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Preparation and Characterization of a Novel Absorber for Formaldehyde

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***Abstract*—Formaldehyde is one of the substances causing sick for human being.Small doses of formaldehyde can cause a variety of symptoms of physical discomfort. High dose and long time exposure to formaldehyde will increase the probability of cancer. However, the content of formaldehyde in the newly renovated room or near the new furniture is very high. To solve the formaldehyde, this paper developed a new kind of sodium carboxymethyl cellulose/carboxyl graphite oxide (CMC/GO-COOH) scaffold via a lyophilization method. Then, this synthetic scaffold was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), hydrophilic test, mechanical property and in vitro detoxification test. There were covalent bonding and hydrogen bonding in the scaffold, indicating the strong interactions between CMC and GO-COOH. There were interconnected network in the structure of synthesized scaffold. The mechanical test suggested that the CMC/GO-COOH scaffold had excellent mechanical strength, which was 3.41±0.12MPa with shrink of 25%. Furthermore, the adsorption of CMC/GO-COOH to formaldehyde wereup to 10.97±1.84 mg/g. The resulting CMC/GO-COOH scaffold held great potential for adsorbing formaldehyde.**

Keywords- CMC/GO-COOH; scaffold ; formaldehyde

I. INTRODUCTION

Formaldehyde is one of the substances causing sick for human being. People may feel uncomfortable when formaldehyde reaches a certain concentration in the room. If the formaldehyde concentration is greater than 0.08 milligram per stere,it can cause redness, itching, throat discomfort, hoarseness, sneezing, chest tightness, asthma or dermatitis. Newly renovated room contains higher level of formaldehyde, which is the main cause of many diseases. Long term exposure to formaldehyde increases the risk of Hodgkin's lymphoma, multiple myeloma, myeloid leukemia and other special cancer.

The adsorption formaldehyde has been investigated byseveral groups for a long time. Specifically, the porous detoxifying scaffold [1,2] based on high specific surface area, had been proved to be an effective material in artificial kidneys. Activated carbon kept the first choice in environment detoxification. Nevertheless, the detoxification efficiency of activated carbon to formaldehyde was rather low. Graphite Oxide (GO)[3] attracted great attentions due to its unique thermal, mechanical and electrical properties. All these specific characteristics were attributed to its unique structure and oxygen-containing groups, such as epoxy, hydroxyl and carboxyl groups and so on. Carboxyl Graphite Oxide (GO-COOH) was important due to its high reactivity, dispersibility and stability. The GO-COOH showed better reactivity and stability than GO for further application.

Herein, CMC and GO-COOH were combined to overcome their own disadvantages alone. GO was prepared by the modified Hummers method. CMC/GO-COOH scaffolds were prepared via a lyophilization method. The CMC/GO-COOH scaffold synthesized was characterized by FT-IR, SEM, mechanical stress. In vitro experiment, the adsorption of CMC/GO-COOH scaffolds for formaldehyde.

II. MATERIALS AND METHODS

Natural graphite powder (180 mesh) was obtained from Qingdao Black Dragon Graphite Co. Ltd., China. Chitosan, urea, creatinine, Vitamin B12 and β2-m were all purchased from Sigma-Aldrich Inc., USA. Potassium permanganate (KMnO4), sulfuric acid (H2SO4, 98wt.%), sodium nitrate (NaNO3), sodium hydroxide (NaOH) and hydrogen peroxide (H2O2) were supplied by Aladdin Reagent Co. Ltd., China. All the chemicals were analytical grade and doubly deionized water was used throughout.

A. Synthesis of Carboxyl Graphite Oxide

GO was synthesized using the modified Hummers method. Natural graphite powder (2g), NaNO3 (1g) and H2SO4 (98wt.%, 46mL) were mixed in a round bottom flask, under magnetic stirring for 12h at -5℃. Next, KMnO4 (6 g) was added to the mixture gradually, and then the mixture was heated to 35℃. After continuous stirring for 1h, distilled water (46mL) was poured into the solution at 80℃. After 30min, water (280mL) along with H2O2 (30wt.%, 40ml) was added under stirring. The reason adding H2O2 was to remove the remaining of KMnO4. Subsequently, the mixture was filtered, and the obtained solid material was put into distilled water. Centrifugation was carried out for 30min at 4000rpm and material obtained from centrifugation was put into water again. The procedure above was repeated until the PH of the material was neutralized up to 7. Finally, the resultant product was dried at 50℃ and GO was obtained in the form of dark brown slice.

The carboxyl of GO was activated by chloroacetic acids according to the reported method. The prepared GO (200mg) was suspended in distilled water (100mL), followed by sonication for about 2h. Then, NaOH(12g) was added to the mixture under stirring. About 30min later, chloroacetic acids (20g) was introduced into the mixture under strong basic condition. After continuous sonication for 2h, the resultant was purified by dialysis, washed with ethanol, and separated by centrifugation. Finally, the product was dried at 60℃ and GO-COOH was obtained.

B. Synthesis of CMC/GO-COOH Scaffolds Carboxyl Graphite Oxide

CMC/GO-COOH scaffolds were prepared via the double-lyophilization method, as shown in Fig.1. The process included two important steps, namely, the synthesis of CS/GO-COOH hydrogels, and subsequent double-lyophilization technique.

CMC(3.1g) was dissolved in distilled water (5%, 55mL) solution under continuous stirring overnight. Meanwhile, a 1.0mg/mL GO-COOH was added into the distilled water and followed by sonication for 2h. The ratio of GO-COOH introduced into the mixture mainly depended on its dissolving capacity in water. In the pre-experiment, the solubility of GO-COOH was 7.0mg/mL. Then, the CMC solution and GO-COOH aqueous dispersion were mixed together under constant stirring. The mixture was agitated for 24h. Then, the mixed solution (25mL) was transferred to a glass bottle (20×40 mm), and frozen at minus 80℃ for 10 h. Subsequently, the sample was first lyophilized at minus 50℃ condition. Finally, the CMC/GO-COOH scaffold was obtained.

C. Characterization

Fourier transform infrared spectrometer (FT-IR, Nicolet iS10, USA) was performed to analysis the interactions between CMC and GO-COOH. The FT-IR was tested in the range of 4000-500cm-1, at 1.5cm-1 resolution and averaging 100 scans.

The surface morphology of CMC/GO-COOH scaffold was observed with a Scanning Electron Microscope (SEM, FEI250, USA), with an accelerated voltage of 10KV. The average diameter of structure was measured from SEM images by Image Program.

The Dynamic Mechanical Analyzer (Electro-Force 3550, USA) was used to measure the dynamic stiffness of scaffolds synthesized. Scaffolds were loaded with the dynamic force until it was at strain of 90%. More specifically, a starting force of 0N was applied and then continuously increased with the movement of 0.5mm/s at a constant frequency of 1HZ.

The Adsorption Experimentwas carried out by OSHA's titerimetricanalysis method[4] for formaldehyde.

D. Statistical Analysis

Data were pooled from at least three independent experiments and presented as mean ± standard deviation (±s) unless indicated otherwise. Differences between groups were analyzed using one-way analysis of variance. All the statistical analyses were performed with SPSS13.0. *$p<0.05$ was considered statistically significant.

III. Results and Discussion

It can be found the characteristic peak of alkoxy (C-O) was displayed at 1054cm-1(shown in Fig1b). The absorption bands at 1736cm-1 and 1634cm-1 were attributed to the stretching vibrations of carbonyl and carboxylic groups, respectively. In Fig.1a, the absorbance band of CMC shifted. This result was attributed to the der Waals interactions between GO-COOH and CMC.The mechanical test suggested that the CMC/GO-COOH scaffold had excellent mechanical strength, which was 3.41±0.12MPa with shrink of 25%. This could be ascribed to the strong interfacial interactions between GO-COOH and the CMC matrix. In addition to the electrostatic interactions, there were the strong hydrogen bonding and covalent bonding formed between the carboxyl groups of GO-COOH and hydroxyl groups of CMC matrix. Strong interfacial adhesion was established between both components. The pores in the scaffolds formed during the lyphilization process. And the average diameter corresponding to these scaffolds was 232±15um. The adsorption of CMC/GO-COOH to formaldehyde wereup to 10.97±1.84 mg/g. After adsorption experiment, there are many blocked, sealed tubular structures. This means that CMC/GO-COOH scaffold held great potential for adsorbing formaldehyde.

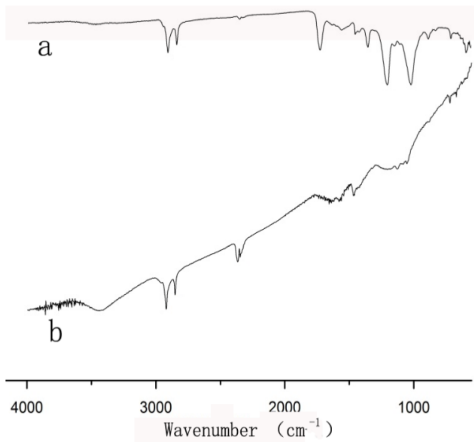

Figure 1. FT-IR curves of synthesized CMC/GO-COOHandGO-COOH scaffold were shown in Fig. 3(a-d), respectively.

Figure 2 (a)SEM photos before adsorbing acetaldehyde(b)SEM photos after adsorbing acetaldehyde

IV. Conclusion

The CMC/GO-COOH scaffold was prepared by a lyophilization method. The structure of the scaffold exhibited interconnected 3D porous network. The scaffold displayed the best adsorption for formaldehyde. In addition, GO-COOH showed excellent miscibility and dispersion with CMC. The porous structure of the scaffold allowed for the efficient elimination of formaldehyde. In all, the CS/GO-COOH scaffold had good affinity to formaldehyde, and had potential in the application of environment.

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