

Cu(II) Ion Adsorption onto Hydroxymethylated Lignin-Chitosan Crosslinked Membrane

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A crosslinked chitosan membrane (I) and a hydroxymethylated lignin-chitosan crosslinked membrane (II) were prepared using glutaraldehyde as the crosslinking agent. Fourier transform infrared spectroscopy (FTIR) was used to identify the chemical structures of the crosslinked membranes and the presence of an absorption peak at 1515 cm⁻¹ indicated the presence of lignin. Scanning electron microscope (SEM) images revealed that membrane (I) possessed a smooth surface, while membrane (II) exhibited a homogeneous embossed surface without any agglomeration. The Cu(II) ion adsorption properties of both membranes were analyzed. The results indicated that the static adsorption capacities of membranes (I) and (II) were 195 µg Cu(II)/cm² and 275 µg Cu(II)/cm², respectively, and their dynamic chelation capacities were 2.89 µg Cu(II)/cm² and 4.59 µg Cu(II)/cm², respectively. Membrane (I) was suitable only for use in aqueous solutions with pH values of 3.5 to 9.0, while membrane (II) maintained its shape even in concentrated hydrochloric acid or 1 M NaOH solution. The Cu(II) ion absorption properties and resistance to acid and alkali of membrane (II) were superior to those of membrane (I), indicating that hydroxymethylation of the lignin-chitosan crosslinked membrane is worthy of further investigation.

Keywords: *Hydroxymethylated lignin; Chitosan; Crosslinked membrane; Adsorption properties*

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INTRODUCTION

Lignin is the second most abundant organic polymer in nature (second only to cellulose). There are about 20 billion tons of lignin on earth (Buranov and Mazza 2008), but its utilization is very limited (Pouteau *et al.* 2003). Lignin is an amorphous, highly branched polyphenolic macromolecular compound with three types of phenyl propyl units, of which a large number are syringyl phenylpropane units and a substantial amount of guaiacyl phenylpropane units (Sjöström 1993; Doherty *et al.* 2011). Although ubiquitous, the chemical reactivity and compatibility of lignin with other materials is low. Zhang *et al.* (2005) incorporated lignosulfonate into a polysulfone network in which the sulfonic acid groups of lignosulfonate acted as a proton transport medium. Nevárez *et al.* (2011) prepared nanocomposite membranes by a vapor-induced phase separation method from lignin and cellulose triacetate. In order to improve the lignin compatibility, it was initially propionated. It has been reported that hydroxymethylation of lignin can increase the hydroxyl group content and activate the resulting reaction groups (Benar *et al.* 1999; Goncalves and Benar 2001). A suitable reagent is then used to modify the structure for practical applications.

Chitosan is a natural polysaccharide. It exhibits good biocompatibility, biodegradability, and film-forming properties, as well as some antibacterial and anticoagulant properties (Hirano 1996; Mi *et al.* 2003; Alonso *et al.* 2009). Chitosan and its modified products are widely used in pharmaceuticals, cosmetics, agriculture, biological and chemical separation systems, tissue engineering, biomaterials, and drug controlled release systems (Kaushik *et al.* 2004). Chitosan-based materials have been extensively studied as reported in the literature for the decontamination of metals from effluents owing to the abundance of amino groups in the structure. A variety of chemical modifications have been applied to enhance the adsorption features of chitosan (Kyzas *et al.* 2013). The *N*-acetylglucosamine unit in chitosan facilitates its linear polymer conformation, and the amino and hydroxyl groups in this structure allow the chitosan macromolecular chains to form hydrogen bonds with one another, which produces good film-forming properties. The resulting chitosan film is valuable for a number of reasons including: non-toxicity, strong hydrophilicity, and good transparency (Musale *et al.* 1999; Ghaffari *et al.* 2007; Wang *et al.* 2012). However, there are some drawbacks for practical applications such as: poor mechanical properties, brittleness, poor water resistance, and low acid resistance. To overcome these limitations the chitosan membrane is often crosslinked with other polymers (Lin *et al.* 2012). Although many applications have been reported, there are limited accounts regarding the use of chitosan membranes for metal ion adsorption and water treatment. To our knowledge, there is no published scientific literature on lignin-chitosan crosslinked membranes.

Therefore, this paper describes an investigation to examine the addition of hydroxymethylated lignin to chitosan using a chemical method to synthesize a hydroxymethylated lignin-chitosan crosslinked membrane, to mitigate some of the performance deficiencies of chitosan-based membranes. The optimized membranes were identified by the characterization of the membrane's thickness and the degree of swelling, as well as its ability to statically and dynamically absorb Cu(II) ions through chelation. Success in this work will not only make use of a voluminous waste product of the paper-making industry, but it will also reduce environmental pollution and alleviate resource waste while reducing the cost of chitosan membrane production. Therefore, preparing a functional membrane that can adsorb metal ions is worthy of extensive research.

EXPERIMENTAL

Reagents

Hydroxymethylated lignin was produced by the method of Çetin and Özman (2003) as follows. The hydroxymethylated lignin was dissolved into an 80% *p*-dioxane/20% water (v/v) solution to form a 3% (w/w) hydroxymethylated lignin solution. The chitosan solution was produced as follows. The chitosan was dissolved with a 2% acetic acid solution to make a 3% (w/w) chitosan solution. Glutaraldehyde, *p*-dioxane, and acetic acid were all of analytical grade; distilled water was also used.

Preparation of Chitosan-crosslinked Membrane (I)

Glutaraldehyde (1.5 mL of a 1% solution) was added to 30 mL of a previously prepared chitosan solution. The mixture was stirred at 30 °C for 6 h and vacuum-defoamed for 2 h to prepare the membrane liquid. The membrane liquid was then poured onto 12 cm x 18 cm aluminum foil and oven-dried at 50 °C for 3 h. During this process

the crosslinking reaction between glutaraldehyde and chitosan occurred. Finally, the crosslinked chitosan membranes were peeled off from the aluminum foil.

Preparation of Hydroxymethylated Lignin-Chitosan-crosslinked Membrane (II)

Hydroxymethylated lignin and chitosan were mixed with a mass ratio of 1:2. Then glutaraldehyde solution (at a concentration of 1%) composing 0.3% of the total mass was added as the crosslinking agent. Glycerol (0.5% of total mass) was then added. In order to get membranes in the same thickness, a similar amount of the mixture with that of membrane (I) was stirred at 25 °C for 6 h and vacuum-defoamed for 2 h to prepare the membrane liquid. As before, the liquid was then poured onto 12 cm x 18 cm aluminum foil and oven-dried at 50 °C for 3 h. During this process, the crosslinking reaction between hydroxymethylated lignin and chitosan occurred. Finally, the crosslinked membranes were peeled from the aluminum foil for use.

Characterization

A Magna-560 Fourier transform infrared spectrophotometer was used for the structural analysis of the membrane. The membrane's surface morphology was characterized using a Quanta 200 scanning electron microscope. A ZLD-300 electronic tensile testing machine was used to measure the tension stress of the crosslinked membrane; the test sample was a 10 cm × 1.5 cm rectangular membrane. A ZUS-4 paper thickness tester was used to measure membrane thickness. Membrane thickness was calculated from the average of 9 fixed points on the square membrane with the aluminum foil support. The thickness of the aluminum foil support was deducted from the total thickness to obtain the membrane's thickness. A TAS-990 atomic absorption spectrophotometer was used to analyze the membrane's absorption of metal ions. The membrane's water swelling properties were determined according to the following procedure. Several 3 cm × 3 cm samples of membrane (I) or (II) were cut and weighed accurately. After being immersed in a pH 7 buffer solution for 24 h, the membrane samples were removed, wiped with filter paper to remove the solution on the surfaces and weighed accurately. The water swelling properties were calculated based on the difference of mass before and after water adsorption.

Cu(II) Absorption Performance of Crosslinked Membranes

Standardization curve for copper ion concentration measured by atomic absorption spectroscopy

Cu(II) ion standard solutions of 1, 2, 3, 4, and 5 µg/mL were prepared using anhydrous cupric sulfate, and a flame atomic absorption spectrophotometer (AAS) was employed to measure the absorbance values of the standard solutions at 247.6 nm. The Cu(II) standard curve was prepared based on the solution concentrations and their absorbance values.

Static absorption capacity of crosslinked membranes for Cu(II) ions

Membrane specimens of 2 cm x 2 cm were cut and immersed in 250 mL of a 100 µg/mL copper sulfate solution. On every other day a 5 mL aliquot of this stock solution was accurately transferred to a 100-mL volumetric flask, which was then diluted to volume using distilled water. The concentration of Cu(II) ions in the volumetric flask was measured using AAS. When the tested copper concentrations approached a constant

value, this indicated that the static absorption of copper ions by the membrane had reached saturation. The static absorption capacity was calculated with the constant copper concentrations.

Dynamic filtration and Cu(II) ion chelation performance of the crosslinked membranes

A dynamic filtration and chelating performance measuring device was prepared according to Musale *et al.* (1999). The dynamic filtration and Cu(II) ion chelation performance of the crosslinked membranes was determined using 250 mL of a 20 µg/mL copper sulfate solution under constant vacuum (absolute pressure of 0.01 to 0.015 MPa). The filtrate was collected at a speed of about 0.2 L/h; and 5 mL of every 50 mL filtrate was accurately transferred to a 25 mL volumetric flask and distilled water was used to adjust to a constant volume. The concentration of Cu(II) ions of each volumetric flask was also measured with AAS at 247.6 nm. According to the standard curve for copper ion concentration, the concentrations of Cu(II) ions in the filtrate and dynamic cumulative chelating capacity of per square centimeter membrane for Cu(II) ions were calculated (the actual membrane area in the ultrafiltration cup was 38.47 cm²).

Resistance of Crosslinked Membranes to Acid or Alkali Aqueous Solutions

Acid or alkali buffers with different pH values of 0.1, 0.28, 0.74, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.6, 11.0, 11.6, 12.0, 12.6, 13.0, and 14.0 were prepared using hydrochloric acid, potassium chloride, potassium biphthalate, sodium hydroxide, potassium dihydrogen phosphate, boric acid, aminoacetic acid, and sodium chloride in various dosages.

Samples of membranes (I) and (II) were separately immersed in these buffers for 10 min, then removed and dried with filter paper. Following this, the samples were closely examined using a Novel biological microscope at 10X to inspect the membrane edges and internal variations to determine their relative acid and alkali resistance.

RESULTS AND DISCUSSION

Thickness of the Crosslinked Membranes

Following drying, both membranes (I) and (II) exhibited smooth, delicate and shiny surfaces. Due to the addition of glycerol, membrane (II) seemed slightly wet. Exhibiting good ductility, it could be bent without fracturing. In addition, it could be stretched, and its tensile strength was in the range of 27 to 28 N. Membrane (I) had a thickness of 12 to 13 µm; membrane (II) thicknesses are shown in Table 1. The analysis shows that the membrane (II) had an average thickness of 12 to 14 µm, similar to the membrane (I). Both types of membranes were thin and homogeneous in thickness.

Table 1. Thickness of Membrane (II)

No.	Average thickness /µm	Standard deviation /µm
1	13.6	0.49
2	13.0	0.12
3	12.5	0.76

Note: Values were obtained from 9 replicates.

FTIR Analysis

Figure 1 presents the FTIR spectra of two crosslinked membranes. These spectra show absorption peaks at 3400 cm^{-1} , which can be attributed to amino (-NH) and hydroxyl (-OH) stretching vibrations, for both membranes. The peaks around 2850 cm^{-1} and 2900 cm^{-1} can be attributed to methyl (-CH₃) and methylene (-CH₂) stretching vibrations. The spectra exhibit absorption peaks at 1650 cm^{-1} due to the carbonyl group (-C=O) stretching vibration.

Normally, the aldehyde group absorption peak is at $\sim 1710\text{ cm}^{-1}$, but this absorbance was absent in both of the two spectra. This implies that the glutaraldehyde had been successfully crosslinked with chitosan or hydroxymethylated lignin. The peak at $\sim 1590\text{ cm}^{-1}$ is attributed to amino (-NH) deformation vibration, whereas the 1090-cm^{-1} peak is ascribed to C-O-C stretching vibration. Membrane (II) had an absorption peak around 1515 cm^{-1} , which can be attributed to aromatic ring (-C=C) stretching vibration, thus indicating the presence of the hydroxymethylated lignin.

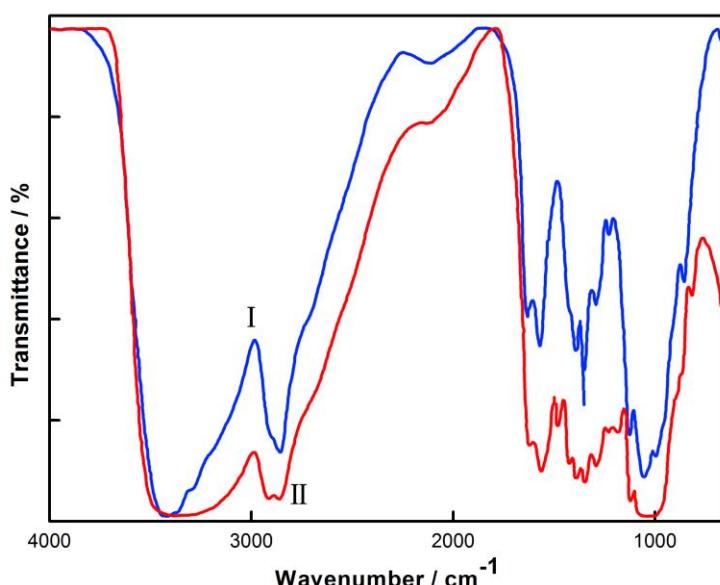


Fig. 1. FTIR spectra of crosslinked membranes (I) and (II)

SEM Analysis of Crosslinked Membranes

Figure 2 shows scanning electron micrographs of the crosslinked membranes. Membrane (II) had a rough microscopic surface, exhibiting homogeneous embossments that may be due to the hydroxymethylated lignin's three-dimensional net-like structure. Because the hydroxymethylated lignin had been grafted onto the chitosan chains, many convexities were apparent at the membrane surface.

The scanning electron microscope photographs, film thickness, and FTIR analysis comparison between the two membranes added further evidence that the crosslinking reaction between hydroxymethyl lignin and chitosan occurred and that a crosslinked membrane resulted.

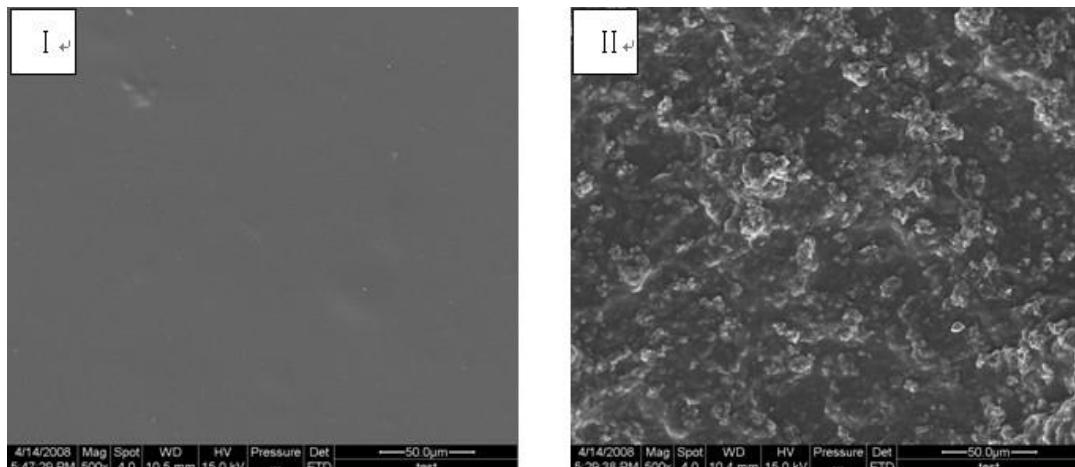


Fig. 2. SEM images of crosslinked membranes (I) and (II)

Water Uptake of Hydroxymethylated Lignin-Chitosan Crosslinked Membrane

The hydroxymethylated lignin-chitosan crosslinked membrane contained both hydroxyl and amino groups. These functional groups can form hydrogen bonds with water molecules, leading to water absorption and membrane swelling. Masses before and after water absorption in a buffer solutions were accurately recorded and the ratio of the mass difference to the mass before water absorption was calculated as the water absorbing swelling ratio (Table 2). The average water absorbing swelling ratio of the membrane (II) was 28.4%, and the neat edges the smooth and delicate surfaces remained throughout the water absorption process.

Table 2. Water Uptake of Crosslinked Membrane (II)

Sample name	Mass before water absorption mg/m ²	Mass after water absorption mg/m ²	Water absorbing swelling ratio %
Hydroxymethylated lignin-chitosan crosslinked membrane	58.7(1.4)	75.4(2.3)	28.4(0.8)

Note: Values represent averages of 3 replicates while numbers in the parentheses are one standard deviation.

Static Cu(II) Ion Absorption Capacity of Crosslinked Membranes

The Cu(II) ion standardization concentration curve was obtained, and the standard curve equation is $[\text{Absorbance}] = 0.1847[\text{Concentration}] + 0.0495$, with a coefficient of determination R^2 of 0.9984. Analysis showed that membranes (II) and (I) had static adsorption capacities of $275 \mu\text{g Cu(II)}/\text{cm}^2$ and $195 \mu\text{g Cu(II)}/\text{cm}^2$, respectively. The capacity of membrane (II), relative to (I), increased by 40.9%.

The dynamic filter chelation capacities of the two membranes for Cu(II) ions are shown in Fig. 3. When the filtrate reached to 250 mL, the dynamic accumulation chelation capacities for Cu(II) ion of membranes (I) and (II) were $2.89 \mu\text{g}/\text{cm}^2$ and $4.5 \mu\text{g}/\text{cm}^2$, respectively. Compared with membrane (I), membrane (II) exhibited a 58.8% larger dynamic chelating capacity. This is probably due to the fact that a large number of amino

and hydroxyl groups, which are functional groups for Cu(II) ion absorption, are being consumed during the process of the crosslinked chitosan membrane preparation using glutaraldehyde as the crosslinker. The introduction of the hydroxymethylated lignin improved dynamic chelation capacity of membrane (II). The network structure of the hydroxymethylated lignin provided the membrane with a coarse surface, which increased the available surface area, allowing for greater absorption of the available Cu(II) ions. Furthermore, the hydroxymethylated lignin possessed carboxylic groups in addition to uncrosslinked hydroxyl groups. Both of these groups possessed unshared electron pairs which could easily chelate copper ions through chemical adsorption (Hao *et al.* 2003). In other words, membrane (II) adsorbed Cu(II) ions via both physical and chemical mechanisms. The Cu(II) ion chelating capacity of membrane (II) per unit area was greater than that of membrane (I), which was a further indication that the introduction of hydroxymethylated lignin by a chemical method improved the membrane's static and dynamic absorption of Cu (II) ions.

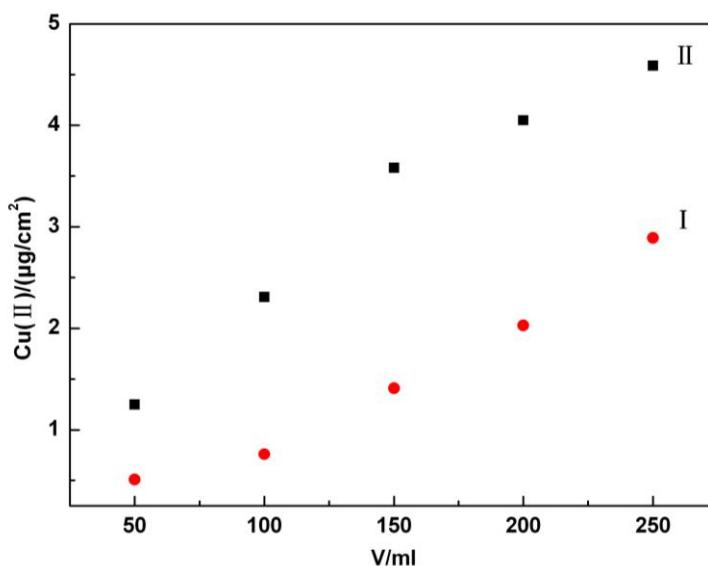


Fig. 3. The dynamic chelating property curves of crosslinked membranes (I) and (II)

Acid or Alkali Resistance of Crosslinked Membranes

Resistance of crosslinked membranes to acid aqueous solutions

Although the crosslinking reaction improved the acid resistance of the membranes, the immersed membrane (I) quickly swelled in the acid buffers with pH values of less than 3.5 and after only 5 min the membrane appeared to be a gluelike aggregation. After immersion for 10 min in the buffers with weaker acidity, membrane (I) samples were curved, but their smooth surface and edges were intact. Hence, a pH value of 3.5 is the lowest for use of membrane (I). Membrane (II) samples exhibited better acid resistance. After immersion for 10 min in the buffers with pH values of 0.1 to 7, the samples swelled slightly (their surface areas enlarged about 1.2 times) but maintained their original shape and edges. All of the swelled samples could be used just as originals. In order to check the resistance of membrane (II) to stronger acidic aqueous solution, the samples were directly immersed in concentrated hydrochloric acid (36-38% w/w). After 10 min, the sample surface area swelled to 1.5 times of its original size. The swelled membrane was very thin, but not fractured even after stirring the solution with a glass rod. This signified

that membrane (II) exhibited strong acid resistance. In comparison to membrane (I), the introduction of hydroxymethylated lignin markedly improved the acid resistance of the chitosan membranes, which is beneficial for expanding the applications of these membranes.

Resistance of crosslinked membranes to alkali aqueous solutions

Chitosan membranes offer weak resistance to alkali aqueous solutions. Membrane (I) swelled slightly following immersion in the buffers with pH values of less than 9.0, but its smooth surface and edges were intact. When the membrane samples were immersed in the buffers with pH values of 9.5 to 13, the samples were quickly swelled. After only 5 min, their surface areas were 1.5 times greater than the original values. These swelled membrane samples were broken and were of no further use. Hence, membrane (I) has a working the pH range of less than 9.0.

Membrane (II) samples presented far better alkali resistance than membrane (I). After immersion in the buffers with pH values of less than 9.0, the membrane samples were slightly swelled and their smooth surfaces and edges were intact. Even after immersion for 24 h, the original shape of samples was not changed. Their strength was largely intact. When the membrane samples were immersed in the buffers with pH values of 9.0 or 9.5, the solutions became slightly yellow, indicating that some of the lignin had dissolved into the alkali solution. As the buffer pH value increased, the yellowing of the aqueous solutions increased. When the membrane samples were immersed in buffers with pH values of 10 to 13 for 24 hrs, the samples were slightly swelled, very thin but not fractured. Their surface areas increased to 1.2 times the original values. When a pH 14 aqueous (1 M NaOH) was used for immersion of the membrane, they still retained their shapes and most of their strength, due to the better alkali resistance of hydroxymethylated lignin.

CONCLUSIONS

1. Hydroxymethylated lignin was used to modify a chitosan membrane. FTIR analysis demonstrated the successful preparation of the crosslinked membranes. SEM images revealed that a chitosan membrane (I) possessed a smooth surface, while membrane (II), prepared from chitosan and hydroxymethylated lignin, exhibited a homogeneous embossed surface, but no any agglomeration.
2. The static adsorption capacities of Cu (II) ions by these two membranes were 195.25 $\mu\text{g}/\text{cm}^2$ and 275.15 $\mu\text{g}/\text{cm}^2$ and for membranes (I) and (II), respectively. The capacity of membrane (II), relative to (I), increased by 40.92%. The dynamic chelation capacities of the two membranes were 2.89 $\mu\text{g}/\text{cm}^2$ for (I) and 4.59 $\mu\text{g}/\text{cm}^2$ for (II). The capacity of membrane (II), relative to (I), increased by 58.82%.
3. Membrane (I) was only suitable to be used in aqueous with pH values of 3.5-9.0, while membrane (II) could keep shape even in concentrated hydrochloric acid or 1 M NaOH solution. Thus, the crosslinking with hydroxylmethylated lignin is very helpful to widen the application of chitosan membranes.

ACKNOWLEDGMENTS

The authors are grateful for the support of the State Forestry Industry Public Welfare projects (NO. 20120480306) and the “Twelfth five” National Science and Technology Program (NO. 2012BAD24B04). We also acknowledge the project of the Science and Technology Agency of Jilin province (NO. 20080705).

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Article submitted: September 24, 2013; Peer review completed: February 7, 2014;
Revised version received: June 12, 2014; Accepted: June 14, 2014; Published: July 8, 2014.