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# Chemical and Surface Properties of Charcoal and Activated Carbon Prepared from Soybean Milk Residue

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## ABSTRACT

Charcoals and activated carbons from soybean milk residue were studied to see the effect of carbonization temperatures between 300°C and 800°C. The chemical and surface properties, such as percent yield, ash, volatile matter, fixed carbon, iodine number, functional groups and surface morpholography were investigated. It was found that the percent yield and volatile matter of carbonized charcoals decreased as the carbonization temperatures increased from 300°C to 800°C. The fixed carbons of charcoals increased with an increase in the carbonization temperatures from 300°C to 800°C. the ash contents of the charcoal were constant for carbonized temperature $\geq$ 400°C. The iodine numbers of activated carbons were higher than regular charcoals for all carbonization temperatures. The iodine numbers of activated carbons were the highest at 500°C, after that they decreased. The peak of phosphate functional groups found in activated carbon increased as carbonization temperatures increased. The porousnous of activated carbon decreased with carbonized temperatures $\geq$ 600°C.

*Keywords*: Soybean milk residue, charcoal, activated carbon, phosphoric acid

## INTRODUCTION

A low-cost by-product of soybean milk drink factory as soybean milk residue, which is generated by pulverizing of soybean. The chemical composition soybean milk residue (obtained from a soybean milk drink factory in Taiwan) includes 18.9% dry matter, 97.1 % organic matter, 16.8 % crude protein, 22.6 % hemicellulose, 29.8% cellulose, 0.87 % acid detergent lignin, 18.8 % non-fiber carbohydrates, 0.95% water-soluble carbohydrates, 115.6 mM total volatile fatty acid (Yang, 2005).The fresh soybean milk residue deteriorates rapidly upon exposure to air because of the high moisture content. This problem becomes more prominent in summer when the ambient temperature is high, and soybean milk drink demand peaks. The disposal of soybean milk residue might add to environmental pollution (Wang *et al*., 2008).

Lignocellulosic materials have been used as precursors for activated carbon, using chemical activating agents, such as phosphoric acid, zinc chloride and potassium hydroxide. The acidic reagents are able to interact with oxygen functional groups in coal and thus catalyze the dehydration and dehydrogenation reactions, resulting in charring and aromatization of the carbon skeleton and creation of the pore structure (Hsu and Teng, 2000). It was found that the phosphoric acid leads to a more heterogeneous pore size distribution (Molina-Sabio and Rodriguez-Reinoso, 2004). The activated carbons could prepare with good yields and high surface areas using chemical activation with phosphoric acid (Fierro *et al.*, 2007). Phosphoric acid is suggested to inflict physical and chemical modifications on the botanical structure by penetration, particle swelling, partial dissolution of the biomass, bind cleavage and reformation of new polymeric structures resistant to thermal decomposition (Girgis and El-Hendawy, 2002).

In this research, soybean milk residue was used as the precursor of charcoal and activated carbon. The phosphoric acid ($H_3PO_4$) was chosen as activating agent. The changes in chemical composition, functional groups, and morphology of charcoal and activated carbon with different carbonization temperatures are used to describe the properties development of charcoal and activated carbon.

## MATERIALS AND METHODS

Soybean milk residue was obtained from a soybean milk drink factory in Phitsanulok (Thailand). Soybean milk residue was dried in oven (SL Shel Lsb 1375 FX) at 105°C for 3 h. After that, the dried samples were carbonized in furnace (Fisher Scientific Isotemp, U.S.A) at 300, 400, 500, 600, 700 and 800°C for about 1 h under closed system in a porcelain crucible and then cooled down to room temperature. The charcoal products at different carbonized temperatures were impregnated with 85 wt.% $H_3PO_4$ (UNIVAR, AR) at a ratio of 1:1 (charcoal:$H_3PO_4$) on a prepared weight by volume basis. After that, the slurries were left overnight at room temperature and, then, dried at 110°C for 24 h. The samples were then activated in closed system with pyrolysis temperatures between 300°C and 800°C and held for 1 h. After cooling down, the activated carbons were leached several times with 0.2 N HCl (AR Merck) then with water until the pH became neutral, and finally with cold water. The washed samples were dried at 110°C to get the final activated carbon and weighed to calculate the activated carbon produced based on feeder charge. The dried soybean milk residue, charcoal and activated carbon were analysed to chemical composition, functional groups, and morphology.

## ANALYTICAL METHODS

The dried soybean milk residue, charcoal and activated carbon were analysed for proximate composition, including moisture content (ASTM D 2867-95, 1996), ash (ASTM D 2866-94, 1996), volatile mater (ASTM D 5832-95, 1996) and fixed carbon (ASTM D 3172-89, 1994). The produced charcoal and activated carbon were determined percentage yield. The iodine number of the charcoal and activated carbon was determined by methods of AWWA B604-74 (1974). The iodine number is a measure of the micropore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution. FTIR spectrum of charcoal and activated carbon were measured by GX, Perkin Elmer, (U.S.A.). The surface morphology was imaged in scanning electron microscopy (LEO 1455 VP electron microscopy, England).

## RESULTS AND DISCUSSION

### *Chemical composition*

Proximate analysis of soybean milk residue and soybean milk residue charcoal show the change in volatile matter and fixed carbon of the soybean milk residue charcoals with carbonization temperatures (Table 1). There is a rapid decrease in volatile matter content of soybean milk residue-charcoal with increasing carbonization temperatures between 300°C and 400°C, followed then by gradually reduction when carbonization temperatures range between 500°C and 800°C. This indicated that the volatile matter of soybean milk residue-charcoal, when carbonized ranges between 500°C and 800°C, are almost released. In the same time, the fixed carbon increased when increasing the carbonization temperatures from 300°C to 400°C and, then, gradually increased in ranges between 500°C and 800°C. The increasing of fixed carbon is mainly attributed to the release of volatile matter. The ash contents are quite constant for all soybean milk residue-charcoals, except for soybean milk residue-charcoal with carbonized at 300°C. This result is described in the same way of fixed carbon.

### *Yields*

Table 2 shows percent yield of charcoal and iodine number of charcoal and activated charcoal from soybean milk residue. It was showed that the percent yield of charcoal decreased gradually with an increasing a carbonization temperatures from 300 to 500°C, then, decreased rapidly at 600°C, followed by quite constant in ranges between 600°C and 800°C. The decrease in percent yield can be attributed to the increased tar release and strongly volatilized occurring between 500°C and 600°C. It showed that the evolved matter can possibly be carbon oxides and various volatile hydrocarbons. The evolution of volatiles in range between 300°C and 500°C can be attributed to the bond cleavage reaction caused by hydrolysis of the lignocellulosic material in the coal during carbonization. The bond cleavage was subsequently followed by extensive cross-linking at higher temperatures, leading to bonding of otherwise volatile materials into the charcoal product with a carbonization temperatures of 300-500°C and, thus, the high carbon yield (Hsu and Teng, 2000). The percent yield of charcoal decreased rapidly from 500°C to 600°C reaches a constant at 600°C to 800°C. This indicated that, for carbonization above 500°C, the cross-linked structure has reached its thermal limit and bond cleavage is accelerated upon heating to cause the decrease in carbon yield. The strong evolution starting at temperatures 500°C also indicates the rupture of the cross-linking network (Hsu and Teng, 2000).

**Table 1** Proximate analysis of soybean milk residue and soybean milk residuecharcoal

| Proximate analysis (%wt) | Soybean milk residue | Soybean milk residue charcoal | | | | | |
|---|---|---|---|---|---|---|---|
| | | Carbonization temperature ($^oC$) | | | | | |
| | | 300 | 400 | 500 | 600 | 700 | 800 |
| Moisture content | 69.18±5.92 | 2.95±0.05 | 2.88±0.03 | 2.00±0.02 | 1.52±0.21 | 1.25±0.06 | 0.99±0.07 |
| Ash | 1.89±0.12 | 0.21±0.02 | 1.13±0.07 | 1.13±0.04 | 1.13±0.05 | 1.13±0.18 | 1.04±0.02 |
| Volatile matter | 27.92±6.55 | 68.84±0.60 | 46.03±1.04 | 31.23±0.46 | 30.99±1.51 | 29.94±0.69 | 27.91±0.58 |
| Fixed carbon | 0.98±0.62 | 28.00±0.61 | 49.96±0.76 | 65.64±0.75 | 66.36±0.38 | 67.68±2.50 | 70.66±0.31 |

**Table 2** Percent yield of charcoal and iodine number of charcoal and activated carbon from soybean milk residue

| Carbonization temperature ($^oC$) | % yield of charcoal | Iodine number (mg $I_2$/g) | |
|---|---|---|---|
| | | Charcoal | Activated carbon |
| 300 | 33.82±3.20 | 431.22 | 855.24 |
| 400 | 31.24±0.95 | 413.65 | 779.02 |
| 500 | 30.65±0.30 | 397.34 | 885.49 |
| 600 | 16.09±0.76 | 452.23 | 546.93 |
| 700 | 15.99±0.76 | 442.73 | 549.70 |
| 800 | 15.14±5.76 | 428.24 | 575.30 |

### *Iodine Number*

The iodine number of soybean milk residue charcoals with treated by different carbonization temperatures of 300-800$^o$C, and activated carbon with $H_3PO_4$ activation by ratio 1:1 and, then, pyrolysed between 300$^o$C and 800$^o$C, were showed in Table 2. It was found that the iodine number of charcoals decrease with the increasing carbonization temperatures from 300 to 500$^o$C and reach a maximum at 600$^o$C, and then decrease with further increase of the temperature. The high iodine number at 300$^o$C may be attributed to unsaturated bond of incomplete carbonized charcoals, with can reacted to iodine. The increase in iodine number, from carbonization temperatures of 500$^o$C to 600$^o$C can be attributed to the release of tars from the cross-linked framework generated by the heat treatment. After that, the temperature above 600$^o$C would induce shrinkage in the carbon structure, leading to the collapse of pores and the decrease of porosity. Additionally, extensive gasification on the exterior portion of the carbon particles can also cause the reduction in porosity (Hsu and Teng, 2000). For the activated carbon, the iodine number reaches maximum (885.49 mg/g) at 500$^o$C and then, rapidly decrease. This result explained that, at the high carbonization temperature, the shrinkage in the untreated charcoals have been occurred, leading to a low in porosity. Furthermore, it was found that the iodine numbers of all activated carbons are higher than the untreated charcoals. This result reflected that $H_3PO_4$ can be effective in developing charcoals of soybean milk residue. It may be attributed to the release of tars from the cross-linked framework of charcoal.

### *FTIR spectrum*

FTIR transmission spectrum of dry soybean milk residue and soybean milk residue charcoal with carbonization temperatures between 300 and 800$^o$C presented in Figure 1. The FTIR spectrum of the dry soybean milk residue presents a board band at 3436.04 cm$^{-1}$ due to a symmetric of O-H stretching vibration of hydroxyl functional groups in phenolic and aliphatic structures (Fierro *et al.*, 2007). The bands at 2925.77 and 2854.97 cm$^{-1}$ can be assigned to the asymmetric and symmetric C-H stretching vibrations in methyl and methylene groups of fatty acids (Casal and Mantsch, 1984). These bands contrast to the δ(C-H) vibrational bands for $–CH_3$- and $–CH_2=$, which are located at 1384.11 and 1456.07 cm$^{-1}$ (Lua and Yang, 2004). The band 1746.87 cm$^{-1}$ can be assigned to the C=O stretching vibration from ketones, aldehydes and carboxyl groups as in lactones, carboxylic acid, ethers, phenols and carboxylic anhydrides (Starck *et al.*, 2004; Mendez *et al.*, 2005; Guo and Rockstraw, 2007). The band at 1645.35 cm$^{-1}$, due to the C=C stretching vibration, can be assigned to alkenes or olefinic groups (Lua and Yang, 2004). The band 1544.12 cm$^{-1}$ has been to the C=C stretching in aromatic rings, quinines, lignin and keto-enols (Lua and Yang, 2004). The band at 1163.31 cm$^{-1}$ has been assigned to C-O stretching mode of alcoholic, phenolic and carboxylic groups (Pradhan and Sandle, 1999; Mendez *et al.*, 2005). The band at 1039.02 cm$^{-1}$ associated with C-O, C-C stretching and C-OH bending in polysaccharides or carbohydrates (Fierro *et al.*, 2007). The very small band at around 800 cm$^{-1}$ appears for charcoal. This band

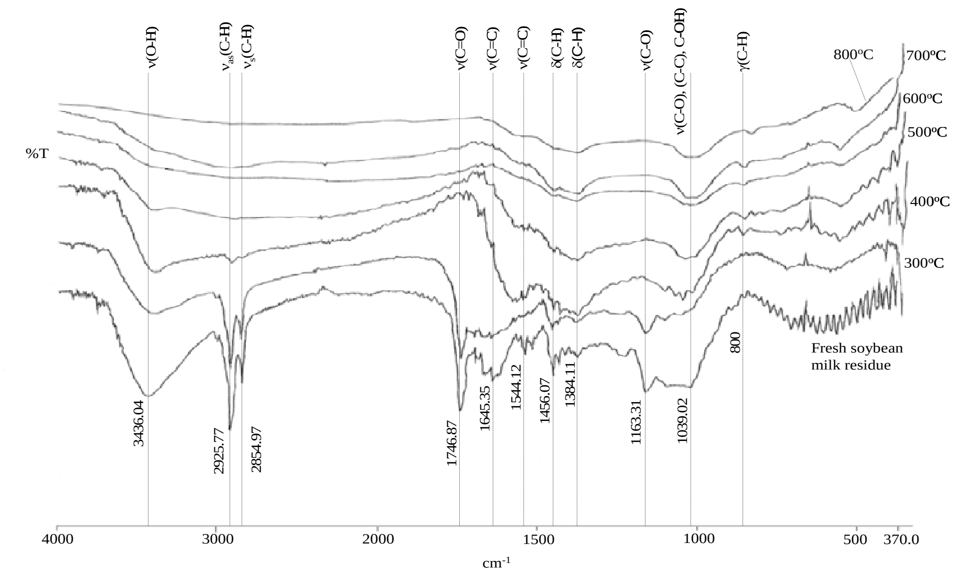


**Figure 1** FTIR transmission spectra of fresh soybean milk residue and soybean milk residue charcoals with carbonization temperatures between 300°C and 800°C

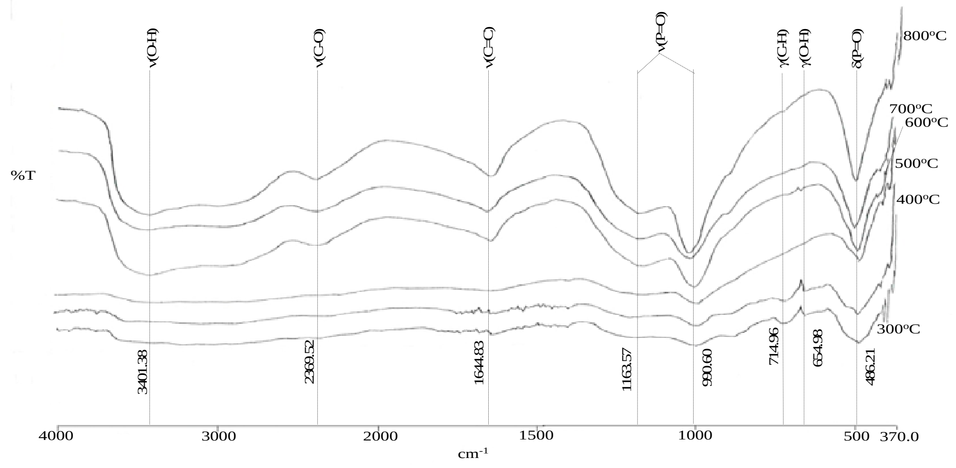


**Figure 2** FTIR transmission spectra of activated carbon prepared from soybean milk residue charcoals with carbonization temperatures between 300°C and 800°C and $H_3PO_4$ activation between 300°C and 800°C.

assigned to aromatic C-H out-of-plane bending vibration. This indicated that the aromatization appeared in the charcoal (Lua and Yang, 2004). It can be seen that the intensities of all bands decreases generally after carbonization temperatures increase from 300°C to 800°C. This indicated that the changes in the surface functional groups and structures by effect of carbonized temperature. It appears therefore that during thermal treatment the majority of the more weakly bound functional groups were removed.

Figure 2 show FTIR transmission spectrum of activated carbon with $H_3PO_4$ activation of charcoals carbonization temperatures between 300°C to 800°C then pyrolysed at 700°C. It was found that the broad bands at 3401.38, 2369.52, 1644.83, 1163.57 $cm^{-1}$ is appear when pyrolyses temperature of charcoal above 600°C. Also, it can be seen that the new bands at 990.60 and 486.21 $cm^{-1}$ increase intensities with increase the carbonization temperatures from 300°C to 800°C of charcoals. The band at 3401.38 $cm^{-1}$ assigned to carboxyl group O-H stretching. The broad band at 2369.52 $cm^{-1}$, which show low intensity, assigned to C-O stretching vibration in ketene groups. This result indicated that the oxidation of activated carbons with prepared from charcoal carbonized above 600°C increase the amount of surface oxygen complexes (Pradhan and Sandle, 1999). The small band 1644.83 $cm^{-1}$, which appeared for charcoals with carbonization temperature above 600°C before activation, due to C=C stretching vibration. The intensity band of 1644.83 $cm^{-1}$ increases slightly with increasing carbonization temperature of charcoal. This indicated that the evolution of carbonization process is occur and the consequent formation of condensed structures (Demirbas, 2000). The new two bands appear at 1163.57 and 990.60 $cm^{-1}$, this might indicate that the presence of phosphate groups, can be attributed to the stretching of P=O bond in a phosphate ester, O-C bond in P-O-C linkage, or P=OOH bond (Corcho-Corral *et al.*, 2006; Guo and Rockstraw, 2007). These bands associated with a band at 486.21$cm^{-1}$ that assigned to $\delta$(P=O) vibration (Wapner *et al.*, 2007). This result indicated that there is phosphorus-containing group in activated carbons. This is due to that the reaction of phosphoric acid with charcoal increase extensive when increase a carbonization temperatures of charcoals. This has been mainly attributed to the decomposition or evaporation of polyphosphoric acid, which were formed through the condensation of the impregnated phosphoric acid by losing water. These acids include species such as $H_3PO_4$, $H_4P_2O_7$ and $H_5P_3O_{10}$ (Hsu and Teng, 2000). The bands at 714.96 and 654.98 $cm^{-1}$, which is disappeared after carbonized charcoals at 500°C, assigned to the C-H out-of-plane bending and hydroxyl group out-of-plane bending.

### ***SEM observations***

The surface images of the charcoals of soybean milk residue prepared at different carbonization temperatures between 300° and 800°C and activated carbon prepared from soybean milk residue charcoals which activated by $H_3PO_4$ and pyrolysis between 300°C and 700°C were showed in Figures 3 and 4. From Figure 3(a), it can be seen that the pores within the fresh soybean milk residue are cellular structure, branched porous texture, quite order and a rough surface. For charcoals which carbonization temperatures between 300°C and 800°C, it seem that the pores within the charcoals are widening and clearing with increase carbonization temperature, but have irregular shape (Figure 3 (b)-(g)). This is a result from the evaporation of the tar or volatile matter during carbonization. It is corresponding to the volatile matter content decreased with an increased carbonization temperature (Table 1). The surface images of the activated carbon, with pyrolysis between 300°C and 500°C, are characteristically irregular and highly clear (Figure 4(a)-(c)). This result may be described that the phosphoric acid produces the development of porosity at temperatures below 500°C leading to highly activated carbon (Molina-Sabio and Rodriguez-Reinoso, 2004). On the other hand, after pyrolysis of 600°C to 800°C, the pores of activated carbon show that there are less pores and a cloudy-like texture (Figure 4(d)-(f)). This is agrees with the results of very low iodine number (Table 2). Because of, at higher pyrolysis temperature to be excessive burn-off of the surface charcoals before activation, and the volume of porosity is larger than the phosphoric acid. In these effects, the intense chemical attack of the phosphoric acid on the surface of charcoals produces the clusters structure, and the resulting would produce a more densely packed structure with reduced porosity (Solum *et al.*, 1995).

## CONCLUSIONS

The percent yield and volatile matter of carbonized charcoals were decreased with the carbonization temperatures increased from 300 to 800°C. There is a rapid decrease in volatile matter content of soybean milk residue-charcoal with increasing carbonization temperatures between 300°C and 400°C, followed then by gradually reduction when carbonized temperature ranges between 500°C and 800°C. The fixed carbon increased when increasing the carbonization temperature from 300 to 400°C and, then, gradually increased in ranges between 500 and 800°C. The ash contents are quite constant for all soybean milk residue-charcoals. The iodine numbers of charcoals decrease with the increasing carbonization temperatures from 300 to 500°C and to a maximum at 600°C, and then decrease with further increase of the temperature. The iodine numbers of all activated carbons were higher than the untreated charcoals and reach maximum at 500°C.

The functional groups on the soybean milk residue charcoal were decreased generally after carbonization temperatures increase from 300°C to 800°C and almost removed at 600°C. The FTIR spectrum of activated carbon with carbonization temperatures between 300°C and 500°C are quite smooth lines. The broad bands at 3401.38, 2369.52, 1644.83, 1163.57 $cm^{-1}$ of activated carbon appeared when pyrolysis temperature of charcoal above 600°C. This indicated that the O-H stretching, C-O stretching and C=C stretching vibration occurred in the activated carbon. The intensity band of 1644.83 $cm^{-1}$ increases slightly with increasing carbonization temperatures of charcoal. This indicated that the evolution of carbonization process is occur and the consequent formation of condensed structures The new bands at 1163.57, 990.60 and 486.21 $cm^{-1}$ of activated carbon increase intensities with increase the carbonization temperatures from 300°C to 800°C of charcoals. This might be indicated that the phosphate groups presented in the activated carbon.

The pores of charcoals with carbonization temperatures between 300°C and 800°C are widening and clearing with increase carbonization temperatures, but have irregular shape. The surface images of the activated carbon, with pyrolysis between 300°C and 500°C, are characteristically irregular and highly clear, however, there are less pores and a cloudy-like texture after pyrolysis of 600°C to 800°C.

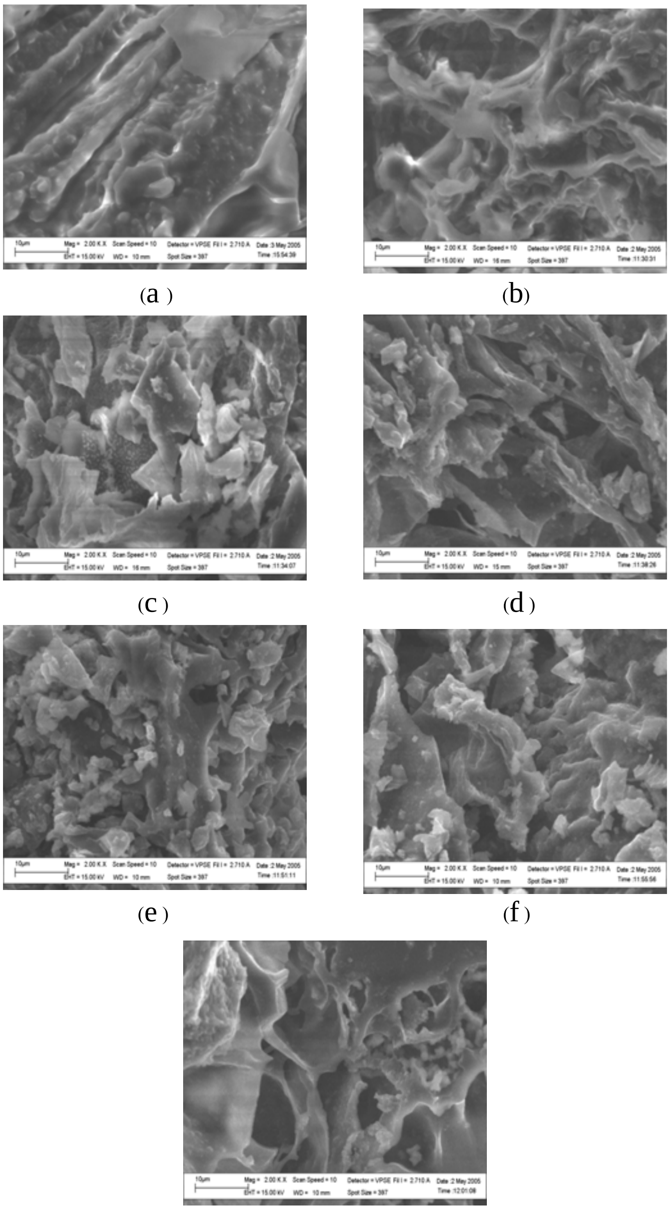
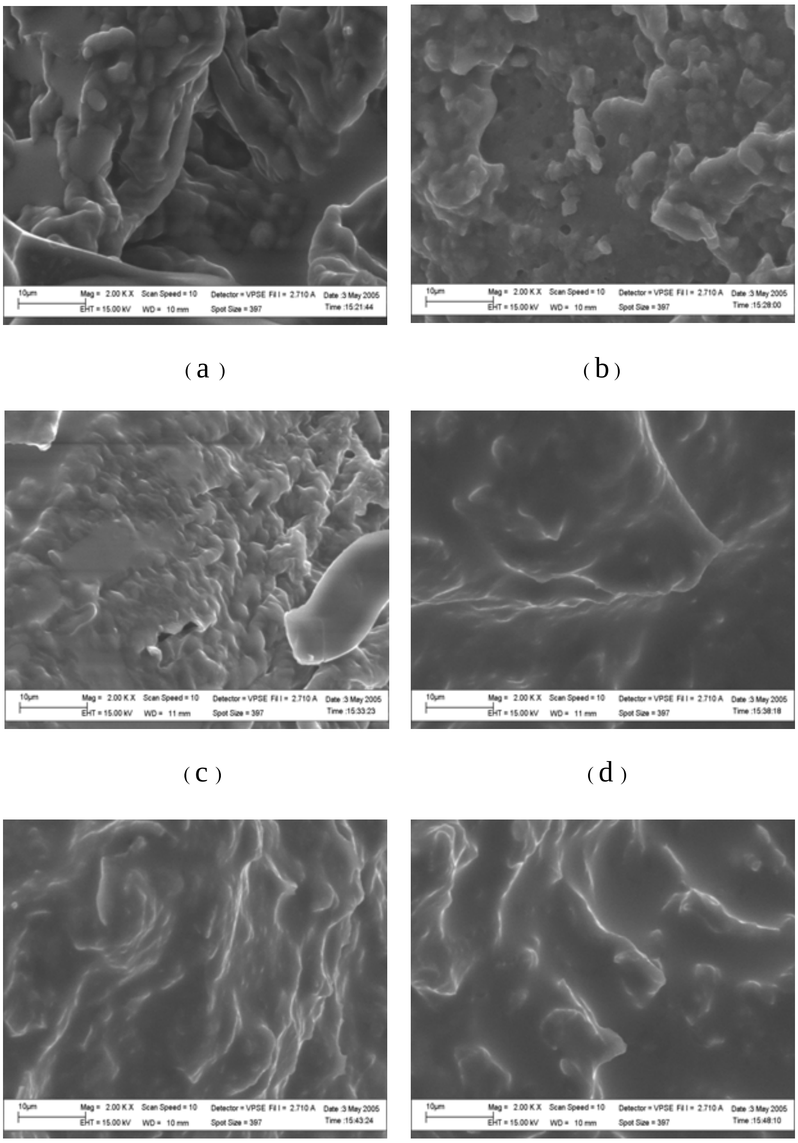

(a )
(b)
(c )
(d )
(e )
(f )
(g )

**Figure 3** SEM images of fresh soybean milk residue (a) and soybean milk residue charcoals with carbonization temperatures at 300°C (b), 400°C (c),500°C (d), 600°C (e), 700°C (f) and 800°C (g)



(a) (b)

(c) (d)

(e) (f)

**Figure 4** SEM images of activated carbon prepared from soybean milk residue charcoals with carbonization temperatures at 300°C to 800°C and $H_3PO_4$ activation and then pyrolysed at 700°C.From charcoal with carbonization temperatures at 300°C (a), 400°C (b), 500°C (c), 600°C (d), 700°C (e) and 800°C (f).

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