ARSENATE BIOSORPTION BY IRON-MODIFIED PINE SAWDUST IN BATCH SYSTEMS: KINETICS AND EQUILIBRIUM STUDIES

María Aranzazú López Leal,[a] Raúl Cortés Martínez,[b,]* Ruth Alfaro Cuevas Villanueva,[a]
Héctor Eduardo Martínez Flores,[b] and Consuelo de Jesús Cortés Penagos [b]

The biosorption of As(V) from aqueous solutions by pine sawdust chemically modified with iron in batch systems was investigated. The loading process of Fe in this biomaterial was achieved by hydrolysis of two different ferric salts. This modification of sawdust is an attempt to improve As(V) biosorption for practical applications. The kinetics and maximum biosorption capacities of the unmodified and modified pine sawdust were evaluated. It was found that the pseudo-second order model described the As(V) biosorption kinetic data and the Langmuir-Freundlich equation described the arsenate sorption equilibrium. These results indicated that the sorption mechanism was chemisorption on a heterogeneous material. The pH effects governing biosorption capacities were also evaluated, showing a decrease as pH value rises, indicating that this biosorption process is highly pH-dependent. The estimated maximum biosorption capacities of As(V), based on the Langmuir-Freundlich fit to the data were, at pH 4, 4.4 mg/g of untreated sawdust, (UN-SW), 12.85 mg/g of ferric chloride modified sawdust (FeCl-SW), and 6 mg/g of ferric nitrate modified sawdust (FeNit-SW); and at pH 7, 2.6 mg/g of UN-SW, 5.9 mg/g of FeCl-SW, and 4.6 mg/g of FeNit-SW. Sorption capacities of iron-modified pine sawdust were evidently higher than other similar biosorbents previously reported.

Keywords: Arsenate; Biosorption; Sawdust; pH; Kinetics; Isotherms

*Contact information: a: Instituto de Investigaciones Químico Biológicas, Universidad Michoacana de San Nicolás de Hidalgo, Edif. B1. CU, Morelia, Michoacán, México; b: Facultad de Químico Farmacobiología, Universidad Michoacana de San Nicolás de Hidalgo. Tzintzuntzan 173 Col. Matamoros, C.P. 58240, Morelia, Michoacán. México; *Corresponding author: raulcortesmtz@gmail.com*

INTRODUCTION

The arsenic contamination of potable groundwater is a worldwide concern and poses a great threat to human health. The potable water supplied in many countries (including Bangladesh, India, Taiwan, Mongolia, Chile, Mexico, and the United-States) contains dissolved arsenic levels in excess of 10 μg/L, which is the maximum level recommended by the World Health Organization. Long-term exposure to arsenic can cause various cancers in the skin, kidneys, bladder, and lungs, as well as neurological and cardiovascular problems (Dupont et al. 2007).

In aquatic environments, arsenic is found as As(III) or As(V), depending on the oxide-reduction conditions. The arsenic (III) species is the most toxic, although the arsenic (V) species is the most movable (Macedo-Miranda and Olguín 2007). Generally, As(V) predominates in surface water, while As(III) is the main species in groundwater.

However, both forms of arsenic can be found in groundwater due to changes on redox conditions and biological activity (Smedley and Kinniburgh 2002).

There are many techniques used to remove arsenic from aqueous systems, such as coagulation-flocculation, chemical precipitation, reverse osmosis, electrodialysis, ultra-filtration, etc. Some of these methods have disadvantages such as incomplete metal removal, high reagent dosages, high energy requirements, and generation of toxic sludge; these disadvantages are often more difficult to manage (Kumari et al. 2005; Alluri et al. 2007). Among these technologies, adsorption is considered one of the most promising due to its being both economical and easy to set up.

Many studies have reported the possible utilization of conventional adsorbents, such as titanium dioxide (Dutta et al. 2004); modified zeolites (Macedo-Miranda and Olguín 2007; Jiménez-Cedillo et al. 2009) or iron oxides and hydroxides (Raven et al. 1998; Lakshmipathiraj et al. 2006). It has also been reported that removal of As(V) can be achieved by different types of biomass, such as crab shell (Vijayaraghavan et al. 2009), coconut fiber, and sawdust (Igwe et al. 2005). Among the chemically modified adsorbents, the solid phases loaded with iron species are particularly efficient in the removal of arsenite and arsenate ions from contaminated waters (Dupont et al. 2007; Guo and Fuhua 2005; Zhang and Itoh 2005).

As a result, the use of waste materials as adsorbents is of current interest for arsenic removal from aqueous systems, since simple and inexpensive modifications of these materials can enhance their sorption properties, producing highly efficient and relatively low-cost adsorbents. Sorption can play a significant role in improving the applicability of industrial or agricultural by-products in the removal of arsenic using simple and cheap chemical modifications. Therefore, it is important to see whether a lignocellulosic substrate loaded with ferric ions can be used for the removal of arsenic from aqueous effluents. This substrate constitutes a by-product of the wood industry. It has no commercial value, since it is rejected by the industry, and a it has high availability in region where this type of industry is intensively developed. Therefore, the aim of this work was to evaluate the effect of iron modification of pine sawdust in the removal of As(V) from aqueous solutions, as well as to determine the influence of pH on the biosorption process.

EXPERIMENTAL

Biosorbent Preparation

Treated and untreated pine sawdust biosorbents were used in this study for biosorption experiments. Pine sawdust (*Pinus michoacana*) was collected from a local wood mill. It was sieved, and the 0.5 mm grain size fraction was selected to carry out the tests. This fraction was then washed thrice with water to remove dust and water-soluble impurities. The material was treated with 50 mL of 0.5 M HCl at 70 ºC for 30 min and washed several times with distilled water as described elsewhere (Srinivasa-Rao et al. 2007). After acid treatment, the sawdust was dried in an oven at 60 °C for 24 hours and then placed in a desiccator for further treatment. This material was identified as unmodified sawdust (UN-SW), and it was used for biosorption experiments.

Sawdust Modification with Fe

Pine sawdust was modified with iron in order to evaluate its arsenate sorption capacity after this treatment. This modification of the biosorbent was carried out by two different procedures, separately. For the first procedure, 10 g of UN-SW were put in reflux with 250 mL of $FeCl_3$ 0.05 M solution for 3 h. The mixture was allowed to cool and was put in reflux again for another 3 h with fresh solution. Then, the modified sawdust with $FeCl_3$ (FeCl-SW) was filtered and washed with distilled water to eliminate any excess iron and chloride ions from the material; the solution was allowed to dry, and the modified material was stored in a desiccator. This method was carried out according to those reported previously, which describe an increase in arsenic and dyes sorption capacities of different iron modified sorbents (Murugesan et al. 2006; Solache-Ríos et al. 2010). Another procedure for iron modification of sawdust was carried out based on the method proposed by Dupont et al. (2007): 10 g of UN-SW were placed in a flask with 250 mL of 0.05 M $Fe(NO_3)_3$ solution. Aliquots of 1 M NaOH were slowly added into the flask under continuous stirring, until the pH rose to a value of 2.8 to 3.2 for approximately 24 h. The sawdust was filtered, washed, and dried as mentioned before. The iron modified sawdust by this method was identified as (FeNit-SW) and used for biosorption experiments.

Kinetic Experiments

Batch type experiments were performed to determine the kinetics of removal of arsenate with the three types of materials: unmodified sawdust (UN-SW), sawdust modified with $FeCl_3$ (FeCl-SW), and sawdust modified with $Fe(NO_3)_3$. 10 mL aliquots of a 2 mg/L $Na_2HAsO_4.7H_2O$ solution at pH 7 and 0.5 g of each type of sawdust were placed in centrifuge tubes and shaken for different periods at room temperature. Later, the samples were centrifuged and filtered to separate the aqueous phase, which was analyzed for total arsenic by an atomic absorption spectrometer with a hydride generation system (AAS). The quantity of arsenic adsorbed was deduced from the initial concentration using the equation,

$$q = \frac{V(C_0 - C_e)}{M} \tag{1}$$

where q is the measured sorption per unit weight of solid, V is the volume of solution, C_0 and C_e are the initial and equilibrium concentrations of arsenic, respectively, and M is the dry weight of biosorbent. All sorption experiments were performed three times to ascertain the reproducibility of the results, and mean values were considered. Blank experiments showed no detectable As(V) adsorbed on the walls of the centrifuge tubes.

Isotherms

Biosorption isotherms were obtained using a batch equilibrium method; 5 mL aliquots of different concentrations of $Na_2HAsO_4.7H_2O$ solutions (ranging from $6.4X10^{-4}$ to 8 mmol/L) were put in contact with 80 mg of the three types of sawdust (UN-SW, FeCl-SW and FeNit-SW) in centrifuge tubes. The tubes were placed in a shaker bath at a constant temperature until equilibrium was attained. Moreover, the samples were centrifuged and filtered. The supernatants were analyzed for arsenic by AAS as described above. The isotherms were carried out at two different pH values (4 and 7) to determine the effect of this variable on arsenate biosorption capacities of the three materials used in this study. These pH values were selected according to the chemical equilibrium diagram for arsenic in aqueous solution, where two different species predominate at pH 4 and 7, and also because the pH of natural water is, in general, between 5 and 7. The pH values were adjusted with 0.1 M HCl and 0.1 M NaOH solutions as required, before adsorption experiments.

RESULTS AND DISCUSSION

Modification of Biosorbent

Biosorbent samples were acid-digested after surface modification to determine concentrations of loaded iron on each type of biosorbent. The total Fe content was determined by AAS on the digested solutions. Results of these digestions showed that FeCl-SW was the sample that presented the highest concentration of iron (5080±2.25 mg/kg), followed by FeNit-SW (3265±9.25), and finally UN-SW (23.35±0.6). These results indicate that the iron modification with $FeCl_3$ was more efficient to modify the pine sawdust with Fe. This fact could lead to an improvement to the arsenate biosorption process. The Fe(III) ions loaded in the lignocellulosic substrate (UN-SW) have nearly the same reactivity than iron oxide surface sites and the active form is the hydrolyzed surface species FeOH, which behaves like an amphoteric site. This approach is based on the hypothesis that the ferric species could cross-link with various functional groups in a dispersive way on the sawdust, maximizing subsequent adsorption for arsenic. A similar behavior has been reported concerning surface modification of different adsorbents with Fe (Dupont et al. 2007; Gu et al. 2005).

Kinetic Experiments

Figure 1 shows the results obtained from biosorption kinetics experiments with UN-SW, FeCl-SW, and FeNit-SW. According to these plots, the arsenate removal by the three types of biosorbents were characterized by a fast increase in arsenate biosorption in the first minutes of contact, especially with UN-SW where arsenate removal occurred almost instantly after the arsenate solution was put in contact with the biosorbent. After this stage, the rate of As(V) uptake was reduced as equilibrium was approached. Furthermore, it can be observed that the quantities of arsenate removed in the experiments with FeCl-SW and FeNit-SW were slightly higher (approximately 32 and 31 μg/g of biosorbent, respectively) than obtained by UN-SW (approximately 25 μg/g biosorbent). After 40 min of contact, significant changes were no longer observed in arsenic concentration, indicating that sorption equilibrium had been attained; as a result, this time was chosen for further biosorption experiments. These results suggest that the modification with iron does not significantly affect the kinetics of arsenate removal by sawdust; however, it does positively affect the quantity of arsenate removed, suggesting that this modification could enhance arsenate biosorption onto sawdust.

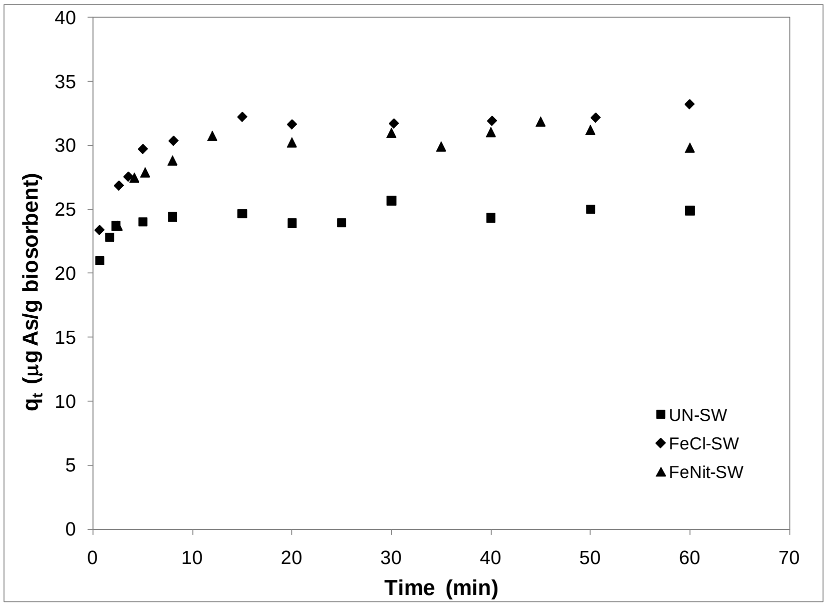

Fig. 1. Arsenate biosorption from aqueous solution by UN-SW, FeCl-SW and FeNit-SW as a function of time

The data obtained from the kinetics tests were adjusted by nonlinear regression analysis to the following models, which have been used for this type of system:

The Lagergren first-order model is represented by the following equation (Lagergren 1898),

$$q_t = q_e(1 - e^{-K_L t}) \tag{2}$$

where K_L is the Lagergren rate constant (h^{-1}), q_t is the amount of ion adsorbed at any given time t (µg/g), and q_e is the amount of ion adsorbed at equilibrium (µg/g).

Ho et al. (2000) used a pseudo-second-order equation on the kinetics removal of heavy metals on peat; this equation is represented on its linear form as follows:

$$\frac{t}{q_t} = \frac{t}{(Kq_e^2)} + \frac{t}{q_e} \tag{3}$$

Rearranging,

$$q_t = \frac{Kq_e^2 t}{1 + Kq_e t} \tag{4}$$

where K is the pseudo-second-order rate constant for adsorption (g/µg h), q_t is the amount of ion adsorbed at any given time t (µg/g), and q_e is the amount of ion adsorbed at equilibrium (µg/g). The pseudo-second-order model is based on the assumption that the rate-limiting step may be chemical sorption or chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

The Elovich rate equation has been commonly used in the kinetics of chemisorption of gases on solids. However, some researchers have applied this model to solid–liquid sorption systems, especially in the sorption of heavy metals (Igwe and Abia 2006; Calero et al. 2009). This model is represented by the following equation (Low 1960),

$$\frac{dq}{dt} = \alpha e^{(-\beta q_t)} \qquad (5)$$

where α is the initial sorption rate (μg/g min); β is the constant related to the surface coverage (g/μg), and q_t is the amount of ion adsorbed at any given time t (μg/g). In case that $\alpha\beta t >> 1$ and applying frontier conditions: $q_t = 0$ at t= 0, y $q_t = q_t$ at $t = t$, Eq. 5 simplifies to (Cheung et al. 2001):

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \qquad (6)$$

Figures 2, 3, and 4 show the fitted plots obtained by nonlinear regression analysis to the above mentioned kinetic models for biosorption of arsenate onto UN-SW, FeCl-SW and FeNit-SW, respectively. Model parameters including kinetic constants and correlation coefficients are presented in Table 1.

It can be observed from the plots that the model that best described the kinetics of arsenate on the three different biosorbents was the pseudo second order model, according to the correlation coefficients obtained for each biosorption system. Lagergren and Elovich models fitted well the biosorption kinetic data, but the pseudo second order model fit experimental data over the whole time range over which the experiments were conducted. Furthermore, the model parameters for the Elovich and Lagergren equations were not completely reliable, since they were not statistically significant at a confidence level of 95%, according to the p-levels obtained from the non-linear regression analyses. The fact that the pseudo second order model best suited the kinetic biosorption data implies that this sorption system is not a first order reaction, and chemical sorption may be the rate limiting step, as suggested by Ho et al. (2000).

Table 1. Kinetics Model Parameters for Arsenate Biosorption on UN-SW, FeCl-SW and FeNit-SW

Model	Kinetic parameters					
	UN-SW		FeCl-SW		FeNit-SW	
Lagergren	K_L= 2.8 min^{-1}	R=0.9952	K_L= 2.2 min^{-1}	R=0.9785	K_L= 26.4 min^{-1}	R=0.9670
Pseudo second order	K_2 = 0.083 g/μg.min	R=0.9978	K_2 = 0.027 g/μg.min	R=0.9930	K_2 = 0.011 g/μg.min	R=0.9970
Elovich	α = 9.32x10^9 μg/g.min β = 1.06 g/μg	R=0.9943	α = 695254 μg/g.min β = 0.504 g/μg	R=0.9958	α = 1856805 μg/g.min β = 0.566 g/μg	R=0.9910

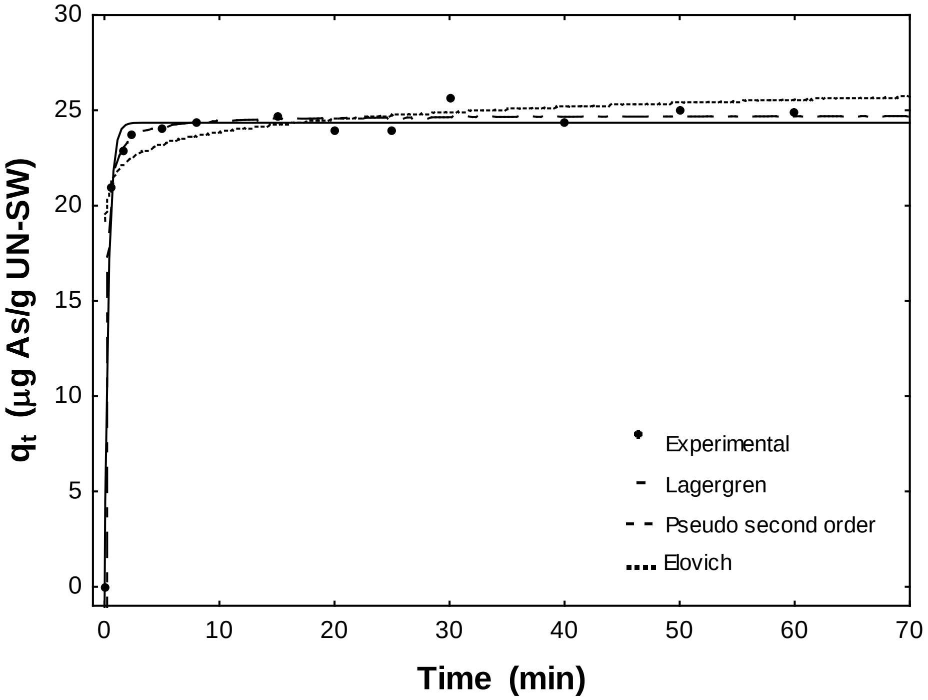

Fig. 2. Arsenate biosorption from aqueous solution by UN-SW as a function of time fitted to the Lagergren, pseudo second order and Elovich models

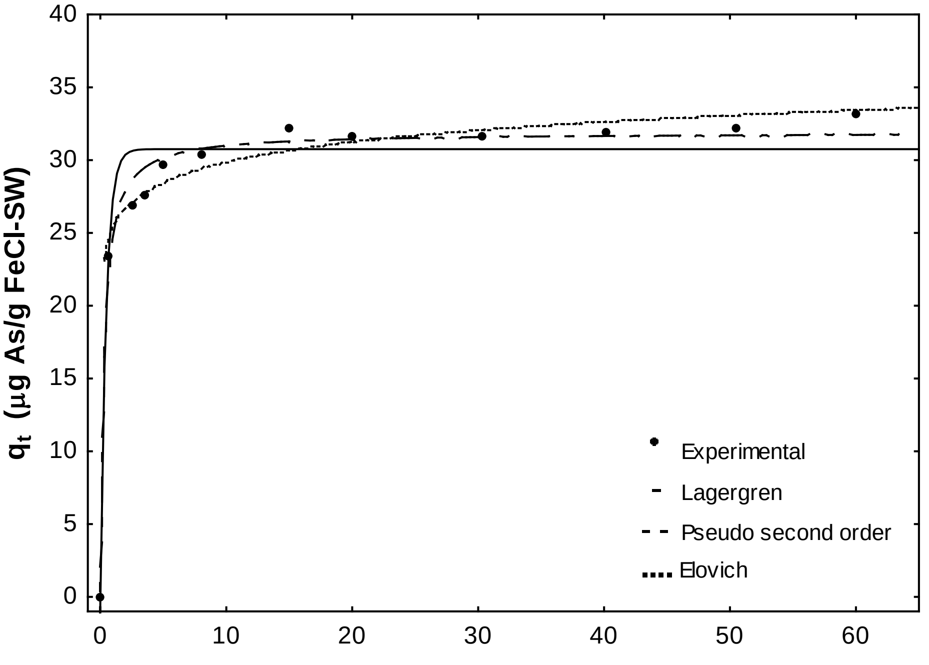

Fig. 3. Arsenate biosorption from aqueous solution by FeCl-SW as a function of time fitted to the Lagergren, pseudo second order and Elovich models

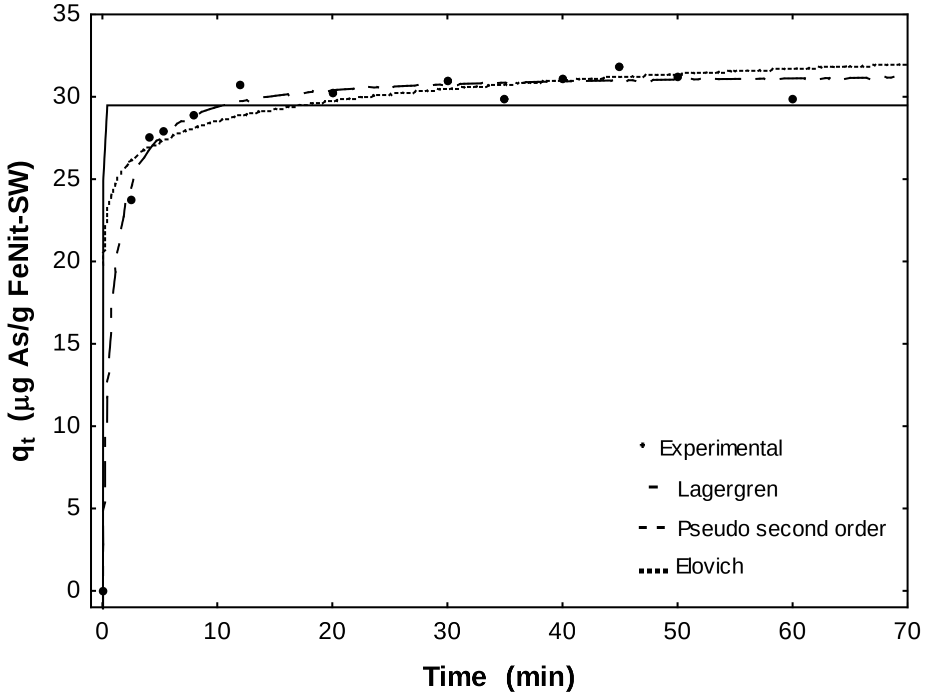

Fig. 4. Arsenate biosorption from aqueous solution by FeNit-SW as a function of time fitted to the Lagergren, pseudo second order and Elovich models

It can also be observed from Table 1 that the pseudo second order kinetic constant for the biosorption of arsenate by UN-SW was slightly higher than for biosorption by FeCl-SW or by FeNit-SW. This fact indicates that arsenic biosorption becomes slower when the sawdust surface is modified with iron. This behavior could be attributed to the different sorption mechanisms existent among the unmodified and modified sawdust. According to Goldberg and Johnston (2001) the arsenate adsorption mechanism onto amorphous oxides, which could be present on the surface of the modified materials, seems to be formation of inner and outer sphere surface complexes. At the pH value used for kinetic experiments (pH=7), As(V) predominantly exists in the negative divalent form $HAsO_4^{2-}$ in aqueous solution. Reed et al. (2000) recognized two forces that play an important role in the adsorption process. These are chemical interaction and electrostatic force. At the pH value used for these experiments (pH=7), arsenic uptake is largely caused by chemical interaction, since the point of zero charge of the active surfaces (hydrous ferric oxides) is between 7.8 and 8.2. The point of zero charge is the pH at which the adsorbent has a net zero surface charge (Onyango et al. 2003). Since the pseudo second order mechanism is based on the assumption that one adsorbate type occupies two sites; the arsenate kinetics are well fitted by this model; thus the arsenate reaction with the binding surfaces (hydrous ferric oxide) on sawdust may be represented as follows (Dupont et al. 2007, Onyango et al. 2003):

$$\text{SW-2(FeOH)} + HAsO_4^{2-} \leftrightarrow \text{SW-}Fe_2HAsO_4 + 2OH^- \qquad (7)$$

Such equilibria consider the formation of monodentate and bidentate surface complexes, as reported elsewhere (Dupont et al. 2007). Hydrous ferric oxide has empty *d*-orbitals, allowing complexation of heavy metal anions through replacement of a hydroxyl group (Reed et al. 2000). The formation of such complexes could lead to the decrease of kinetic constants related to iron-modified sawdust since a chemical bond is involved in the biosorption process.

A wide range of equilibrium sorption times and kinetic sorption parameters have been reported in the literature with various arsenate-biosorbent systems. For example, a 60 min equilibrium biosorption time has been reported (Kumari et al. 2005) for arsenate and arsenite biosorption onto plant biomass (*Moringa oleifera*); A rapid initial uptake was observed in the first minutes of contact; after this stage, sorption equilibrium was reached. A similar behavior was found by Ishikawa et al. (2004) for arsenate removal by animal biopolymers; they reported that equilibrium was achieved in about 60 min after a rapid initial arsenate removal. In addition, Stanić et al. (2009) found arsenic sorption onto an iron (III) modified natural zeolitic tuff was fast and that most of the arsenic(V) was adsorbed in less than 30 min. This behavior is in agreement with the arsenate kinetic data presented herein, where biosorption equilibrium is reached in about 40 min for modified and unmodified sawdust.

However, higher arsenate sorption equilibrium times have been reported for different types of sorbents. For instance, Onyango et al. (2003) found a 48 h sorption equilibrium time for arsenate removal by iron-conditioned zeolite. Gu and Deng (2007) reported that arsenate adsorption by iron-containing mesoporous carbon reached equilibrium in about 3 h. Even arsenate removal by a fungal biosorbent (*Penicillium purpurogenum*) has been reported to have higher biosorption rates, around 3 h until equilibrium was achieved (Say et al. 2003). It is important to note that there are several parameters that determine the equilibrium sorption time. These include agitation rate in the aqueous phase, physical properties of the adsorbent, (e.g. protein and carbohydrate composition, surface charge density, porosity, surface area, etc), amount of adsorbent, properties of the ions to be removed, initial concentration of ionic species, and the presence of other metal ions that may compete with the ionic species of interest for the active binding sites. Therefore, it is difficult to compare the adsorption rates reported (Say et al. 2003). However, it is also important to notice that if the sorption rate is fast on a particular biosorbent, this could benefit further applications of such an biosorbent in dynamic systems.

Isotherms

The sorption isotherms of arsenate biosorption using UN-SW, FeCl-SW, and FeNit-SW at different pH values are shown in Figs. 5 and 6, respectively. Experimental data from these plots were fitted to the following isotherm models by nonlinear regression analysis,

$$\text{Freundlich:} \qquad q_e = K_F C_e^{1/n_F} \tag{8}$$

where q_e is the amount of solute per unit weight of adsorbent (mg/g), C_e is the solute concentration in the solution at equilibrium (mg/L), K_F is the equilibrium constant indicative of adsorption capacity, and n_F is the adsorption equilibrium constant whose reciprocal is indicative of adsorption intensity,

$$\text{Langmuir:} \quad q_e = \frac{q_o\, a_L\, C_e}{1 + a_L\, C_e} = \frac{K_L\, C_e}{1 + a_L\, C_e} \tag{9}$$

where, q_e is the amount of solute per unit weight of adsorbent (mg/g), C_e is the solute concentration in the solution at equilibrium (mg/L), q_o is the amount of solute retained per unit weight of adsorbent in forming a complete monolayer on the surface (mg/g), a_L is the constant related to the energy or net enthalpy of adsorption, and K_L is the Langmuir constant, (L/g), and

$$\text{Langmuir-Freundlich:} \quad q_e = \frac{K_{LF} C_e^{\,1/n}}{1 + a_{LF} C_e^{\,1/n}} \tag{10}$$

where, q_e is the amount of solute per unit weight of adsorbent (mg/g), C_e is the solute concentration in the solution at equilibrium (mg/L), K_{LF} and a_{LF} are empirical constants.

According to the results at pH 4 (Fig. 5), it can be observed that the amount of As(V) adsorbed by the three different materials was increased by raising the initial arsenate concentration, following a nonlinear type isotherm. Nonlinear isotherms were also reported for adsorption of arsenate on iron (III)-modified zeolitic tuff (Stanić et al. 2009). Experimental data showed two different sections within the studied concentration range: in the first, the amount of adsorbed arsenate increased gradually, until the slope of the curve decreased gradually in the second part.

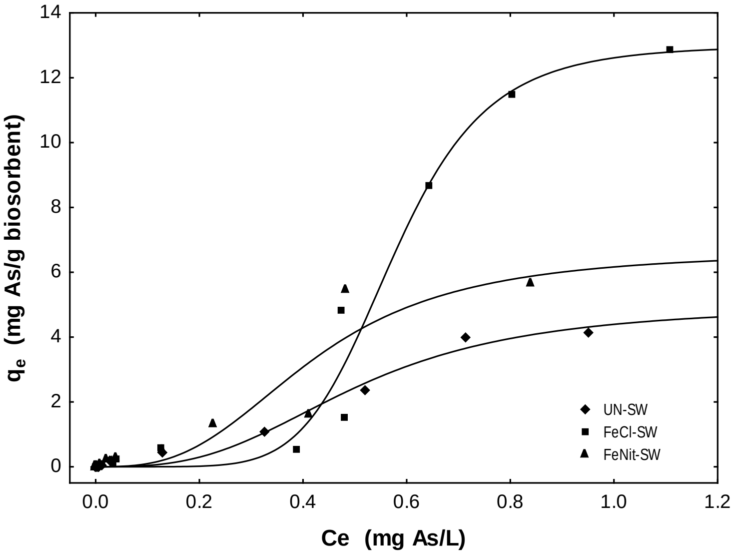

Fig. 5. Langmuir-Freundlich isotherm applied to the arsenate biosorption from aqueous solution, at pH=4

From these data it can also be observed that arsenate adsorption showed different behaviors according to the type of biosorbent used in each experiment, since the Fe-modified biosorbents showed higher sorption capacities than the unmodified pine sawdust. In particular, FeCl-SW showed a significantly higher sorption capacity than FeNit-SW and UN-SW at these experimental conditions.

For the case of biosorption isotherms obtained at pH 7, a similar behavior was observed (Fig. 6), where FeCl-SW was the biosorbent that presented higher arsenate sorption capacity. It is important to notice that the FeCl-SW material showed a higher Fe content than FeNit-SW and UN-SW. In general, it was observed from the adjustment of the experimental data to the Langmuir-Freundlich isotherm that the maximum sorption of arsenate increased as iron content on the sawdust increased, indicating that Fe content plays an important role in the arsenate biosorption by these biosorbents. Similar results have been reported for arsenate adsorption by natural and Fe-modified pozzolane (Serrano-Gómez et al. 2010). In addition, the arsenate biosorption capacities of the three types of materials were higher at pH 4 than at pH 7. The pentavalent arsenic exists in the monovalent ($H_3AsO_4^-$), and divalent anion ($H_2AsO_4^{2-}$) forms in the pH range from 2 to 9. According to the results, one can establish that the removal of arsenate from aqueous solutions by biosorption onto unmodified and iron-modified sawdust is highly dependent on pH of the solution, since this parameter can affect the surface charge of the adsorbent, as well as the degree of ionization and speciation of the adsorbate. In the case of arsenate biosorption onto UN-SW, the sorption capacity was enhanced at pH 4, since the anion biosorption is favored at this pH value due to the point of zero charge of the UN-SW (between 6 and 6.9). For the iron-modified biosorbents, the point of zero charge of the active surfaces is around 7.9 to 8.2, and the arsenate biosorption is favored at both pH values used in these experiments, so the differences in sorption capacity at a lower pH could be attributed to the arsenate speciation under such experimental conditions.

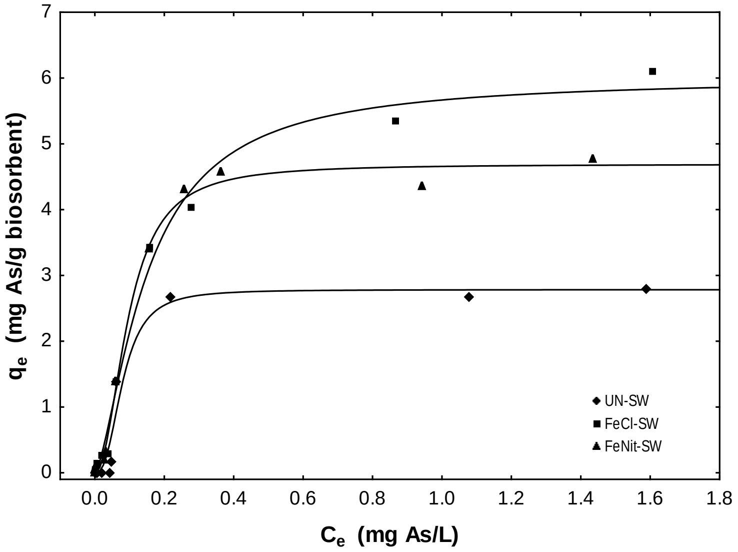

Fig. 6. Langmuir-Freundlich isotherm applied to the arsenate biosorption from aqueous solution, at pH=7

It is important to mention that all isotherm data were best adjusted by the Langmuir-Freundlich model, based on the correlation coefficients (*R*) obtained by nonlinear regression analyses, which range from 0.9448 to 0.9983 (Table 2). The Freundlich and Langmuir models tested to fit the equilibrium experimental data showed significantly lower *R* values in all cases. At low adsorbate concentrations, the Langmuir-Freundlich isotherm (Equation 9) effectively reduces to the Freundlich isotherm and thus does not obey Henry's Law. At high sorbate concentrations, this isotherm predicts a monolayer sorption capacity characteristic of the Langmuir isotherm (Ho et al. 2002).

Table 2. Langmuir-Freundlich Isotherm Parameters for Arsenate Biosorption onto UN-SW, FeCl-SW and FeNit-SW at Different pH Values

Parameter	pH value	Biosorbent		
		UN-SW	FeCl-SW	FeNit-SW
K_{LF} (mg/g)(mg/L)$^{1/nLF}$	pH 4	37.36	427.75	84.44
	pH 7	20.33	101.79	64.7
a_{LF} (mg/L)	pH 4	1.97	1.74	2.37
	pH 7	12.4	6.71	10.41
$1/n$	pH 4	0.336	0.158	0.34
	pH 7	0.382	0.672	0.475
R	pH 4	0.9932	0.9883	0.9448
	pH 7	0.9831	0.9962	0.9983

The Langmuir-Freundlich model has been widely used to describe equilibrium adsorption data on heterogeneous surfaces. Thus, the fact that the arsenate equilibrium data fits well with in this, suggests that As(V) biosorption onto UN-SW, FeCl-SW and FeNit-SW are of heterogeneous nature. Similar results have been reported for arsenate sorption by different types of adsorbents, including iron-modified materials (Stanić et al. 2009; Valencia-Trejo et al. 2010). These results are in agreement with the fact that the main As(V) sorption mechanism on the iron oxyhidroxides present on the active surfaces of the FeCl-SW and FeNit-SW seem to be the inner and outer sphere complexation, which implies heterogeneous sorption sites that have different energy and may explain the high correlation coefficient of Langmuir-Freundlich equilibrium model in all biosorption systems in this study. The estimated maximum biosorption capacities of As(V), based on the Langmuir-Freundlich fit to the data, are, at pH 4, 4.4 mg/g of UN-SW, 12.85 mg/g of FeCl-SW, and 6 mg/g of FeNit-SW; and at pH 7, 2.6 mg/g of UN-SW, 5.9 mg/g of FeCl-SW, and 4.6 mg/g of FeNit-SW. It can be clearly observed that the arsenate biosorption capacity was enhanced when the sawdust was modified with iron under different experimental conditions. FeCl-SW showed the best As(V) biosorption capacity of all materials tested. The exponent n values are not close to unity (Table 2). This suggested that the arsenate sorption data obtained in this study better fit the Freundlich form rather than the Langmuir form.

A comparison of the removal capacities of selected sorbent materials towards As(V) is given in Table 3. As(V) uptake determined in this work was higher than that of activated carbon, iron (III)-modified zeolitic tuff, iron oxide coated sand, natural iron ores, hematite, fly ash, and acid-washed crab shells, but lower than that reported for Fe(III) loaded resin, goethite, *Lessonia nigrescens, Xanthoria parietina*, and Fe(III)-treated *Staphylococcus xylosus*. Compared with other biosorbents, pine sawdust seems to be a good alternative for the removal of As(V) species from aqueous solutions, particularly if this material is modified with iron.

Table 3. Arsenate Maximum Sorption Capacities (Q_{max}) of Selected Sorbent Materials

Adsorbent	Q_{max} (mg/g)	pH	Reference
UN-SW	4.4	4	This work
FeCl-SW	12.85	4	This work
FeNit-SW	6.0	4	This work
Iron (III)-modified zeolitic tuff	1.55	6-7	(Stanić et al. 2009)
Iron-containing mesoporous carbon	5.15	7.85	(Gu and Deng 2007)
Iron oxide coated sand	0.412	7.6	(Thirunavukkaresu et al. 2003)
Fe(III) loaded resin	59.93	1.7	(Rau et al. 2003)
Natural iron ores	0.397	4.5-6.5	(Zhang et al. 2004)
Hematite	0.4	--	(Zhang et al. 2004)
Goethite	24.72	5	(Matis et al. 1999)
Activated carbon	1.2	--	(Bunnaul et al. 1999)
Fly ash	0.194	6.9	(Bertocchi et al. 2006)
Acid-washed crab shells	8.25	2.5	(Niu et al. 2007)
Lessonia nigrescens	45.2	2.5	(Hansen et al. 2006)
Xanthoria parietina	60.3	--	(Sarı and Tuzen 2010)
Fe(III)-treated *Staphylococcus xylosus*	61.34	--	(Aryal et al. 2010)

-- not reported

CONCLUSIONS

1. In general, it can be concluded that pine sawdust has favorable properties for the biosorption of arsenates from aqueous solutions and these properties are enhanced by modifying its surface with iron compounds.
2. The pseudo-second- order model described As(V) biosorption kinetics using the three types of materials.
3. The isotherm experimental data was best described by the Langmuir-Freundlich model.
4. These results indicate that the mechanism involved in the As(V) biosorption in the unmodified and modified sawdust biosorbents is related to chemisorption on heterogeneous surfaces.

5. It was found that the biosorption of arsenate is higher at pH 4 than at pH 7, since maximum biosorption capacities of the three types of materials occurred at pH 4, where As(V) monovalent species predominate in aqueous solution.

ACKNOWLEDGMENTS

The authors acknowledge financial support provided by Coordinación de la Investigación Científica-UMSNH and are grateful to the technical support of B. Villalobos-Castañeda and B. Cortés for style correction.

REFERENCES CITED

Alluri, H. K., Ronda, R. S., Settalluri, S. V., Bondili, S. J., Suryanarayana, V., and Venkateshwar, P. (2007). "Biosorption: An eco-friendly alternative for heavy metal removal," *Afr. J. Biotechnol.* 6(25), 2924-2931.

Aryal, M., Ziagova, M., and Liakopoulou-Kyriakides, M. (2010). "Study on arsenic biosorption using Fe(III)-treated biomass of *Staphylococcus xylosus*," *Chem. Eng. J.* 162(1), 178-185.

Bertocchi, A. F., Ghiani, M., Peretti, R., and Zucca, A. (2006). "Red mud and fly ash for the remediation of mine sites contaminated with As, Cd, Cu, Pb and Zn," *J. Hazard. Mater.* 134(1-3), 112-119.

Bunnaul, P., Saejen, R., Arryku, S., and Kooptarnond, K. (1999). "Removal of arsenic(V) from water by adsorption on aluminum and ferric hydroxides," *J. Am. Water Work Assoc.* 65, 548-552.

Calero, M., Hernáinz, F., Blázquez, G., Martín-Lara, M. A., and Tenorio, G. (2009). "Biosorption kinetics of Cd (II), Cr (III) and Pb (II) in aqueous solutions by olive stone," *Braz. J. Chem Eng.* 26(2), 265-273.

Cheung, C. W., Porter, J. F., and Mckay. G. (2001). "Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char," *Water Res.* 35(3), 605-612.

Dupont, L., Jolly, G., and Aplincourt, M. (2007). "Arsenic adsorption on lignocellulosic substrate loaded with ferric ion," *Environ. Chem. Lett.* 5(3), 125-129.

Dutta, P. K., Raya, A. K., Sharma, V. K., and Millero, F. J. (2004). "Adsorption of arsenate and arsenite on titanium dioxide suspensions," *J. Colloid Interf. Sci.* 278(2), 270-275.

Goldberg, S., and Johnston, C. T. (2001). "Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling," *J. Colloid. Inter. Sci.* 234(1), 204-216.

Gu, Z., and Deng, B. (2007). "Use of iron-containing mesoporous carbon (IMC) for arsenic removal from drinking water," *Env. Eng. Sci.* 24(1), 113-121.

Gu, Z., Fang, J., and Deng, B. (2005). "Preparation and evaluation of GAC based iron-containing adsorbents for arsenic removal," *Environ. Sci. Technol.* 39, 3833-3843.

Guo, X., and Fuhua, C. (2005). "Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater," *Environ. Sci. Technol.* 39(17), 6808-6818.

Hansen, H. K., Ribeiro, A., and Mateus, E. (2006). "Biosorption of arsenic (V) with *Lessonia nigrescens*," *Miner. Eng.* 19(5), 486-490.

Ho, Y. S., Porter, J. F., and McKay, G. (2002). "Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems," *Water Air Soil Pollut.* 141(1-4), 1-33.

Ho, Y. S., Mckay, G., Wase, D. A. J., and Forster, C.F. (2000). "Study of the sorption of divalent metal ions onto peat," *Adsorp. Sci. Technol.* 18(7), 639-650.

Igwe, J. C., and Abia, A. A. (2006). "A bioseparation process for removing heavy metals from waste water using biosorbents," *Afr. J. Biotechnol.* 5(12), 1617-1179.

Igwe, J. C., Nwokennaya, E. C., and Abia, A. A. (2005). "The role of pH in heavy metal detoxification by biosorption from aqueous solutions containing chelating agents," *Afr. J. Biotechnol.* 4(10), 1109-1112.

Ishikawa, S. I., Sekine, S., Miura, N., Suyama, K., Arihara, K., and Itoh, M. (2004). "Removal of selenium and arsenic by animal biopolymers," *Biol. Trace Elem. Res.* 102(1-3), 113-127.

Jiménez-Cedillo, M. J., Olguín, M. T., and Fall, Ch. (2009). "Adsorption kinetic of arsenates as water pollutant on iron, manganese and iron–manganese-modified clinoptilolite-rich tuffs," *J. Hazard. Mater.* 163(2-3), 939-945 .

Kumari, P., Sharma, P., Srivastava, S., and Srivastava, M. M. (2005). "Arsenic removal from the aqueous system using plant biomass: A bioremedial approach," *J. Ind. Microbiol. Biotechnol.* 32(11-12), 521-526.

Lagergren, S. (1898). "Zur theoric dersogenannten Adsorption geloster Stoffe," *Kungliga Svenska Ventenskapsatemiens Handlinger* 24, 1-39.

Lakshmipathiraj, P., Narasimhan, B. R. V., Prabhakar, S., and Bhaskar Raju, G. (2006). "Adsorption of arsenate on synthetic goethite from aqueous solution," *J. Hazard. Mater.* 136(2), 281-287.

Low, M. J. D. (1960). "Kinetics of chemisorption of gases on solids," *Chem. Rev.* 60(3), 267-312.

Macedo-Miranda, M. G., and Olguín, M. T. (2007). "Arsenic sorption by modified clinoptilolite-heulandite rich tuffs," *J. Incl. Phenom. Macrocycl. Chem.* 59(1-2), 131-142.

Matis, K. A., Lehmann, M., and Zouboulis, A. I. (1999). "Modelling sorption of metals from aqueous solution onto mineral particles: The case of arsenic ions and goethite ore," In: Misaelides et al. (eds.), *Natural Microporous Materials in Environmental Technology*, Kluwer, The Netherlands, 463-472.

Murugesan, G. S., Sathishkumar, M., and Swaminathan, K. (2006). "Arsenic removal from groundwater by pretreated waste tea fungal biomass," *Bioresource Technol*. 97, 483-487.

Niu, C. H., Volesky, B., and Cleiman, D. (2007). "Biosorption of arsenic (V) with acid-washed crab shells," *Water Res.* 41(11), 2473-2478.

Onyango, M. S., Matsuda, H., and Ogada, T. (2003). "Sorption kinetics of arsenic onto iron-conditioned zeolite," *J. Chem. Eng. Jpn.* 36(4), 477-485.

Rau, I., Gonzalo, A., and Valiente, M. (2003). "Arsenic (V) adsorption by imobilized iron mediation. Modeling of the adsorption process and influence of interfering anions," *React. Funct. Polym.* 54(1-3), 85-94.

Raven, K. P., Jain, A., and Loeppert, R.H. (1998). "Arsenite and arsenate adsorption on ferrihydrite: Kinetics, equilibrium, and adsorption envelopes," *Environ. Sci. Technol.* 32(3), 344-349.

Reed, B. E., Vaughan, R., and Jiang, L. Q. (2000). "As(III), As(V), Hg, and Pb removal by Fe-oxide impregnated activated carbon," *J. Environ. Eng.-ASCE.* 126(9), 869-873.

Sarı, A., and Tuzen, M. (2010). "Biosorption of As(III) and As(V) from aqueous solution by lichen (*Xanthoria parietina*) biomass," *Sep. Sci. Technol.* 45(4), 463-471.

Say, R., Yilmaz, N., and Denizli, A. (2003). "Biosorption of cadmium, lead, mercury, and arsenic ions by the fungus *Penicillium purpurogenum*," *Sep. Sci. Technol.* 38(9), 2039-2053.

Serrano-Gómez, J., López-González, H., Olguín M. T., and Bulbulian, S. (2010). "As(V) adsorption by unmodified and iron modified pozzolane," *J. Incl. Phenom. Macrocycl. Chem.* 67(1-2), 153-158.

Smedley, P. L., and Kinniburgh, D. G. (2002). "A review of the source, behaviour and distribution of arsenic in natural waters," *Appl. Geochem.* 17, 517-568.

Solache-Ríos, M. J., Villalva-Coyote, R., and Díaz-Nava, M. C. (2010). "Sorption and desorption of Remazol Yellow by a Fe-zeolitic tuff," *J. Mex. Chem. Soc.* 54(1), 59-68.

Srinivasa-Rao, P., Suresh-Reddy, K. V. N., Kalyani, S., and Krishnaiah, A. (2007). "Comparative sorption of copper and nickel from aqueous solutions by natural neem (*Azadirachta indica*) sawdust and acid treated sawdust," *Wood Sci. Technol.* 41(5), 427-442.

Stanić, T., Daković, A., Živanović, A., Tomaševic´-Čanović, M., Dondur, V., and Milićevic, S. (2009). "Adsorption of arsenic (V) by iron (III)-modified natural zeolitic tuff," *Environ. Chem. Lett.* 7(2), 161-166.

Thirunavukkaresu, O. S., Viraraghavan, T., and Subramanian, K. S. (2003). "Arsenic removal from drinking water using iron oxide-coated sand," *Water Air Soil Pollut.* 142(1-4), 95-111.

Valencia-Trejo, E., Villicaña-Méndez, M., Alfaro-Cuevas-Villanueva, R., Garnica-Romo, M. G., and Cortés-Martínez, R. (2010). "Effect of temperature on the removal of arsenate from aqueous solutions by titanium dioxide nanoparticles," *J. Applied Sci. Environ. Sanit.* 5(2), 171-184.

Vijayaraghavan, K., Mahadevan, A., Joshi, U. M., and Balasubramanian, R. (2009). "Biosorption of As(V) onto the shells of the crab (*Portunus sanguinolentus*): Equilibrium and kinetic studies," *Ind. Eng. Chem. Res.* 48(7), 3589-3594.

Zhang, F. S., and Itoh, H. (2005). "Iron oxide-loaded slag for arsenic removal from aqueous system," *Chemosphere.* 60(3), 319-325.

Zhang, W., Singh, P., Paling, E., and Delides, S. (2004). "Arsenic removal from contaminated water by natural iron ores," *Miner. Eng.* 17(4), 517-524.

Article submitted: April 11, 2011; Peer review completed: May 26, 2011; Revised version received: January 16, 2012; Accepted: January 29, 2012; Published: February 2, 2012.