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Adsorptive capacity of ethylenediamine treated oxidised rice straw for sulfur dioxide

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ABSTRACT

The introduction of sulfur dioxide (SO_2) into the atmosphere is of major concern causing acid rain. Thus, the modified rice straw was prepared via sequential reactions of the active groups on rice straw with potassium permanganate ($KMnO_4$) followed by the alkaline molecule, ethylenediamine, to adsorb SO_2. The experimental parameters were optimized as the concentration of potassium permanganate of 5%, the concentration of ethylenediamine of 10%, the moisture content of 200%, as well as the reaction temperature of room temperature. Experiments show that the modified rice (Straw–$KMnO_4$–NH_2) has better adsorption capacity for SO_2 and its saturated sulfur capacity could reach ~340 mg/g, which was much better than that of the raw straw and other reported modified samples. The performance of the Straw–$KMnO_4$–NH_2 was characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), scanning electron micrographs (SEM), and elemental analysis.

1. Introduction

Fossil fuel, fired power plants, auto exhausts and other industrial chemical emissions are the major sources of sulfur dioxide (SO_2). SO_2 can react slowly with oxygen to form the trioxide that subsequently reacts with water to form sulfuric acid (Jeon et al., 2008). The introduction of SO_2 into the atmosphere is of major concern causing acid rain. Many methods have been devised to reduce emissions of SO_2, and these can be broadly classified into two general categories: absorption of SO_2 in liquids and adsorption by solids (Xue et al., 2010). Wet methods, such as lime–limestones scrubbers, are highly efficient but they tend to require large capital investment and produce sludge, which must be disposed (Song, Meng, & Yang, 2008). Recently, more attention has been invested in developing dry methods for removal of SO_2 because of their potential simplicity and lower cost. One such method that shows great promise is using modified rice straw to adsorb SO_2 (Lu & Do, 2004).

Rice straw is one of the abundant lignocellulosic agricultural residue, especially in china (Binod, Sindhu, Singhania, & Vikram, 2010). As per FAO statistics, world annual rice straw produce was about 650–975 million tons globally, only a little part of those is going as cattle feed. The effective utilization of those straws is hard to find, most of them are burned (Chen & Yu, 2011; Dohnani, Nozire, Gaillard-Martinie, Puard, & Doreau, 2003; Pan, Zhou, Zhou, & Lian, 2010). Presently, with high price of petrochemical and people's recognition about the ecological environment and health problems, the utilization of rice straw is given more attention.

Besides some impurities like gum, rice straw is mainly composed of cellulose, hemicellulose, lignin, and water (Kong & Eichhorn, 2005). Cellulose is a linear crystalline macromolecule consisting of regio- and enantioselective β-1, 4-glycosidic linked D-glucose units (Li, Tabil, & Oguocha, 2007), and each unit contains three reactive hydroxyl groups. The large surface area and porosity give cellulose a certain adsorption capacity, and the presence of hydroxyl groups has created favorable conditions for chemical modification, which could further improve the adsorption properties of cellulose (Buranov & Mazza, 2008). Lignin, as a complex phenolic polymer, is composed of four alcohol monomers (P-coumaric alcohol, coniferyl alcohol, 5-hydroxy coniferyl alcohol, sinapic alcohol), and the phenolic hydroxyl, carbonyl, carboxyl, benzene and other active groups also create the possibility of chemical modification (Donaldson, 2007; Thevenot & Dignac, 2010). Several modification methods, e.g., esterification, etherification and graft copolymerization, have been developed for the modification of cellulose-based materials (Bertoti, Luporini, & Esperidiao, 2009; Chauvelon, Gergaud, Saulnier, & Lourdin, 2002; Hassan & Khan, 2009). Other chemical methods, such as sulfonation and hydroxymethylation, have been used in the modification of lignin-based materials (Crestini, Sermanni, & Dimitris, 1998; Shin & Roger, 2005). However, previous researches have just modified cellulose

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or lignin individually, no more studies on utilizing cellulose and lignin of rice straw simultaneously. Moreover, the reported investigations about chemical modification of rice straw mainly focused on esterification, etherification and graft copolymerization, the oxidation modification is rarely studied, let alone oxidating rice straw by potassium permanganate followed by amine functionalization. Additionally, the previous researches about application of modified straw mainly in adsorption of metal ions or organic matter, yet such reports on adsorption of SO_2 by modified straw was barely found.

Therefore, our researches focused on the adsorption properties of rice straw oxidated by potassium permanganate followed by ethylenediamine on SO_2. The effect of the different modifiers, the concentration of potassium permanganate and the moisture content on adsorption properties of rice straw were investigated. Finally, the changes of the element content, surface functional groups, crystallinity and surface morphology before and after modification were also analyzed by the chemical characterizations.

2. Experimental

2.1. Materials

The rice straw was obtained from a county farmland of Sichuan province in china, and was mainly composed of cellulose (37.3–38.1%), hemicellulose (18.3–19.9%), lignin (35.2–36.1%), and water (∼8%). The ethylenediamine, potassium permanganate, dimethyl formamide, sulfuric acid, phosphorus oxychloride, hydrogen peroxide, sodium periodate were purchased from Ke Long Chemical Reagent Company (Chengdu, China). All chemicals were of analytical grade. The gas of SO_2 was supplied by the Tian Yi Co. Ltd. (Chengdu, China).

2.2. Modification of rice straw

The immersing of rice straw in the dimethyl formamide solution called pretreatment was carried out for 4 h at room temperature, followed by extensive washing with water. Then the product of pretreatment (10 g) was put into flask. After this, a mixture of 5% potassium permanganate solution (200 mL), and 10% sulfuric acid (10 mL) was added. The reaction was carried out at room temperature for 1 h. After reaction, the product was washed with water until the pH of 7, and dried at 70 °C.

The oxidated straw was immersed in the 10% ethylenediamine solution under continuous magnetic stirring at 70 °C for 2 h. After reaction, the product was washed with extensive water until the pH of 7, and dried at 70 °C. Finally, the modified straw (Straw–$KMnO_4$–NH_2) was obtained.

2.3. Adsorption procedure of SO_2

The rice straw (6 g) either modified or unmodified was taken into fixed reactor (30 mm diameter, 300 mm high) with a certain amount of distilled water. Then the mixture gas of SO_2 and N_2, initial SO_2 concentration of 1500 ppm, went through the reactor at 300 mL/min. The residual gas of export was absorbed by 3% H_2O_2, and the absorbing liquid was titrated by 0.01 mol/L NaOH solution, then the desulphurization rate was calculated.

When desulphurization rate fell to 20%, adsorption procedure was stopped. Finally, the saturated sulfur capacity of samples was calculated. The flow chart of adsorption for SO_2 is shown in Fig. 1.

2.4. Characterization

The changes of element content of rice straw before and after modification were analyzed by an elemental analyser (Italian Elementar Analysen-systeme GmbH, EURO EA3000). IR analyses were carried out using an FT-IR spectrometer (Nicolet Co. Ltd., Nicolet 6700). About 2 mg of straw was mixed with 200 mg of spectroscopic grade KBr, and the FT-IR spectral were recorded with a detector at 4 cm^{-1} resolution and 16 scans per sample. XRD was measured by a Philips-3KWX Rigaku wide angle X-ray diffractometer (WAXD) at scan speed of 9° min^{-1}. For SEM analysis, the rice straw was shadowed with gold and then examined with a S-450 (Hitachi Co. Ltd.) scanning electron microscopy, which was operated at 20 kV.

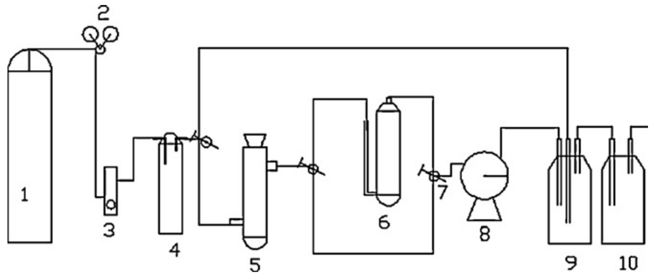

Fig. 1. Flow chart of adsorption of SO_2. (1) Mixed cylinders; (2) pressure reducing valve; (3) rotameter; (4) glass humidifier; (5) fixed reactor; (6) H_2O_2 absorption tube; (7) three-way valve; (8) wet type gas meter; (9) tail gas absorption bottles; (10) magenta detection bottle.

3. Results and discussion

3.1. The mechanism

The inter-reactive activities of ethylenediamine with the raw straw directly are poor, thus the potassium permanganate as oxidant was used first to react with rice straw to produce some new active groups. The oxidation of potassium permanganate of rice straw belongs to non-selective oxidation, and alcoholic hydroxyl of cellulose can be oxidated into aldehyde, carboxyl and semi-acetal groups. Meanwhile, potassium permanganate can also oxidate phenol hydroxyl and methoxy of the lignin into quinone, and the benzene ring will be destroyed. And then, the aldehyde and carboxyl groups react with ethylenediamine, introducing the amine. Carboxyl reacts with ethylenediamine by acid–base neutralization, and the C=O bond of carbonyl occurs addition reaction with ethylenediamine. Thus, the potassium permanganate during modification performs two roles: one is oxidating rice straw to produce more new active groups, another is as oxidant attaching on surface of rice straw. Therefore, the mechanism of desulfurization of the Straw–$KMnO_4$–NH_2 can be represented by the following two reactions:

$$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow 2MnSO_4 + K_2SO_4 + 2H_2SO_4 \qquad (1)$$

$$\text{Straw–}KMnO_4\text{–}NH_2 + SO_2 + H_2O \rightarrow [\text{Straw–}KMnO_4\text{–}NH_3{}^{+}]SO_3 \qquad (2)$$

3.2. Influencing factors on adsorption behavior of rice straw

3.2.1. Effect of the different modifiers

Some chemical modifiers have been studied previously in modification of rice straw (Li, Wu, Mu, & Lin, 2011; Liu, Yang, & Zhang, 2008; Sun, Sun, Fowler, & Baird, 2004), and the effect of different modifiers on the adsorption behavior of rice straw on SO_2 was studied by varying modifier, such as phosphorus oxychloride ($POCl_3$), hydrogen peroxide (H_2O_2), sodium periodate ($NaIO_4$), and potassium permanganate ($KMnO_4$), at a constant concentration of 5%, and moisture content of 200% at room temperature. The results of Table 1 reveal that the adsorption capacity of modified samples on

Table 1
The adsorption capacity of samples modified by different modifiers on SO_2.

Modifier	Adsorption capacity (mg/g)	Nitrogen content (%)
None	19.73	1.25
$POCl_3$	34.89	2.44
H_2O_2	25.52	1.23
$NaIO_4$	39.65	2.39
$KMnO_4$	341.62	3.80

SO_2 were better than that of the raw straw, especially the straw oxidated by potassium permanganate was much better than the other samples. This may be due to that the potassium permanganate, as a non-selective efficient oxidant, oxidated more hydroxyl of straw into carbonyl, carboxyl and other active functional groups, which could react with ethylenediamine effectively. Thus, the amount of amine introduced was more than other samples, resulting in the increase of adsorption capacity accordingly. On the contrary, the H_2O_2 and $NaIO_4$, as elective efficient oxidants, could only oxidate a little part of designated active hydroxyl groups, which led to lower adsorption capacity.

Besides, the potassium permanganate attaching to the sample would oxidate a part of SO_2, further improving the adsorption capacity of Straw–$KMnO_4$–NH_2. Also, as can be seen from Table 1 that the adsorption capacity and nitrogen content of samples accord with positive correlation to some extent.

3.2.2. Effect of the concentration of potassium permanganate

By keeping a constant moisture content (200%), the adsorption capacity of the rice straw oxidated by different concentrations of potassium permanganate from 1% to 10% was studied at room temperature. As shown in Fig. 2, the results reveal that the adsorption capacity of modified samples increased sharply with the increase of the concentration of potassium permanganate until 5%. Then it was level off when the concentration of potassium permanganate was above 5%. This can be easily explained based on the available alcoholic hydroxyl, phenol hydroxyl and methoxy groups of raw straw. At lower concentration of potassium permanganate, the increase in the concentration of potassium permanganate resulted in the increase of the extent of oxidation, and led to advancing the amine content of Straw–$KMnO_4$–NH_2, and correspondingly raised adsorption capacity. However, at higher concentrations of potassium permanganate (above 5%), the accessible hydroxyl groups of raw rice straw were depleted, which led to a constant amine content in Straw–$KMnO_4$–NH_2, as well as the adsorption capacity of modified samples on SO_2.

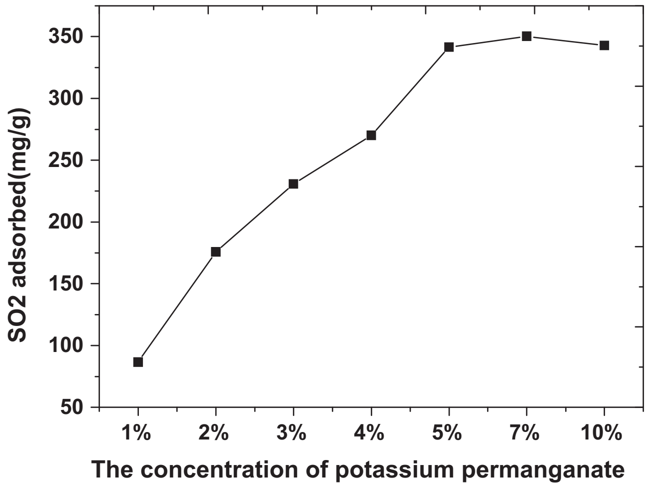

Fig. 2. Effect of the concentration of potassium permanganate on adsorption of SO_2.

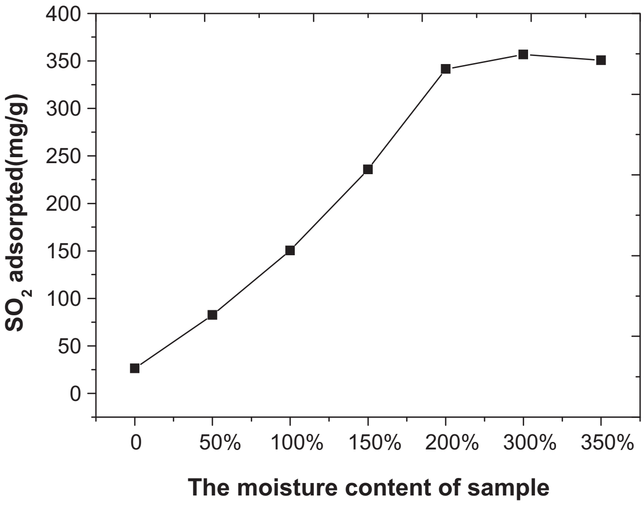

Fig. 3. Effect of the moisture content of sample on adsorption of SO_2.

Table 2
Analysis of Element content.

Sample	C (%)	H (%)	N (%)	O (%)
Raw straw	38.38	6.51	0.99	54.12
Pretreated straw	38.33	6.29	0.97	54.41
Oxidated straw	25.80	4.85	0.89	63.46
Straw–$KMnO_4$–NH_2	22.76	4.76	3.80	63.68

3.2.3. Effect of the moisture content

The effect of moisture content on the adsorption behavior of modified straw was studied by varying moisture content from 0 to 350% at a constant concentration of potassium permanganate (5%) at room temperature. From Fig. 3, it can be seen that the adsorption capacity of Straw–$KMnO_4$–NH_2 on SO_2 increases with the increase of moisture content until the moisture content of 200%, and it will not increase any more by extending moisture content. This maybe due to that (i) as can be seen from mechanism of desulfurization, water was indispensable in the reactions of desulfurization, and played a key role during the removal of SO_2; (ii) the pore of modified product would expand in water condition, which promoted the adsorption capacity of Straw–$KMnO_4$–NH_2; (iii) water, as a solvent, could make amine stable, which further improved the ability of the desulfurization. When these functions reached a certain level, excess water would not work, the adsorption capacity of modified straw remained constant.

3.3. Elementary analysis

Element content of the raw straw, pretreated material, oxidated straw and Straw–$KMnO_4$–NH_2 are shown in Table 2. The element content of straw nearly did not change after pretreating by dimethyl formamide. As for the sample oxidated by potassium permanganate, the C content decreased from 38.38% down to 25.80%, and the H content reduced from 6.51% to 4.85%. Nevertheless, the O content increased from 54.12% to 63.46%, This maybe due to that the C–C, C–H and benzene ring structure of straw were destroyed by potassium permanganate, and a large number of defects bit combined O atoms, thus resulting in the increase of oxygen content. Meanwhile, the introduction of potassium permanganate led to further increase of oxygen content. After modification, the N content increased markedly from 0.89% to 3.80%, it can be easily explained based on the introduction of the amine after reaction with ethylenediamine.

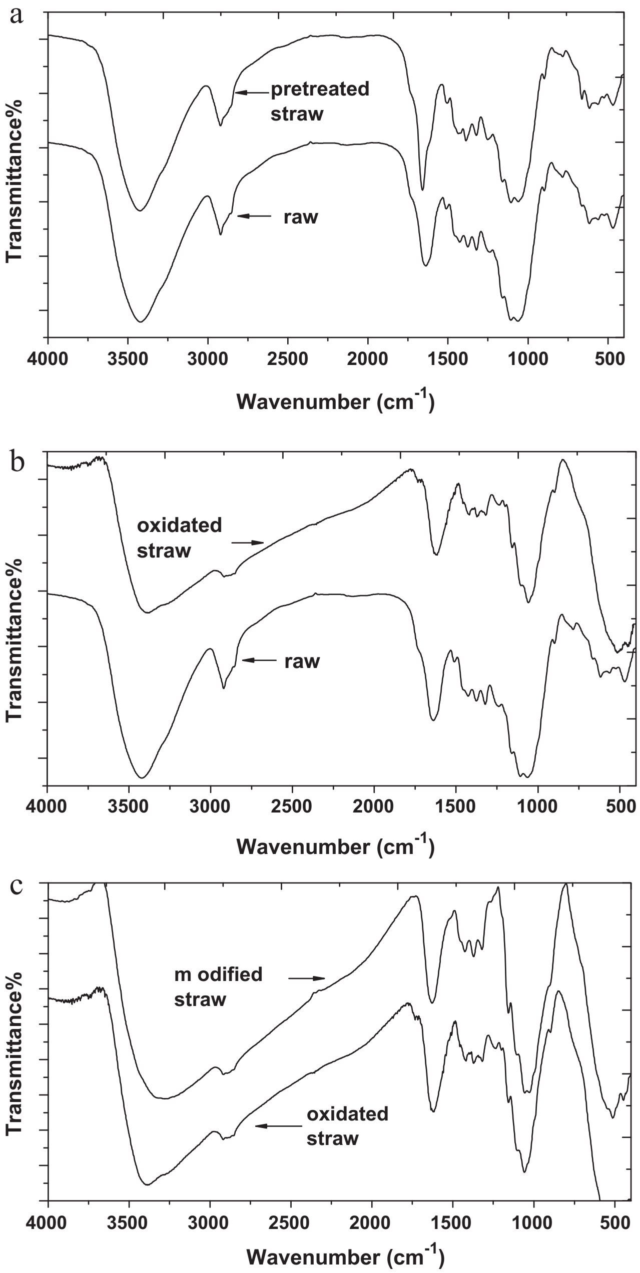

Fig. 4. FT-IR spectra of (a) comparison between raw straw and pretreated straw, (b) comparison between raw straw and oxidated straw, (c) comparison between oxidated straw and Straw–KMnO$_4$–NH$_2$.

3.4. FT-IR analysis

The IR spectra of the raw and the treated straw are shown in Fig. 4. The spectrum of the raw straw exhibited O–H stretching absorption around 3422 cm^{-1}, C–H stretching absorption around 2900–3000 cm^{-1}, C═O stretching absorption around 1638 cm^{-1}, and the alcohol hydroxyl stretching absorption around 1420–1260 cm^{-1}. These absorption peaks are consistent with those of the typical cellulose backbone (Zhang, Price, & Daly, 2006). Besides, the benzene stretching absorption around 1512 and 785 cm^{-1}, the phenolic hydroxyl stretching absorption around 1238 cm^{-1} were exhibited as well. These characteristic peaks are the typical lignin backbone (Alemdar & Sain, 2008; Reddy, Sardashti, and Simon (2010), Sun, Jing, Fowler, Wu, and Rajaratnam (2011). In the case of the pretreated straw, almost the same absorption peaks to those of the raw straw were observed except that O–H stretching absorption peak around 3422 cm^{-1} decreased, and moved to the high wave number of 3434 cm^{-1} (Fig. 4a). Those changes can be explained based on the fracture of hydrogen bond and the expansion of micropore after immersing in dimethyl formamide solution. Moreover, compared with the raw straw (Fig. 4b), the characteristic peaks of benzene at 1512 and 785 cm^{-1} in the oxidated straw disappeared, which was attributed to the modification of the lignin. The decrease of the band between 1420 and 1260 cm^{-1} and the peak at 1238 cm^{-1} in the oxidated straw indicated that both the alcohol hydroxyl and the phenolic hydroxyl were oxidated simultaneously, and accordingly appeared the carbonyl stretching absorption peak at 1720 cm^{-1}. The intensity of these peaks between 663 and 467 cm^{-1} increased, which was due to the increase of aliphatic aldehydes and ketones after oxidation. As for the Straw–KMnO$_4$–NH$_2$ (Fig. 4c), the characteristic absorption peaks of –NH$_2$ at 3385 cm^{-1} and 1020–1220 cm^{-1} increased markedly as a result of the introduction of amine.

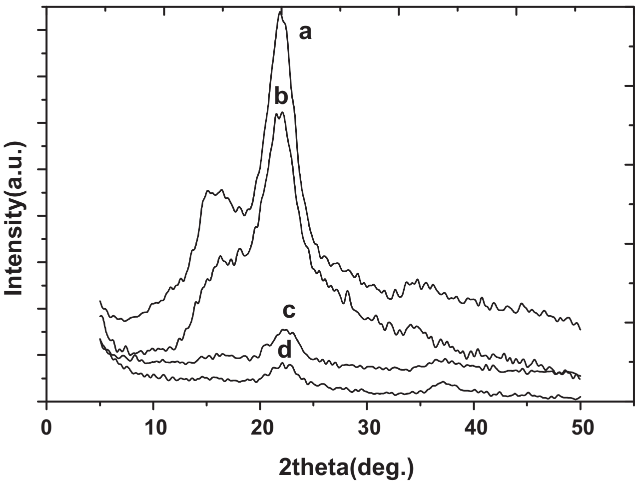

Fig. 5. XRD patterns of (a) raw rice straw, (b) pretreated straw, (c) oxidated straw, and (d) Straw–KMnO$_4$–NH$_2$.

3.5. XRD analysis

The XRD patterns of the raw straw, pretreated material, oxidated straw and Straw–KMnO$_4$–NH$_2$ are shown in Fig. 5. The diffractions at 2θ of 14.7°, 22.5°, and 39.7° were observed, which was attributed to the typical crystalline form of rice straw as reported in the references (Kong & Eichhorn, 2005; Wada, Heux, & Sugiyama, 2004; Yin et al., 2007). For the pretreated straw, the crystalline form and the peak intensity did not change. However, compared with the raw straw, the peak intensity of the oxidated straw declined markedly indicating the decrease in crystallinity. This maybe due to the oxidation effect of the potassium permanganate, which destroyed hydrogen bond and benzene, translated crystalline regions into non-crystalline regions. Thus, the accessibility and reactivity of functional groups were improved observably, as well as the possibility of combination with amine. After functionalization with ethylenediamine, the crystallinity did not change mainly.

3.6. SEM analysis

The surface morphology of the raw and modified straw is shown in Fig. 6. The raw straw has a very smooth and compact surface, and some grains are observable along the vertical section. The surface of the pretreated straw is quite similar to that of the raw straw.

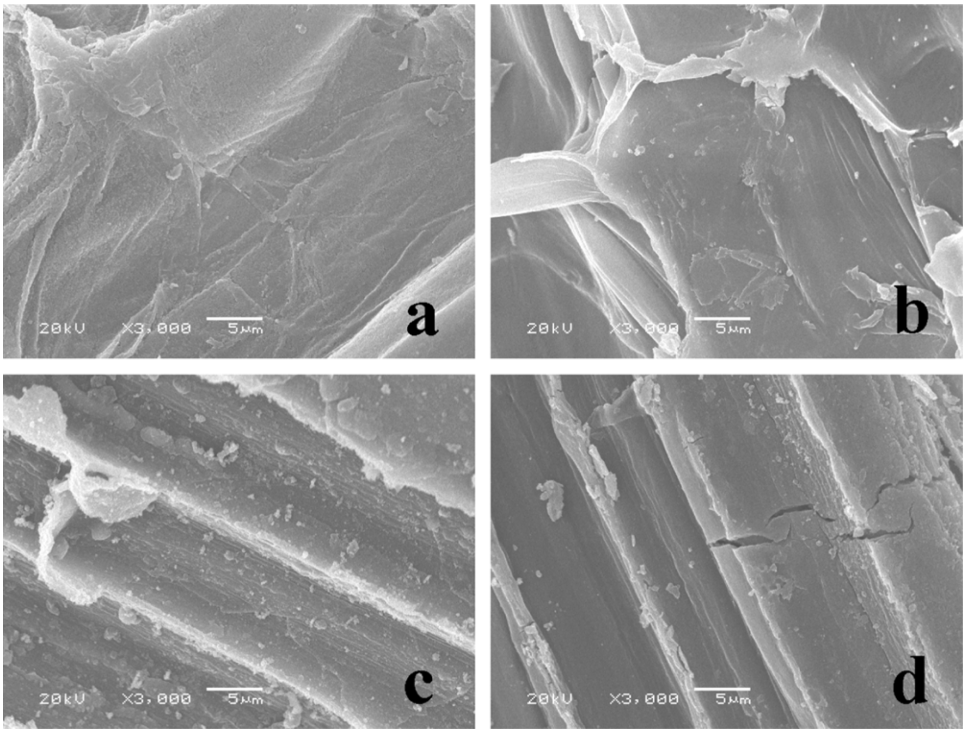

Fig. 6. SEM images of (magnification, 3000×): (a) raw rice straw, (b) pretreated straw, (c) oxidated straw, and (d) Straw–$KMnO_4$–NH_2.

However, after reacting with potassium permanganate, the surface of the straw becomes rough and attaches some material, which is presumably potassium permanganate as mentioned in mechanism. As for the Straw–$KMnO_4$–NH_2, almost the same surface morphology to that of oxidated straw is observed except the emergence of some fractures. Thus, there is only a little effect of functionalization with ethylenediamine on the surface morphology of oxidated straw observed by SEM.

4. Conclusions

The adsorption properties of rice straw oxidated by potassium permanganate followed by ethylenediamine on SO_2 were extensively studied under different conditions. The modification parameters were optimized as the concentration of potassium permanganate of 5%, the moisture content of 200%, as well as the reaction temperature of room temperature, and the saturated sulfur capacity of Straw–$KMnO_4$–NH_2 could reach ~340 mg/g, which was much better than that of raw straw or other reported modified samples. The characterization results show that the C and H content of rice straw decreased while the O and N content increased after modification, and the marked decrease of crystallinity of Straw–$KMnO_4$–NH_2 compared to the untreated straw improved the accessibility and reactivity of functional groups, as well as the possibility of combination with amine. FTIR analysis revealed that the decrease of hydroxy, the disappearance of benzene, and the increase of aldehyde proved that the cellulose and lignin of rice straw were utilized simultaneously. Besides, the increase of characteristic absorption peaks of amine indicated the success of amine functionalization. The surface of the Straw–$KMnO_4$–NH_2 became rough and attached some potassium permanganate after modification. Seeing from above, all these changes are beneficial to improve the adsorption capacity of rice straw. Therefore, it can be concluded from these results that the Straw–$KMnO_4$–NH_2 has great effective applications in adsorption of SO_2 and has potential industrial value.

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