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Dyes and Pigments 67 (2005) 175–181

DYES and PIGMENTS

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# Effect of chemical modification on dye adsorption capacity of peanut hull

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Received 27 July 2004; received in revised form 13 August 2004; accepted 9 December 2004
Available online 19 February 2005

## Abstract

In this paper, the roles played by three major functional groups (amino, carboxyl and hydroxyl groups) in the biomass of peanut hull in adsorption of six dyes were investigated. These functional groups in peanut hull were chemically modified individually to determine their contribution to the adsorption of ionic dyes. The dyes used were methylene blue (MB), brilliant cresyl blue (BCB), neutral red (NR), amaranth (Am), sunset yellow (SY) and fast green FCF (FG). It was found that carboxyl group inhibited the adsorption of anionic dyes but it was major functional group in the adsorption of cationic dyes, hydroxyl group was important functional group in the adsorption of all six dyes and the effect of methylation of amino group was not significant on the adsorption of six dyes.

*Keywords:* Chemical modification; Dye adsorption; Peanut hull; IR spectrum; XRD

## 1. Introduction

Dyes are a kind of organic compounds which can bring bright and firm color to other substances. Synthetic dyes usually have a complex aromatic molecular structure which possibly comes from coal-tar based hydrocarbons such as benzene, naphthalene, anthracene, toluene, xylene, etc. The complex aromatic molecular structures of dyes make them more stable and more difficult to biodegrade [1,2]. Today there are more than 10,000 dyes available commercially [3]. Synthetic dyes have been increasingly used in the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and food industries. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharged into environmental water bodies. For some dyes, the dye concentration of less than 1 ppm in receiving water bodies is highly visible, so that even small quantities of dyes can color large water bodies. This not only affects aesthetic merit but also inhibits sunlight penetration and reduces photosynthetic action. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic [4,5].

The conventional methods for removal of dyes from wastewaters include coagulation and flocculation [6], oxidation or ozonation [7,8], membrane separation [9] and adsorption [10]. Activated carbon is popular and effective dye sorbent, but its relatively high price, high operating costs and problems with regeneration hamper its large scale application. Therefore, there is a growing need in finding low cost, renewable, locally available materials as sorbent for the removal of dye colors.

Some low cost botanic materials had directly been used as sorbent for dye adsorption from wastewater, which included apple pomace, wheat straw [11], orange

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doi:10.1016/j.dyepig.2004.12.003

peel [12], banana peel [13], maize cob [3], maize stalk [14], rice husk [15], barley husk [16], peanut hull [17], wood chip [18], palm fruit bunch [19,20], sawdust [21], bark [22], leaf [23], coir pith [24], banana pith [25], bagasse pith [26] and aquatic plants [27,28]. But few researches had been done about the interaction between functional groups in biomaterial and a variety of dyes. In this paper, the roles played by three major functional groups (amino, carboxyl and hydroxyl groups) in the biomass of peanut hull in adsorption of six dyes were investigated. The aim of this study was to identify the possible dye adsorption mechanisms of peanut hull. The dyes selected as sorbate were three cationic dyes: methylene blue (MB), brilliant cresyl blue (BCB), neutral red (NR) and three anionic dyes: amaranth (Am), sunset yellow (SY), fast green FCF (FG).

## 2. Materials and methods

### 2.1. Preparation of dye solutions

The dyes used in this study are listed in Table 1. Their chemical structures are shown in Fig. 1. Six dyes (MB, BCB, NR, Am, SY and FG), in commercial purity, were used without further purification. The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 200 mg/l. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to needed initial concentrations. The initial pH of each dye solution was adjusted with 0.1 M $HNO_3$ or NaOH using pH meter to its effective adsorption pH value obtained from the results of earlier experiments.

### 2.2. Preparation of peanut hull sorbent

The peanut hull used in this study was obtained from a local market. The collected biomaterial was extensively washed with tap water to remove soil and dust, sprayed with distilled water then dried in an oven at 80 °C to a constant weight. Dry biomass was crushed into powder and sieved to different particle sizes, then the biomaterial of uniform size (80–100 mesh) was preserved in the desiccator for further chemical modification.

Table 1
The general data of six dyes used in this study

| Trade name | Classification | C.I. no | FW | $\lambda_{max}$ (nm) |
|---|---|---|---|---|
| MB | Phenothiazine | 52015 | 373.9 | 670 |
| BCB | Phenoxazine | 51010 | 317.8 | 630 |
| NR | Phenazine | 50040 | 288.8 | 530 |
| Am | Monoazo | 16185 | 604.49 | 520 |
| SY | Monoazo | 15985 | 452.37 | 490 |
| FG | Triphenylmethane | 42053 | 808.86 | 620 |

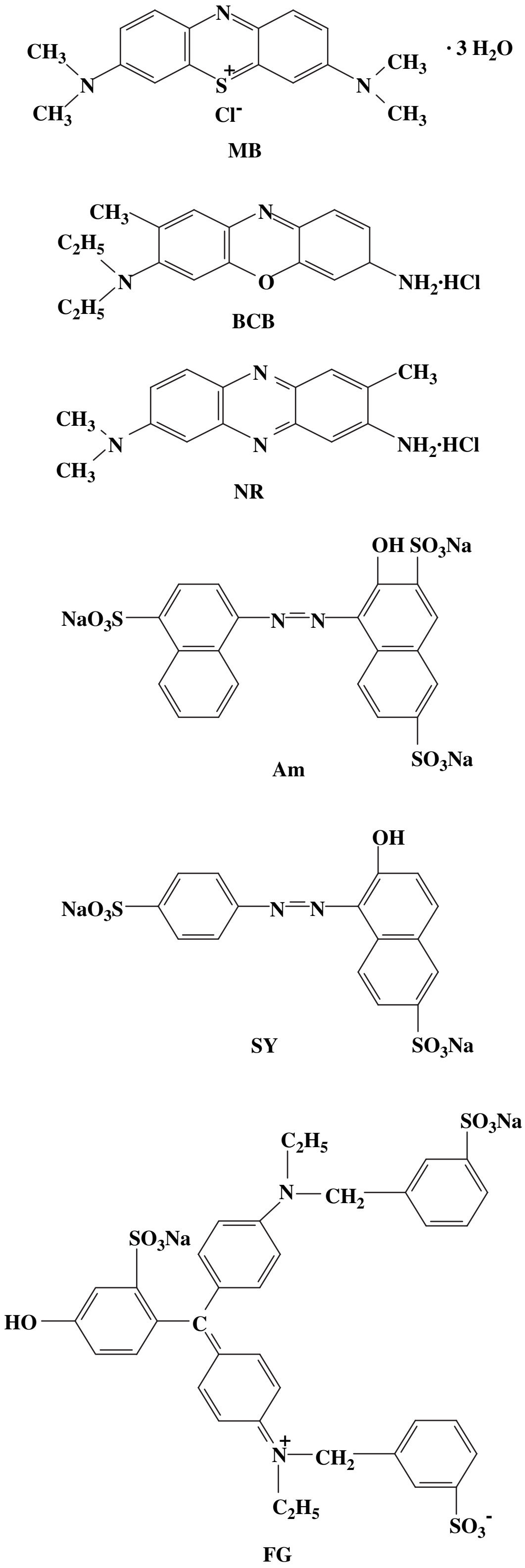

Fig. 1. Chemical structures of the six dyes used in this study.

### 2.3. Chemical modification of the biomaterial

#### 2.3.1. Methylation of amino group

The modification of amino group was made according to the same method previously reported [29,30], by shaking at ambient temperature 9 g (dry weight) of the raw biomass in 180 ml of formaldehyde (HCHO) and 360 ml of formic acid (HCOOH) for 6 h at 125 rpm. Then the treated biomaterial was thoroughly washed with distilled water, filtered and dried. This treatment resulted in methylation of amino group. The general reaction scheme is:

$$\mathrm{RNH_2 + 2HCHO + 2HCOOH \rightarrow RN(CH_3)_2 + 2CO_2 + 2H_2O}$$

#### 2.3.2. Esterification of carboxyl group

The carboxyl group of the biomass was methanol esterified following a similar method previously described [31]. Esterification was carried out by heating biomass of 9 g suspended in 633 ml of 99.9% pure methanol and 5.4 ml of concentrated hydrochloric acid (HCl) given a final acidic concentration of 0.1 M HCl under reflux for 48 h. Then the esterified biomaterial was thoroughly washed with distilled water, filtered and dried. The general reaction scheme of this treatment is:

$$\mathrm{RCOOH + CH_3OH \xrightarrow{H+} RCOOCH_3 + H_2O}$$

#### 2.3.3. Acetylation of amino and hydroxyl group

According to the method previously used [32], total acetylation of amino and hydroxyl group of the sorbent was carried out by refluxing the biomass suspension in acetic anhydride at 80 °C for 10 h. Then the acetylated biomaterial was thoroughly washed with distilled water, filtered and dried. The general reaction scheme of this treatment is:

$$\mathrm{RNH_2 + (CH_3CO)_2O \rightarrow RNHCOCH_3 + CH_3COOH}$$

$$\mathrm{RCH_2OH + (CH_3CO)_2O \rightarrow RCH_2OCOCH_3 + CH_3COOH}$$

### 2.4. Dye adsorption experiments

The adsorption experiments of cationic dyes were carried out in a rotary shaker at 150 rpm and at ambient temperature using 250 ml shaking flasks containing 100 ml dye solutions. The concentration and initial pH value of dye solution were 100 mg/l and 5.0, respectively. Four flasks were used for each dye. Raw, methylated, esterified and acetylated biomaterials (0.2 g) were respectively added to four flasks of each dye, then the flasks were sealed up to prevent change of volume of the solution during the experiments. After shaking the flasks for 24 h, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by filtration with a 200 mesh/inch stainless steel sieve then centrifugation. Dye concentrations in the supernatant solutions were determined.

The adsorption experiments of anionic dyes were carried out following a similar method as cationic dye adsorption, but the concentration and initial pH value of dye solution were 50 mg/l and 2.0, respectively. Furthermore, 0.5 g of raw, methylaed, esterified and acetylated biomaterials were used and the adsorption time was 36 h.

### 2.5. Dye concentration determination

Dye concentrations were estimated by measuring adsorbance at maximum wavelengths of dyes with a 752W UV–vis Grating Spectrophotometer (Shanghai, China) and computing from the calibration curves. The amounts of dyes sorbed by the biomaterials were calculated using the following equation:

$$q = (C_0 - C_e)V/W$$

where $q$ (mg/g) is the amount of dye sorbed by biomass, $C_0$ and $C_e$ (mg/l) are the initial and equilibrium liquid-phase concentration of dye, respectively, $V$ (l) is the initial volume of dye solution, and $W$ (g) is the weight of the biomass.

The experiments were conducted in duplicate and the negative controls (with no sorbent) and were simultaneously carried out to ensure that adsorption was by peanut hull biomass and not by the container.

### 2.6. IR spectra and XRD study

The IR spectra of raw and chemically modified sorbents were obtained using a Fourier transform infrared spectrometer (BIO-RAD FTS-40). For IR spectra, 5 mg of biomass was encapsulated in 400 mg of KBr. Translucent disk was made by pressing the

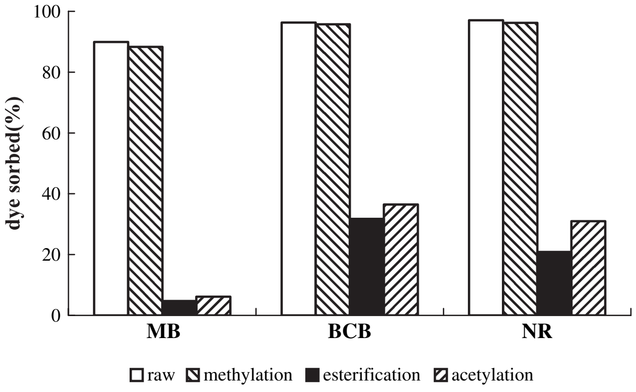

Fig. 2. Effect of chemical modification on adsorption of MB, BCB, NR by peanut hull.

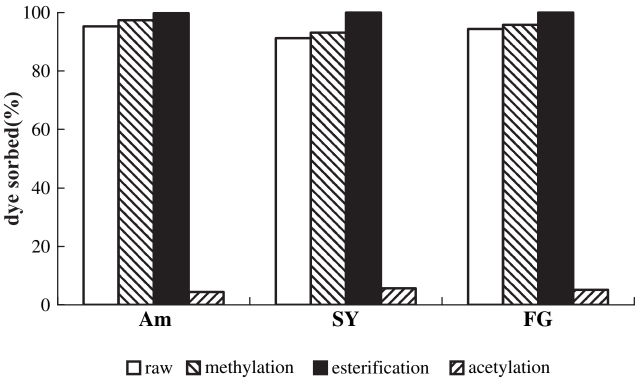

Fig. 3. Influence of chemical modification on adsorption of Am, SY, FG by peanut hull.

ground mixed material with the aid of a bench press (955 kg for 10 min).

Crystallinities of the raw and chemically modified sorbents were determined by X-ray diffraction using a diffractometer (X'TRA ARL) operated at 50 kV and 40 mA. The scanning scope and scanning speed were 5–55° and 10°/min, respectively, using Cu $K_{\alpha}$ radiation.

## 3. Results and discussion

### 3.1. Effect of dye adsorption by chemical modification

The effects of chemical modification on the removal ratios of cationic dyes are shown Fig. 2. None of chemical modification increased dye adsorption ratios. After amino group methylation, removal capacities of three dyes decreased, but only a little. Esterification of carboxyl group induced rapid decrease of three dye adsorptions; this experimental result proved that carboxyl group was major functional group in the adsorption of cationic dyes. Total acetylation of amino and hydroxyl groups also decreased the adsorption percentages of all three dyes, but decrease extent was less than that of esterification, it indicated that hydroxyl group also was important functional group in the adsorption of cationic dyes.

Fig. 3 showed the influences of chemical modification on adsorption percentages of anionic dyes. Methylation of amino group increased slightly the adsorption ratios of three dyes. After carboxyl group esterification, three dyes were completely removed from solution, it indicated that the carboxyl group bearing negative charge inhibited the adsorption of anionic dyes and in case removing the negative charge of carboxyl group by esterification, dye uptake capacities were obviously increased. Total acetylation of amino and hydroxyl groups extremely decreased the adsorption ratios of all three dyes, it showed that hydroxyl group was important functional group in the adsorption of anionic dyes.

### 3.2. Influence of IR spectra and XRD by chemical modification

The IR spectra of raw and chemically modified biomaterials are shown in Figs. 4–7. From Fig. 5, it could been seen, the broad mixed stretching vibration adsorption band of amino and hydroxyl groups at 3392 $cm^{-1}$ was reduced, it was the result of methylation. Fig. 6 showed that esterification brought reduction of stretching vibration adsorption band of carboxyl group at 1730 $cm^{-1}$. Fig. 7 indicated that the stretching

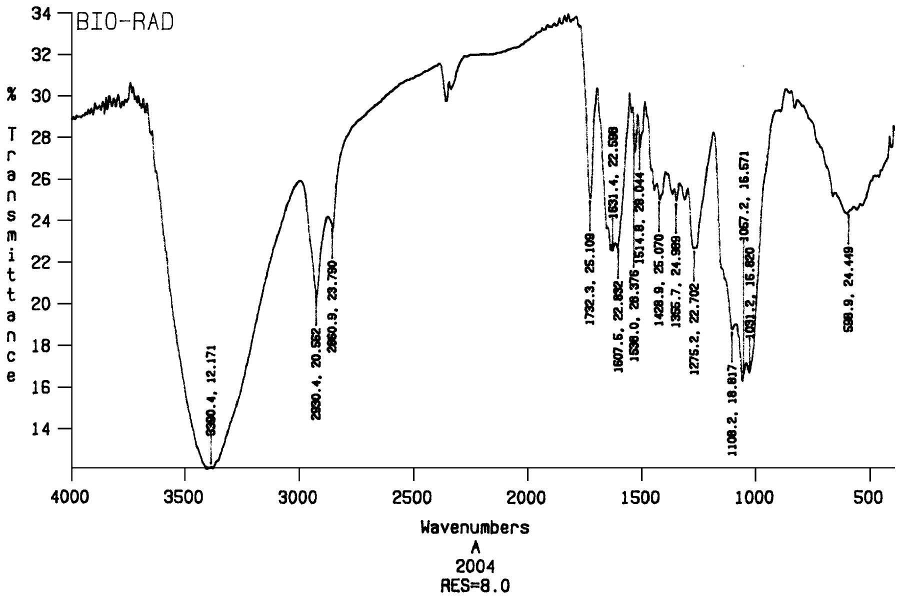

Fig. 4. The IR spectrum of raw sorbent.

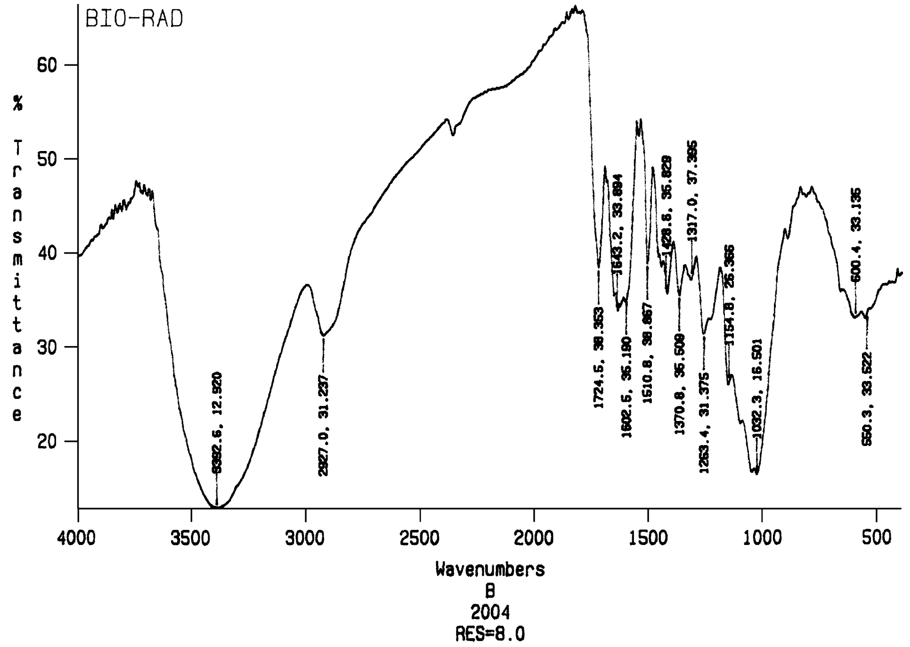

Fig. 5. The IR spectrum of methylation sorbent.

vibration adsorption band of carboxyl group at 1746 $cm^{-1}$ was obviously increased due to acetylation of amino and hydroxyl groups, and besides, an increase of the adsorption band at 1235 $cm^{-1}$ also could been found.

The XRD diagrams of raw and chemically modified sorbents are shown in Fig. 8. The XRD pattern of raw sorbent showed typical spectrum of cellulosic material, having main and secondary peaks at $2\theta$ of 22° and 16°, respectively [33]. The main peak is taken as indicative of the presence of highly organized crystalline cellulose, while the secondary peak is a measure of a less organized polysaccharide structure. The XRD diagram of methylation sorbent was very similar to that of raw sorbent. After carboxyl group esterification, the main and secondary peak heights in XRD diagram was increased, it indicated that the crystallinity of esterified sorbent was actually increased. Total acetylation of amino and hydroxyl groups induced disappearance of the secondary peak in XRD diagram.

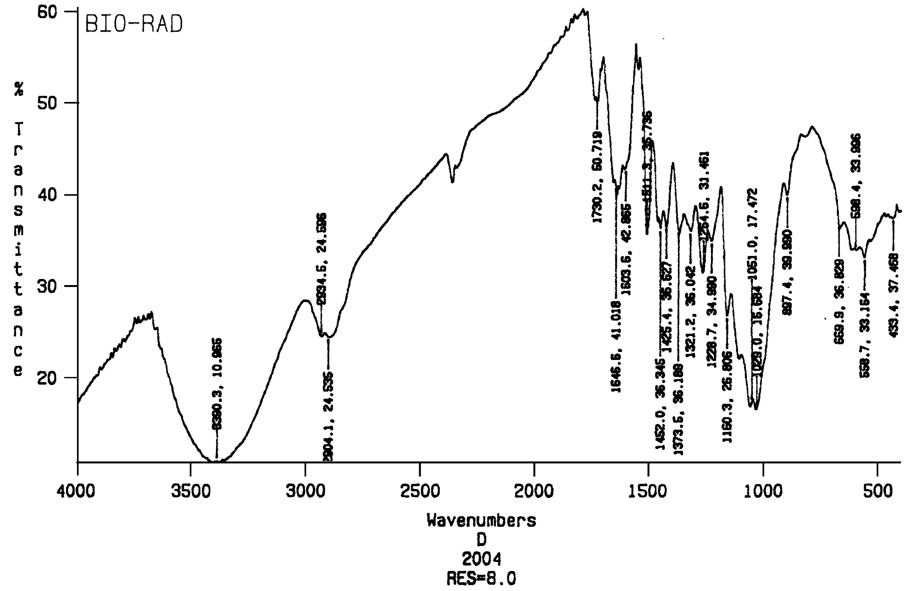

Fig. 6. The IR spectrum of esterification sorbent.

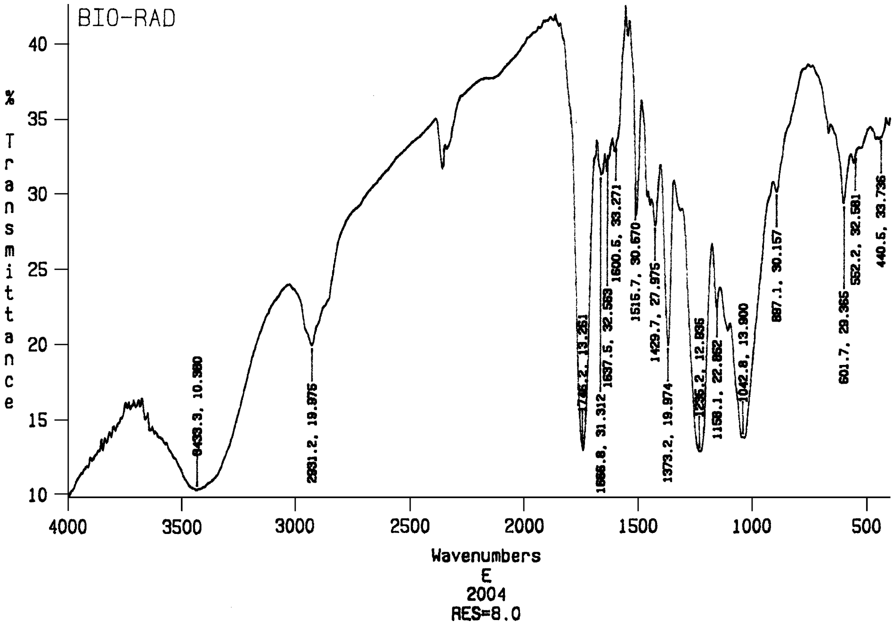

Fig. 7. The IR spectrum of acetylation sorbent.

## 4. Conclusions

Studies on effects of chemical modification on dye adsorption on sorbent derived from peanut hull suggested the following conclusions:

- The effect of methylation of amino group on ionic dye adsorption was not significant. The possible reason was that at ambient temperature, the methylation could not be carried out completely due to the tough cell wall of peanut hull.

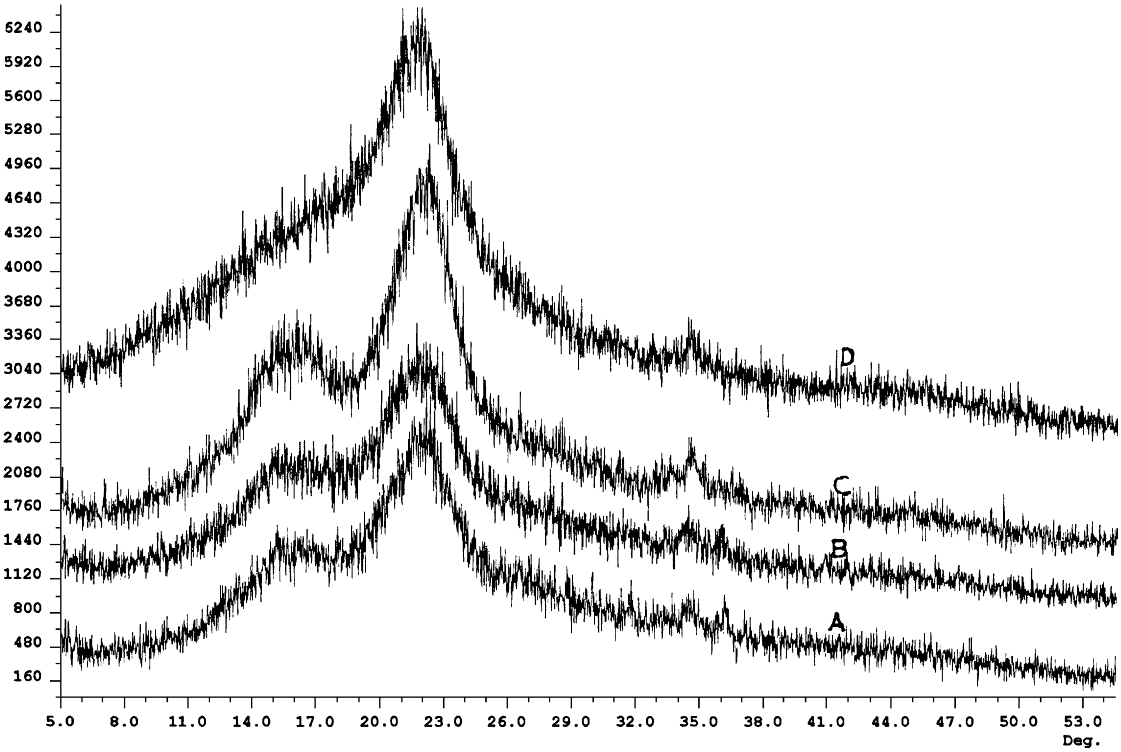

Fig. 8. XRD diagrams of raw and chemically modified sorbents. A: raw sorbent, B: methylation sorbent, C: esterification sorbent, D: acetylation sorbent.

- The carboxyl group inhibited the adsorption of anionic dyes because of its negative charge and in case removing the negative charge of carboxyl group by esterification, anionic dye uptake capacity was obviously increased. The carboxyl group was major functional group in the adsorption of cationic dyes.
- The hydroxyl group was important functional group in the adsorption of cationic and anionic dyes.

## Acknowledgments

This work was financially supported by the Key Laboratory of Bioresource Protection and Utilization of Anhui Province, the Anhui Educational Bureau and the Anhui Normal University, China.

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