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A Study on Adsorption Membrane of Tannery Wastewater Based on Low Temperature Plasma

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***Abstract*—The tanning industry produced a large amount of tannery wastewater and solid waste, resulting in environmental pollution and waste of resources, which has become an urgent need to be solved. In this study, a gelatin-based graphene oxide composite adsorption membrane was prepared and treated with low temperature plasma to enhance its adsorption performance. The results showed that the surface functionalization degree of the composite membrane treated by plasma was effectively improved. In the adsorption experiments of Cr^{3+} and methylene blue, the adsorption capacity has increased by 78% and 107% respectively. The results provide an effective reference for the research on the adsorbent material of tannery wastewater.**

***Keywords*—low temperature plasma; GO; Gelatin; absorption**

I. Introduction

The rapid development of the tanning industry has led to the production of a large amount of tannery wastewater and solid waste. Tannery wastewater contains a large amount of dyes and heavy metal ions, which may cause environmental pollution and even poison human health. At the same time, the production of collagen-rich tanning solid waste has also caused a lot of waste of resources. In order to maintain the sustainable development of the tanning industry, it is of great significance to reduce the pollution and waste reuse in the tanning industry [1].

Adsorption method is one of the most widely used tannery wastewater treatment methods, and it has the characteristics of good adsorption effect and easy operation. Massive studies have been carried out both at home and abroad on adsorption of heavy metals and dyes. Haroun et al prepared a series of gelatin/hydrolyzed PET (polyterephthalic acid)/chitosan composites for the adsorption of acid red 150 [2]. Qiu et al prepared gelatin / montmorillonite composites, and studied the adsorption properties of this material on Cr^{3+} in aqueous solution[3]. A graphene oxide/chitosan aerogel was prepared by Yu et al in freeze-drying, which can quickly remove Cu^{2+} in water under high pH, low ionic strength and high temperature conditions[4]. Li et al. founded a sulfhydryl functionalized graphene oxide (GO)/chitosan composite, which showed good adsorption performance for Cu^{2+}, Pb^{2+} and Cd^{2+}[5]. Cheng et al. synthesized a series of graphene oxide/biopolymer three-dimensional porous gels, and their studies showed that the obtained porous gels could effectively remove cationic dyes and heavy metal ions in wastewater[6]. These studies indicated the feasibility of graphene oxide modification of adsorbent materials and the superiority of collagen as an adsorbent material.

Low temperature plasma (LTP) can destroy the chemical bonds on the surface of materials to form new crosslinked structures or new chemical groups, and is therefore widely used for surface modification. Saxena et al treated the polyethersulfone (PES) membrane with Ar-O_2 plasma to enhance the hydrophilicity and permeation flux of the membrane[7]. Kwong et al. treated the polyester synthetic tanning with CF_4 plasma to improve the hydrophobicity of the surface [8]. However, the current research on gelatin-based go adsorbents is not in-depth, nor has LTP technology been applied to the modification of such adsorbents.

In this study, a gelatin-based graphene oxide (GO/gelatin) composite adsorption film was prepared by crosslinking gelatin with GO. The adsorption properties of composite films modified by N_2 and O_2 LTP treatment were studied. Cr^{3+} and methylene blue existed in tannery wastewater were selected as the objects for adsorption experiments. The results showed that LTP treatment can improve the functional degree and adsorption properties of the membrane effectively. In the adsorption experiments of Cr^{3+} and methylene blue, the adsorption capacity of the composite film was increased by 78% and 107% respectively after treated with O_2 plasma for 15min. The results of this study provide a useful reference for the research of green and environmental tanning wastewater treatment materials.

II. Experimental

A. Preparation of GO/Gelatin Composite Membrane

The composite membrane was prepared as follows: 2.0 g gelatin was dissolved to 50 mL deionized water at 50℃ to obtain a gelatin solution, adding 15 wt% of a plasticizer of triethylene glycol with stirring, and plasticating for 30 min. Appropriate amount of GO was dispersed in deionized water to prepare a dispersion solution of 1 mg/mL (60mL), added to the gelatin solution slowly and stirred evenly. The mixed solution was vacuum defoamed, injected into a mold, and dried at 35℃ blasting conditions to obtain a composite film. After the composite film was peeled off from the mold, it was placed in a sealed container containing a saturated $Mg(NO_3)_2\cdot 6H_2O$ solution (relative humidity RH of 50 ± 2%) at 25℃, and the humility was equilibrated for 3 days or more.

B. Low Temperature Plasma Treatment of Composite Membrane

0.1g GO/gelatin composite film was treated with O_2 for 15 min in a LTP treatment apparatus (gas flow rate: 40 mL/min;

discharge power: 200 W). Change the gas and treat another composite membrane with N_2 in the same way for 15 min.

C. Characterization of GO/Gelatin Composite Membrane

The surface of the sample before and after the plasma treatment was observed with a scanning electron microscope (SEM). The elemental and group content of the surface of the material was analyzed by X-ray photoelectron spectroscopy (XPS). The remaining metal ion concentration and dye concentration in the solution were determined by an atomic emission spectrometer and an ultraviolet-visible spectrophotometer in an adsorption experiment. The capacity of adsorption is calculated by the following formula:

$$\theta = (X_o - X_\alpha)\varsigma/\mu. \quad (1)$$

C_o and C_a are the initial and residual adsorbate concentrations (mg/L) after adsorption, V is the solution volume (L), and m is the mass of the composite film (g).

III. Results and Discussion

A. Effect of Plasma Treatment on Surface Morphology of Composite Membranes

Fig.1 shows the surface morphology of the composite film before and after the treatment with O_2 plasma. Compared with the untreated composite film, the surface of the composite film becomes rough and exhibits a gully-like surface topography after treatment for 15 min. This can be explained by the etching effect of the plasma. During the process, O_2 dissociates oxygen radicals, oxygen anions and other chemically active particles, interacting with the molecular chains and side groups of gelatin on the surface of the composite membrane, and volatile products are formed, thereby causing the effect of etching. The surface morphology of the N_2 treated composite film is similar to O_2 treated composite film.

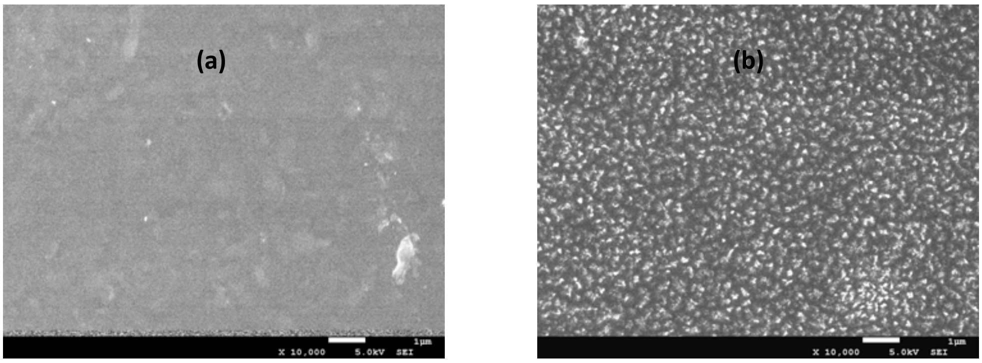

FIGURE I. SEM OF COMPOSITE FILMS TREATED WITH O_2 LOW TEMPERATURE PLASMA: (A) UNTREATED, (B) 15 MIN

B. Effect of Plasma Treatment on Surface Elements and Groups of Composite Membranes

Table 1 shows the change in elemental content of the surface before and after plasma treatment. Table 2 shows the content of the four groups of C-C/C=C (284.7 eV), C-OH (285.6 eV), C-N/C-O-C (286.3 eV) and C=O/C(O)-N (288.0 eV). After treated with O_2 plasma for 15 min, the content of C on the surface of the membrane is decreased, the content of N and O is increased; the content of C-C/C=C and C-OH is decreased slightly and the content of C-N/C-O-C and C=O /C(O)-N is increased. This can be attributed to chemical reactions during processing mostly. When the composite membrane is subjected to O_2 plasma, the active particles dissociated by O_2 react with C-C/C=C, C-N, and C-OH on the surface to form a C-O group and further form the C (O)-N and C=O groups. At the same time, the plasma etches the surface, causing some internal nitrogenous groups to be exposed to the surface is also worked.

TABLE I. C, N, O CONTENT OF COMPOSITE MEMBRANES TREATED WITH LOW TEMPERATURE PLASMA

Elements	Untreated	Treated by N_2 Low-temperature Plasma (15min)	
		O_2	N_2
C 1s /%	67.38	62.83	65.26
N 1s /%	13.60	15.19	16.20
O 1s /%	19.02	21.99	18.54

After N_2 plasma treated for 15 min, the content of N and O on the surface of the composite membrane is increased, while the content of C is decreased; the content of C-OH, C-N/C-O-C and C-C/C=C is decreased, the C=O/C(O)-N content is increased. The high energy active particles dissociated by N_2 react with the C-C/C=C of the surface, resulting in a decrease in the content of C element and an increase in the content of N. The nitrogen-containing radical reacts with C-OH, so that the content of C-OH is decreased, the content of C=O/C(O)-N is increased. At the same time, the oxygen-containing group is exposed by etching, thereby the content of O increases.

TABLE II. PEAK FITTING RESULTS OF C 1S OF COMPOSITE FILMS TREATED WITH LOW TEMPERATURE PLASMA

	Untreated	Treated by N_2 Low-temperature Plasma (15min)	
		O_2	N_2
C-C/C=C /%	41.25	34.64	39.36
C-OH /%	28.55	24.17	27.38
C-N/C-O-C /%	5.64	11.54	5.48
C=O/C(O)-N /%	24.56	29.65	27.79

C. *Effect of Plasma Treatment on Adsorption Properties of Composite Membranes*

The adsorption kinetics curve of Cr^{3+} ions in the composite membrane before and after low temperature plasma treatment is shown in Fig. 2. The saturated adsorption capacity of the untreated composite membrane was only 8.35 mg/g; The adsorption performance of the composite membrane treated by different low temperature plasma treatment for 15 min was improved to different extents, especially the composite membrane treated by O_2 low temperature plasma for 15 min, the saturated adsorption capacity was 14.87 mg/g, which increased by 78%. According to the analysis, after the low-temperature plasma treatment, the gas is excited into active particle to react with the composite film, and groups such as C=O/C(O)-N which can coordinate with Cr^{3+} are generated. At the same time, the formation of a large number of gullies on the surface of the composite membrane by etching also contributes to adsorption.

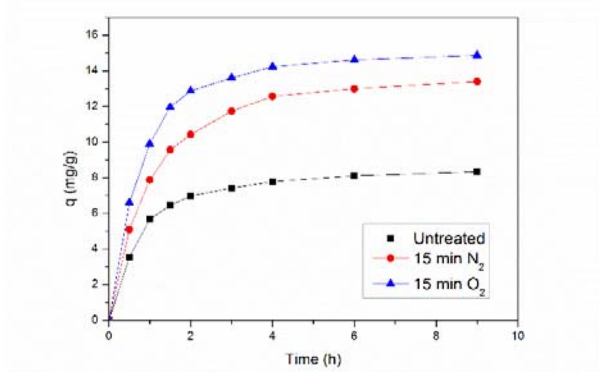

FIGURE II. ADSORPTION OF CR^{3+} BY COMPOSITE FILMS AFTER 15 MIN LOW TEMPERATURE PLASMA TREATMENT

Figure 3 shows the adsorption kinetics of the composite membrane to methylene blue before and after low temperature plasma treatment. The saturated adsorption capacity of the untreated composite membrane was only 9.13 mg/g; The adsorption performance of the composite membrane treated by different low temperature plasma treatment for 15 min was improved to different extents, especially the composite membrane treated by O_2 low temperature plasma for 15 min, the saturated adsorption capacity was 18.93 mg/g, which increased by 107%. It can be seen from the analysis that after the low temperature plasma treatment, the composite membrane generates a large number of negatively charged groups such as C-N/C-O-C and C=O/C(O)-N, which act on the positively charged methylene blue to promote the adsorption properties of the membrane. At the same time, the formation of a large number of gullies on the surface also worked on adsorption effect.

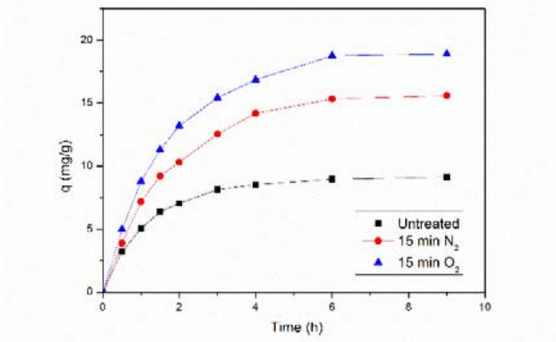

FIGURE III. ADSORPTION OF METHYLENE BLUE BY COMPOSITE FILMS AFTER 15 MIN LOW TEMPERATURE PLASMA TREATMENT

IV. SUMMARY

In this study, a gelatin-based graphene oxide composite adsorption film was prepared from gelatin and GO as the base material, and low temperature plasma treatment was used to enhance the adsorption performance of the composite membrane. The results showed that the adsorption performance of the composite film could be improved by introducing groups and etching with the low-temperature plasma. The adsorption capacity of Cr^{3+} and methylene blue by the composite film treated with O_2 plasma for 15min was increased by 78% and 107% respectively. It is also demonstrated that LTP treatment can improve the functional degree and adsorption properties of the membrane effectively, and will provide a useful reference for the research of green and environmental treatment technology and adsorption film materials in tanning wastewater.

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