Effects of Formaldehyde Modification of Eucalyptus Bark on Cr(VI) Adsorption

Shuangquan Yao,[a,b,1] Cong Gao,[a,b,1] Shuangxi Nie,[a,b] Fenjie Niu,[a,b] Shuangfei Wang,[a,b] and Chengrong Qin [a,b,*]

The adsorption effects, thermodynamics, and kinetics of formaldehyde-modified eucalyptus bark on Cr(VI) was investigated. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) were used to verify the adsorption capacity difference between unmodified and modified eucalyptus bark. The results demonstrated that the surface area and active group content was increased by modification, which was conducive to the adsorption of Cr(VI). The effects of pH, time, temperature, initial Cr(VI) concentration, and adsorbent dosage and on adsorption were investigated. The optimal adsorption capacity was 16.50 mg.g^{-1} under the conditions of 50 mg.L^{-1} initial Cr(VI) concentration, pH 2.0, 3 g.L^{-1} adsorbent dosage, 50 °C, and 120 min. The fitting of kinetics indicated that the adsorption was governed by multiple factors. The thermodynamic parameters $\triangle H^0 > 0$ showed that the adsorption process was an endothermic reaction. The value $\triangle S^0 > 0$ indicated that liquid-solid interface disorder increased during the adsorption process and showed a good adsorption performance.

Keywords: Eucalyptus bark; Formaldehyde modified; Adsorption; Cr(VI); Kinetics; Thermodynamics

*Contact information: a: Department of light Industrial and Food Engineering, Guangxi University, Nanning, 530004, PR China; b: Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control, Nanning 530004, PR China; *Corresponding author: qin_chengrong@sina.com*
[1] *These authors contributed equally to this work.*

INTRODUCTION

Chromium has a positive and negative effect in nature (Rieke 2017). This is due to its two main forms: Cr(III) and Cr(VI) (Johnson *et al*. 2017; Lee *et al*. 2017). Cr(III) has been used to enhance insulin, promote glucose metabolism, promote the synthesis of cholesterol, and inhibit fatty acids production (Houton *et al*. 2016; Yang *et al*. 2016), and it is also one of the essential elements of mammalian metabolism (Zhang *et al*. 2015a; Aharchaou *et al*. 2016). However, Cr(VI) is toxic, carcinogenic, and teratogenic (Arulkumar *et al*. 2012); it has been listed as one of the highest levels of toxic substances (Fakhriyan *et al*. 2016). Therefore, the removal of the Cr(VI) pollution from wastewater is an urgent problem.

In general, adsorption is used to remove heavy metals; the most mature adsorption material is activated carbon (Shafeeyan *et al*. 2015; Jorge *et al*. 2016). Activated carbon adsorbent can be used to remove Cr(VI) (Khraisheh *et al*. 2016; Maneerung *et al*. 2016). Doke and Khan (2017) prepared activated charcoal from wood apple shell by chemical activation and used this adsorbent to remove Cr(VI) from aqueous solutions. Batch adsorption studies revealed that the activated charcoal has a significant capacity for Cr(VI) adsorption. The removal of Cr(VI) from aqueous solutions by activated carbon has been investigated (Ali and Alrafai 2016). The optimum conditions for maximum removal of

Cr(VI) ion from aqueous solutions about 99% (w/w) were reported as 0.80 g of activated carbon, 25 min, and 50.0 mg.L^{-1} Cr(VI). The study showed that activated carbon can be used as a low cost, ecofriendly, and effective sorbent for the removal of Cr(VI) from aqueous solutions. Cr(VI) adsorption from aqueous solution by an agricultural waste is a very effective method (Khan *et al.* 2016, Mohan *et al*. 2005). It is a simple and resourceful process. The adsorption of Cr(VI) from aqueous solutions onto different agricultural wastes such as sugarcane bagasse, maize corn cob, and Jatropha oil cake under various experimental conditions has been studied (Garg *et al*. 2007). The results showed that agricultural wastes can be an attractive low-cost alternative for removal of chrome from wastewater. The comparative adsorption efficiency of *Picea smithiana* and activated charcoal for removal of Cr(VI) from aqueous solution has been investigated (Mittal *et al*. 2015). The study indicates that *Picea smithiana* has 76% (w/w) removal efficiency for Cr(VI) compared with activated charcoal. *Picea smithiana* has high adsorption efficiency compared with other bio-waste materials.

Agricultural forest waste has great potential and advantages in the adsorption of Cr(VI) (Yang *et al*. 2009; Qiu *et al*. 2015), but there is little information on the use of eucalyptus bark as a bioabsorbent. In recent years, China's growth of eucalyptus has been particularly rapid, especially in Guangxi, where the demand for eucalyptus is highest (Harrington *et al*. 2015; Zhang *et al*. 2015b; Engler *et al*. 2016). In 2015, the average production of wood was 25 million m^3, with the resulting bark of 7.5 million m^3. Eucalyptus bark is composed mainly of cellulose, hemicellulose, lignin, and pectin (Yan *et al*. 2015; Yu *et al*. 2016). The surface contains a large amount of active substances, such as -COOH, -OH, and -NH_2 (Gao *et al*. 2016). These active groups have a good adsorption of metal ions.

This paper focuses on the effects of formaldehyde modified eucalyptus bark on adsorption of Cr(VI). To demonstrate its potential as adsorbent, the adsorption capacities of the eucalyptus bark and of activated carbon were compared. To study the effect of modification on the adsorption capacity of eucalyptus bark, its structure was characterized with or without modification using scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The effects of initial Cr (VI) concentration, pH, adsorption, reaction time, and reaction temperature on adsorption were studied. In order to understand the mechanism of adsorption, the kinetics and thermodynamics were studied. This report provides a basis for Cr(VI) removal from wastewater using agricultural forest waste.

EXPERIMENTAL

Materials

Cr(VI) standard reserve fluid, Cr(VI) standard wastewater, and chromogenic agent was obtained from Cheng du Kelon chemical reagent factory (Cheng du, China). Activated carbon, acetone, diphenylcarbazide, and 40% (w/w) formaldehyde were purchased from Analytik-Jena instrument company (Jena, Germany); other chemicals were purchased from Alladdin (Shanghai, China). All assay reagents were obtained from Sigma (St. Louis, USA). All of the chemicals used were analytical grade.

Methods

The eucalyptus bark was washed with deionized water, dried at 60 °C, and then crushed (between 40 and 60 mesh). To compare the adsorption effect, the activated carbon also needed pretreatment before adsorption. The operation was as follows: the powder activated carbon was soaked for 24 h with 0.1 $mol.L^{-1}$ HCl. It was washed to neutral pH before drying at 110 °C. To avoid the release of color by bark into the aqueous solution during adsorption, it was modified by formaldehyde (Park *et al*. 2007a). A total of 5 mL of aqueous formaldehyde was added to 100 mL of 0.1 $mol.L^{-1}$ HCl, and 10 g of ground, washed bark was added to this solution. The final mixture was stirred and heated at 60 °C for 3 h until the mixture became thick slurry. The slurry (pretreated bark) was washed with deionized water until the pH of the filtrate was more than 5. Finally, the bark was air-dried and sieved (Sarin and Pant 2006).

The cross-sectional morphology of eucalyptus bark with or without formaldehyde modified was observed by SEM (S-3400N, Hitachi, City, Japan) (Yao *et al*. 2015). The eucalyptus bark powder was fractured in liquid nitrogen and then coated with gold before SEM imaging under 10000× magnification.

FTIR spectra of eucalyptus bark with or without formaldehyde modification were examined with a Nexus 470 spectrometer (HP, City, USA) using 16 scans and a frequency range of 500 to 4000 cm^{-1}. Signal averages were obtained at a resolution of 4 cm^{-1}. Samples were oven-dried at 105 °C for 6 h, mixed with KBr in a ratio of 1 : 10 mg (eucalyptus bark powder: KBr), and pressed under vacuum to form pellets (Yao *et al*. 2015; Yuan *et al*. 2010). For measuring the intensity at a specific wave number, two specimens of each sample were tested, and the results were averaged (González *et al*. 2011).

Later, 100 mL of 40 $mg.L^{-1}$ Cr(VI) was added to deionized water, and then 0.3 g of washed bark was added to this solution. The initial pH of the slurry was adjusted by 0.1 $mol.L^{-1}$ HCl or NaOH to pH 3. The final mixture was stirred and heated at 30 °C for 90 min. The filtrate was collected, and the concentration of Cr(VI) was determined by diphenylcarbohydrazide spectrophotometry (Ahmadi and Shadizadeh 2015). The calculation of adsorption capacity is shown in Eq. 1. The static adsorption of pretreated activated carbon was the same as that of the pretreated eucalyptus bark,

$$q_e = v(p_1 - p_2)/m \tag{1}$$

where q_e is the adsorption capacity ($mg.g^{-1}$), v is the volume of the sample (L), p_1 is the initial concentration of the sample ($mg.L^{-1}$), p_2 is the concentration of the sample after reaction ($mg.L^{-1}$), and m is the dosage of adsorbent (g).

RESULTS AND DISCUSSION

Comparison of Adsorption Capacity

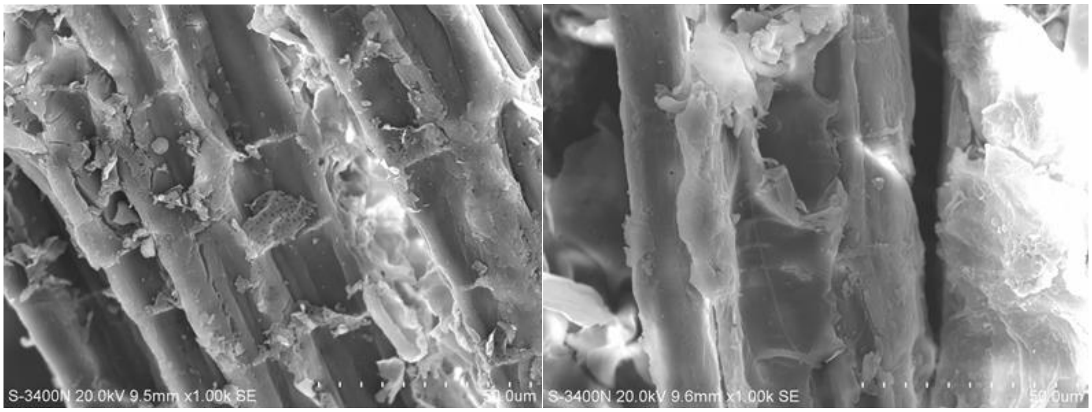
The adsorption capacity of eucalyptus bark with or without modified and activated carbon is shown in Table 1. Cr(VI) could be adsorbed by eucalyptus bark, but its adsorption capacity was 3.03 $mg.g^{-1}$, only half that of activated carbon (6.38 $mg.g^{-1}$). To be suitable for commercial applications, the adsorption capacity of eucalyptus bark would need to be improved. The adsorption capacity of formaldehyde-modified eucalyptus bark was 6.45 $mg.g^{-1}$, which was higher than that of activated carbon. This means that the adsorption efficiency was improved, the dissolution of the colored substance in the bark was effectively prevented, and the error of the follow-up measurement was decreased by the crosslinking of formaldehyde. Due to the high cost and non-renewable characteristics of activated carbon, cheap eucalyptus bark has a greater advantage. In fact, the effect of eliminating waste was achieved by using the formaldehyde-modified eucalyptus bark as the adsorbent.

Table 1. Comparisons for Adsorption Capacity of Eucalyptus Bark

Adsorbent	Cr(VI) Concentration (mg.L^{-1})	Adsorption Capacity (mg.g^{-1})
Eucalyptus bark	3.91	3.03
Modified eucalyptus bark	0.66	6.45
Activated carbon	0.88	6.38

Morphology Analysis

Morphological changes of the eucalyptus bark on account of its modification were observed by SEM (Fig. 1). The unmodified sample was rough, with many fragmented materials on the surface (Fig. 1a). The fragments were located close together on the surface. Most of these fragments were identifiable as dust, pectin, and materials other than cellulose, lignin, and hemicellulose. Additionally, most of these substances had poor adsorption capability. After pretreatment, a clean and smooth surface appeared (Fig. 1b). The dust, pectin, and other materials were detached from the surface. The basic structure of the bark was destroyed in the course of its modification. The surface of modified eucalyptus bark became more porous. The fiber bundles were stratified and denuded. The outer layer of the fiber bundle became loose. A larger porosity was achieved as some of the fibers were gathered in a cage. For these reasons, the surface area of the sample was enlarged. At the same time, the poor adsorption capability components were stripped away. Therefore, Cr(VI) adsorption was stronger in formaldehyde-modified eucalyptus bark.



(a) (b)

Fig. 1. SEM pictures of (a) unmodified eucalyptus bark, and (b) modified eucalyptus bark)

FTIR Spectroscopy

FTIR is a powerful technique that can be used to investigate changes in functional groups resulting from modification of biomaterials. When chemical groups interact on a molecular level, a spectral adsorption band shift occurs. These changes could be an indication of good adsorption of eucalyptus bark. The spectra of samples with or without modified bark (Fig. 2) showed the typical signal pattern expected, based on the compositions of the materials. The two spectra had the same general patterns, with some differences. In Fig. 2a, the peak at 3452 cm^{-1} was attributed to O-H stretching vibration formed by the hydroxyl group of polysaccharides and water (Sun *et al*. 2013). This peak moved to 3421 cm^{-1} and was obviously enhanced in Fig. 2b. Thus, the modified sample had more hydroxyl content. The signal at 2900 cm^{-1} was due to the methylene bending vibration (Liu *et al*. 2007). It moved to 2920 cm^{-1} and was more prominent in Fig. 2b, indicating that the content of methylene groups was increased by formaldehyde modification. In Fig. 2b, the peak at 1636 cm^{-1} was due to the stretching vibration of carbonyl groups, indicating that during the modification the condensation of formaldehyde and eucalyptus bark resulted in the formation of hemiacetal (Calvini *et al*. 2004; Saito *et al*. 2009). In addition, a band at 2300 cm^{-1} represented C≡N, Si-H, B-H, S-H, P-H... stretching vibrations due to the other components of eucalyptus bark. There was no obvious change based on a comparison of Fig. 2c with Fig. 2b, and no new groups appear to have been generated. A possible reason was that adsorption process was dominated by physical adsorption.

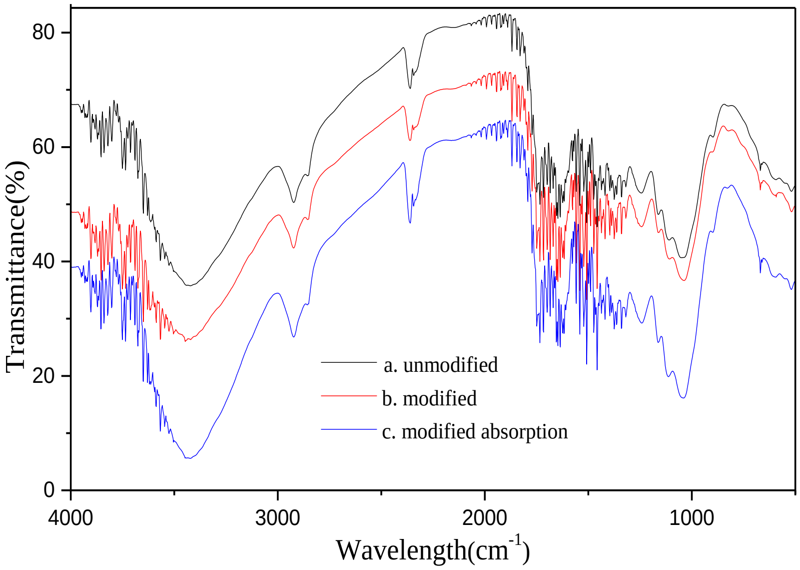


Fig. 2. FTIR of eucalyptus bark with or without modification

Effect of pH on Adsorption

Cr(VI) is a very strong oxidizing agent, and bark contains a diverse collection of chemical species, some of which can be oxidized by the Cr(VI) (Park *et al.* 2005b). Because Cr(III) is the other highly stable oxidation number of chromium, one can expect that when Cr(VI) oxidizes something, the product will mostly be Cr(III) (Elangovan *et al*. 2008; Murphy *et al.* 2009). There are many articles that discuss this, including the effects of such conversions on the amounts of chromium adsorbed onto cellulosic materials of various types (Mohanty *et al.* 2006; Park *et al*. 2007b, 2008). An increased ionic strength inhibited the Cr(VI) reduction. The presence of other heavy metals, such as Cr(III), Ni(II), or Zn(II), only slightly affected the Cr(VI) reduction. Although the above various parameters could affect the reduction rate of Cr(VI) by biomass, these effects were relatively smaller than those of pH and temperature (Park *et al*. 2005a).

100 mL of 50 $mg.L^{-1}$ Cr(VI) was added to waste water, and then 0.3 g of washed bark was added to this solution. The final mixture was stirred and heated at 30 °C for 90 min. The change rule of equilibrium adsorbed amount was investigated by changing pH. The results are shown in Fig. 4.

The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry in solution (Mohanty *et al.* 2006). When pH changed from 1 to 3, the change of the equilibrium adsorption capacity was small. It decreased from 9.89 $mg.g^{-1}$ to 9.57 $mg.g^{-1}$. The downward trends of the equilibrium adsorption capacity increased obviously when pH exceeded 3; it was 4.61 $mg.g^{-1}$ when pH was 5. This could be explained that since Cr(VI) co-exists in different forms, such as $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$ in acidic medium, and the lowering of pH causes the surface of the adsorbent to be protonated to a higher extent, a strong attraction exists between these oxyanions of Cr (VI) and the positively charged surface of the adsorbent (Garg *et al.* 2007; Gupta *et al.* 2010). It has also been postulated that under acidic conditions, Cr(VI) could be reduced to Cr(III) in the presence of an adsorbent:

$$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow Cr^{3+} + 7H_2O$$

Whereas at high pH there will be abundance of negatively charged OH^- in aqueous solution, causing hindrance between negatively charged ions $Cr_2O_7^{2-}$; CrO_4^{2-}, etc. and negatively charged adsorbent, resulting in a decrease of adsorption. When the pH was 1, the modified bark had a certain degree of hydrolysis. The optimal pH of the reaction was 2. Our results are consistent with other workers (Goel *et al.* 2005; Garg *et al.* 2007; Gupta *et al.* 2010).

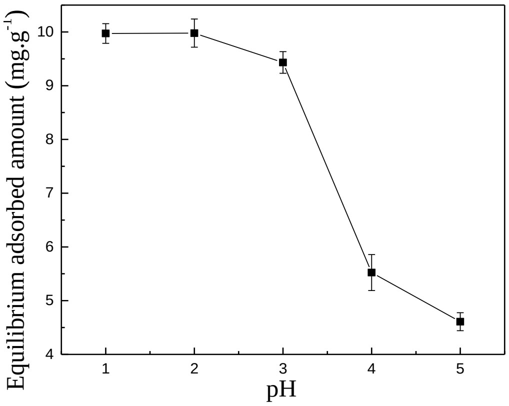


Fig. 3. Influence of pH on metal adsorption

Effect of the Initial Cr(VI) Concentration on Adsorption

Cr(VI) (100 mL) was added to deionized water, and 0.3 g of washed bark was added to this solution. The initial pH of the slurry was adjusted by 0.1 $mol.L^{-1}$ HCl or NaOH to pH 3. The final mixture was stirred and heated at 30 °C for 90 min. The change rule of equilibrium adsorbed amount was investigated by evaluating the change of the initial concentration of Cr(VI). The results are shown in Fig. 3. When the concentration of Cr(VI) changed from 20 $mg.L^{-1}$ to 50 $mg.L^{-1}$, the equilibrium adsorbed amount showed linear growth, from 6.45 $mg.g^{-1}$ to 14.08 $mg.g^{-1}$. The equilibrium adsorbed amount decreased when the concentration of Cr(VI) exceeded 50 $mg.L^{-1}$; it was 14.46 $mg.g^{-1}$ at 60 $mg.L^{-1}$ Cr(VI). Due to the increase of Cr(VI) concentration on the surface of the adsorbent and the acceleration of Cr(VI) diffusion, the equilibrium adsorbed amount increased with the increased Cr(VI) concentration. The active site of the adsorbent was surrounded by Cr(VI) ions for the concentration increases. As a result, the equilibrium adsorbed amount increased slowly, even flattening. Hence, the optimal initial Cr(VI) concentration of the reaction was 50 $mg.L^{-1}$.

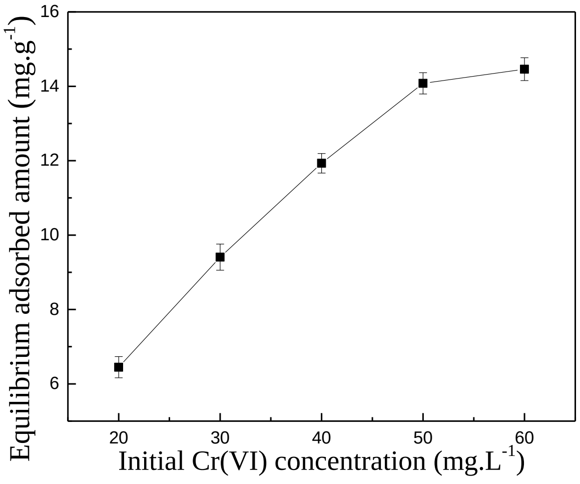


Fig. 4. Effect of initial Cr(VI) concentration on the adsorbed amount

Effect of Adsorbent Dosage on Adsorption

100 mL of 50 mg.L^{-1} Cr(VI) was added to waste water and then 0.3 g of washed bark was added to this solution. The initial pH of the slurry was adjusted by 0.1 mol.L^{-1} HCl or NaOH to pH 2. The final mixture was stirred and heated at 30 °C for 90 min. The change rule of equilibrium adsorbed amount was investigated by changing the adsorbent dosage.

The results are shown in Fig. 5. When the adsorbent dosage changed from 0.1 g to 0.3 g, the equilibrium adsorbed amount decreased almost linearly, from 18.35 mg.g^{-1} to 9.51 mg.g^{-1}. The decline was slowing down when the adsorbent dosage exceeded 0.3 g; it was 6.21 mg.g^{-1} when the adsorbent dosage was 0.5 g. A possible reason was that the adsorption saturation was easily achieved when the absorbent dosage was small. When the adsorbent dosage was 0.3 g, the removal rate of Cr(VI) was close to 100 %. It was no longer increased when the adsorbent dosage was beyond 0.3g. The optimal absorbent dosage of the reaction was 0.3 g.

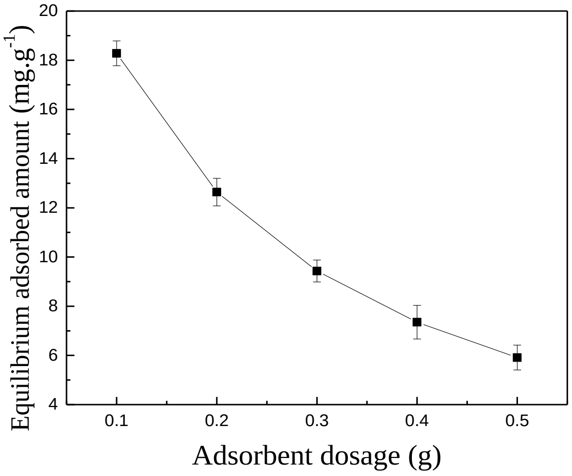


Fig. 5. Adsorbent dosage on influence of the adsorbed amount

Effect of Temperature on Adsorption

100 mL of 50 mg.L^{-1} Cr(VI) was added to waste water, and then 0.3 g of washed bark was added to this solution. The initial pH of the slurry was adjusted by 0.1 mol.L^{-1} HCl or NaOH to pH 2. The final mixture was stirred and heated for 90 min. The change rule of equilibrium adsorbed amount was investigated by change temperature. The result is shown in Fig. 6.

When the temperature was changed from 30 °C to 50 °C, the equilibrium adsorbed amount increased rapidly, from 9.42 mg.g^{-1} to 9.93 mg.g^{-1}. The growth trend decreased when the temperature exceeded 50 °C; the adsorption was 9.95 mg.g^{-1} at 70 °C. This result is because the adsorption response may have been an endothermic reaction, and the positive reaction was facilitated by temperature increase. The optimal temperature of the reaction was 50 °C.

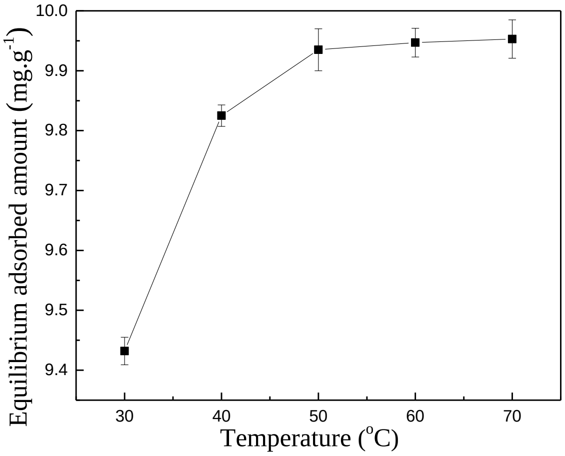


Fig. 6. Temperature on influence of the adsorbed amount

Effect of Time on Adsorption

100 mL of 50 mg.L^{-1} Cr(VI) was added to waste water, and then 0.3 g of washed bark was added to this solution. The initial pH of the slurry was adjusted by adding portions of 0.1 mol.L^{-1} HCl or NaOH to reach pH 2. The final mixture was stirred and heated at 50 °C. The change rule of equilibrium adsorbed amount was investigated by changing time. The result is shown in Fig. 7.

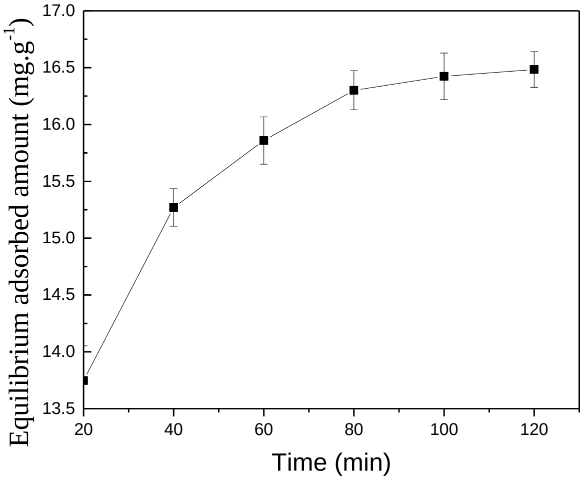


Fig. 7. Time on influence of the adsorbed amount

When the time changed from 20 min to 80 min, the equilibrium adsorbed amount increased rapidly, from 13.75 mg.g^{-1} to 16.23 mg.g^{-1}. The growth trend decreased when the time exceeded 80 min; it was 16.41 mg.g^{-1} at 120 min. The optimal time of the reaction was 120 min. The optimum conditions were as follows: 50 mg.L^{-1} initial Cr(VI) concentration, pH 2.0, 3 g.L^{-1} adsorbent dosage, temperature 50 °C, and time 120 min.

Adsorption Kinetics

The kinetics of the adsorption of Cr(VI) by modified eucalyptus bark was studied under the optimal conditions. The adsorption kinetics curve was obtained, which showed the relationship between the adsorption capacity *q* and the adsorption time *t*. The result is shown in Fig. 7. The establishment of adsorption kinetics played an important role in the study of adsorption mechanism. The adsorption kinetics of Cr(VI) in modified eucalyptus bark was analyzed by the pseudo-first order adsorption kinetics (Eq. 2) and the pseudo-second order adsorption kinetics equation (Eq. 3) (Iqbal *et al*. 2009; (Giri *et al*. 2012). The fitting results are shown in Table 2,

$$1/q_t = 1/q_e + K_1/(q_e t) \tag{2}$$

$$t/q_t = 1/(K_2 q e^2) + t/(q_e) \tag{3}$$

where k_1 is the pseudo first order adsorption rate constant (min) and k_2 is the pseudo second order adsorption rate constant (g.mg^{-1}.min^{-1}).

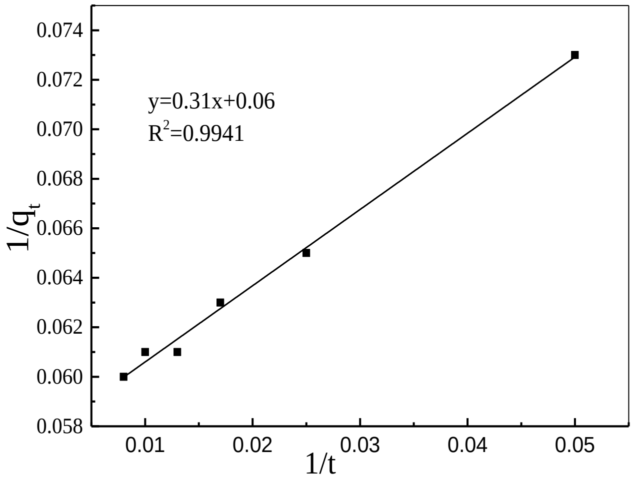


Fig. 8. Pseudo-first order kinetics curve

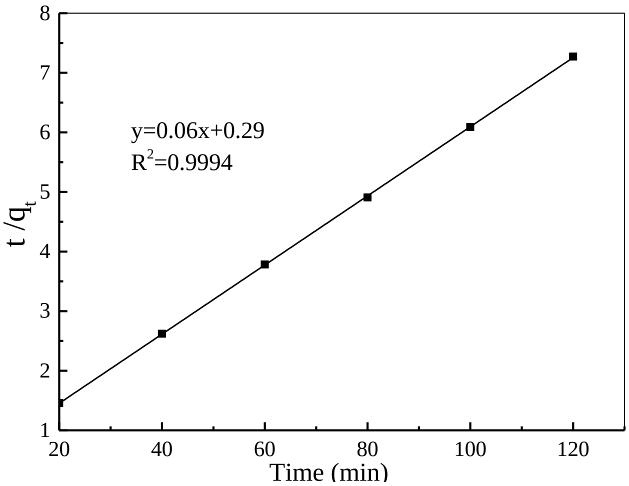


Fig. 9. Pseudo-second order kinetics curve

The linear correlation coefficients are shown in Table 2. The adsorption of the modified eucalyptus bark to Cr (VI) was well described by the pseudo first order adsorption kinetics and the pseudo second order adsorption kinetics. Thus, the adsorption process of modified eucalyptus bark to Cr (VI) could not be definitively assigned to one or the other rate model.

Table 2. Fitting Results of the Kinetics Curves

Kinetics	Equation	Parameters
Pseudo-first order	$1/q_t=0.31/t+0.58$	$q_e=17.39$, $k_1=5.36$, $R^2=0.9941$
Pseudo-second order	$t/q_t=0.06t+0.29$	$q_e=17.24$, $k_2=0.01$, $R^2=0.9994$

Adsorption Thermodynamics

The thermodynamics of the adsorption of Cr(VI) by modified eucalyptus bark was studied under different temperatures. The results are shown in Table 3. The feasibility and nature of the adsorption process were evaluated by the standard Gibbs free energy (ΔG^0), enthalpy (ΔH^0), and entropy change (ΔS^0). The calculation ΔG^0 is shown in Eq. 4. The values of ΔH^0 and ΔS^0 were obtained as the slope and intercept in Fig. 10.

$$\Delta G^0 = -RT\ln K_c \tag{4}$$

$$K_c = q_e/C_e \tag{5}$$

$$\ln K_c = -\Delta H^0/RT + \Delta S^0/R \tag{6}$$

Table 3. Results of Adsorption Thermodynamic Experiment

	30 °C	40 °C	50 °C	60 °C	70 °C
C_e (mg.L^{-1})	0.25	0.21	0.16	0.14	0.12
q_e (mg.g^{-1})	16.58	16.60	16.61	16.62	16.63
ΔG^0 (Kj.mol^{-1})	-10.57	-11.34	-12.50	-13.23	-14.04
ΔH^0 (KJ.mol^{-1})	16.25				
ΔS^0 (J.mol^{-1}.k^{-1})	88.51				

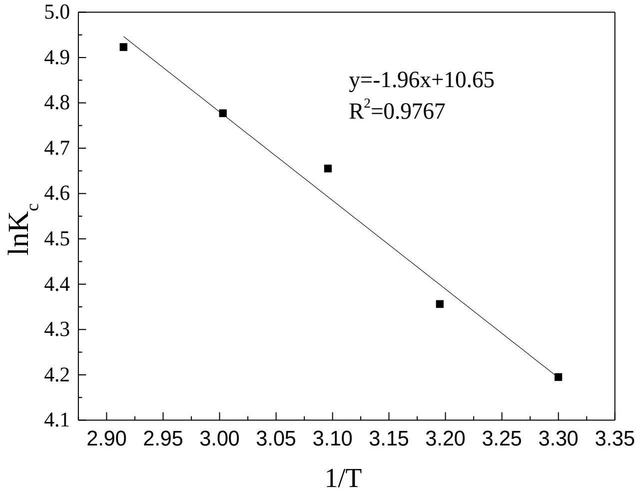


Fig. 10. Linear relationship between ln(K_c) and 1/T

CONCLUSIONS

1. The effect of modifying eucalyptus bark with phenol-formaldehyde (PF) treatment on the adsorption of Cr(VI) was positive, and the dissolution of the colored material was effectively inhibited by PF modification. The adsorption capacity of the modified eucalyptus bark was increased as the surface area and the content of active groups was increased. The optimum conditions were as follows: 50 mg.L^{-1} initial Cr(VI) concentration, pH 2.0, 3 g.L^{-1} adsorbent dosage, temperature 50 °C, and time 120 min. The optimal adsorption capacity was 16.50 mg.g^{-1}.

2. Adsorption kinetics studies revealed that the adsorption process of modified eucalyptus bark to Cr(VI) was not distinguishable between pseudo-first-order and pseudo-second-order, which is consistent with a multi-factor control process. Thermodynamics showed that the adsorption was spontaneous and entropy increasing endothermic process.

ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China (31760192) as well as the Guangxi Natural Science Foundation of China (2016GXNSFBA380234). This project was sponsored by the National Natural Science Foundation of China (21466004) and the research funds of The Guangxi Key Laboratory of Clean Pulp & Papermaking and Pollution Control. The authors thank the Project for Graduate Study Overseas of Guangxi University for research assistance.

REFERENCES CITED

Aharchaou, I., Rosabal, M., Liu, F., Battaglia, E., Vignati, D. A. L., and Fortin, C. (2016). "Bioaccumulation and subcellular partitioning of Cr(III) and Cr(VI) in the freshwater green alga *Chlamydomonas reinhardtii*," *Aquatic Toxicology* 182, 49. DOI: 10.1016/j.aquatox.2016.11.004

Ahmadi, M. A., and Shadizadeh, S. R. (2015). "Experimental investigation of a natural surfactant adsorption on shale-sandstone reservoir rocks: Static and dynamic conditions," *Fuel* 159, 15-26. DOI: 10.1016/j.fuel.2015.06.035

Ali, I. H., and Alrafai, H. A. (2016). "Kinetic, isotherm and thermodynamic studies on biosorption of chromium(VI) by using activated carbon from leaves of *Ficus nitida*," *Chemistry Central Journal* 10, 1-7. DOI: 10.1186/s13065-016-0180-1

Arulkumar, M., Thirumalai, K., Sathishkumar, P., and Palvannan, T. (2012). "Rapid removal of chromium from aqueous solution using novel prawn shell activated carbon," *Chemical Engineering Journal* 185–186, 178-186. DOI: 10.1016/j.cej.2012.01.071

Calvini, P., Conio, G., Lorenzoni, M., and Pedemonte, E. (2004). "Viscometric determination of dialdehyde content in periodate oxycellulose. Part I. Methodology," *Cellulose* 11, 99-107. DOI: 10.1023/b:cell.0000014766.31671.8d

Doke, K. M., and Khan, E. M. (2017). "Equilibrium, kinetic and diffusion mechanism of Cr(VI) adsorption onto activated carbon derived from wood apple shell," *Arabian Journal of Chemistry* 10, S252-S260. DOI: 10.1016/j.arabjc.2012.07.031

Elangovan, R., Philip, L., and Chandraraj, K. (2008). "Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies," *Journal of Hazardous Materials* 152(1), 100-112. DOI: 10.1016/j.jhazmat.2007.06.067

Engler, B., Becker, G., and Hoffmann, S. (2016). "Process mechanization models for improved *Eucalyptus* plantation management in Southern China based on the analysis of currently applied semi-mechanized harvesting operations," *Biomass & Bioenergy* 87, 96-106. DOI: 10.1016/j.biombioe.2016.02.021

Fakhriyan, G., Mousavi, H., and Sajjadi, S. M. (2016). "Speciation and determination of Cr (III) and Cr (VI) by directly suspended droplet microextraction coupled with flame atomic absorption spectrometry: An application of central composite design strategy as experimental design tool," *Analytical Methods* 8(25), 5070-5078. DOI: 10.1039/c6ay00566g

Gao, P., Zhou, Y., Meng, F., Zhang, Y., Liu, Z., Zhang, W., and Xue, G. (2016). "Preparation and characterization of hydrochar from waste eucalyptus bark by hydrothermal carbonization," *Energy* 97, 238-245. DOI: 10.1016/j.energy.2015.12.123

Garg, U. K., Kaur, M. P., Garg, V. K., and Sud, D. (2007). "Removal of hexavalent chromium from aqueous solution by agricultural waste biomass," *Journal of Hazardous Materials.* 140, 60-68. DOI: 10.1016/j.jhazmat.2006.06.056

Giri, A. K., Patel, R., and Mandal, S. (2012). "Removal of Cr (VI) from aqueous solution by *Eichhornia crassipes* root biomass-derived activated carbon," *Chemical Engineering Journal* 185–186, 71-81. DOI: 10.1016/j.cej.2012.01.025

Goel, J., Kadirvelu, K., Rajagopal, C., Garg, V. K. (2005). "Removal of lead(II) by adsorption using treated granular activated carbon: batch and column studies," *Journal of Hazardous Materials* 125 (1–3) :211-220. DOI: 10.1016/j.jhazmat.2005.05.032

González, D., Santos, V., and Parajó, J. C. (2011). "Manufacture of fibrous reinforcements for biocomposites and hemicellulosic oligomers from bamboo," *Chemical Engineering Journal* 167, 278-287. DOI: 10.1016/j.cej.2010.12.066

Gupta, V. K., Rastogi, A., Nayak, A. (2010). "Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material," *Journal Of Colloid And Interface Science* 342 (1) :135-141. DOI: 10.1016/j.jcis.2009.09.065

Harrington, T. C., Huang, Q., Ferreira, M. A., and Alfenas, A. C. (2015). "Genetic analyses trace the Yunnan, China population of *Ceratocystis fimbriata* on pomegranate and taro to populations on eucalyptus in Brazil," *Plant Disease* 99, 106-111. DOI: 10.1094/PDIS-01-14-0056-RE

Houton, E., Comar, B. P., Pitak, C. M. B., Coles, E. S. J., Ryder, E. A. G., Piligkos, S., Brechinc, D. E. K., and Jones, L. F. (2016). "Solvothermal synthesis of discrete cages and extended networks comprising $\{Cr(III)_3O(O_2CR)_3(oxime)_3\}^{2-}$ ($R = H, CH_3, C(CH_3)_3, C_{14}H_9$) building blocks," *RSC Advances* 6(77), 73668-73676. DOI: 10.1039/c6ra14811.

Iqbal, M., Saeed, A., and Zafar, S. I. (2009). "FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste," *Journal of Hazardous Materials* 164, 161-171. DOI: 10.1016/j.jhazmat.2008.07.141

Johnson, D. B., Hedrich, S., and Pakostova, E. (2017). "Indirect redox transformations of iron, copper, and chromium catalyzed by extremely acidophilic bacteria," *Frontiers in Microbiology* 8, 211. DOI: 10.3389/fmicb.2017.00211

Jorge, M., Christian Schumacher, A., and Seaton, N. A. (2016). "Simulation study of the effect of the chemical heterogeneity of activated carbon on water adsorption," *Langmuir* 18, 9296-9306. DOI: 10.1021/la025846q

Khan, T., Isa, M. H., Mustafa, M. R. U., Yeekchia, H., Baloo, L., Manan, T. S. B. A., and Saeed, M. O. (2016). "Cr(VI) adsorption from aqueous solution by an agricultural waste based carbon," *RSC Advances* 6, 56365-56374. DOI: 10.1039/c6ra05618k

Khraisheh, M. A. M., Al-Degs, Y. S., Allen, S. J., and Ahmad, M. N. (2016). "Elucidation of controlling steps of reactive dye adsorption on activated carbon," *Industrial & Engineering Chemistry Research* 41, 1651-1657. DOI: 10.1021/ie000942c

Lee, C. G., Lee, S., Park, J. A., Park, C., Lee, S. J., Kim, S. B., An, B., Yun, S. T., Lee, S. H., and Choi, J. W. (2017). "Removal of copper, nickel and chromium mixtures from metal plating wastewater by adsorption with modified carbon foam," *Chemosphere* 166, 203. DOI: 10.1016/j.chemosphere.2016.09.093

Liu, C. F., Sun, R. C., Zhang, A. P., and Ren, J. L. (2007). "Preparation of sugarcane bagasse cellulosic phthalate using an ionic liquid as reaction medium," *Carbohydrate Polymers* 68, 17-25. DOI: 10.1016/j.carbpol.2006.07.002

Maneerung, T., Liew, J., Dai, Y., Kawi, S., Chong, C., and Wang, C. H. (2016). "Activated carbon derived from carbon residue from biomass gasification and its application for dye adsorption: Kinetics, isotherms and thermodynamic studies," *Bioresource Technology* 200: 350. DOI: 10.1016/j.biortech.2015.10.047

Mittal, S., Vaid, U., Najar, G. N., and Babu, J. N. (2015). "Removal of hexavalent chromium from aqueous solution: A comparative study of cone biomass of "*Picea smithiana*" and activated charcoal," *Desalination & Water Treatment*. 2015. DOI: 10.1080/19443994.2015.1038594

Mohan, D., Singh, K. P., and Singh, V. K. (2005). "Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth," *Industrial & Engineering Chemistry Research* 44: 1027-1042. DOI: 10.1021/ie0400898

Mohanty, K., Jha, M., Meikap, B. C., and Biswas, M. N. (2006). "Biosorption of Cr(VI) from aqueous solutions by *Eichhornia crassipes*," *Chemical Engineering Journal* 117(1), 71-77. DOI: 10.1016/j.cej.2005.11.018

Murphy, V., Tofail, S. A. M., Hughes, H., and Mcloughlin, P. (2009). "A novel study of hexavalent chromium detoxification by selected seaweed species using SEM-EDX and XPS analysis," *Chemical Engineering Journal* 148(2–3), 425-433. DOI: 10.1016/j.cej.2008.09.029

Park, D., Lim, S. R., Yun, Y. S., and Park, J. M. (2007a). "Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-coupled reduction," *Chemosphere* 70, 298-305. DOI: 10.1016/j.chemosphere.2007.06.007

Park, D., Yun, Y. S., Ji, Y. K., and Park, J. M. (2008). "How to study Cr(VI) biosorption: Use of fermentation waste for detoxifying Cr(VI) in aqueous solution," *Chemical Engineering Journal* 136(2), 173-179. DOI: 10.1016/j.cej.2007.03.039

Park, D., Yun, Y. S., Jo, J. H., and Park, J. M. (2005a). "Effects of ionic strength, background electrolytes, heavy metals, and redox-active species on the reduction of hexavalent chromium by *Ecklonia* biomass," *Journal of Microbiology & Biotechnology* 15(4), 780-786.

Park, D., Yun, Y. S., and Park, J. M. (2005b). "Use of dead fungal biomass for the detoxification of hexavalent chromium: Screening and kinetics," *Process Biochemistry* 40(7), 2559-2565. DOI: 10.1016/j.procbio.2004.12.002

Park, D., Yun, Y.-S., and Park, J. M. (2007b). "Reduction of hexavalent chromium with the brown seaweed *Ecklonia* biomass," *Chemosphere* 66(5), 939. DOI: 10.1016/j.chemosphere.2006.05.068

Qiu, B., Xu, C., Sun, D., Wang, Q., Gu, H., Zhang, X., Weeks, B. L., Hopper, J., Ho, T. C., and Guo, Z. (2015). "Polyaniline coating with various substrates for hexavalent chromium removal," *Applied Surface Science* 334, 7-14. DOI: 10.1016/j.apsusc.2014.07.039

Rieke, R. D. (2017). "Chromium," in: *Chemical Synthesis using Highly Reactive Metals*, John Wiley & Sons, Inc., pp. 443-446. DOI: 10.1002/9781118929124.ch16

Saito, T., Hirota, M., Tamura, N., Kimura, S., Fukuzumi, H., Heux, L., and Isogai, A., (2009). "Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions," *Biomacromolecules* 10, 1992-1996. DOI: 10.1021/bm900414t

Sarin, V., and Pant, K. K. (2006). "Removal of chromium from industrial waste by using eucalyptus bark," *Bioresource Technology* 97, 15-20. DOI: 10.1016/j.biortech.2005.02.010

Shafeeyan, M. S., Wan, M. A. W. D., Shamiri, A., and Aghamohammadi, N. (2015). "Adsorption equilibrium of carbon dioxide on ammonia-modified activated carbon," *Chemical Engineering Research & Design* 104, 42-52. DOI: 10.1016/j.cherd.2015.07.018

Sun, S. L., Wen, J. L., Ma, M. G., and Sun, R. C. (2013). "Successive alkali extraction and structural characterization of hemicelluloses from sweet sorghum stem," *Carbohydrate Polymers.* 92, 2224-2231. DOI: 10.1016/j.carbpol.2012.11.098

Yang, Z. H., Wang, B., Chai, L. Y., Wang, Y. Y., Wang, H. Y., and Su, C. Q. (2009). "Removal of Cr(III) and Cr(VI) from aqueous solution by adsorption on sugarcane pulp residue," *Journal of Central South University*. 16, 101-107. DOI: 10.1007/s11771-009-0017-3

Yang, Y., Sun, Y., Liao, S., Wu, Z., and Yu, R. (2016). "Bimetallic gold-silver nanoclusters fluorescent probes for Cr(III) and Cr(VI)," *Analytical Methods* 8(39), 7237-7241. DOI: 10.1039/c6ay02270g

Yan, P., Xu, Z., Zhang, C., Liu, X., Xu, W., and Zhang, Z. C. (2015). "Fractionation of lignin from eucalyptus bark using amine-sulfonate functionalized ionic liquids," *Green Chemistry* 17, 4913-4920. DOI: 10.1039/c5gc01035g

Yao, S., Nie, S., Yuan, Y., Wang, S., and Qin, C. (2015). "Efficient extraction of bagasse hemicelluloses and characterization of solid remainder," *Bioresource Technology* 185, 21-27. DOI: 10.1016/j.biortech.2015.02.052

Yu, D., Chen, M., Wei, Y., Niu, S., and Xue F. (2016). "An assessment on co-combustion characteristics of Chinese lignite and eucalyptus bark with TG–MS technique," *Powder Technology* 294, 463-471. DOI: 10.1016/j.powtec.2016.03.016

Yuan, T.-Q., Xu, F., He, J., and Sun, R.-C. (2010). "Structural and physico-chemical characterization of hemicelluloses from ultrasound-assisted extractions of partially delignified fast-growing poplar wood through organic solvent and alkaline solutions," *Biotechnology Advances* 28, 583-593. DOI: 10.1016/j.biotechadv.2010.05.016

Zhang, J., Gu, C., Tong, Y., Gou, J., Wang, X., and Tu, J. (2015a). "Microstructure and corrosion behavior of Cr and Cr–P alloy coatings electrodeposited from a Cr(III) deep eutectic solvent," *RSC Advances* 5, 71268-71277. DOI: 10.1039/c5ra13056e

Zhang, K., Zheng, H., Chen, F. L., Ouyang, Z. Y., Wang, Y., Wu, Y. F., Lan, J., Fu, M., and Xiang, X. W. (2015b). "Changes in soil quality after converting *Pinus* to *Eucalyptus* plantations in southern China," *Solid Earth* 6, 115-123. DOI: 10.5194/se-6-115-2015

Article submitted: June 14, 2017; Peer review completed: August 12, 2017; Revised version received: September 6, 2017; Accepted: September 7, 2017; Published: October 11, 2017.
DOI: 10.15376/biores.12.4.8986-9000