

Effects of Different Solvents on the Surface Acidic Oxygen-containing Functional Groups on *Xanthoceras sorbifolia* Shell

Linan Liu,^a Lihua Wang,^{a,b,*} Liming Yin,^a Wenhong Song,^a Jinghua Yu,^a and Ye Liu^a

This study reports the preparation of a novel biomaterial from a forestry residue - *Xanthoceras sorbifolia* shell (XSS) - by solvent modification. The effects of acid and base (hydrochloric acerbic, acetic acid, sodium hydroxide, ammonia water) and some organic solvents (ethanol, acetone, ethyl acetate, chloroform, petroleum ether, and n-hexane) on the surface acidic functional groups (SAFGs) on XSS were investigated. The amount of SAFGs was quantified using acid and alkali chemical titration methods, and the characteristics of virgin XSS were compared with treated ones by FT-IR spectroscopy. It was found that acid solutions can increase the concentration of SAFGs, while alkaline solutions reduce it. The XSS treated in 0.5 M HCl has the largest number of total acidic functional groups and phenolic hydroxyl groups. The shell extracted with 2 M acetic acid has the highest concentration of carboxyl. The SAFG contents were remarkably increased by treatments with ethanol and acetone, due to the outstanding enhancement of phenolic hydroxyl. These changes in the SAFGs of XSS brought about by treatments with various solutions could be a theoretical foundation for modifying this residue to create a new type of highly efficient absorbent material.

Key words: *Xanthoceras sorbifolia* shell; Acidic functional group; Phenolic hydroxyl; Carboxyl; Solvent modification

Contact information: a: Institute of Applied Ecology, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China; b: University of Chinese Academy of Sciences, 19 Yuquan Road, Shijingshan District, Beijing 100039, China; *Corresponding author: lhwang@iae.ac.cn

INTRODUCTION

The applications of biomaterial in separation technology have been noted in the past decade due to serious concerns regarding the environment and economics, as well as their versatile properties (Srinivasan and Viraraghavan 2010). The surface chemical characteristics of a biomaterial determine its adsorption efficiencies. These characteristics are highly dependent on the ratio and the components of surface oxygen-/ nitrogen-containing functional groups. Acidic oxygen-containing functional groups, based on their carboxyl and phenolic hydroxyl groups, contribute to the polarity of bio-sorbents and thus increase their adsorption capability for polar compounds or heavy metals (Toles *et al.* 1999; Liu *et al.* 2005).

Earlier results showed that acid modification of the biomaterials could improve their adsorption performance. A phosphoric acid-activation method, by providing the greatest contact between almond shells and air during carbonization, increased the quantity of surface functional groups and therefore enhanced copper uptake with different oxygen-containing groups participating (Toles *et al.* 1999). Liu *et al.* (2007) conducted a two-step acid-base surface modification of activated carbon for Cr adsorption. The

modification for activated carbon, in which raw biomaterial was oxidized in boiling HNO_3 and then treated with a mixture of NaOH and NaCl , increased the BEF surface area and total number of surface oxygen acid groups, and the result achieved the higher Cr(VI) adsorption capacity and adsorption rate.

There have been many studies focused on the application performance, especially on the adsorption capacity of raw or treated biomaterials, while the chemical characteristics of biomaterial itself have not been deeply studied. The superficial knowledge about the chemical characters of the material itself and the mechanisms of its surface effects have made it important to further investigate and excavate the potential utilities of the rich biomass resources.

Xanthoceras sorbifolia Bunge, also named yellow horn, a Chinese endemic plant, is distributed in 16 northern provinces (municipalities and autonomous regions) of China (Cheng 2004; Li *et al.* 2012). The State Forestry Administration of China has planned to develop 1.1 million hectares of this species as a kind of bio-energy tree, principally in the "Three-North Area", for its seed-rich oil content and widely ecological adaptability on marginal land. Separating the seed kernel from its fruit for biodiesel purpose would leave behind 45% husk and 25% seed coat in weight as a residue lacking in any significant industrial and commercial uses. Li *et al.* (2013) reported that treating with IL solution in different concentration and microwave irradiation would remove some components from husks and lead to a change on the surface structure and the amount of pores, which could affect its adsorption capacity for oil. Yao *et al.* (2009) measured the seed coat adsorption of methylene blue from aqueous solution and found the dye solution pH had a significant effect on the adsorption ability of the seed coat. These indicated that the adsorption mechanism should be an ion exchanging process during which the hydroxyl ions from the adsorbent are forced into the solutions and, that different solvents and pH value could change the surface properties of this biomass both from its porosity and chemical functional groups, thus affecting the adsorption capacity for pollutants.

The objective of this study was to analyze the husk of *Xanthoceras sorbifolia* for its molecular structure and surface chemistry, to investigate its mechanism of surface functional groups, and to validate the feasibility of developing it as multi-purpose material. The husk is modified by immersing its powder into different intensities of acid, alkali, and organic solvents to elucidate their effects on the surface acid oxygen-containing functional groups.

EXPERIMENTAL

Materials

Xanthoceras sorbifolia Bunge shell was collected from Wudan forest farm (42°55'N, 119°01'E), Chifeng, Inner Mongolia, China, where the plant has been cultivated for more than 50 years. The shell was washed with distilled water to remove dirt, dried in an air oven at 105 °C to a constant weight, finely crushed, passed through a 0.9-mm sieve, and stored in plastic bottles for further use. Its basic properties were measured by the following methods, and those results were shown in Table 1.

The moisture and ash content of the shell were measured according to the standard methods used for food (GB5009.3; GB/T5009.4-2003). Its bulk density was determined by the national standard measurement method used for wood-derived activated carbon (GB/T 12496.1-1999). The zero point of charge (pH_{pzc}) was determined

using a procedure similar to that described by Nomanbhay and Palanisamy (2005), and a Prado's titration method mentioned above was used to calculate the amount of acidic functional groups.

Table 1. Basic Properties of Powdered *Xanthoceras sorbifolia* Shell

| BD (g/cm ³) | MC (%) | AC (%) | pH _{PZC} | SAFG (mmol/g) | | |
|----------------------------|-----------|-----------|-------------------|------------------|------|------|
| | | | | CG | PHG | TAFG |
| 0.34 | 7.37 | 6.11 | 6 | 0.7 | 2.99 | 3.69 |

BD: Bulk density, MC: Moisture content, AC: Ash content, pH_{PZC}: Point of zero charge, SAFG: Surface acidic functional groups, CG: Carboxyl group, PHG: Phenolic hydroxyl group, TAFG: Total acidic functional group

XSS Modification

The shell (20 g) was modified by placing 250-mL solutions of HCl, NaOH, acetic acid, and ammonia, each with concentrations 0.1, 0.5, 1, and 2 M, in different 500-mL closed conical flasks. The solid matter was filtered from the mixture after 48 h of agitation at 130 RPM at room temperature and washed with distilled water until it was neutral. Finally, it was dried in an air oven at 105 °C to constant weight. Controlled trials were conducted by immersing the materials in water simultaneously.

Functional Group Measurement

The amount of total acidic functional groups was measured using Prado's titration method with a slight modification (Boehm 1994), updated by replacing direct heating reflux with a constant-temperature ultrasonic water bath (Kang *et al.* 2012). Briefly, shells (0.1 g) treated with different solvents were placed in different closed conical flasks, which were cleaned of CO₂ by use of a stream of N₂. Then, 20 mL of 0.1 M Ba(OH)₂ solutions were added before shaking the bottle gently to soak the samples. N₂ was bubbled into the bottles again.

The bottles were plugged and placed in ultrasonic waves at 50 °C for 10 min, while in a constant-temperature water bath at 95 °C for 4 h. Then, the suspension was filtered into conical flasks containing 20 mL of 0.2 M HCl, and the residues, flasks, and filter paper were then thoroughly washed with distilled water free of CO₂. The filtrate and liquid detergent were merged, and the mixture was titrated with a standard solution of 0.2 M NaOH to pH 8.4 (measured by a pH meter).

The primary procedures to measure the quantity of carboxylic acid groups were similar to the steps above, but the reacting solution was changed to 50 mL of 0.2 M Ba(CH₃COO)₂ solutions, and in the last procedure the mixture was titrated with a standard solution of 0.1 M NaOH to pH 9.8. To reduce errors and confirm the results, each experiment was repeated in triplicate under the same conditions. Blank tests (without sorbents) were also conducted. The functional group contents (mmol·g⁻¹) were calculated according to the equations shown in Table 2.

Table 2. Formulas for Three Kinds of Acidic Functional Groups

| Functional groups | Numbering of equation | Calculating formula |
|-------------------------------|-----------------------|---|
| Total acidic functional group | (1) | $T_{ac} = \frac{(V - V_0) \times C}{W_s}$ |
| Carboxyl group | (2) | $T_{COOH} = \frac{(V - V_0) \times C}{W_s}$ |
| Phenolic hydroxyl group | (3) | $T_{OH} = T_{ac} - T_{COOH}$ |

Note: The number of these functional groups may be calculated by reference to the formulas of Prado. T_{ac} , T_{COOH} , and T_{OH} represent the concentration of total acidic functional group, carboxyl groups, and phenolic hydroxyl groups ($\text{mmol}\cdot\text{g}^{-1}$). V is the volume of the standard NaOH solution titrating the experimental sample (mL). V_0 is the volume of the standard NaOH solution titrating the blank sample (mL). C is the concentration of the standard NaOH solution ($\text{mol}\cdot\text{L}^{-1}$). W_s is the weight of the sample (g).

RESULTS AND DISCUSSION

The Effect of Treatment by Different Acid and Alkali Solvents on the Acidic Functional Group Concentration of *Xanthoceras sorbifolia* Shell

To improve the biological activity and application performance of porous biomass materials, some researchers have modified the surface functional groups of the materials with chemical methods such as acid or alkali treatment (Shafeeyan *et al.* 2010; Cong *et al.* 1984; Shen *et al.* 2009). Four kinds of strong and weak acid and alkali solvents with each of four different concentrations, including almost the fullest extent of pH value, were used to modify the shell, and their effects on its surface acidic functional group concentration are shown in Fig. 1. Compared with the control (untreated shell), the general trend is that the alkaline treatment reduced the contents of the total acidic functional groups significantly, and the lowest amount of acidic functional groups was found on the shell immersed in NaOH solution. The reduction can be attributed to the decrease in phenolic hydroxyl content (Fig. 1). With increase of ammonia solution concentration, carboxyl content slightly increased, and that of phenolic hydroxyl and total acid function group decreased accordingly. For NaOH solution treatment, carboxyl content slightly increased at low concentrations ($\leq 0.5 \text{ mol}\cdot\text{L}^{-1}$) and decreased at high concentrations ($\geq 1.0 \text{ mol}\cdot\text{L}^{-1}$), respectively. The other two acidic groups significantly decreased with increasing NaOH concentration. Changes to the surface functional groups and of phenolic hydroxyl on biomass with alkaline pre-treatment at different pH have been reported by Sab *et al.* (2007).

The effect of acid treatments depended on the acid types and their concentrations. Acetic acid could enhance the content of total acidic groups at all concentrations used, while HCl increased the content at low solvent concentrations ($\leq 0.5 \text{ M}$) but decreased them at high solvent concentrations ($\geq 1.0 \text{ M}$). Under our experimental conditions, the most abundant acidic functional groups were on the shell treated with 0.5 M HCl, due to the highest phenolic hydroxyl content and a high carboxyl content. The acetic acid

lowered the phenolic hydroxyl content, so the increase in total acidic groups is credited with the carboxyl enhancement. From a pH perspective, taking the 0.1 M solvents as an example whose pH value were measured and listed as follows: HCl 1, acetic acid 3, ammonia 10, and NaOH 13, with the pH value increasing sharply, these acidic functional groups decreased significantly. A previous study showed that higher H⁺ concentrations in low-pH solutions would lead to the protonation of the most active groups on the surface of biomass shells (Zachara *et al.* 1986), which resulted in an increase in the concentration of surface acidic functional groups. At high pH values (over its isoelectric point), deprotonation can occur on the shell (Wang *et al.* 2013) and generate negative charge, causing the material to be more soluble, allowing it to adsorb or coordinate some kind of metal or organic cation to occupy the position of H⁺, reducing its surface acidity.

There are several impossible reasons for the different effects that resulted from modifying this material using acid and alkali solvents. Some solvents may clean up dust surrounding the surface of the shell, exposing more functional groups that can be changed or consumed because of reacting with these solutions (Zhu *et al.* 2008). In addition, strong acid or alkali solvents can destroy the surface structure, breaking some chemical bonds in functional groups.

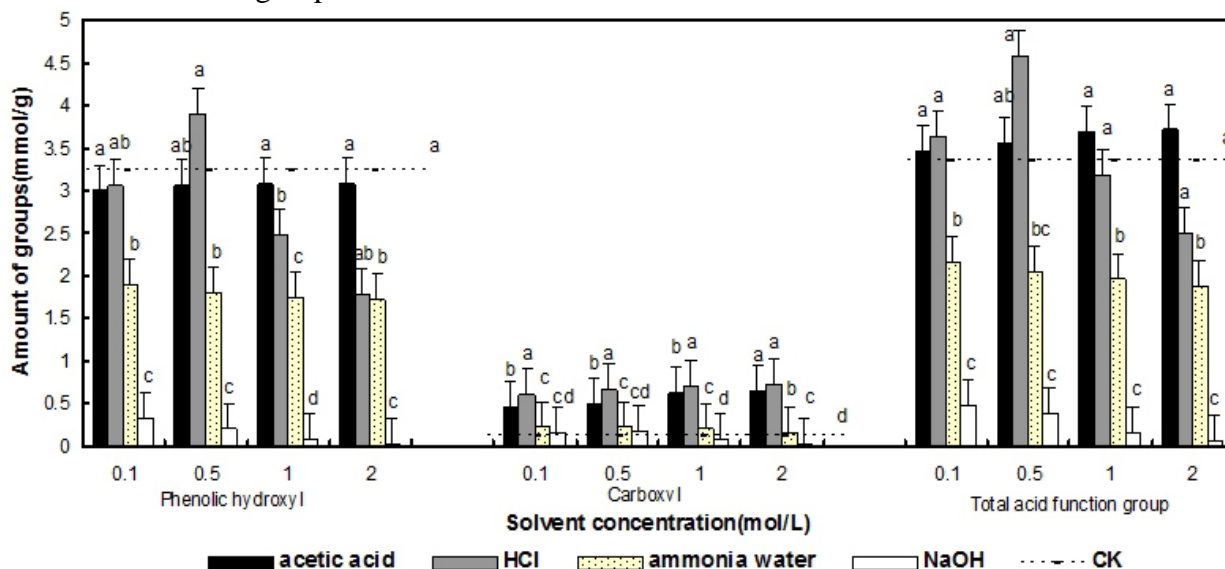
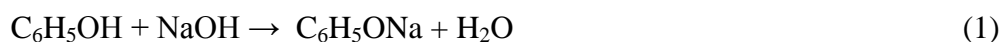


Fig. 1. The acidic functional group concentration of *Xanthoceras sorbifolia* shell immersed in different acid and alkali solvents. Different small letters mean significant difference at the 0.05 level.

In chemical terms, the carboxylic acid of acidic functional groups contains carboxyl and carbonyl, and the latter may change to the former in solutions with high levels of protons. In this study, the concentration of carboxyl increased significantly after the shell was treated with HCl and acetic acid, especially with HCl treatment. This may be attributed to the hydrolysis of HCl treatment that destroyed some hydrogen bonds and exposed more H⁺, leading to higher consumption of alkali liquor during the titration process (Wang *et al.* 2012). For alkaline solution, sodium hydroxide is a strong alkali, leading to a neutralization reaction when in contact with phenol hydroxyl, an organic weak acid, generating sodium phenolate and water. The equation for this process is:



Therefore, acidic functional groups of the shell immersed in NaOH and ammonia water were reduced and the surface polarity abated, which may increase its adsorption performance for nonpolar substances (Su *et al.* 2007; Valdes *et al.* 2002). However, the reason why its carboxyl content increased after NaOH and ammonia treatment is not yet clear. It is obvious that strong alkali can produce serious damage to the structure of biomass fiber leading to a remarkable reduction of acid functional groups (Wang *et al.* 2012). By contrast, immersing in NaOH solution under mild conditions will not generate new acid oxygen-containing functional groups, such as carboxyl or phenolic hydroxyl groups, on the surface of materials (Mei *et al.* 2010). These findings now have been verified by the present observations: when the concentrations of NaOH within 0.1 M, carboxyl content showed no apparent difference compared with the control and a decreasing trend at a NaOH concentration higher than 0.1 M. Fan *et al.* (2001) suggested modifying sorbents by reducing their surface oxygen-containing functional groups, such as lactone and carboxyl acid, to increase their hydrophobicity for the purpose of removing organic pollutants in water. Therefore, our results, *i.e.*, reducing the surface acidic functional groups with NaOH and ammonia treatments, can provide a theoretical basis for modifying sorbents to adsorb nonpolar organic substances.

Effect of Treatment by Different Organic Solvents on the Acidic Functional Group Concentration of *Xanthoceras sorbifolia* Shell

Some organic solvents will modify the surface structure and functional groups of biomass to some degree (Sun *et al.* 2004; Ren *et al.* 2007). Therefore, the effect of treatments was examined by different organic solvents on the acidic functional group concentration of the XSSB. No significant difference was found in the contents of carboxyl groups, and immersion in water-insoluble organic solvents (ethyl acetate, chloroform and petroleum ether, and n-hexane) did not significantly change the contents of total acidic functional groups and phenolic hydroxyl. It is worth noting that the total acidic functional group concentration was remarkably increased by treatment with water-soluble organic solvents (ethanol and acetone) due to the outstanding enhancement of phenolic hydroxyl (Fig. 2).

The acting mechanism with respect to organic solvents on acidic functional groups of this biomass is unclear. The ethanol molecule contains a polarized hydrogen bond, which will generate alkoxy anions and protons upon ionization, as follows: $\text{CH}_3\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O}^- + \text{H}^+$. Alcohol is often used as an economical and easily recycled extractor of alkaloids, and it also can remove most impurities on the surface of materials (Liang and Wen 2006). Some researchers also found that free alkaloids and their salts are generally soluble in methanol and ethanol, which are also used as common alkaloid extraction solvents (Yates and Powell 1988; Yang *et al.* 1998). Thus, modifying the shell with ethanol not only can expose more acidic functional groups by cleaning up the surface impurities that insoluble in water, but it may also have certain effects on the removal of alkaloids, leading to relatively higher concentrations of acidic functional groups. Hayouni *et al.* (2007) reported that acetone and other organic agents had a significant impact on the extraction of polyphenols from biomass. The six hydrogens in acetone show light chemical activation due to the absorption of an electron by carbonyl. To a certain extent, hydrogen atoms in methyl can make it a weak acid and chelate chemical compositions in the shell to generate polyphenols or other acid chemical substance that will consume NaOH in the process of titration.

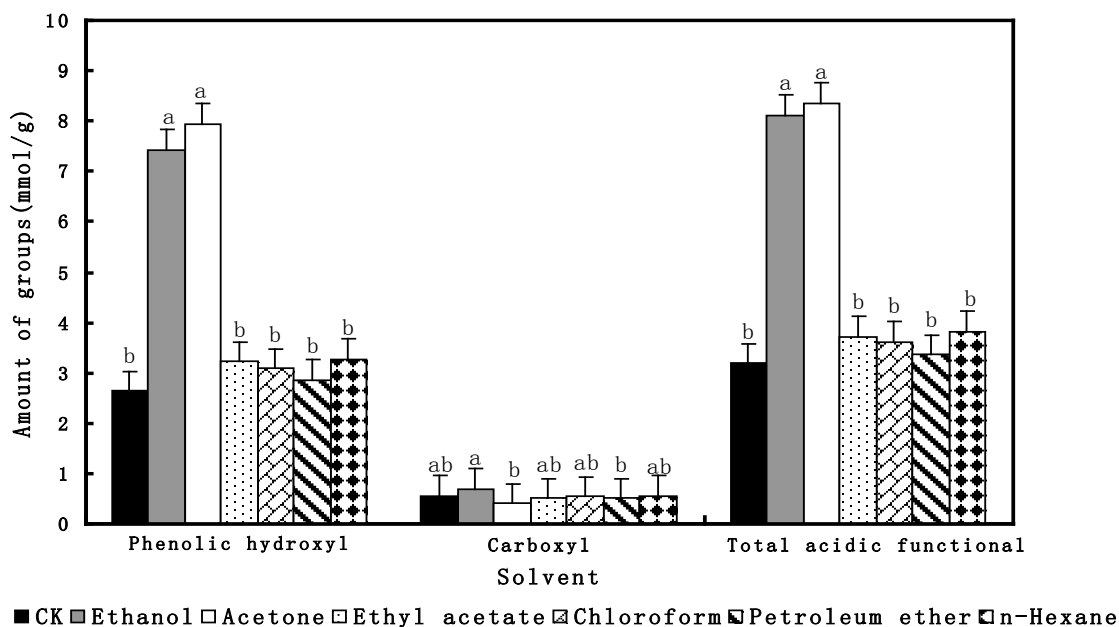


Fig. 2. The acidic functional group concentration of *Xanthoceras sorbifolia* shell immersed in different organic solvents

FT-IR Spectra

Several kinds of XSS with different treatments that have shown obvious effects on the amount of acid functional groups through the titration process were chosen for analysis by the FT-IR spectra, and the results were given in Fig. 3. By comparing the absorption peaks of eight samples, obvious changes in absorption can be observed, especially the difference of 2 M NaOH treatment from the others.

For acid (HCl and acetic acid) treatments, the intensity and type of absorption peaks were extremely similar, but those were different from the alkali (NaOH and ammonia) treatments. Obviously, the band intensities for carbonyl absorbance at 1737 cm^{-1} to 1752 cm^{-1} and 1242 cm^{-1} ($-\text{O}-\text{C}-(\text{C}=\text{O})-\text{CH}_3$ group) increased significantly from the treatments of 0.5 M HCl, 2 M HCl, and 2 M acetic acid to those with 2 M ammonia, water, and 2 M NaOH (Sun *et al.* 2000). The result was consistent with the analysis in Part 1. Meanwhile, increased absorption peaks at 1520 cm^{-1} (aromatics), 1106 cm^{-1} (C=C or $-\text{OH}$ and $-\text{CHO}$ bands), and 1372 cm^{-1} (symmetric stretching of COO of pectin) also can be observed.

Another increased absorption peak at 1020 to 1220 cm^{-1} (C-N) can be found when compared with control samples. The evolution of the FT-IR spectra with ethanol and acetone are illustrated in spectra c and d. The similar spectral profiles indicate similar structures of the modified shells. However, the increased absorption peaks appear at 1105 cm^{-1} ($-\text{OH}$ or $-\text{CHO}$) and 1031 cm^{-1} compared with untreated shells. For these hydroxyl bands, some small differences were clearly identified. The absorbance for the unchanged hydroxyl band at 3420 cm^{-1} decreased from spectra a-g to spectrum h due to these treatments.

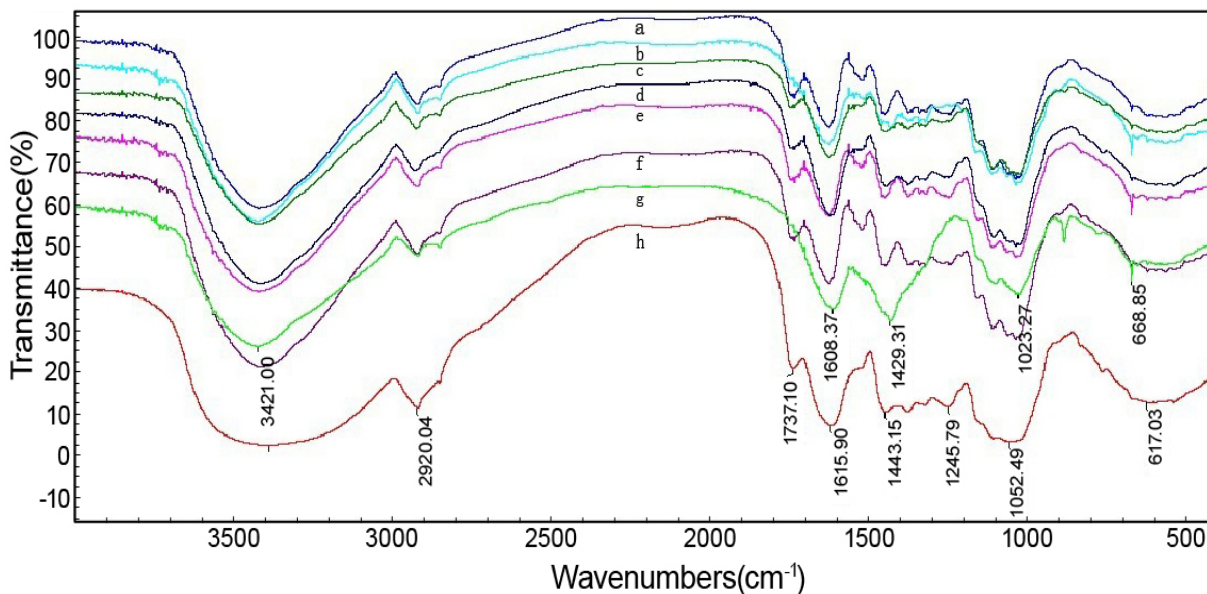


Fig 3. FT-IR spectra of treated shell (spectrum a-g: 0.5 M HCl, 2 M ammonia water, ethanol, acetone, 2 M acetic acid, 2 M HCl, and 2M NaOH), and unmodified shell (spectrum h)

CONCLUSIONS

1. The surface acidity or basicity is an important criterion for interpreting the surface chemistry of biological adsorbent materials (Foo *et al.* 2011). Different concentrations of acidic or basic solutions and organic solutions had different influences on the acid functional groups of *Xanthoceras sorbifolia* shell.
2. FT-IR spectra comparison demonstrated that although the bands of C=O and –OH in the acid-treated shell were much higher than those in the alkali-treated shell, the main functional groups found in the natural shell remained practically unchanged after the pre-treatment. Moreover, the presence of carboxyl and hydroxyl groups showed potential as proton donors to be used in coordination with cations (Iqbal *et al.* 2009; Vázquez *et al.* 2012), which provide a possibility for this material to be used as a biosorbent to adsorb heavy metals.
3. In this study, we have not examined the effect of the adsorption of heavy metals and organic pollutants, but our results still highlight the potential of *Xanthoceras sorbifolia* shell as an efficient raw precursor for the preparation of biosorbent. More importantly, our results present a basis for further research into and manufacturing of a new kind of highly efficient biological material.

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