

Removal of arsenic (V) from aqueous solutions using chemically modified sawdust of spruce (*Picea abies*): Kinetics and isotherm studies

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ABSTRACT: Arsenic is a ubiquitous element in the environment and occurs naturally in both organic and inorganic forms. Under aerobic condition, the dominant form of arsenic in waters is arsenate, which is highly mobile and toxic. Arsenic poisoning from drinking water remains a serious world health issue. There are various standard methods for arsenic removal from drinking waters (coagulation, sorption, ion-exchange reactions or methods of reverse osmosis) and alternative methods, such as biosorption. Biosorption of arsenic from natural and model waters by native or chemically modified (with urea or ferric oxyhydroxides) plant biomass prepared from sawdust of *Picea abies* was studied. The kinetic of the adsorption process fitted well the pseudo second order adsorption model and equilibrium was achieved after 2 h. The results showed that biosorption was well described by both Langmuir and Freundlich isotherms. The maximum biosorption capacity of the sawdust modified with ferric oxyhydroxides, evaluated by Langmuir adsorption model, was 9.259 mg/g, while the biosorption capacity of unmodified biosorbent or biosorbent modified with urea was negligible. The adsorption capacity is comparable to results published by other authors, suggesting that the prepared chemically modified biosorbent has potential in remediation of contaminated waters.

Keywords: Adsorption; Bioremediation; Biosorption; Plant biomass

INTRODUCTION

Arsenic compounds are common contaminants in the environment. Because of arsenic toxicity and induced carcinogenicity (Eblin *et al.*, 2006; Hughes, 2002), higher arsenic concentration in the environment represents serious problems for human health, especially for populations in Bangladesh, Western Bengal, Vietnam, China, Mexico and Chile. The danger of elevated arsenic concentration in waters in these countries was underlined by WHO, which estimated the recommended limit for arsenic concentration in drinking waters up to 10 µg/L (WHO, 1996). The conventional technologies for arsenic removal from waters are based on processes of coagulation, sorption, ion-exchange reactions or methods of reverse osmosis. Materials used in these processes are Fe (0), Fe (III) oxyhydroxides, Mn (II), Al (III), apatite, silicate sands, carbonates, sulphides, ash or various types of coal (Chmielewska *et al.*, 2008; Daus

et al., 2004; DeMarco *et al.*, 2003; Hiller *et al.*, 2007; Lin and Wu, 2001; Sato *et al.*, 2002; Song *et al.*, 2006). Nowadays, there is a trend to use the alternative and low-cost materials for arsenic removal from the waters in laboratory or medium-scale experiments. Effectiveness of chemically modified or native biomass in processes of arsenic removal was evaluated and proved by various authors (Abdel-Ghani *et al.*, 2007; Boddu *et al.*, 2008; Čerňanský *et al.*, 2007; Loukidou *et al.*, 2003; Malakootian *et al.*, 2009; Murugesan *et al.*, 2006; Rahaman *et al.*, 2008; Seki *et al.*, 2005).

The aim of this study was to evaluate effectiveness of chemically modified with Fe (III) or urea or unmodified plant biomass prepared from sawdust of *Picea abies* to remove arsenic from model or natural arsenic contaminated water. The influence of various initial arsenic concentrations was also tested and the kinetics of the adsorption process was evaluated. This experiment was realized in the laboratories of the

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MATERIALS AND METHODS

Preparation of biosorbents

The plant biomass was prepared from sawdust of *Picea abies* (160 €/t of biomass). The sawdust was washed with great amount of deionized water, sieved and part of fraction under 0.2 mm was used in the experiments as chemically unmodified biosorbent. The other part of fraction was used to prepare biosorbents modified with urea and ferric Fe(III) oxyhydroxides. To prepare Fe(III) modified biomass, the sawdust fraction was homogenized with a mixture of prepared iron oxyhydroxide and NaOH solution and dried in the oven overnight according to procedure proposed by Pokhrel and Viraraghavan (2006). To prepare biosorbent modified with urea, the sawdust fraction (10 g) was agitated (140 rpm) in the presence of urea (200 g/L) for 24 h, then rinsed with deionized water and dried in oven (80 °C) overnight. The third chemical modification was a combination of previous two procedures, when the sawdust fraction was coated with Fe(III) oxyhydroxides in the presence of urea.

Biosorption of arsenic from natural waters

The natural water contaminated with arsenic (concentration of total arsenic was 230 µg/L) was collected from Poša (Eastern Slovakia). The volume of 50 ml of contaminated water was transferred into 250 mL beaker and 1 g of native or chemically modified biosorbent prepared from sawdust was added. The system was agitated at 140 rpm for 2 h. The agitation time was selected according to preliminary and kinetic studies, since 2 h were required to reach equilibrium. After 2 h, the biosorbent was separated by filtration, washed with deionized water and then the amount of arsenic in residual solution was measured. Dry weight of biosorbent was measured after drying at 105 °C. All the experiments were carried out in triplicates.

Kinetic and equilibrium adsorption experiments

The stock solution was prepared by dissolution of arsenic species Na_2HAsO_4 (Merck, Germany) in distilled water. The initial concentrations of As(V) in prepared model solutions varied from 20 up to 500 mg/L. The pH value was adjusted to 8 (pH value, when all of As(V) in solution is ionized) using the solution of 1M NaOH. 0.5 g of chemically modified or unmodified biosorbent was

then transferred into the 50 mL solution with desired As(V) concentration and agitated on rotatory shaker (Unimax 2100, Heidolph, Germany) at 140 rpm. After desired time (15 to 240 min) the biosorbents were separated from solution by filtration. Arsenic in solution was then stabilized with concentrated HCl and the amount of total arsenic was determined. Dry weight of biomass was measured after drying at 105 °C. All the experiments were carried out in triplicates.

Experimental data analysis

The experimental data were analyzed using Freundlich (1906) and Langmuir (1918) adsorption isotherms and pseudo first and pseudo second order kinetic model. The linear equations of isotherm and kinetic models were used to gain appropriate constants and to evaluate experimental data.

Linear Freundlich equation was used as:

$$\log S_{eq} = \log K_F + N \log C_{eq} \quad (1)$$

Where, K_F and N are the Freundlich constants. K_F is the indicator for adsorption capacity of the adsorbent when the concentration of adsorbate at equilibrium is unitary. N represents the heterogeneity factor, which characterizes surface with energetically nonequivalent sites.

Linear Langmuir equation was used as:

$$\frac{C_{eq}}{S_{eq}} = \frac{1}{kS_m} + \frac{C_{eq}}{S_m} \quad (2)$$

Where, S_m is the maximum adsorption capacity corresponding to complete monolayer coverage (mg/g) and k is the Langmuir constant that relates to the energy of adsorption (L/mg). C_{eq} represents equilibrium concentration of As(V) in solution (mg/L) and S_{eq} amount of As(V) adsorbed onto biomass at equilibrium concentration (mg/g).

By integrating and applying the boundary conditions ($t=0$ and $S_t=S_{eq}$) to the pseudo first order rate expression of Lagergren (1889), the original expression may be described by the following equation:

$$\ln \left(\frac{S_{eq} - S_t}{S_t} \right) = -k_1 t \quad (3)$$

Where, k_1 is the pseudo first order kinetic constant (1/min) and S_t represent adsorption capacity (mg/g) of

biosorbent at time t (min).

According to Ho and McKey (1999), the linearized form of pseudo second order rate expression was used as:

$$\frac{t}{S_t} = \frac{t}{S_{eq}} + \frac{1}{k_2 S_{eq}^2} \quad (4)$$

Where, k_2 represent pseudo second rate constant (g/mg/min).

Analytical procedures

For the determination of total arsenic in samples, a laboratory electrochemical analyser EcaFlow 150 (Istran, Bratislava, Slovakia) was used, which applies flow-through electrochemical coulometry and in-electrode coulometric titrations.

RESULTS AND DISCUSSION

Arsenic removal efficiency by adsorbents from natural water

The As (V) removal efficiency from natural waters contaminated with arsenic (0.230 mg/L) by four different biosorbents was compared using the batch-wise method. The most effective adsorbent was the Fe(III) modified sawdust (Fig. 1), which removed nearly 100 % of arsenic. The Fe (III) oxyhydroxide modification of biosorbent was also successfully applied in other studies (Pokhrel and Viraraghavan, 2008). The application of chemical treatment with urea was based on assumption, that urea should create new adsorption positions. Apparently,

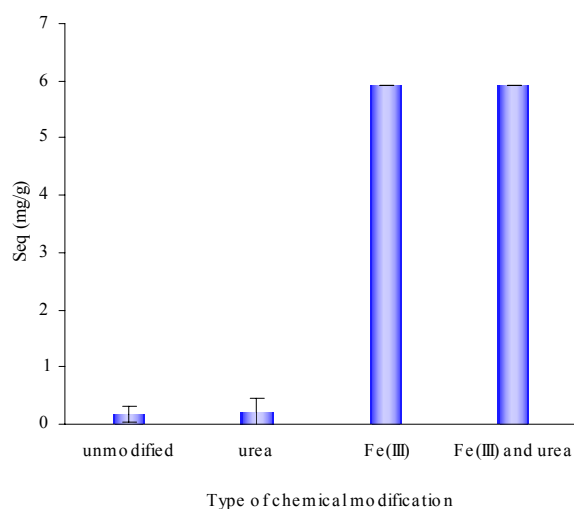


Fig. 1: The effect of chemical modification on the adsorption capacity of sawdust prepared from spruce (*Picea abies*) for removal of arsenic (0.230 mg/L) from natural contaminated water

adsorption capacity decreased after modification of unmodified or Fe (III) modified biomass, assuming diverse effect had taken place, probably revealing the complexation activity of urea as an chelating agent that occupies the adsorption positions on the adsorbent surface. The adsorption capacity of chemically unmodified biomass was negligible (Fig. 1). Hence, it is assumed that only iron is responsible for As(V) removal and spruce sawdust is only enhancing the mechanical properties of the prepared hybrid adsorbent. Therefore, the Fe (III) modified adsorbent was used in following kinetic and equilibrium experiments.

Kinetic experiments

Fig. 2 shows that within the first 60 min a rapid uptake of As (V) takes place. After this time, the rate of As (V) uptake was reduced as the equilibrium approached. The equilibrium for As (V) bisorption onto modified sawdust was reached after 120 min. Therefore, this time was chosen for further batch adsorption experiments. The experimental data presented in Fig. 2 could be fitted well for the pseudo first ($r^2 = 0.968$) and pseudo second ($r^2 = 0.984$) order model of adsorption rate. However, the best adjustment was observed for the pseudo second order kinetic, which is based on the assumption that rate limiting step is chemisorption (Ho, 2006). According to work of Goldberg and Johnston (2001), the mechanism of As (V) adsorption onto amorphous oxides seems to be formation of inner and outer sphere surface complexes. Thus, the formation of chemical bound is involved. The calculated value of pseudo second order rate constant was 0.012 g/mg/min. However, the pseudo second kinetic model may not indicate the diffusion mechanism, which is essentially associated with adsorption. Hence, the integrated intraparticle diffusion model developed by Weber and Morris (1963) was used to explore the possibility of intraparticle diffusion resistance affecting the adsorption. The model was used as:

$$S_t = K_i t^{1/2} + C \quad (5)$$

Where, K_i is the diffusion rate constant (mg/g/min) and value of C (mg/g) is proportional to boundary layer thickness (Kannan and Sundaram, 2001). It has been reported that the adsorption capacity decreases when the thickness of boundary layer decreases (Aksu, 2001). If the plot of adsorption capacity (S_t) versus the square root of time is linear, the intra particle diffusion is involved and if the line passes through the origin, diffusion in the biosorbent is the only controlling step. However, only within the first 100 min the plot presented

Removal of arsenic (V) from aqueous solutions

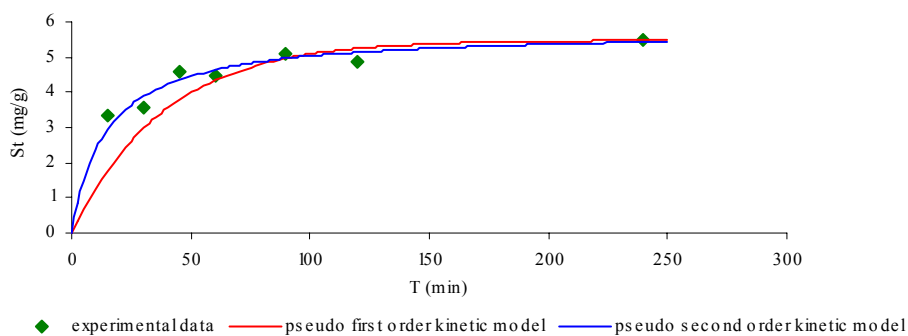


Fig. 2: Pseudo first and pseudo second kinetic models of As (V) adsorption onto sawdust chemically modified with Fe (III) oxyhydroxides (initial concentration of As (V) was 90 mg/L)

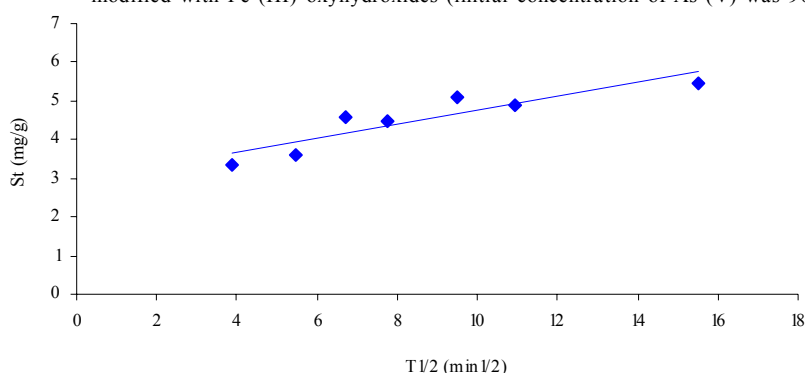


Fig. 3: Intraparticle diffusion model (initial concentration of As (V) was 90 mg/L)

in Fig. 3 shows relevant linearity ($r^2=0.917$) and the intercept (C) has higher value than zero (2.037). Therefore, some boundary layer control must be involved and intraparticle diffusion is not the rate limiting factor.

Adsorption isotherms

The experimental data for As (V) removal from aqueous solution were analyzed using Langmuir and Freundlich equilibrium isotherm models. The evaluation of the correlation between experimental data and equilibrium models is important for design of the most appropriate adsorption system for As (V) removal. The adjustable constants for Langmuir and Freundlich equations are presented in Table. 1. The Freundlich equation predicts that the adsorption capacities for the adsorbate will increase as long as there is an increase in the adsorbate concentration. The experimental results follow well Freundlich model ($r^2=0.968$). However, the adsorption capacity of the spruce sawdust modified with Fe (III) resulted to plateau within experimental concentration range of As (V) (Fig. 4). Hence, the correlation coefficient for Langmuir isotherm is higher ($r^2=0.984$). Therefore it is assumed that limited adsorption

capacity of the adsorbent up to S_{max} (9.86 mg/g), which is comparable with other related studies using ferric modified organic adsorbents or inorganic reagents (Lorenzen *et al.*, 1995; Singh *et al.*, 1996). However, the adsorption capacity is lower when compared to biomass modified with cationic polyelectrolyte (Loukidou *et al.*, 2003). The mechanism of As (V) adsorption on the surface of amorphous Fe (III) oxyhydroxides involves both inner and outer sphere complexation (Goldberg and Johnston, 2001; Jonsson and Sherman, 2008). That implies heterogenous adsorption sites that have different energy and may explain the high correlation coefficient of Freundlich equilibrium model.

The Freundlich equation parameter should also be used as a relative measure of the adsorption capacity when the concentration of As (V) is unitary. At equilibrium concentration of 1 mg/L of As (V), 1 g of prepared hybrid adsorbent removed 1.369 mg of arsenic from solution. It have been observed a slight decrease of pH of the bulk solution during the kinetic and equilibrium adsorption experiments (from 8 to 7.6). The comparison of pH value in arsenic solutions before and after the adsorption experiment confirmed the

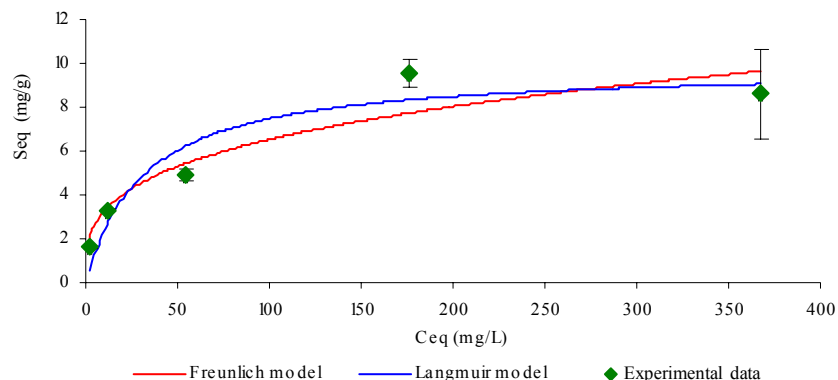


Fig. 4: Langmuir and Freundlich model of As (V) adsorption onto sawdust chemically modified with Fe (III) oxyhydroxides

Table 1: Adjustable parameters and correlation coefficients for Langmuir and Freundlich isotherms calculated from experimental data of As (V) adsorption onto sawdust prepared from spruce (*Picea abies*) coated with Fe (III) oxyhydroxides

Langmuir isotherm constants			Freundlich isotherm constants		
S_m	k	r^2	K_F	N	r^2
9.259	0.049	0.984	1.369	0.336	0.968

S_m , maximum uptake capacity of the adsorbent (mg/g); k , Langmuir binding constant; K_F , adsorption capacity when the concentration of the metal ion in equilibrium is unitary; N , Freundlich constant related to the adsorption intensity

observation of Mamisahebei *et al.* (2007), who observed the slight increase in concentration of H^+ in solution after biosorption. The decrease of pH value was probably resulting from mechanism of As (V) adsorption onto the surface of adsorbent.

CONCLUSION

The major conclusions based on the experimental study were:

1. Adsorbent prepared by chemical modification of spruce (*Picea abies*) using Fe (III) oxyhydroxide showed high affinity for As (V). The adsorption experiments revealed its possible application for arsenic removal from natural contaminated waters;
2. The adsorption kinetic data were well described by both pseudo first and pseudo second order rate expressions. However, the correlation coefficient was more adjustable for pseudo second model, assuming chemisorptions as the uptake mechanism. Intraparticle diffusion was not proved as a possible rate limiting step of arsenic removal and
3. The maximum adsorption capacity of Fe (III) modified sawdust was 9.259 mg/g. However, the experimental data fitted well both Langmuir and Freundlich isotherm models.

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