located at 2$\theta = 11.37$, 20.36, and 26.05°. However, the peaks corresponding to CNTs and POSS are not obvious in the composite curve, which may be due to the relatively low CNTs and POSS content in the composite. The thermal stability of samples was further investigated by thermograms (TG), as shown in Figure 4b. The samples were heated from 50 to 800 °C at a heating rate of 10 °C/min under argon. The TG curves of CS and composite were divided into three stages. CS is a crystal with a melting point, in the first stage, the temperature of free water losing its connection with intermolecular forces is 78−89 °C, and the weight loss is about 3.34%. Second, the crystal water with stronger bond is lost, and the maximum decomposition temperature of main chain fracture is 266 °C with a weight loss about 7.17%. Lastly, the weight of CS loss is 60.17%, this stage weight caused by the final decomposition and the temperature is 560−688 °C. The prepared POSS-CNTs-CS composite was obtained by the freeze-drying method. After freeze-drying, there will be some crystal water in the solid. In the TG curve, it can be found that the decline trend of the composite curve at 100−200 °C is significantly faster than that of the CS monomer. When the temperature was higher than 200 °C, the TG curve of the composite decreased more slowly than that of CS, indicating that the thermal stability of the POSS-CNTs-CS composite was improved by doping POSS and CNTs. When the temperature was higher than 317 °C, the curve of the POSS-CNTs-CS composite showed the stability of relative advantage, and the weight loss of CS mass was 30.09%, while the weight loss of POSS-CNTs-CS composite was only 19.68%.

The scanning electron microscopy (SEM) images of the POSS-CNTs-CS composite are shown in Figure 5. It can be found from Figure 5a that there are filamentous CNTs.
Figure 5. (a, b) SEM images and (c–f) elemental mappings of the prepared POSS-CNTs-CS composite.

attached to the surface of the smooth CS, which can prove the attachment of CNTs in the CS. The POSS cannot be clearly seen in SEM images due to its small particle size. In addition, the SEM element maps were used to further characterize the elements in the composite. As shown in Figure 5b–f, C, N, O, and Si elements can be clearly observed, indicating that POSS and CNTs have been successfully added into composite.

CS is a positively charged polyelectrolyte with strong adsorption ability, and the adsorption capacity was further enhanced after doping CNTs. The \(-\text{NH}_2\) \(-\text{OH}\) group in CS can combine with the \(-\text{SO}_3\) group in methyl orange (MO) dye solution and the \(-\text{NH}_2\) \(-\text{SO}_3\) group in Congo red through intermolecular force, thus producing adsorption effect. To evaluate the adsorption capacity of POSS-CNTs-CS composite for MO and CR dyes, the prepared POSS-CNTs-CS composite was used to adsorb MO and CR dye solution. The adsorption kinetics was studied by fitting the adsorption experimental data, and pseudo-first-order model and pseudo-second-order model adsorption equation were used to analyze the data.

The pseudo-first-order model

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t
\]

The pseudo-second-order model

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}
\]

In the formula, \(t\) represents the adsorption time, \(q_t\) is the capacity of adsorption at time \(t\) (mg/g), and \(q_e\) is the capacity of adsorption (mg/g) at equilibrium. \(K_1\) and \(K_2\) represent the pseudo-first and pseudo-second kinetic rate constants, respectively. The fitted data of kinetic adsorption are shown in Table 1. As for POSS-CNTs-CS composite, the correlation coefficients of the pseudo-first-order model and the pseudo-second-order model were \(R^2 > 0.943\) and \(R^2 > 0.999\) for MO systems, respectively. In addition, the correlation coefficients of the pseudo-first-order model and the pseudo-second-order model were \(R^2 > 0.891\) and \(R^2 > 0.999\) for CR systems, as shown in Figure 6a,b. At 120 min, the adsorption of MO by the POSS-CNTs-CS composite and CS reached equilibrium, and the \(q_t\) values were 63.23 mg/g and 22.43 mg/g, respectively. Moreover, it can be clearly seen that the prepared POSS-CNTs-CS composite shows higher adsorption capacity for MO dye solution. The same result can also be observed in the CR system, the \(q_t\) of CS and POSS-CNTs-CS composite were 167.89 and 314.97 mg/g, respectively. The results show that compared with CS, the adsorption capacity of the POSS-CNTs-CS composite is greatly enhanced after adding POSS and CNTs. To better compare the adsorption properties of the prepared POSS-CNTs-CS composite with other similar composite materials, the relevant results are summarized in Table 2. It is worth noting that the POSS-CNTs-CS composite in this work shows better adsorption property for MO and CR dyes.

3. CONCLUSIONS

In summary, CS was modified with POSS and CNTs by intermolecular forces. POSS was grafted onto CS molecules to improve the stability of CS. Carbon nanotube is a kind of nanomaterials with large surface area, good mechanical properties, and adsorption capacity. The addition of the carbon nanotubes can effectively improve the adsorption performance of the composite. Compared with CS, the prepared POSS-CNTs-CS composite showed enhanced adsorption capacity of for MO and CR solution. The excellent adsorption properties of prepared POSS-CNTs-CS composite make it show potential applications in food, wastewater treatment, and medical treatment. This work also provides new ideas for the preparation of CS-based multi-composite.

4. EXPERIMENTAL SECTION

4.1. Materials. The used chitosan, carbon nanotubes (CNTs), and γ-aminopropyl triethoxysilane were all purchased from Aladdin Chemicals (Shanghai, China). Methyl orange (MO) and Congo red (CR) were obtained from Sinopharm Chemical Reagent Co. Ltd. (analytical reagent grade, Shanghai, China). Tetrahydrofuran, acetic acid, concentrated hydrochloric acid, and sodium hydroxide were purchased from Sinopharm Chemical Reagent Co. Ltd. (analytical reagent grade). The aqueous water was purified with a two-stage Millipore Milli-Q water purification system. All reagents were used without further purification.

4.2. Preparation of POSS. Octa-amino polyhedral oligomeric silsesquioxanes were synthesized according to the method reported by Feher et al. and Seckin et al. γ-aminopropyl triethoxysilane (5 mL), concentrated hydrochloric acid (7.5 mL) and anhydrous methanol (90 mL) were added to a 250 mL three-necked flask, and stirred at 70 °C for 19 h. Then, an equal volume of tetrahydrofuran was added to the mixture and a white precipitate appears. The white precipitate was washed by tetrahydrofuran repeatedly to

Table 1. Kinetic Parameters of the Composite and Chitosan Adsorbed MO or CR

| dye       | composite and chitosan absorbed MO or CR | pseudo-first-order model | pseudo-second-order model |
|-----------|------------------------------------------|--------------------------|---------------------------|
|           |                                          | \(q_e\) (mg/g) | \(R^2\) | \(K_1\) (min\(^{-1}\)) | \(q_e\) (mg/g) | \(R^2\) | \(K_2\) (g/mg.min\(^{-1}\)) |
| MO        | CS                                       | 22.43                    | 0.992          | 0.07038               | 25.70                      | 0.985    | 0.00250                      |
|           | POSS-CNTs-CS                             | 63.23                    | 0.943          | 0.29918               | 69.88                      | 0.999    | 0.00442                      |
| CR        | CS                                       | 167.89                   | 0.981          | 0.00899               | 178.57                     | 0.981    | 0.000012                     |
|           | POSS-CNTs-CS                             | 314.97                   | 0.891          | 0.17814               | 341.30                     | 0.999    | 0.00080                      |
remove impurities in the product, and the finally sample was dried to obtain POSS solid particles.

4.3. Preparation of POSS-CNTs-CS Composite. POSS-CNTs-CS was synthesized according to the following method:31,49,50 0.6000 g of CS powder was dissolved in 2% acetic acid solution under ultrasound for 30 min, then 5 mg of CNTs and 10 mg of POSS were added to the mixture and sonicated for 10 min. The obtained mixture solution was stirred for about 12 h under a water bath at 40 °C. After the reaction, the solution was slowly added to the configured alkaline coagulant (H₂O:MeOH:NaOH = 4:5:1, v/v) at room temperature and continuously stirred for 6 h to form POSS-CNTs-CS composite. Finally, the composite was dried by deionized water for 3 days to remove impurities. After the dialysis, the composite was dried in a lyophilizer at −50 °C for 3−5 days to remove water.51−54

4.4. Adsorption Experiment Studies. The adsorption properties of the composites were performed by removal of methyl orange (MO) and Congo red (CR) by a UV−vis spectrophotometer (752-type, Sunny Hengping Scientific Instrument Co. Ltd., Shanghai, China). Equilibrium adsorption experiments were conducted by adding 0.08 g POSS-CNTs-CS composite into 50 mg/L MO or 200 mg/L CR solution at room temperature. The absorbance of the dye solution was measured at certain intervals.

4.5. Characterization. The composites used in this study were dried at −50 °C by a FD-1C-50 lyophilizer instrument from Beijing Boyikang Experimental Instrument Co., Ltd. (Beijing, China). The atomic force microscopy (AFM) pictures of POSS were measured with a nanoscope model Multimode & Scanning Probe Microscopy (Veeco Instrument, USA). The infrared spectra were characterized by a Fourier infrared spectroscopy (Nicolet Corporation, America) using the KBr sheet method. X-ray diffraction (XRD) was measured on an X-ray diffractometer equipped with a Cu Ka X-ray radiation source and a Bragg diffraction setup (SMART LAB, Rigaku, Japan). The nanostructures of the composites were studied by a field-emission scanning electron microscopy (SEM) (S-4800II, Hitachi, Japan) with 5−30 kV accelerating voltage. Thermogravimetry (TG) was conducted by using a NETZSCHTA 409 PC Luxxsi mutaneous thermal analyzer (Netzsch Instruments Manufacturing Co, Ltd., Germany) in

Figure 6. Kinetic adsorption of (a) q versus t plots and (b) t/q versus t plots for MO; (c) q versus t plots and (d) t/q versus t plots for CR.

Table 2. Comparison of the Adsorption Capacity of the Composite to MO and CR Dye

| adsorbent                        | dye       | adsorption capacity (mg/g) | references |
|----------------------------------|-----------|---------------------------|------------|
| PbS/ZnO                          | MO        | 159                       | [37]       |
| ZnFe₂O₄/graphene                 | MO        | 2.31                      | [22]       |
| chitosan/organic rectorite       | MO        | 5.56                      | [38]       |
| composite                        | polyaniline nano-adsortent | 75.9                  | [39]       |
| hexagonal-shaped nanoporous      | MO        | 18.8                      | [40]       |
| carbon                           | modified fly ash with Ca(OH)₂/Na₃FeO₄ | 23.8                  | [41]       |
| graphene oxide                   | MO        | 16.83                     | [42]       |
| biochar adsorbent                | MO        | 39.37                     | [43]       |
| m-CS/c-Fe₂O₄/MWCNTs              | MO        | 31.52                     | [44]       |
| PVA/MF                           | CR        | 221.43                    | [45]       |
| CS/CTAB                          | CR        | 352.5                     | [26]       |
| CS-VTM                           | CR        | 62.2                      | [46]       |
| Sn(II)-BDC MOF                   | CR        | 95.2                      | [47]       |
| ZnFe₂O₄/MgAl-LDH                 | CR        | 294.12                    | [48]       |

Table 2. Comparison of the Adsorption Capacity of the Composite to MO and CR Dye
argon gas. The transmission electron microscope (TEM) (HT7700, Hitachi High-Technologies Corporation, Japan) was used to characterize the morphology of the materials. UV−vis spectra were measured by Shimadzu UV-2550 system (Shimadzu Corporation, Japan).

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### Notes

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