Rice Husk Char/Poly-(Acrylic Acid-co-acrylamide) Superabsorbent Hydrogels: Preparation, Characterization, and Swelling Behaviors

Xin Pan, Xiao-Wei Zhuang,* and Shun-Wei Chen

A series of novel rice husk char/poly-(acrylic acid(AA)-co-acrylamide(AM)) superabsorbent hydrogels were synthesized by graft copolymerization. The effects of the rice husk char (RHC) loading on their miscibility, shapes, and chemical structures were studied, and their swelling behaviors, kinetics, and pH response were evaluated. During the preparation, RHC reacted with acrylic acid. The RHC at lower loads (< mass ratios of RHC and AA of 1%) was scattered well within the polymer matrix, but an excessive load might result in the formation of large agglomerates. The swelling capacity and swelling rate of the hydrogels first were both increased with the rising RHC loading to 1% and then declined with further RHC loading. The superabsorbent hydrogel containing 1% RHC had the highest water absorbency (869 g/g in deionized water and 97 g/g in 0.9% NaCl solution).

Keywords: Rice husk char; Superabsorbent hydrogels; Swelling behavior; pH Sensitivity

Contact information: Zhejiang Provincial Key Laboratory of Biological and Chemical Utilization of Forest Resource, Zhejiang Forestry Academy, Box 399, Hangzhou, Zhejiang 310023 China;
** Corresponding author: zhuangxw@aliyun.com*

INTRODUCTION

Superabsorbents are the hydrophilic polymers that physically and/or chemically crosslink into three-dimensional networks (Bao *et al*. 2011). Generally, a superabsorbent can absorb abundant water or other aqueous solutions. Because of superior properties compared to traditional materials such as sponges, they are widely used in hygiene (Kosemund *et al*. 2009), agriculture (Guo *et al*. 2005; Liang *et al*. 2009), drug delivery (Reddy *et al*. 2011; Oun *et al*. 2014), and water purification (Zheng *et al.* 2010; Wang *et al.* 2011). The research on the use of superabsorbents as water and fertilizer managing materials for the renewal desert environment (Banedjschafie and Durner 2015) and slow release fertilizers (Li *et al*.2016; Yamamoto *et al*. 2016) has attracted great attention, and encouraging results have been observed, as they can reduce irrigation water consumption, lower the death rate of plants, and increase plant growth rate (Parvathy *et al.* 2014).

Superabsorbents are biocompatible, biodegradable, renewable, and nontoxic (Guilherme *et al*. 2005; Murthy *et al*. 2006; Pourjavadi *et al*. 2006). Many substances have been loaded into the polymer matrix, such as cellulose (Yoshimura *et al.* 2006; Chang *et al.* 2010), starch (Pourjavadi *et al.* 2010; Zou *et al.* 2012), chitosan (Mahdavinia *et al.* 2004; Zhang *et al.* 2007), and complex substances (Perez and Francois 2016; Qi *et al.* 2016) because of their biodegradability, abundance, low generation costs, and multifunctional character.

Rice husk chars (RHCs) result from the thermal treatment of rice husks. The rice husks are rich in cellulose and lignin, which is very suitable for the production of chars.

Thermal processing leads to the pore development within the RHCs, which make RHCs a potential adsorption material (Shen *et al.* 2014). The RHCs also contain plenty of silica and porous silica, which are also widely applied in adsorption, separation, and catalysis (Witoon *et al.* 2008; Jullaphan *et al.* 2009), so RHCs have large specific surface areas (Paethanom and Yoshikawa 2012). RHCs have been added into superabsorbents, where they contributed to strong methylene blue adsorption (Azevedo *et al.* 2017). Thus, superabsorbents with RHCs can be used for wastewater treatment (Hafida *et al.* 2015), recovery or containment of marine crude oil spills (Nguyen and Pignatello 2013), and soil amendment (Ekebafe *et al.* 2013).

The annual production of RHC was very large in China. In this work, RHCs were chosen and used to prepare RHC/poly-(acrylic acid-co-acrylamide) (RHC/P) superabsorbents through graft polymerization. Also, the swelling behaviors were compared. The new preparation route for RHC/P would reduce the production costs and improve the properties (*e.g.* thermal stability and swelling at varying pHs).

EXPERIMENTAL

Materials

RHC and reagents

The RHCs (average particle size = 74 μm) were obtained from the Zhejiang Provincial Key Laboratory of Biological and Chemical Utilization of Forest Resources (Hangzhou, China).

Other materials used in this study included ammonium pursulfate (APS) and N,N'-methylenebisacrylamide (NMBA), acrylic acid (AA) (distilled under reduced pressure before use), acrylamide (AM) (all from Tianjin Chemical, Tianjin, China), and NaOH (Chengdu Kelong Chemical, Chengdu, China).

All the substances were analytically pure, and all of the solutions were prepared in deionized water.

Preparation of RHC/P superabsorbent hydrogels

A series of RHC/P superabsorbent hydrogels were synthesized (Huang *et al.* 2012). Specifically, to 5 g of acrylic acid in a 250-mL four-necked flask (with a thermometer, a condenser, a stirrer, and a nitrogen line), an appropriate amount of NaOH solution was added slowly under an ice bath, until reaching 60% molar neutralization. The resulting solution was heated and kept at 60 ºC for 30 min under a nitrogen atmosphere.

Into the above solution, acrylamide (0.83 g), NMBA (1 mg/mL, 1.2 mL), APS (2 mg/mL, 2.9 mL), and deionized water (17.5 mL) were slowly added under continual stirring. The authors designed four loads of RHC (0.0025 g, 0.005 g, 0.01 g, and 0.025 g) in the blends, that corresponded to the RHC and AA mass ratios of 0.5%, 1%, 2%, and 5%, respectively (the same below). The water bath was heated to 70 ºC and kept for 3 h until complete polymerization.

The resulting product RHC/P was cut into pieces, which were then dried at 70 ºC under vacuum to a constant weight. The PAA (AA-co-AM) superabsorbent hydrogels were also prepared in the above way except for the addition of RHC. All of the samples were milled and sieved to 40-mesh to 80-mesh.

Methods

Fourier transform infrared spectroscopy (FTIR)

The samples were spectroscopically analyzed on a Nicolet 6700 FTIR meter (Thermo Scientific, Madison, USA) within 4000 cm^{-1} to 400 cm^{-1} over 36 scans at a resolution of 2 cm^{-1}. The test samples were vacuum-dried and prepared by the KBr-disk method.

Thermogravimetric analysis (TGA)

The thermal stability was studied on an STA 409 PC Luxx thermal analyzer (Netzsch-geraetebau GmbH, Schulstr, Germany) with a temperature range = 30 ºC to 900 ºC, a heating rate at 10 ºC/min, flow rate of 40 mL/min, and a dry nitrogen purge.

Surface morphology

All samples were fixed on aluminum stubs and coated with gold. Then micrographs were explored on an S-3400N scanning electron microscope (Hitachi, Tokyo, Japan).

Specific surface area measurements

The Brunauer-Emmett-Teller specific surface area (BET) was determined by N_2 physisorption using an ASAP 2020 automated system (Micromeritics, Norcross, USA). Then 0.5 to 0.9 g of sample was degassed in the ASAP 2020 at 160 °C for 4 h prior to the analysis, followed by N_2 adsorption at -196 °C. BET analysis was carried out for a relative vapor pressure of 0.01 to 0.3 at -196 °C.

Measurement of water absorption and swelling kinetics

Specifically, a dry superabsorbent hydrogel (*ca*. 0.10 g) was soaked in 500 mL of deionized water at room temperature for 4 h, until reaching the swelling equilibrium. The swollen sample was then filtered through a 100-mesh screen and separated from the unabsorbed water. The water swelling ratio (W; g/g) of the hydrogel was calculated as follows,

$$W = (W_s - W_d) / W_d \tag{1}$$

where W_s and W_d were the weights of the swollen and dry sample (g), respectively. Each sample was tested in triplicate.

The swelling kinetics was measured. The dried samples (each 0.10 g) were soaked in excessive deionized water. The swollen samples were isolated using a mesh screen and weighed at a preset interval. This procedure was repeated until a constant weight was reached. The water absorbency at any time was calculated from Eq. 1.

Swelling at varying pHs and in saline solutions

Any external solution was regulated to the required pH using 1 mol/L NaOH or HCl solution. The same method was used as the measurement of water absorbency in deionized water.

The swelling in salt solution was measured as follows. A sample (0.10 g) was poured into 250 mL of 0.9% (W/V) NaCl solution and then at a certain time interval, the solution swollen ratio was determined by Eq. 1. The determination condition used was the same as for the measurement of balanced water absorbency in deionized water.

RESULTS AND DISCUSSION

FTIR

Figure 1 shows the FTIR spectra of the RHC, RHC/P, and PAA. The RHC shows three peaks at 1604 cm^{-1}, 1100 cm^{-1}, and 798 cm^{-1}, that corresponded to the stretching of COO-, Si-O, and P-O, respectively (Fig. 1a). The PAA showed peaks at 1569 cm^{-1}, 1455 cm^{-1}, 1408 cm^{-1}, and 1325 cm^{-1}, which revealed the presence of COO- (Fig. 1c). Moreover, the grafting of acrylic acid (RHC-g-PAA) made the absorption band of Si-O shift from 1100 cm^{-1} to 1050 cm^{-1} and resulted in the appearance of some new peaks of PAA (Fig. 1b). Compared with PAA, the spectrum of RHC-g-PAA showed some new peaks (Fig. 1b), including the Si-O stretching of RHC (1050 cm^{-1}), P-O stretching of RHC (783 cm^{-1}), C=O band (1677 cm^{-1}), and the associated –OH stretching vibration of the hydroxyl groups (3440 cm^{-1}). The FTIR results suggested the occurrence of a reaction between RHC and acrylic acid during the polymerization.

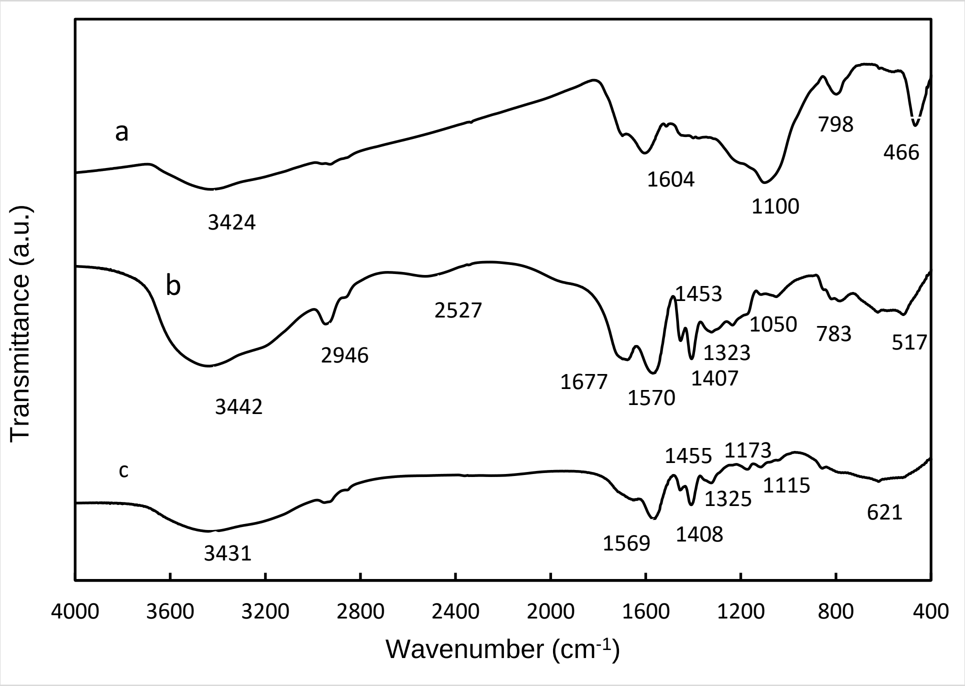


Fig. 1. IR spectra of (a) RHC, (b) RHC/P, and (c) PAA

TGA

Figure 2 depicts the TGA curves of the superabsorbent hydrogels, RHC and RHC/P with varying RHC contents.

Table 1 lists the thermal decomposition temperatures (TDTs) of 10% and 50% weight loss and char yields. The char yield of RHC was 70.31%, so there were no data of TDT of 50% weight loss for RHC. Clearly, the thermal stability of RHC was much more than that of P(AA-co-AM). So, the RHC/P has a higher TDT than that without RHC, which indicated that the thermal stability could be enhanced by the introduction of RHC particles into the polymer networks. These findings were attributed to the heat barrier effect of RHC. Furthermore, the TDTs of hydrogels rose with the increase of RHC content, which was possibly ascribed to the dispersion effect on the thermal stability.

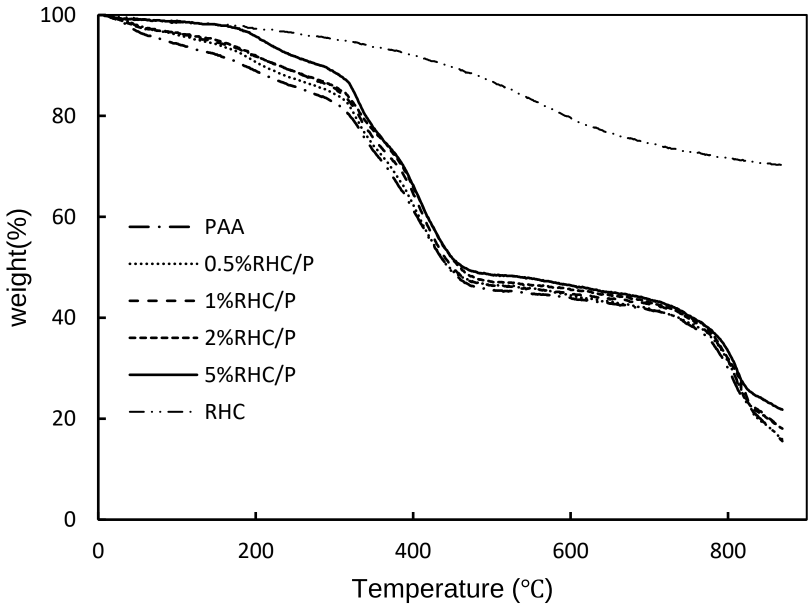


Fig. 2. TGA curves of PAA and RHC/P with various RHC content at a heating rate of 10 °C /min

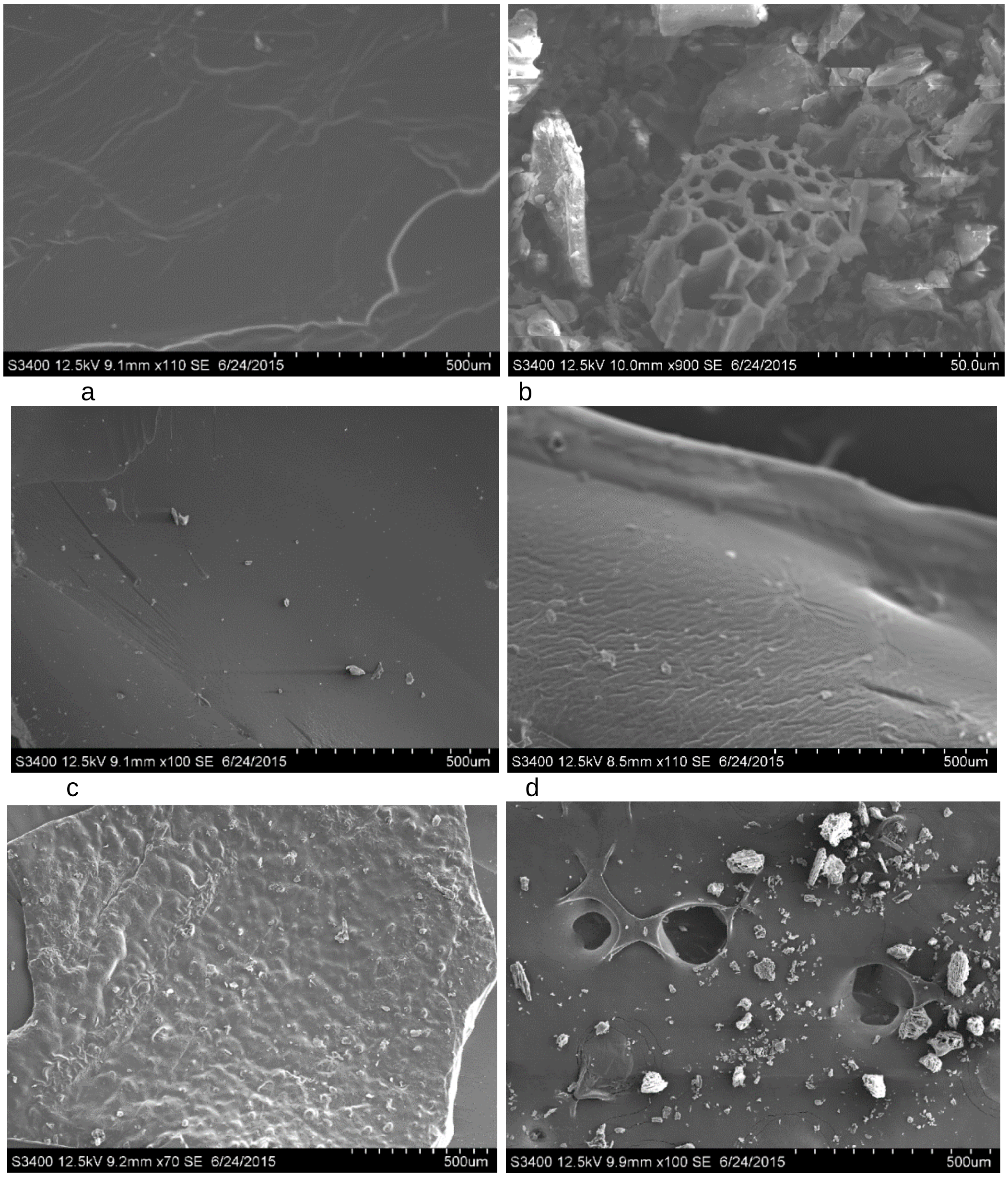
Table 1. TGA Data of Prepared Samples

Samples	T10%	T50%	Char Yield (%)
P(AA-co-AM)	184	445	15.55
0.5% RHC/P	207	446	15.92
1% RHC/P	228	450	17.80
2% RHC/P	228	459	18.04
5% RHC/P	281	464	21.79
RHC	441		70.31

Morphology

Because the water absorbency of a hydrogel is affected by its porosity (Bao *et al*. 2011), its microstructural morphology is a key property to be studied. Figure 3 shows the SEM images of dried PAA, RHC, and RHC/P. Clearly, the PAA hydrogel had a very smooth cross-section, which might have been closely related to its crosslinking polymer networks. The RHC/P hydrogels that contained 0.5% and 1% RHC (mass ratios of RHC and AA) both show a very compact cross-section morphology (Figs. 3c and 3d). This indicated the homogeneous dispersion of RHC within the polymer matrix and the presence of RHC-matrix interfacial interaction. In comparison, the RHC-doped sample has an undulant and coarse surface, which facilitates the water penetration into the polymeric network, and then may improve the water absorbency of the resulting superabsorbent (Pourjavadi *et al.* 2007; Hua and Wang 2009).

When the amounts of RHC increased to 2% and 5%, the hydrogels had very different cross-sections (Figs. 3e and 3f). Clearly, the RHC and matrix micro-phases were separated at a large scale, making the hydrogel structures relatively loose, which might have been because the RHC aggregated in the matrix during the reactions (Huang *et al.* 2012).



a b

c d

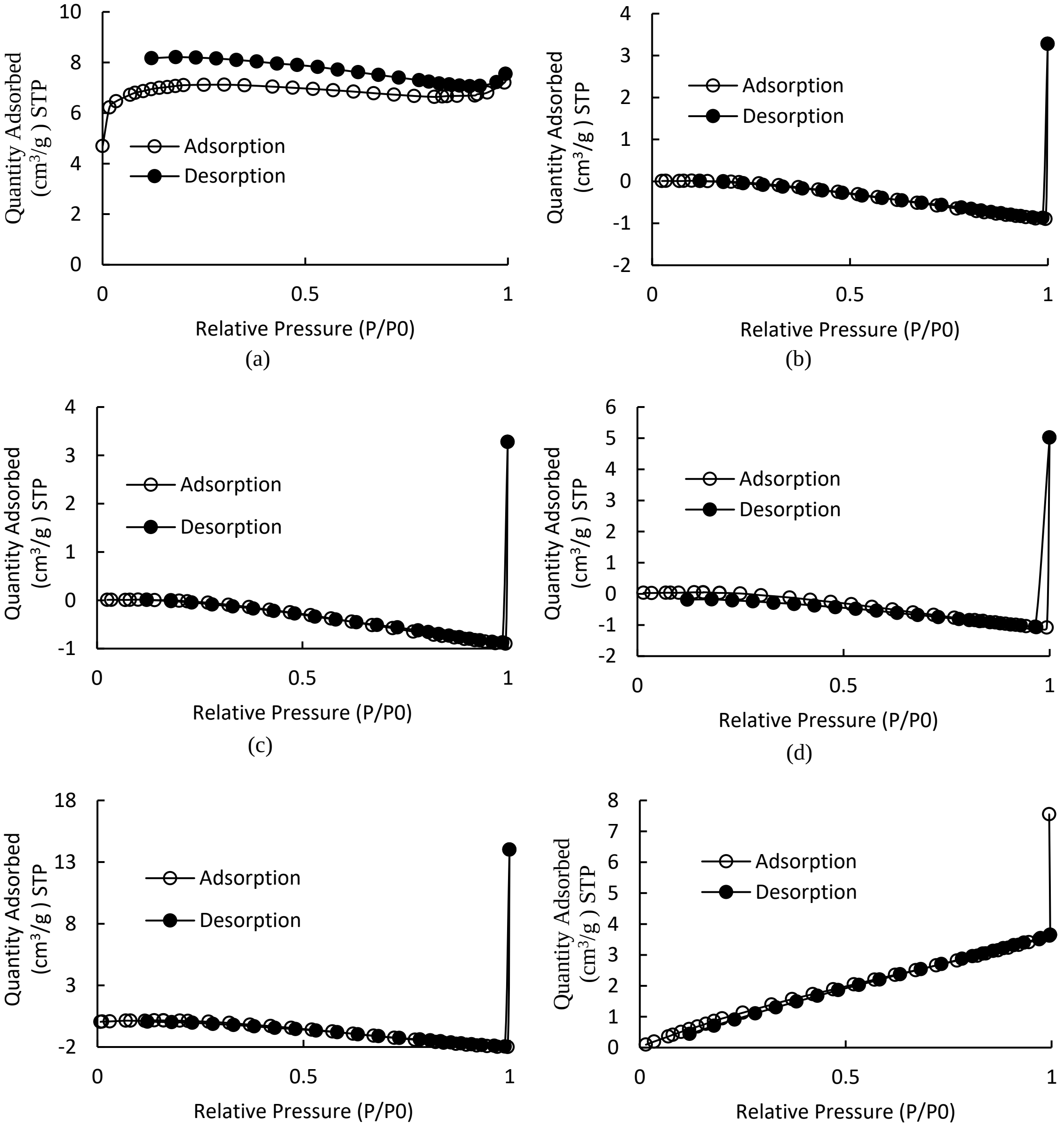
e f

Fig. 3. Scanning electron micrographs of PAA (a), RHC (b), and RHC/P containing 0.5% (c), 1% (d), 2% (e), and 5% (f) RHC

Specific Surface Area

The adsorption/desorption isotherms of the samples obtained under conditions described above are shown in Fig. 4. The RHC exhibited a Type (I) isotherm. Because of the specific surface area of PAA and RHC/P was relatively small, the PAA and RHC/P did not exhibit typical isotherms.

Table 2 shows the specific surface area of the RHC and the RHC/P superabsorbent hydrogels that contained different RHC contents. The specific surface area of PAA was smallest. The specific surface area of the samples increased with the increase of the content of RHC. This facilitated the water penetration into the polymeric network and improved the performance of water absorbency.



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

Fig. 4. N_2 adsorption/desorption isotherms of RHC (a), PAA (b), and RHC/P containing 0.5% (c), 1% (d), 2% (e), and 5% (f) RHC

Table 2. N_2-BET Specific Surface Area of Prepared Samples

Samples	BET (m^2/g)
P(AA-co-AM)	0.0053
0.5% RHC/P	0.0518
1% RHC/P	0.0991
2% RHC/P	0.3983
5% RHC/P	6.9529
RHC	23.9515

Swelling Behaviors of Superabsorbent Hydrogels

Figure 5 shows the swelling capacities of the RHC/P superabsorbent hydrogels that contained different RHC contents in deionized water. Clearly, the swelling ratios of the hydrogels rose with the increase of the RHC loading to 1% and then decreased.

The RHC/P that contained 1% RHC had the largest swelling capacity in deionized water compared with PAA (869 g/g *vs.* 679 g/g), and this noticeable improvement might have been mainly because the monomer was superfluous in the reaction system when the amount of RHC was low. The monomer (AA) turned out to be a homopolymer, which did not benefit the water absorbency. When the crosslinking density is constant, the homopolymer content decreases with the rise of RHC content (Finkenstadt and Willett 2005).

The hydrophilic groups in the polymer networks were intensified by the presence of surface functional groups (*e.g.* COO- and C=O) in RHC. Moreover, due to the nanostructure of RHC, the homogeneous dispersion of RHC within the matrix might have affected the microstructures of the polymer networks and thereby influenced the swelling capacity. Moreover, the synergetic intermolecular interactions between the RHC and the polymer networks contributed to the absorbance of water or other fluids, which improved the swelling capacity. However, the swelling capacity of RHC/P decreased clearly when the amount of RHC was above 1%, which might have been because the grafting ratio and molecular weight of the grafted PAA chains both decreased (Huang *et al.* 2012). Another possible reason was that the excessive RHC tended to aggregate and weakened the RHC-network synergetic interactions, as confirmed by the SEM images (Figs. 3e and 3f).

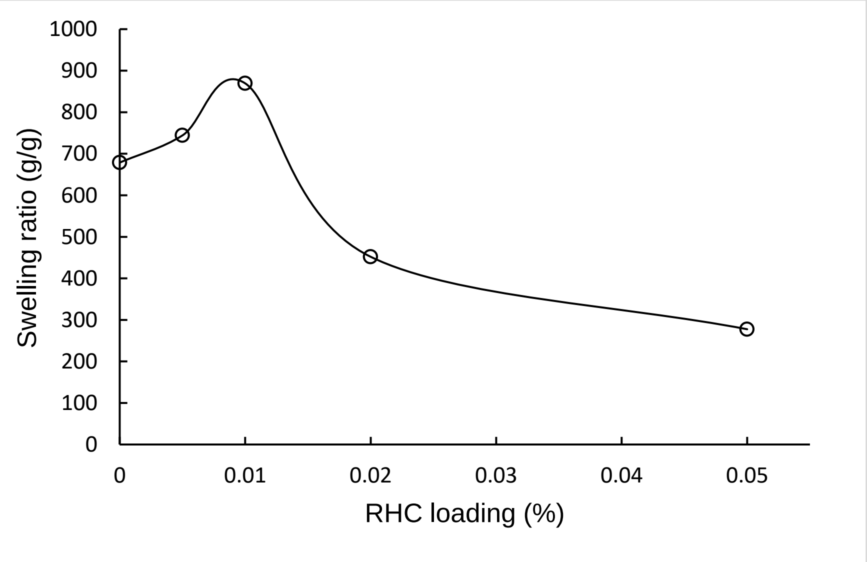


Fig. 5. Swelling capacities of RHC/P superabsorbent hydrogel with various RHC in deionized water

The RHC in the matrix also affected the water diffusion rate during the swelling. Figure 6 shows the swelling rates in deionized water of the RHC/P that contained different RHC amounts. The swelling rates of all of the RHC/P were higher from 0 min to 60 min and the water absorbencies of RHC/P (containing 0%, 0.5%, 1%, 2%, and 5% RHC) were 510 g/g, 618 g/g, 676 g/g, 289 g/g, and 192 g/g, respectively. Then the swelling rates in the deionized water slowly dropped and a swelling equilibrium was achieved after approximately 125 min.

The swelling rates of the RHC/P hydrogels with < 1% RHC were slightly higher than PAA at the initial stage. The swelling rates of the hydrogels were enhanced after the introduction of RHC into the polymer network because the presence of surface COO- and C=O on RHC made the polymeric networks more affinitive towards water molecules. Another reason might have been that the higher porosity of RHC provided more free volume for water penetration into the polymeric network. In contrast, the swelling rates seemingly decreased at the initial stage when the amount of RHC was above 2%. One of the possible explanations was that the aggravation of excessive RHC and the weakened RHC-network synergetic interactions decreased the swelling rates.

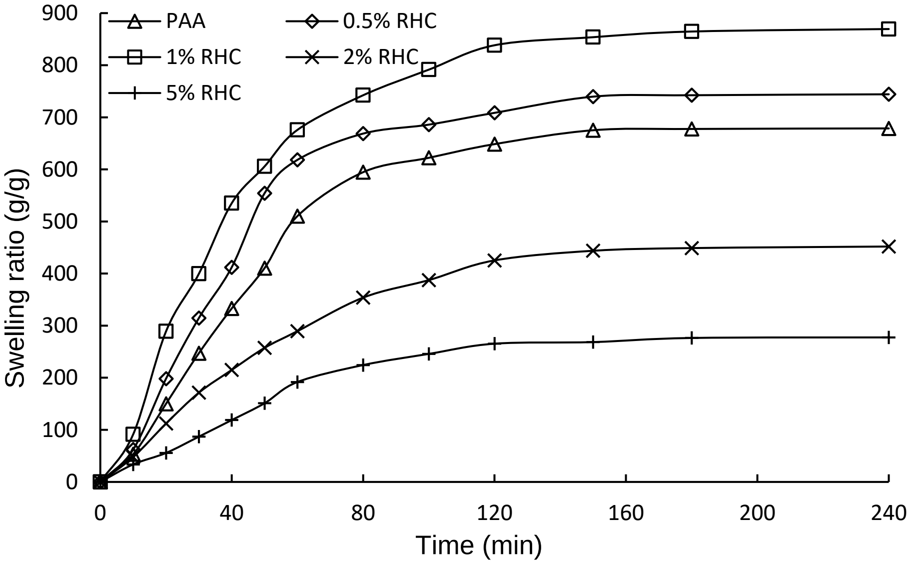


Fig. 6. Swelling rates of PAA and RHC/P superabsorbent hydrogels with various RHC in deionized water

Swelling kinetics can be expressed using the Voigt-based viscoelastic model (Kabiri *et al.* 2003; Irani *et al.* 2013) according to Eq. 2,

$$St = P\,(1 - \mathrm{e} - t\,/\,r) \qquad (2)$$

where St (g/g) is the swelling capability at time t (min), P (g/g) is a power parameter indicating the theoretical balance of water absorption, and r (min) is the rate parameter (time required to reach 63% of its ultimate swelling). To calculate r, the equation with slight modification and plotted Ln [1 - (St / P)] *versus* t was used. The slope P reflects lower water adsorption and a smaller r reflects a higher swelling rate (Wang and Wang 2009).

Results show the rate parameters for the superabsorbent hydrogels (0%, 0.5%, 1%, 2%, and 5%) were 51.23 min, 44.71 min, 44.99 min, 55.90 min, and 56.82 min, respectively, and their P-values were 679 g/g, 744 g/g, 869 g/g, 452 g/g, and 277 g/g, respectively. These data suggested that introducing a small amount (< 1%) of RHC into the superabsorbent hydrogels could improve the swelling rate and water absorbency.

Effect of pH and Salt Solution on Water Absorbency

Figure 7 shows the swelling behaviors of RHC/P hydrogels containing different RHC contents at varying pHs. Clearly, the RHC/P hydrogels containing < 1% RHC always had higher water absorbency than the PAA. When the amount of RHC was above 1%, the water absorbency of RHC/P under varying pH was weakened visibly, which was similar to the RHC in deionized water. All samples were kept nearly constant from a pH of 6 to 8, which could be explained as a buffer action of –COOH and -COO- (Lee and Wu 1996). This was very dominant in the superabsorbents containing –COOH and -COO-. However, the buffer action disappeared after the addition of abundant acid or base.

Under abundant acid (pH<4), most of the carboxylate was protonated. The hydrogen-bonding interaction among carboxylate groups was strengthened and the additional physical crosslinking was generated. However, the electrostatic repulsion among carboxylate group was restricted. So, the network tends to shrink and consequently swelling values are decreased.

The reason for the swelling loss in the highly basic solutions (pH>10) was due to the "charge screening effect" of excess Na+ in the swelling media, which shields the carboxylate anions and prevents effective anion-anion repulsion (Bao *et al.* 2011).

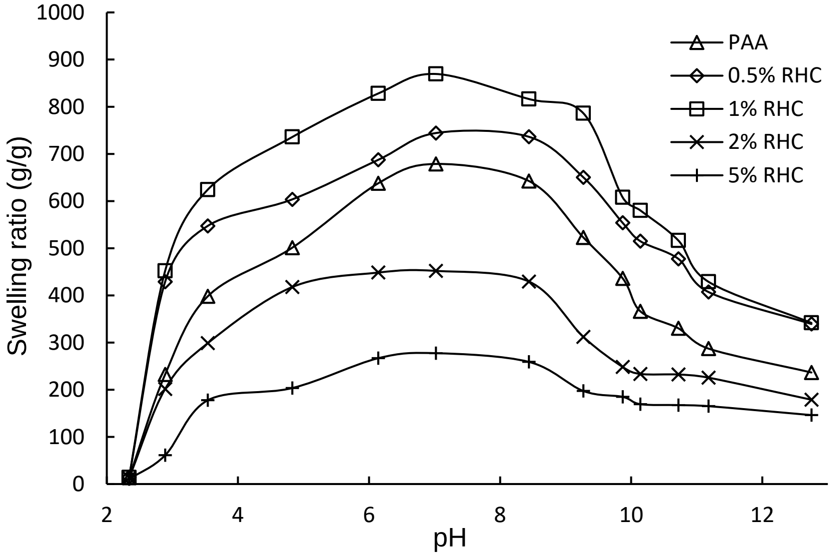


Fig. 7. Swelling rates of PAA and RHC/P superabsorbent hydrogels with various RHC at different pHs

Figure 8 shows the swelling capacities of RHC/P superabsorbent hydrogels that contained different RHC amounts in 0.9% NaCl solution. The swelling ratios of the hydrogels declined sharply compared to the use of deionized water. In fact, this observation is common in the swelling experiments of polyelectrolyte hydrogels (Ostroha *et al.* 2004; Saunders *et al.* 2008). This may have been explained as follows: the charge screening effect caused by the counter ions (Na+) in the salt solution could clearly weaken the electrostatic repulsion and thereby decrease the osmotic pressure between the hydrogel networks and the external solution. However, the swelling kinetics of RHC/P in 0.9% NaCl solution were similar to those in deionized water.

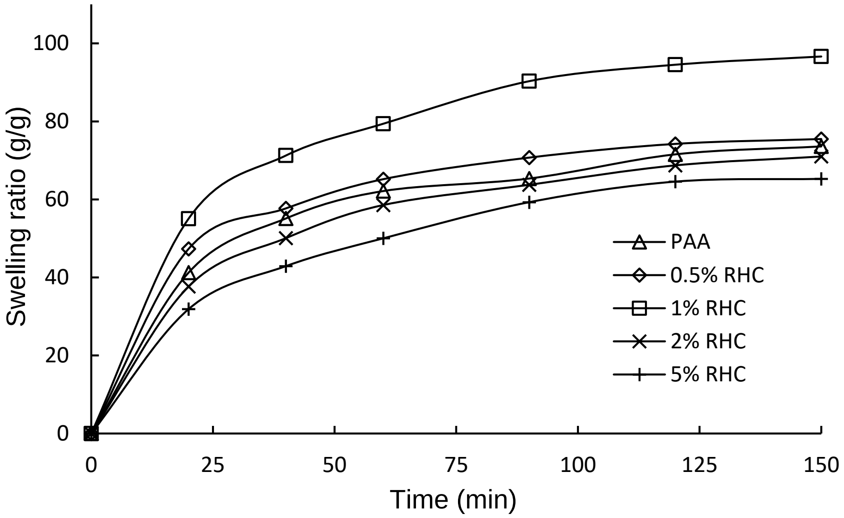


Fig. 8. Swelling rates of PAA and RHC/P superabsorbent hydrogels with various RHC in 0.9% NaCl solution

CONCLUSIONS

1. A series of rice husk char / poly-(acrylic acid-co-acrylamide) (RHC/P) superabsorbent hydrogels were synthesized by using APS as a free radical initiator in the presence of NMBA as a crosslinking agent. Due to the hydrogen bonds and possible covalent bonds between the RHC and polymer chains, a relatively lower content (< 1%) of RHC could be dispersed well within the polymer matrix, and it effectively enhanced the intermolecular interactions between the components.
2. An excessive amount of RHC might form large agglomerates and weaken the interfacial interactions, resulting in the micro-phase separation between the components. Furthermore, the RHC greatly influenced the swelling behaviors and swelling kinetics of the superabsorbent hydrogel. The swelling capacities and swelling rates of the hydrogels increased with increased RHC content (< 1%), and then decreased with further increase in the RHC loading.
3. The Voigt-based viscoelastic model was suitable to represent the swelling kinetics of the RHC/P superabsorbent hydrogel composites. The RHC/P that contained 1% RHC showed the highest swelling capacities (869 g/g in deionized water and 97 g/g in 0.9% NaCl solution), which were much higher than the PAA. The water absorbency for this hydrogel showed buffer action in a pH value from 6 to 8 that resulted from the –COO groups on the polymer chains.
4. An SEM investigation revealed that the superabsorbent incorporated with RHC exhibited a coarse surface. The TGA implied that the introduction of RHC into the polymeric network was helpful for the improvement of thermal stability of corresponding superabsorbents. Therefore, the RHC/P superabsorbent hydrogels that contained suitable RHC content might have potential applications in many areas.

ACKNOWLEDGEMENTS

The authors are thankful for the support from the Scientific Research plan of the Zhejiang province (No. 2014C32039), and the Scientific Research group of the Zhejiang province Key laboratory of Biological, and Chemical Utilization of Forest Resource.

REFERENCES CITED

Azevedo, A. C. N.D., Vaz, M. G., Gomes, R. F., Pereira, A. G. B., Fajardo, A. R., and Rodrigues, F. H. A. (2017). "Starch/rice husk ash based superabsorbent composite: High methylene blue removal efficiency," *Iranian Polymer Journal* 26(2), 93-105. DOI: 10.1007/s13726-016-0500-2

Bao, Y., Ma, J., and Li, N. (2011). "Synthesis and swelling behaviors of sodium carboxymethyl cellulose-g-poly(aa-co-am-co-amps)/mmt superabsorbent hydrogel," *Carbohydrate Polymers* 84(1), 76-82. DOI: 10.1016/j.carbpol.2010.10.061

Banedjschafie, S., and Durner, W. (2015). "Water retention properties of a sandy soil with superabsorbent polymers as affected by aging and water quality," *Journal of Plant Nutrition and Soil Science* 178(5), 798-806. DOI: 10.1002/jpln.201500128

Chang, C., Duan, B., Cai, J., and Zhang, L. (2010). "Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery," *European Polymer Journal* 46(1), 92-100. DOI: 10.1016/j.eurpolymj.2009.04.033

Ekebafe, M. O., Ekebafe, L, O., Maliki, M. (2013). "Utilisation of biochar and superabsorbent polymers for soil amendment," *Science Progress* 96(1), 85-94. DOI: 10.3184/003685013X13587941096281

Finkenstadt, V. L., and Willett, J. L. (2005). "Reactive extrusion of starch-polyacrylamide graft copolymers: Effects of monomer/starch ratio and moisture content," *Macromolecular Chemistry & Physics* 206(16), 125-129. DOI: 10.1002/macp.200500157

Guilherme, M. R., Campese, G. M., Radovanovic, E., Rubira, A. F., Feitosa, J. P. A., and Muniz, E. C. (2005). "Morphology and water affinity of superabsorbent hydrogels composed of methacrylated cashew gum and acrylamide with good mechanical properties," *Polymer* 46(19), 7867-7873. DOI: 10.1016/j.polymer.2005.06.068

Guo, M., Liu, M., Falu Zhan, A., and Wu, L. (2005). "Preparation and properties of a slow-release membrane-encapsulated urea fertilizer with superabsorbent and moisture preservation," *Industrial & Engineering Chemistry Research* 44(12), 4206-4211. DOI: 10.1021/ie0489406

Hafida, F. H., Aiouaz, N, and Dairi N. (2015). "Synthesis and properties of chitosan-graft-polyacrylamide/gelatin superabsorbent composites for wastewater purification," in: *2015 International Conference on Polymer Materials Science and Engineering* 17(7), 29-30.

Hua, S., and Wang, A. (2009). "Synthesis, characterization and swelling behaviors of sodium alginate- g -poly(acrylic acid)/sodium humate superabsorbent," *Carbohydrate Polymers* 75(1), 79-84. DOI: 10.1016/j.carbpol.2008.06.013

Huang, Y., Zeng, M., Ren, J., Wang, J., Fan, L., and Xu, Q. (2012). "Preparation and swelling properties of graphene oxide/poly(acrylic acid- co -acrylamide) super-absorbent hydrogel nanocomposites," *Colloids & Surfaces A: Physicochemical & Engineering Aspects* 401, 97-106. DOI: 10.1016/j.colsurfa.2012.03.031

Irani, M., Ismail, H., and Ahmad, Z. (2013). "Preparation and properties of linear low-density polyethylene-g-poly (acrylic acid)/organo-montmorillonite superabsorbent hydrogel composites," *Polymer Testing* 32(3), 502-512. DOI: 10.1016/j.polymertesting.2013.01.001

Jullaphan, O., Witoon, T., and Chareonpanich, M. (2009). "Synthesis of mixed-phase uniformly infiltrated sba-3-like in sba-15 bimodal mesoporous silica from rice husk ash," *Materials Letters* 63(15), 1303-1306. DOI: 10.1016/j.matlet.2009.03.001

Kabiri, K., Omidian, H., Hashemi, S. A., and Zohuriaan-Mehr, M. J. (2003). "Concise synthesis of fast-swelling superabsorbent hydrogels: Effect of initiator concentration on porosity and absorption rate," *European Polymer Journal* 39(7), 1341-1348. DOI: 10.1016/S0014-3057(02)00391-9

Kosemund, K., Schlatter, H., Ochsenhirt, J. L., Krause, E. L., Marsman, D. S., and Erasala, G. N. (2009). "Safety evaluation of superabsorbent baby diapers," *Regulatory Toxicology & Pharmacology* 53(2), 81-9. DOI: 10.1016/j.yrtph.2008.10.005

Liang, R., Yuan, H., Xi, G., and Zhou, Q. (2009). "Synthesis of wheat straw-g-poly(acrylic acid) superabsorbent composites and release of urea from it," *British Journal of Community Nursing* 77(2), 181-187. DOI: 10.1016/j.carbpol.2008.12.018

Li, X. d., Li, Q., Xu, X., Su, Y., Yue, Q. Y., and Gao, B. Y. (2016). "Characterization, swelling and slow-release properties of a new controlled release fertilizer based on wheat straw cellulose hydrogel," *Journal of the Taiwan Institute of Chemical Engineers* 60(6), 564-572. DOI: 10.1016/j.jtice.2015.10.027

Mahdavinia, G. R., Pourjavadi, A., Hosseinzadeh, H., and Zohuriaan, M. J. (2004). "Modified chitosan 4. Superabsorbent hydrogels from poly(acrylic acid-co-acrylamide) grafted chitosan with salt- and pH-responsiveness properties," *European Polymer Journal* 40(7), 1399-1407. DOI: 10.1016/j.eurpolymj.2004.01.039

Murthy, P. S. K., Mohan, Y. M., Sreeramulu, J., and Raju, K. M. (2006). "Semi-IPNs of starch and poly(acrylamide-co-sodium methacrylate): Preparation, swelling and diffusion characteristics evaluation," *Reactive & Functional Polymers* 66(12), 1482-1493. DOI: 10.1016/j.reactfunctpolym.2006.04.010

Nguyen, H. N., and Pignatello, J. J. (2013). "Laboratory tests of biochars as absorbents for use in recovery or containment of marine crude oil spills," *Environmental Engineering Science* 30(7), 374-380. DOI: 10.1089/ees.2012.0411

Lee, W. F., and Wu, R. J. (1996). "Superabsorbent polymeric materials. I. Swelling behaviors of crosslinked poly(sodium acrylate-co-hydroxyethyl methacrylate) in aqueous salt solution," *Journal of Applied Polymer Science* 62(7), 1099-1114. DOI: 10.1002/(SICI)1097-4628(19961114)62:7%3C1099::AID-APP16%3E3.0.CO;2-1

Ostroha, J., Pong, M., Lowman, A., and Dan, N. (2004). "Controlling the collapse/ swelling transition in charged hydrogels," *Biomaterials* 25(18), 4345-4353. DOI: 10.1016/j.biomaterials.2003.11.019

Oun, R., Plumb, J. A., and Wheate, N. J. (2014). "A cisplatin slow-release hydrogel drug delivery system based on a formulation of the macrocycle cucurbit[7]uril, gelatin and polyvinyl alcohol," *Journal of Inorganic Biochemistry* 134C(3), 100-105. DOI: 10.1016/j.jinorgbio.2014.02.004

Paethanom, A., and Yoshikawa, K. (2012). "Influence of pyrolysis temperature on rice husk char characteristics and its tar adsorption capability," *Energies* 5(12), 4941-4951. DOI: 10.3390/en5124941

Parvathy, P. C., Jyothi, A. N., John, K. S., and Sreekumar, J. (2014). "Cassava starch based superabsorbent polymer as soil conditioner: Impact on soil physico-chemical and biological properties and plant growth," *Clean Soil Air Water* 42(11), 1610-1617. DOI: 10.1002/clen.201300143

Perez, J. J., and Francois, N. J. (2016). "Chitosan-starch beads prepared by ionotropic gelation as potential matrices for controlled release of fertilizers," *Carbohydrate Polymers* 148(5), 134-142. DOI: 10.1016/j.carbpol.2016.04.054

Pourjavadi, A., Barzegar, S., and Mahdavinia, G. R. (2006). "MBA-crosslinked Na-alg/CMC as a smart full-polysaccharide superabsorbent hydrogels," *Carbohydrate Polymers* 66(3), 386-395. DOI: 10.1016/j.carbpol.2006.03.013

Pourjavadi, A., Barzegar, S., and Zeidabadi, F. (2007). "Synthesis and properties of biodegradable hydrogels of κ -carrageenan grafted acrylic acid-co-2-acrylamido-2-methylpropanesulfonic acid as candidates for drug delivery systems," *Reactive & Functional Polymers* 67(7), 644-654. DOI: 10.1016/j.reactfunctpolym.2007.04.007

Pourjavadi, A., Jahromi, P. E., Seidi, F., and Salimi, H. (2010). "Synthesis and swelling behavior of acrylated starch-g-poly (acrylic acid) and acrylated starch-g-poly (acrylamide) hydrogels," *Carbohydrate Polymers* 79(4), 933-940. DOI: 10.1016/j.carbpol.2009.10.021

Reddy, N. N., Varaprasad, K., Ravindra, S., Reddy, G. V. S., Reddy, K. M. S., Reddy, K. M. M., and Raju, K. M. (2011). "Evaluation of blood compatibility and drug release studies of gelatin based magnetic hydrogel nanocomposites," *Colloids & Surfaces A: Physicochemical & Engineering Aspects* 385(1), 20-27. DOI: 10.1016/j.colsurfa.2011.05.006

Qi, X. H., Liu, M. Z., and Chen, Z. B. (2016). "Fast-swelling oxidized starch phosphate-poly (acrylate/ acrylamide/2-acryloylamino-2-methyl-1-propanesulfonic acid) superabsorbent composite," *Polymer Engineering & Science* 56(11), 1267-1274. DOI: 10.1002/pen.24360

Saunders, J. R., Abusalih, S., Khaleque, T., Hanula, S., and Moussa, W. (2008). "Modeling theories of intelligent hydrogel polymers," *Journal of Computational & Theoretical Nanoscience* 5(10), 1942-1960. DOI: 10.1166/jctn.2008.1001

Shen, Y., Zhao, P., Shao, Q., Ma, D., Takahashi, F., and Yoshikawa, K. (2014). "*In-situ*, catalytic conversion of tar using rice husk char-supported nickel-iron catalysts for biomass pyrolysis/gasification," *Applied Catalysis B: Environmental,* 152-153(1), 140-151. DOI: 10.1016/j.apcatb.2014.01.032

Wang, W., and Wang, A. (2009). "Preparation, characterization and properties of superabsorbent nanocomposites based on natural guar gum and modified rectorite," *Carbohydrate Polymers* 77(4), 891-897. DOI: 10.1016/j.carbpol.2009.03.012

Wang, L., Zhang, J., and Wang, A. (2011). "Fast removal of methylene blue from aqueous solution by adsorption onto chitosan-g-poly (acrylic acid)/attapulgite composite," *Desalination* 266(1-3), 33-39. DOI: 10.1016/j.desal.2010.07.065

Witoon, T., Chareonpanich, M., and Limtrakul, J. (2008). "Synthesis of bimodal porous silica from rice husk ash *via* sol-gel process using chitosan as template," *Materials Letters* 62(s 10-11), 1476-1479. DOI: 10.1016/j.matlet.2007.09.004

Yamamoto, C. F., Pereira, E. I., Mattoso, L. H. C., Matsunaka, T., and Ribeiro, C. (2016). "Slow release fertilizers based on urea/urea–formaldehyde polymer nanocomposites," *Chemical Engineering Journal* 287(1), 390-397. DOI: 10.1016/j.cej.2015.11.023

Yoshimura, T., Matsuo, K., and Fujioka, R. (2006). "Novel biodegradable superabsorbent hydrogels derived from cotton cellulose and succinic anhydride: Synthesis and characterization," *Journal of Applied Polymer Science* 99(6), 3251-3256. DOI: 10.1002/app.22794

Zhang, J., Wang, Q., and Wang, A. (2007). "Synthesis and characterization of chitosan- g -poly(acrylic acid)/attapulgite superabsorbent composites," *Carbohydrate Polymers* 68(2), 166-173. DOI: 10.1016/j.carbpol.2006.11.018

Zheng, Y., Hua, S., and Wang, A. (2010). "Adsorption behavior of Cu^{2+}, from aqueous solutions onto starch- g -poly(acrylic acid)/sodium humate hydrogels," *Desalination* 263(1-3), 170-175. DOI: 10.1016/j.desal.2010.06.054

Zou, W., Yu, L., Liu, X., Chen, L., Zhang, X., and Qiao, D., and Zhang, R. (2012). "Effects of amylose/amylopectin ratio on starch-based superabsorbent polymers," *Carbohydrate Polymers* 87(2), 1583-1588. DOI: 10.1016/j.carbpol.2011.09.060

Article submitted: January 12, 2017; Peer review completed: March 26, 2017; Revised version received: May 8, 2017; Accepted: May 9, 2017; Published: May 16, 2017.
DOI: 10.15376/biores.12.3.4795-4809