Asian Journal of Chemistry; Vol. 27, No. 2 (2015), 477-481

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.16970

Effect of Chemical Treatment on Morphology, Structure and Properties of Peanut Shells

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Received: 1 January 2014; *Accepted*: 2 April 2014; *Published online*: 10 January 2015; AJC-16600

In the present work, different chemical modification methods have been used to treat raw peanut shell. Characterization of different samples is carried out with SEM, FTIR and XRD. The effect of cationic dye sorption from aqueous solution by using different peanut shells has also been investigated. SEM and FTIR show that some components of raw peanut shell have been removed during the chemical modification and many cavities of various dimensions are clearly evident on the surface of modified peanut shells. Moreover, there are some especial chemical interactions between raw peanut shell and modifying agents, which lead to significant changes in the groups of raw peanut shell surface. XRD of raw peanut shell displays a typical spectrum of cellulosic material. Compared to raw peanut shell, cellulosic crystal style of modified peanut shells is not obviously changed, but the crystallinity of cellulose increased. Maximum sorption capacity of peanut shells for malachite green is obtained by modification of organic solvents (99.99 %), higher than that of raw peanut shells (80.22 %). The base treated peanut shells also enhance the malachite green sorption (94.32 %).

Keywords: Peanut shell, Chemical modification, Cellulose, Malachite green.

INTRODUCTION

In China, peanut shell is an abundantly available by-product of the peanut blanching or oil extracting industries. The annual generation of peanut shell is estimated to be around 4.5 million tonnes, accounting about one-third of the annual gross production throughout the world[1]. However, as a low-value agricultural waste material, most of peanut shells are either burned for energy or abandoned, resulting in a tremendous waste of natural resources and environmental pollution. Therefore, any possible usage of peanut shells, especially on an industrial scale, will yield economic as well as environmental dividends.

Native peanut shells mainly consist of cellulose, hemicelluloses, proteins, polyphenols, luteolin and coarse fatness, *etc.*[2,3]. Among them, the amount of cellulose is about 65.7-79.3 %, which is the highest in peanut shells[4]. Cellulose is a carbohydrate homopolymer consisting of β-D-glucopyranose units joined together by β-1, 4-glycosidic linkages[5]. As presented in Fig. 1, this macromolecule contains three reactive hydroxyl groups at C-2, C-3 and C-6 atoms representing a favorable characteristic of peanut shells to be a potential adsorbent material.

Witek-Kerouac *et al.*[6] used peanut shells as an absorbent to remove Cu(II) and Cr(III) ions from aqueous environment. The obtained results and their comparison to other biosorbents reported in the literature showed that peanut shell biomass were an attractive, alternative low-cost biosorbent for removal of heavy metal ions from aqueous media. Adsorption experiments using peanut shell ash as an adsorbent have also been reported on other metal ions[7-9] such as Pb^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+}. Recently, several authors reported that peanut shells can be modified with some especial chemical treatment techniques to improve its adsorption properties[10,11]. Liu *et al.*[10] found that Hg^{2+} and Cd^{2+} can be adsorbed rapidly by peanut shells modified with epichlorohydrin and ethylenediamine. However, most of the above studies have obtained only equilibrium adsorption data or measured the kinetics and thermodynamic parameters of adsorption on peanut shells and few works focused on the effect of chemical treatment on the morphology or structure of peanut shells. Moreover, the study about the removal of dyes using chemical modified peanut shells has been less reported[12].

In this study, chemically modified adsorbents have been prepared by treating raw peanut shells with three different chemical methods. Scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray diffractometer (XRD) have been used to characterize these adsorbents. The influences of chemical treatments on the adsorption capacity of peanut shells for malachite green, a basic and cationic dye, have also been investigated.

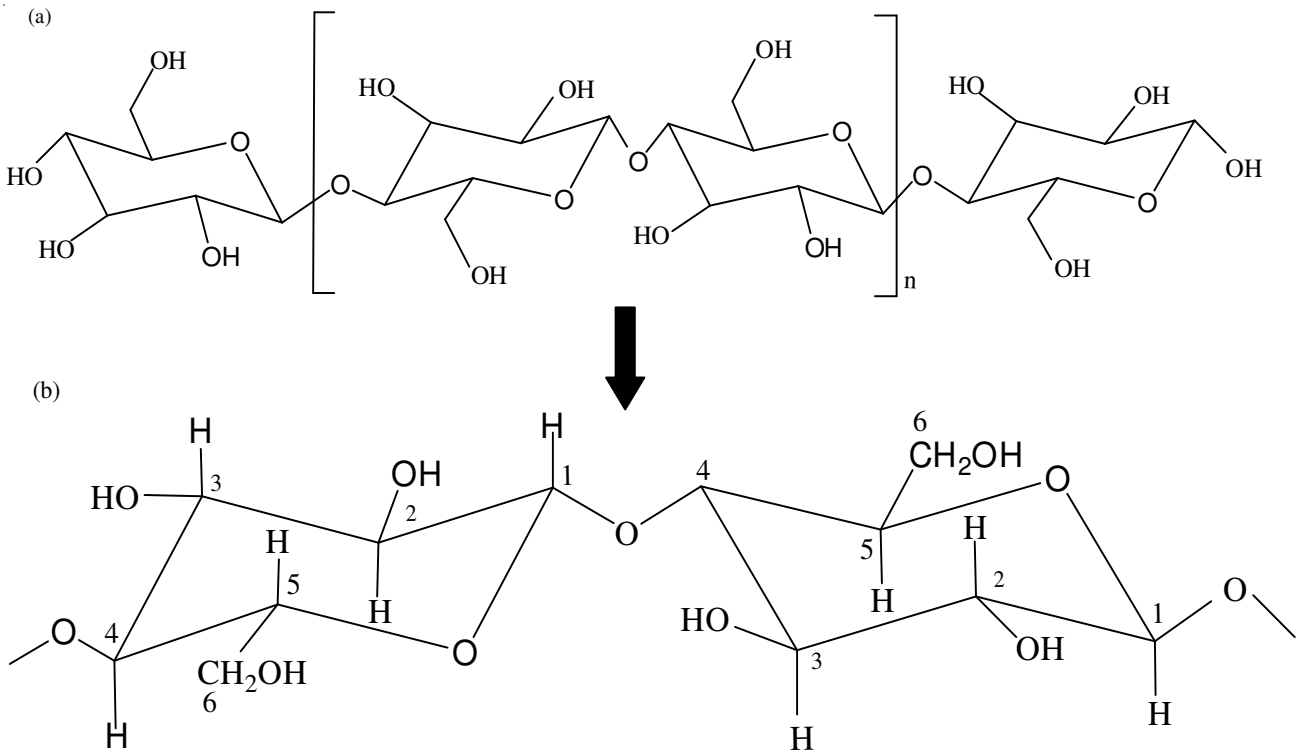

Fig. 1. Structure of cellulose (a) and cellobiose unit (b)

EXPERIMENTAL

Raw peanut shells used in the present study were collected from a local market in Zibo (City in Shandong province, China). The collected peanut shells were extensively washed several times with tap water to remove soil and dirt, then rinsed in an ultrasonic bath with deionized water and dried at 110 °C for 24 h in an even drier. Finally, the dried samples were crushed to the desired particle size. Malachite green (Fig. 2) (Sigma Aldrich, USA) was used without further purification. Other chemicals used were of AR grade and all solutions were prepared with distilled water.

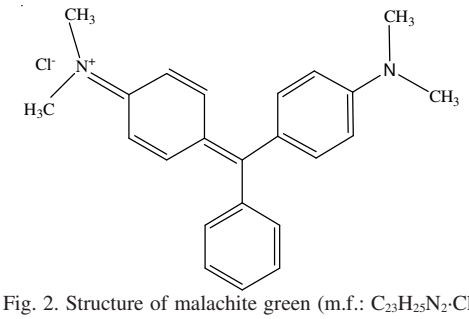

Fig. 2. Structure of malachite green (m.f.: $C_{23}H_{25}N_2 \cdot Cl$)

Modification of peanut shells

Modification with acid: 8 g crushed peanut shells were mixed with 150 mL of hydrochloric acid solution (1 mol/L) and the mixture was heated to 70 °C for 5 h with occasional stirring. The obtained samples were left overnight and then filtered to remove the unused hydrochloric acid. Modified peanut shells were washed several times with distilled water to provide neutral pH oven-dried for 10 h and stored in a desiccator.

Modification with base: 5 g crushed peanut shells were mixed with 200 mL of NaOH solution (1 mol/L) at 60 °C for 10 h. The mixture was then filtered, rinsed with water, oven-dried and stored in a desiccator. The obtained mixture was then filtrated with a 100-mesh stainless screen, rinsed with distilled water for three times, oven-dried at 65 °C for 12 h and stored in a desiccator for used.

Modification with organic solvents: The organic solvents modification of peanut shells was made according to the reported method[10,13]. 10 g of peanut shells were mixed with 80 mL of NaOH solution (1.25 mol/L) and 30 mL of epichlorohydrin at 40 °C for 1 h. The mixture was then filtered, rinsed with water, oven-dried. Modified peanut shells (MPS) were prepared by adding 10 mL ethylenediamine solution, 100 mLwater and 1 g $NaCO_3$ to each 10 g peanut shells modified with epichlorohydrin. The mixture was then mixed by agitation at 60 °C for 2 h. Modified peanut shells were oven-dried and stored in a desiccator. To facilitate the following discussion, peanut shells before and after modification were marked raw peanut shell (raw peanut shell), **MPS1** (acid-modified peanut shell), **MPS2** (base-modified peanut shell) and **MPS3** (organic solvent-modified peanut shell), respectively.

The morphological information of peanut shells was provided by scanning electron microscopy (SEM; FEI Sirion 200, NLD). The molecular structure analyses of all the samples were carried out with Fourier transform infrared spectra (FTIR, Nicolet 5700, USA). Sample structures were analyzed by X-ray diffraction (XRD, D8 Advance, GER) with $CuK_{\alpha 1}$ radiation. All the measurements were performed at room temperature.

The adsorption experiments were performed according to previous study[14]. 20 mL of malachite green solution (initial concentration 300 mg/L, initial pH 7) was mixed with 0.40 g

of peanut shells and maintained under shaking at 30 °C on a thermostated shaker (SHZ-92A) until adsorption equilibrium reached. The suspension of the adsorbent and dye solution was separated by a centrifugation at 4500 rpm for 20 min. The absorbencies of malachite green solution were measured by using UV-visible spectrometer (Model TU-1901, CHI) at 617 nm. Then, the concentrations of the solutions were determined by using linear regression equation ($y = 0.0875x + 0.0086$, $R^2 = 0.9994$ (0.1-1 mg/L); $y = 0.1092x - 0.0189$, $R^2 = 0.9997$ (1-10 mg/L)) obtained by plotting a calibration curve for dye over a range of concentrations. All experiments were conducted in triplicate. Then, the percent removal (%) of organic dyes was calculated using the following equation:

$$\text{Removal}\ (\%) = \frac{C_0 - C_e}{C_0} \times 100\ \% \quad (1)$$

RESULTS AND DISCUSSION

Effect of chemical treatment on the morphology of peanut shells: The morphological changes occurred during the chemical modification can be observed by comparing the SEM images of different samples. Fig. 3a showed that there are large irregular fragments and particle-like impurities in the surface morphology of raw peanut shell. Compared with raw peanut shell, the surface morphologies of **MPS1**, **MPS2** and **MPS3** become neater and particle-like impurities are almost removed after different chemical treatments (Fig. 3b-d). Moreover, many cavities of various dimensions are observed in the SEM for all modified samples. The size of these cavities is in the range of 1-3 μm. These significant changes after treatments may be arising from the corrosive action of dilute acids and alkalis. The presence of cavities indicates that there is a large exposed surface area of peanut shells and the dye molecules should easily penetrate into the lignocellulosic structure.

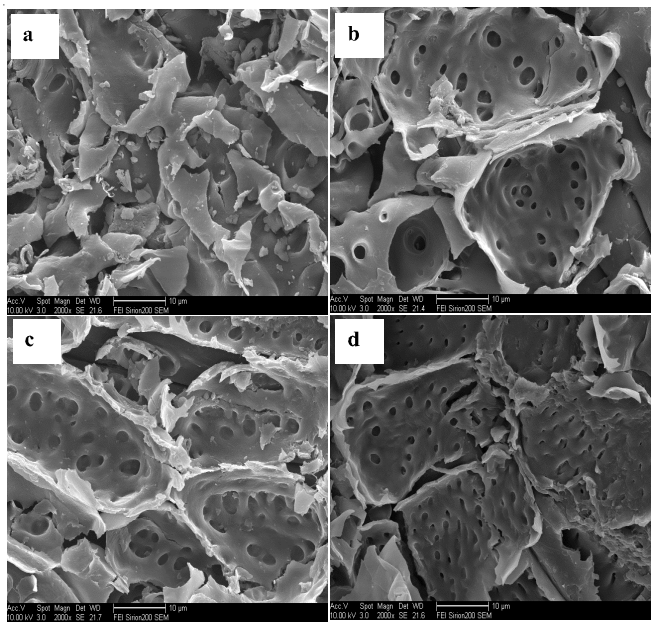

Fig. 3. SEM morphologies of (a) raw peanut shell, (b) **MPS1**, (c) **MPS2** and (d) **MPS3**

Effect of chemical treatment on the chemical structure of peanut shells: To further understand the changes of the components, FTIR spectra are recorded to compare the modified peanut shells with the raw sample. FTIR spectrum of raw peanut shell is similar to that of previous studies[1,15-17]. A wide and strong -OH stretching band observed between 3400-3300 cm^{-1} is ascribed to the presence of polyphenols, luteolin, cellulose and hemicellulose. Also, this broad band related to hydrogen bonding verifies that water is still remaining in the samples. The absorption band at 1736.6 cm^{-1} is ascribed to the stretching vibrations of the carboxyl groups on the edges of layer planes or to conjugated carbonyl groups (C=O in carbonyls, luteolin or lactones groups). Stretching absorption band at 1638.1 cm^{-1} is assigned to C=C present in olefinic vibrations in aromatic region. Absorption bands at 1462.6, 1423.7 and 1374.3 cm^{-1} are assigned as C-H bending vibrations that show the presence of luteolin, sugar, cellulose and hemicellulose. Two strong bands observed at 1265.2 and 1051.2 cm^{-1} are assigned to C-O-C and C-O-(H) stretching vibrations, respectively, present in luteolin, cellulose and hemicellulose (Fig. 4a).

Fig. 4b-d exhibit the comparison spectra of raw and **MPS1**, **MPS2**, **MPS3**, respectively. From Fig. 4-b,c, it can be observed that FTIR spectra of **MPS1** and **MPS2** is essentially the same as that of raw peanut shell, which indicate that the acid or base treatment does not change the structure of raw peanut shell significantly. However, there are some slight decreases in the intensities of some adsorption bands (2000-500 cm^{-1}), which indicate some components, such as polyphenols, hemicelluloses, carboxylic acids and luteolin, have been removed during the above chemical treatments. Beyond that, the decrease of functional group contents may represent some intermolecular hydrogen bonds breaking[18].

After raw peanut shell is modified with organic solvents, FTIR spectrum of **MPS3** shows that one peak (1736 cm^{-1}) disappears and some broad bands (2000-500 cm^{-1}) weaken (Fig. 4d). These results indicate that some complex chemical reactions have gone through during epichlorohydrin-ethylenediamine treatment of raw peanut shell[10].

Effect of chemical treatment on crystalline structure of peanut shells: Materials with crystalline structures can diffract and form specific patterns if X-ray is used to irradiate samples, which can be used to study the inner microstructures of samples. As shown in Fig. 5a, the XRD pattern of raw peanut shell displays typical spectrum of cellulosic material. Two peaks present at 2θ of 22° and 16° correspond to cellulose-I and II, respectively[18,19]. The peak at 2θ of 22° is the main peak, representing the presence of a highly organized "crystalline" cellulose structure, whereas the smaller peak at 2θ of 18° represents a less organized "amorphous" cellulose structure.

XRD diagrams of all modified samples are essentially the same as those of raw peanut shell except one difference (Fig. 5b-d). There is some slight increase in the degree of crystallinity of cellulose after treatment with different reagents, as evident from the sharper diffraction peaks of (Fig. 5b, c and d) compared to those of (Fig. 5a). These results can be explained by the fact that chemical reagents only reach the surfaces of amorphism and crystal areas and the chemical

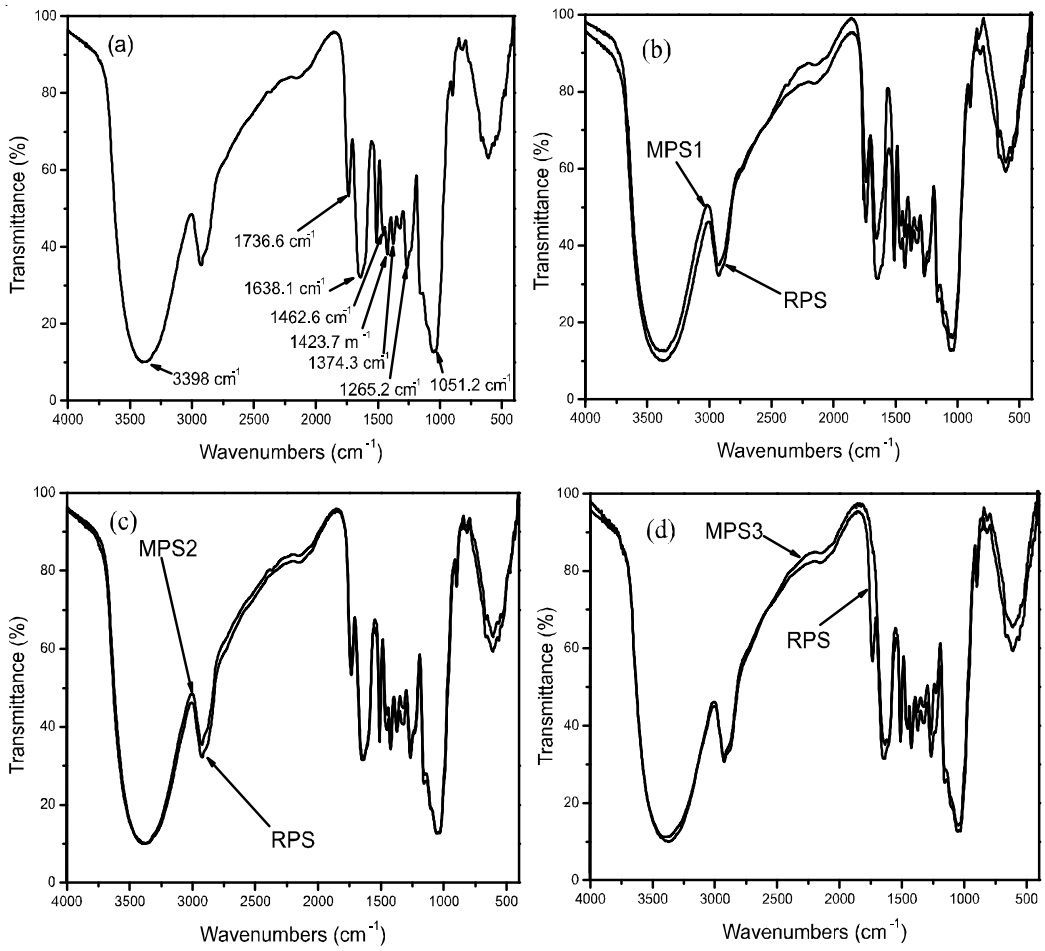

Fig. 4. FTIR spectra of raw peanut shell (a) and modified peanut shells (b,c,d)

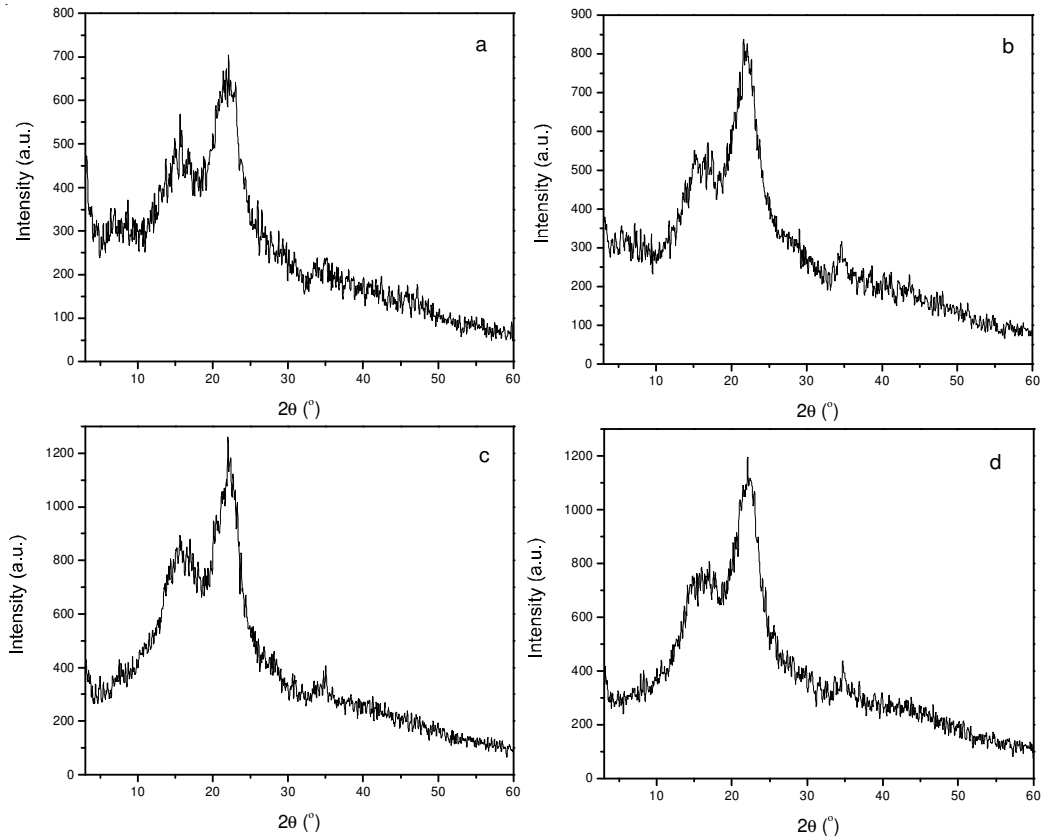

Fig. 5. X-ray diffraction patterns of (a) raw peanut shell, (b) **MPS1**, (c) **MPS2** and (d) **MPS3**

interaction only take place between the crystal areas. As a result, the cellulosic crystal style in chemically-treated samples is not obviously changed. On the other hand, the increased crystallinity of cellulose can be attributed to the chemical treatments, which have removed some amounts of the non-crystallinity components including polyphenols, hemicelluloses and luteolin, increased the proportion of cellulose and therefore, resulted in a slight increase of the crystallinity of the cellulosic rich preparations. Moreover, the greater hydrolyzation of the amorphous areas than crystalline areas shall be taken into account[18].

Effect of chemical treatment on the adsorption properties of peanut shells: Fig. 6 shows the effect of chemical modification on the removal ratios of malachite green. The chemical modifications result in increasing the malachite green uptake of raw peanut shell from 78.62 to 93.36 and 99.99 % for **MPS2** and **MPS3** respectively, whereas it results in decreasing the uptake from 80 to 47.72 % for **MPS1**.

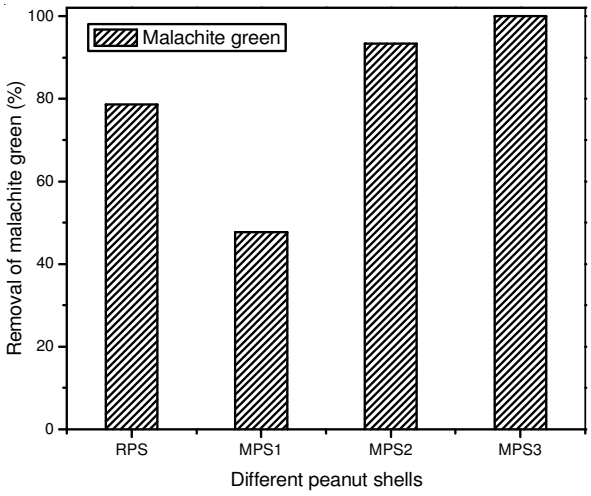

Fig. 6. Influence of chemical modification on adsorption of malachite green by peanut shells

As it can be seen from Fig. 1, there are a number of hydroxyl groups in cellulose, which plays an important role in the sorption of cationic dyes from aqueous solution[20]. The result of base treating is to remove some base soluble materials from raw peanut shells and a number of hydroxyl groups have been bared. Moreover, as shown in SEM, the larger pore size or higher porosity may be convenient for the dye molecules to penetrate into the lignocellulosic structure and interact therein with more hydroxyl groups. Maximum sorption capacity of peanut shells for malachite green is obtained by modification of epichlorohydrin and ethylenediamine, which indicates that the grafting of the amino group may be produce some positive influence on the adsorption of malachite green. Moreover, the use of organic solvents can help in the removal of organic impurities in raw peanut shell.

Acid modification has also removed impurity content of raw peanut shell and increased porosity, but as the number of positively charged surface sites increases during the acid treatment, the electrostatic repulsion between the positively charged dye and the surface of the modified peanut shells is higher[21,22]. This may be the reason for **MPS1** have obtained the lowest percentage removal of malachite green (32.38 %).

Conclusion

In summary, influences of three different chemical treatments on the morphology, structure and properties of peanut shells have been investigated. SEM and FTIR show that some components of raw peanut shell have been removed during the chemical modification and many cavities of various dimensions are clearly evident on the surface of modified peanut shells. Moreover, there are some especial chemical interactions between raw peanut shell and modifying agents, which lead to significant changes in the groups of raw peanut shell surface. XRD of raw peanut shell displays the typical spectrum of cellulosic material. Compared to raw peanut shell, cellulosic crystal style of modified peanut shells is not obviously changed, but the crystallinity of cellulose increased. The results from the sorption of malachite green show that the organic solvents or base modified peanut shells have an excellent sorption capacity than that of raw peanut shell. These modified peanut shells should be a promising and low cost adsorbent for the removal of malachite green in industrial wastewater treatment.

ACKNOWLEDGEMENTS

This work was financed by the Natural Science Foundation of Shandong Province (No. ZR2011EL033). The authors also thank the Scientific Research Foundation from Shangdong University of Technology (No. 410010).

REFERENCES

1. T. Xu and X. Liu, *Chin. J. Chem. Eng*., **16**, 401 (2008).
2. F. Gao, H. Ye, Y. Yu, T. Zhang and X. Deng, *Food Chem*., **129**, 920 (2011).
3. R. Han, P. Han, Z. Cai, Z. Zhao and M.J. Tang, *Environ. Sci*., **20**, 1035 (2008).
4. Y.Z. Shi and Y.H. Wu, *J. Peanut Sci*., **37**, 41 (2008).
5. L. Wojnarovits, C.M. Foldvary and E. Takacs, *Radiat. Phys. Chem*., **79**, 848 (2010).
6. A. Witek-Krowiak, R.G. Szafran and S. Modelski, *Desalination*, **265**, 126 (2011).
7. S.W. Liao, C.I. Lin and L.H. Wang, *J. Taiwan Inst. Chem. E*, **42**, 166 (2011).
8. H.R. Wu, C.I. Lin and L.H. Wang, *J. Taiwan Inst. Chem. E*, **42**, 658 (2011).
9. S. Taha, S. Ricordel and I. Cisse, *Energy Procedia*, **6**, 143 (2011).
10. Y. Liu, X.M. Sun and B.H. Li, *Carbohydr. Polym*., **81**, 335 (2010).
11. Q. Li, J. Zhai, W. Zhang, M. Wang and J. Zhou, *J. Hazard. Mater*., **141**, 163 (2007).
12. H. Li, J. Liao, T. Xiang, R. Wang, D. Wang, S. Sun and C. Zhao, *Desalin. Water Treatment*, **309**, 1 (2013).
13. S. Li, L. N. Zhang and J. Fan, *Biol. Chem. Eng*., **42**, 30 (2008).
14. J. Li, Q. Gao, H. Ua Zhang, Y. An Zhou and H. Wang, *J. Macromol. Sci. A*, **49**, 674 (2012).
15. H. F. Lv, J. P. Zhai, Q. Li and J. Zhou, *Environ. Pollut. Con*., **29**, 837 (2007).
16. E. Apaydin-Varol and A.E. Pütün, *J. Anal. Appl. Pyrolysis*, **98**, 29 (2012).
17. H.P. Yang, R. Yan, H.P. Chen, D.H. Lee and C. Zheng, *Fuel,* **86**, 1781 (2007).
18. Y.F. He, Y.Z. Pang, Y.P. Liu, X.J. Li and K.S. Wang, *Energy Fuels*, **22**, 2775 (2008).
19. Y. Sun, L. Lu, H.B. Deng, J.Z. Li, B.H. He, R.C. Sun and P.K. Quyang, *BioResources*, **3**, 297 (2008).
20. R. Gong, Y. Sun, J. Chen, H. Liu and C. Yang, *Dyes Pigments*, **67**, 175 (2005).
21. C. Pradeep Sekhar, S. Kalidhasan, V. Rajesh and N. Rajesh, *Chemosphere*, **77**, 842 (2009).
22. B.H. Hameed and M.I. El-Khaiary, *J. Hazard. Mater*., **154**, 237 (2008).