

Treatment of wastewater containing arsenic using *Rhazya stricta* as a new adsorbent

Nadia Badr · Khairia M. Al-Qahtani

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Abstract The effective removal of heavy metals from aqueous wastes is among the most important issues for many industrialized countries. Removal of arsenic (As) from aqueous solutions was studied using *Rhazya stricta* biomass. The batch experiments are carried out to investigate the effect of the significant process parameters such as pH, contact time, solute concentration and adsorbent dose. The optimum pH required for maximum adsorption was found to be 5. The equilibrium data for the adsorption of As(V) on *R. stricta* are tested with various adsorption isotherm models such as Langmuir, Freundlich, Tempkin and Generalized equation. Results indicate the following order to fit the isotherm: Langmuir (1 and 2) > Tempkin > Generalized form > Freundlich. A comparison of two kinetic models showed that our data fitted well to the Elovich model.

Keywords Biosorption · Arsenic · *Rhazya stricta* · Adsorption isotherm · Adsorption kinetics

Introduction

Arsenic (As) contamination has received widespread attention owing to its high toxicity to plants, animals and humans as inorganic arsenicals are proven carcinogens to human (Ng 2005). It is a member of the nitrogen family with both metallic and nonmetallic properties, and is ubiquitous in the environment (soil, water, air and also in living matters) (Tamaki and Frankenberger 1992). Arsenic exists in natural waters both in inorganic and organic forms. The inorganic form of arsenic is more toxic compared to its organic form. Inorganic arsenic is the predominant form in contaminated ground water. Arsenic exists in two oxidation states: arsenite, As (III) and arsenate, As (V) according to oxidation-reduction conditions (Pokhrel and Viraraghavan 2006). The As (III) species is the most toxic, although the As (V) species is the most movable (Macedo-Miranda and Olguin 2007). Generally, As (V) predominates in surface water, the thermodynamically stable state of arsenic in oxic waters, while As (III) is the main species in ground water, and predominates in reduced redox conditions. However, both forms of arsenic can be found in ground water due to changes on redox conditions and biological activity (Cullen and Reimer 1989 and Smedley and Kinniburgh 2002).

Although the occurrence of arsenic in the environment is mainly from minerals and geogenic sources, human activities such as mining, burning of fossil fuels, medicine, electronic, use of arsenic-containing chemicals in agriculture (pesticides, herbicide, insecticides, fertilizer, etc.), livestock (cattle and sheep dips) and as wood

N. Badr (✉)
Department of Environmental Sciences, Faculty of Science,
Alexandria University,
Alexandria, Egypt
e-mail: nadia_badr65@hotmail.com

K. M. Al-Qahtani
Department of Chemistry, Faculty of Science,
Princess Nora Bint, Abdel-Rahman University,
Riyadh, Saudi Arabia

preservatives also cause arsenic distribution in the environment (Bissen and Frimmel 2003 and Sharma and Sohn 2009).

Arsenic is accumulated in human beings from drinking water as well as from agricultural crops and vegetables. The WHO guideline for As in drinking water has been changed from 50 to 10 mg/L (Mohan and Pittman 2007). However, millions of people in the developing countries are at risk of having drinking water with As concentration above the guideline. Water contamination with arsenic is an urgent and extensive problem that requires immediate actions (Rahman 2002). In addition to the problem of As in drinking water, groundwater containing elevated levels of As has been used to irrigate rice crops during the dry season in some parts of south and southeast Asia. This practice has resulted in accumulation of As in paddy soils and elevated transfer of As to the food chain (Meharg and Rahman 2003). The range of arsenic in uncontaminated soil ranges from <1 to 95 mg kg⁻¹. Elevated levels of arsenic in agricultural soil could pose a serious threat to plants and human health and the environment as whole (Duxbury et al. 2003).

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 toxic sludge; these disadvantages are more difficult to manage (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.

Adsorption is evolving as a front line of defense. It is the ability of the adsorbate to adhere or attach to the adsorbent. It is a well-established separation technique to remove dilute pollutants as well as to recover valuable products from aqueous solutions. Adsorption is divided into two; one due to forces of physical nature called van der Waals force. This adsorption is relatively weak and plays an unimportant part in connection with surface reactions since they are not sufficiently strong to influence appreciably the reactivity of the molecule adsorbed. The second type is considerably stronger. The adsorbed molecules are held to the surface by valence force of the same type as those occurring between bound atoms in the molecules. This is known as chemisorption.

Selective adsorption utilizing biological materials, mineral oxides, activated carbons, or polymer resins has generated increasing excitement (Benjamin et al. 1996). Many studies have reported the possible utilization of conventional adsorbents, such as titanium dioxide (Dutta et al. 2004), iron oxide (Lakshminathiraj et al. 2006). It has been also reported that removal of As (V) can be achieved by different types of biomass, such as coconut fiber and sawdust (Igwe et al. 2005) and crab shell (Vijayaraghavan et al. 2009). The research for highly biomass sorption is expected to improve the potential for the introduction of new materials, which are likely to be competitive and cost-efficient for the sorption of metals. The biomass of *Rhazya stricta* was selected for this study. This is a native poisonous plant that increases in abundance over large areas of deteriorated rangelands in the Riyadh area. The plant is an evergreen dwarf shrub of the Apocianaceae family. Although no reports of livestock poisoning by the plant, heavy grazing puts the *R. stricta* in a competitive advantage over valuable range plants. The plant has a pharmacological value and could have a potential value as source of pesticides (Assaeed 2007). The objective of this study is to evaluate the capacity of the biomass of *R. stricta* to remove As (V) from different aqueous solutions. Batch adsorption process has been used to evaluate the maximum adsorption capacity of *R. stricta* biomass. The main parameters considered are pH, contact time, initial metal ions concentration and biosorbent concentration.

Materials and methods

Plant species used as biosorbent

R. stricta is an evergreen, perennial, cushion-shaped herb belonging to the family Apocynaceae, which includes about 1,300 herbs, shrubs and trees belonging to about 300 genera mostly grow in tropical and subtropical regions (Boulos 1995). Plants of this family are of medicinal and economic value. This plant is one of Chaemophytes that grow either from seed or vegetation plant chives (Abo Elfateh 1997). It branched from the base to height of 115 cm, spread to about 235 cm and has adventitious roots spread over a large

area in the soil (Migahid and El-Sheikh 1977). The phenological aspects show that there is a regular life cycle started from the perennial plant or the seed after the seasonal rains during November, the flowering starts at the beginning of January and the fruiting at the middle of it (Migahid and El-Sheikh 1977). This plant accumulates high content of Na, K, Ca and Cl in their tissues to generate low water potential to adapt to high temperature and drought (Larcher 1995).

Preparation of biosorbent

A biomass of *R. stricta* was used as a biosorbent of As (V). Samples of the biomass were collected from the polluted area around second industrial area, Riyadh City, Saudi Arabia. The whole plant (leaves, stem and roots) was washed first with tap water, de-ionized water and oven-dried at 80 °C for 24 h, grinding in a ball mill and sieved to particle size range 0.3–0.6 mm.

Reagents and equipment

Doubly distilled water was throughout employed. Initial solutions with different concentration of As (V) were prepared using Na₃AsO₄ (Merck, Ltd., UK). The pH adjustment of the solutions was made with aliquots of 1.0 mol l⁻¹ of HNO₃ utilizing a pH/mV hand-held meter (Crison pH meter, PH 25)

Batch biosorption studies

The effect of pH on Arsenic ions adsorption onto *R. stricta* was carried out at 100 mg l⁻¹ initial As (V) concentration with 0.5 g/100 ml biomass at 25 °C for 3 h equilibrium time. The initial pH values were adjusted in range of 1–9 with 0.1 M HCl or 0.1 M NaOH. The suspensions were shaken using agitation speed (150 rpm) for 3 h, and the amount of As(V) ions adsorbed was determined. Mamisahebei et al. (2007) stated that the removal of As(V) by pretreated waste tea fungal biomass, increased by increase in agitation speed from 50 to 150 rpm. They explained this by the fact that the increasing agitation rate decreases the boundary layer resistance to mass transfer in the bulk and increases the driving force of As(V) ions.

The effect of adsorbent dose (*R. stricta* biomass) of 1, 1.5, 2, 2.5, and 3 g/l on the uptake of As(V) with

initial concentrations of (25–125 mg l⁻¹) was investigated at pH 5. The mixtures were mixed slowly in a rotary shaker at an agitation rate of 150 rpm and kept in an isothermal (25 °C) for 3 h, then the amount of metals adsorbed was determined.

The effect of time on the adsorption process was carried out for different initial concentrations of As(V) (25–125 mg l⁻¹) using 0.5 g of *R. stricta* biomass and pH 5. Samples of 1 ml were collected from flasks at required time intervals 5–180 min and centrifuged for 5 min. Similar procedure was followed for another flask containing the same metal concentration without plant biomass to be used as a blank. The clear solutions were analysed for residual heavy metal concentrations by inductively coupled plasma atomic emission spectroscopy from Varian supplier. All the experiments are duplicated, and only the mean values are reported. The maximum deviation observed was less than 5 %. The removal efficiency of metal was calculated according to the following equation:

$$\%R = \frac{C_o - C_F}{C_o} \times 100 \quad (1)$$

Where C_o and C_F (milligrams per liter) are the initial and final concentration of element, respectively.

The adsorption capacity q_e after equilibrium (milligrams per gram) was calculated by the following mass balance relationship:

$$q_e = \frac{(C_o - C_e) \times V}{W} \quad (2)$$

Where C_o and C_e (milligrams per liter) are the initial and equilibrium liquid–solid phase concentrations of element, respectively, V is the volume of the solution (liter) and W is the mass of adsorbate (grams).

Results and discussion

Influence of solution initial pH

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent, the degree of ionization and speciation of the adsorbate. In order to establish the effect of pH on the biosorption of As(V) ions, the batch equilibrium studies at different pH values were

carried out in the range of 1–9. The relation between the initial pH of the solution and the percentage removal of As(V) is shown in Fig. 1. It was found that the biosorption rate of As(V) is all parabolic, which indicates that there exists an optimum range of pH value. The percentage removal of As(V) is increased from 52 to 83 % with increasing the initial pH from 2 to 5. The sharpest increase in As(V) uptake was obtained at pH=5. In strong acidic solution, competes for active biosorption site with As(V) ion impedes biosorption process by biomass, and biosorption amount of As(V) decreases with acidity increasing. While in alkaline solution, hydrates formed with hydrolyzation of As(V) precipitate on the surface of biomass, and can decrease the biosorption activity. Moreover, the relative distribution of dissolved arsenic is influenced by pH and the redox conditions. Under mildly reducing conditions and at pH=6 and 9, As(V) exists predominately as $\text{H}_2\text{As}_2\text{SO}_4^-$ and is likely to form a complex with iron oxide-coated biomass. At higher pH, the hydroxyle ions (OH ions) in solution can compete with the arsenite ions and so adsorption of As(V) will be reduced (Pokhrel and Viraraghavan 2006). The pH effects governing biosorption capacities of arsenate ions by Fe-modified pine sawdust were evaluated by Lopez Leal et al. (2012). Their results indicated that the biosorption process is highly dependent on pH of solution where values decrease as pH increase and recorded higher biosorption capacities at pH=4 than at pH=7. They attributed this finding to the fact that the change in pH values can affect the surface charge of the adsorbent as well as the degree of ionization and speciation of the adsorbate. The removal of As(V) from aqueous solution by pretreated waste tea fungal biomass was studied by Mamisahebei et al.

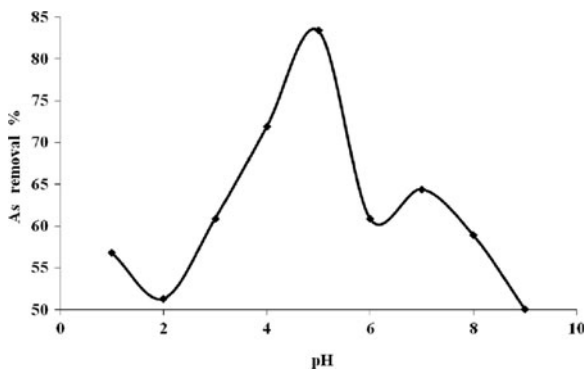


Fig. 1 Effect of pH on the adsorption of As(V) by *R. stricta* biomass

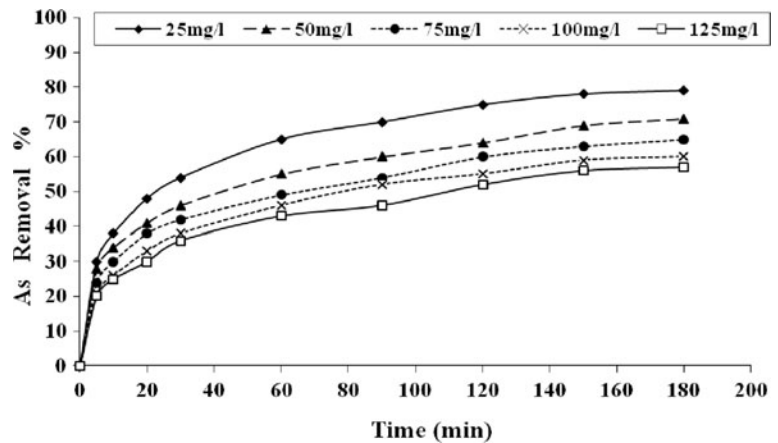
(2007). They found that the optimum biosorption takes place in the pH range of 6–8.

Effect of initial concentration and time on As(V) removal

Effect of initial concentration on As(V) removal by biomass of *R. stricta* was studied at different initial concentrations ranging from 25 to 125 mg l^{-1} keeping pH=5, adsorbent dose (2 g l^{-1}), stirring speed at 150 rpm and different contact times (5–180 min). The removal of As(V), with different concentrations, increased with time and attained the maximum value at about 150 min, and thereafter, it remained almost constant (Fig. 2). It was found that, more than 65 % removal of As(V) in its lower initial concentration (25 mg l^{-1}) occurred in the first 60 min. However, 43 % removal of As (V) was recorded for its higher initial concentration (125 mg l^{-1}). Thus, the removal of As(V) was dependent on the initial concentration and contact time. Further, the removal was rapid in early stages and finally attained almost constant value for longer contact time with negligible effect on the rate of adsorption of As(V) (Fig. 2). Hence, the equilibrium time obtained is 180 min for As(V) removal on *R. stricta* biomass. 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 (surface charge density, porosity and surface area), 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 sites (Say et al. 2003).

It is worth noting that the nature of adsorbent and the available adsorption sites are the most important parameters affecting the rate of adsorption. The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. In the initial stages of adsorption of As(V), the concentration gradient between the film and the available pore sites is large, and hence the rate of adsorption is faster. The rate of adsorption decreases in the later stages of the As(V) adsorption probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent. At low concentration, the ratio of available surface to the initial As(V) concentration is larger, so the removal is higher. However, in case of

Fig. 2 Effect of contact time and initial metal concentration on the adsorption of As(V) by *R. stricta* biomass



higher concentrations, this ratio is low; hence, the As(V) removal percentage is lesser.

A wide range of equilibrium sorption times 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*. Stanic et al. (2009) found arsenic sorption onto an iron (III) modified natural zeolitic stuff was fast, and that most of the As(V) was adsorbed in less than 30 min. 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. 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). However, it is also important to note that if the sorption rate is fast on a particulate biosorbent, this could benefit further application of such a biosorbent in dynamic systems.

Effect of adsorbent dose and initial concentration on As(V) removal

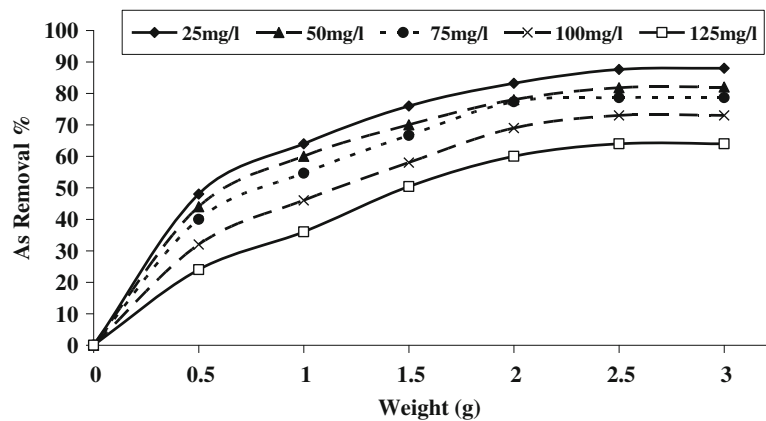
Study on the effect of adsorbent dose for As(V) removal is important to get the trade-off between the adsorbent dose and the percentage removal of As(V) resulting in an optimum adsorbent amount. The influence of adsorbent amount, varying from (1.0, 1.5, 2.0, 2.5 and 3.0 g/l) onto the As(V) adsorption at different initial As(V) concentration (25–125 mg.l⁻¹), is shown in Fig. 3. The results showed that As(V) removal

percentage reached almost 90 % at lower initial concentration (25 mg.l⁻¹) as dose increased from 0.5 to 2.5 g.l⁻¹. However, the removal percentage decreases from 88 to 60 % as the initial As(V) concentrations increased from 25 to 125 mg.l⁻¹. The decrease in the percentage removal of As(V) can be explained with the fact that all adsorbents had a limited number of active sites, which would have become saturated above a certain concentration. Increase of the initial metal concentration results in a decrease in the initial rate of external diffusion and increase in the intra-particle diffusion. The increase in As(V) removal with the adsorbent dose can be attributed to increased surface area and the sorption sites.

Adsorption isotherm study

Adsorption isotherm is important to describe the adsorption mechanism for the interaction of As(V) on the adsorbent surface (Ho et al. 2000). The adsorption isotherm indicates how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches equilibrium state (Bello et al. 2008). The equilibrium studies are useful to obtain the adsorption capacity of *R. stricta* for As(V) removal. An adsorption isotherm is characterized by certain constants that express the surface properties and the affinity of the adsorbent towards As(V) and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants. The equilibrium data for the adsorption of As(V) using *R. stricta* fit into various isotherm models which results in a suitable model that can be used for the design of an adsorption process (Smith 1981). In the present

Fig. 3 Effect of initial metal concentration and adsorbent dose on As(V) removal percentage



study, four equilibrium models are analysed to investigate the suitable adsorption isotherm as the adsorbent developed is new.

Langmuir isotherm

The Langmuir isotherm (Langmuir 1916) has been used extensively by many authors for the adsorption of heavy metals, dyes, organic pollutant and gases onto activated carbon, clay, agriculture wastes, etc. The Langmuir equation is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute on specific homogenous sites of the adsorbent surface containing a finite number of identical sites. The energy of the adsorption is constant, and there is no transmigration of the adsorbate in the plane of the surface (Crini et al. 2007).

The non-linear equation of Langmuir isotherm model can be expressed in the following non-linear form:

$$q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

Where C_e and q_e are as defined above in Eq. (2); K_a is the adsorption equilibrium constant (liters per milligram) that is related to the apparent energy of adsorption; Q_m is the maximum monolayer capacity of the adsorbent (milligrams per gram). Equation (3) can be linearized into four different forms as shown in Table 1 and Eqs. (4)–(7), which give different possibilities to parameter estimation (Kinniburgh 1986).

The results obtained from Langmuir model for the removal of As(V) onto *R. stricta* biomass are represented in Table 2. The correlation coefficients for all linear forms

of Langmuir model are $R^2 > 0.95$ with forms 1 and 2 being the best fitted for the equilibrium data site $R^2 > 0.99$. This high value indicates a good agreement between the experimental values and isotherm parameters and also confirms the monolayer adsorption of As(V) *R. stricta* biomass surface as well as the homogenous nature of biomass surface i-e each molecule of *R. stricta* has equal adsorption activation energy. The essential characteristics of Langmuir isotherm and adsorption favourability can be expressed in terms of dimensionless constant called the separation factor or equilibrium parameter (R_L), which is defined by the following equation (Kadirvelu et al. 2001):

$$R_L = \frac{1}{1 + K_a C_o} \quad (4)$$

Where K_a is the Langmuir constant and C_o is the initial concentration of As(V) with different concentration as mentioned from (25–125 mg.l⁻¹). The value of R_L is found in the range of (0.01–0.014) i-e ($0 < R_L < 1$) which confirms the favourable adsorption process for As(V) removal using *R. stricta* under condition used in this study. The values of R_L are near to zero which favours the irreversible adsorption. Moreover, values of R_L indicate the type of the isotherm to be either unfavourable ($R_L > 1$) or linear ($R_L = 1$). Though the R^2 value obtained is reasonably high (> 0.99) in order to find out if a better fit is possible with other isotherms available in the literature.

Freundlich isotherm

Herbert Max Finlay Freundlich, a German physical chemist, presented an empirical adsorption isotherm

Table 1 The four linear forms of Langmuir model

Form	Linear equation	Plot	Slope	Intercept
Langmuir-1	$\frac{1}{q_e} = \frac{1}{Q_m} + \frac{1}{Q_m K_a} \times \frac{1}{C_e}$ (4)	$1/q_e$ vs. $1/C_e$	$1/Q_m K_a$	$1/Q_m$
Langmuir-2	$\frac{C_e}{q_e} = \frac{1}{Q_m K_a} + \frac{1}{Q_m} \times C_e$ (5)	C_e/q_e vs. C_e	$1/Q_m$	$1/Q_m K_a$
Langmuir-3	$q_e = Q_m - \left(\frac{1}{K_a}\right) \times \frac{q_e}{C_e}$ (6)	q_e vs. q_e/C_e	$1/K_a$	Q_m
Langmuir-4	$\frac{q_e}{C_e} = Q_m K_a - K_a q_e$ (7)	q_e/C_e vs. q_e	K_a	$Q_m K_a$

equation which is based on adsorption on a heterogeneous surface with interaction between adsorbed molecules (Freundlich 1906). The equation can be written in non-linear form as:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{5}$$

Where K_F is the Freundlich constant indicative of the relative adsorption capacity of the adsorbent related to the bonding energy and can be defined as the adsorption or distribution coefficient. It represents the quantity of element adsorbed onto adsorbent for unit equilibrium concentration. The constant “ n ” gives an indication of how favourable the adsorption processes are. The slope $1/n$ is a measure of adsorption intensity or surface heterogeneity that represents the deviation from linearity of adsorption as follows: if the value of $1/n=1$, the adsorption is linear, $1/n<1$, the adsorption process is chemical, if $1/n>1$, the adsorption is a favourable physical process

Table 2 Isotherm parameters obtained from the four linear forms of Langmuir model for the adsorption of As(V) onto *R. stricta*

Isotherm model	Isotherm parameters	<i>R. stricta</i> biomass concentrations	
		2.0 g l ⁻¹	3.0 g/l
Langmuir-1	Q_m (mg g ⁻¹)	149.000	101.500
	$K_a \times 10^3$ (l mg ⁻¹)	66.780	85.750
	R^2	0.994	0.998
Langmuir-2	Q_m (mg g ⁻¹)	162.000	162.000
	$K_a \times 10^3$ (l mg ⁻¹)	56.720	59.590
	R^2	0.995	0.998
Langmuir-3	Q_m (mg g ⁻¹)	154.000	187.000
	$K_a \times 10^3$ (l mg ⁻¹)	0.062	0.091
	R^2	0.956	0.979
Langmuir-4	Q_m (mg g ⁻¹)	161.100	100.600
	$K_a \times 10^3$ (l mg ⁻¹)	56.830	87.960
	R^2	0.964	0.963

and adsorption is cooperative (Crini et al. 2007). Equation (5) is conventionally used in the linear form by taking the logarithmic of both sides as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

Therefore, a plot of $\log q_e$ versus $\log C_e$ enables the constant K_F and n to be determined (Fig. 4) and the coefficients isotherm in Table 3. The correlation coefficients, $R^2>0.96$, obtained from Freundlich model are comparable to that obtained from Langmuir model linear form (Fig. 5). This result indicates that the experimental data fitted well to Freundlich model but is not good as Langmuir model. The value $1/n>1$ indicates that the adsorption is a favourable physical process (Crini et al. 2007). However, it signifies that the surface of the plant biomass under investigation is heterogenous in nature and corresponds to the L-type of normal Langmuir isotherm (Khalid et al. 2000; Fytianos et al. 2000).

Comparing with other biomasses, the biosorption capacity of As(V) by *Lessonia nigrescens* at low pH (2.5) was explained satisfactorily both by the Freundlich and the Langmuir isotherms (Hansen et al. 2006).

Tempkin isotherm

Tempkin isotherm equation (Tempkin and Pyzhev 1940) contains a factor that explicitly takes into account adsorbing species–adsorbate interactions. It assumes that: the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate–adsorbate repulsions and the adsorption is a uniform distribution of maximum binding energy (Kavitha and Namasivayam 2007). In addition, it assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. It has commonly been written in the following equations (Aharoni and Sparks 1991).

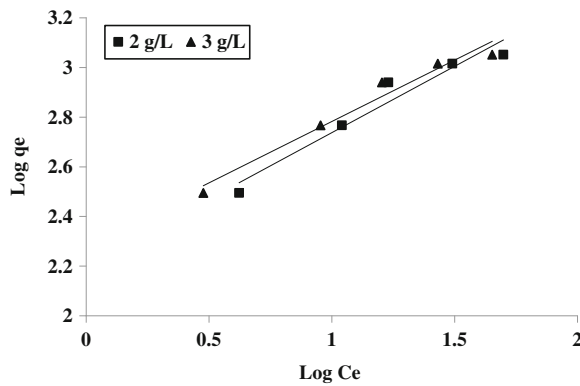


Fig. 4 Freundlich isotherm of As(V) adsorbed onto *R. stricta*

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \text{ (non-linear form)} \tag{7}$$

$$q_e = B_T \ln A_T + B_T \ln C_e \text{ (linear form)} \tag{8}$$

Where $B_T = (RT)/b_T$, T is the absolute temperature in Kelvin and R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. The constant b_T is related to the heat of adsorption; A_T is the equilibrium binding constant (liters per minute) corresponding to the maximum binding energy (Akkaya and Ozer 2005). The adsorption data can be analysed according to Eq. 8. A plot of q_e versus $\ln C_e$ at constant temperature enables the determination of the isotherm constants A_T and b_T and represented in Fig. 6, and the value of constants and correlation coefficients are

Table 3 Comparison of the coefficients isotherm parameters using different isotherm models for As(V) adsorption onto *R. stricta*

Isotherm model	Isotherm parameters	<i>R. stricta</i> biomass concentrations	
		2.0 g/l	3.0 g/l
Freundlich	$1/n$	1.76	1.96
	n	0.57	0.51
	K_F	17.62	19.43
	R^2	0.971	0.980
Tempkin	A_T	0.167	0.121
	B_T	34.5	22.5
	b_T	71.7	109.9
	R^2	0.989	0.992
Generalized form	N_b	0.369	0.459
	K_G	37.23	32.56
	R^2	0.981	0.982

reported in Table 3. The correlation coefficients $R^2 = 0.989$ and 0.992 confirm the better fit of equilibrium data as compared with the Freundlich isotherm model. But Tempkin isotherm model is not good as Langmuir 1 and 2.

Generalized isotherm equation

A generalized isotherm equation was tested for correlation of the equilibrium data (Kargi and Cikla 2006). Linear form of the generalized isotherm is given by:

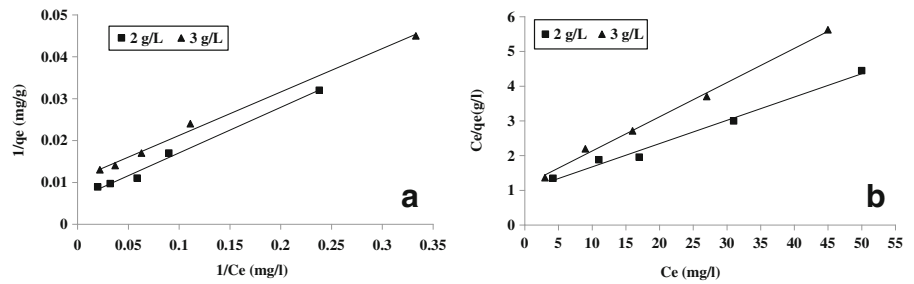
$$\log \left[\frac{Q_m}{q_e} - 1 \right] = \log K_G + N_b \log C_e \tag{9}$$

Where K_G is the saturation constant (milligrams per liter); N_b the cooperative constant; Q_m the maximum adsorption capacity of the adsorbent (milligrams per gram; obtained from Langmuir isotherm model); q_e (milligrams per gram) and C_e (milligrams per liter) are the equilibrium As(V) concentrations in the solid and liquid phases, respectively. Figure 7 shows a plot of $\log [(Q_m/q_e) - 1]$ versus $\log C_e$; the intercept gave $\log K_G$ and the slope gave N_b constants. Parameters related to each isotherm were determined by using linear regression analysis, and the square of the correlation coefficients (R^2) have been calculated. A list of the parameters obtained together with R^2 values is given in Table 3. Apparently, the generalized adsorption represents the equilibrium data reasonably well. The R^2 values were 0.981 and 0.982 which reflects that the generalized isotherm showed less agreement with the experimental data compared with Langmuir 1 and 2 isotherms.

Final remarks on isotherm study

The experimental equilibrium data are found to be fitted well with the Langmuir (1 and 2) isotherm model which indicates the monomolecular adsorption of As(V) onto *R. stricta*. It is also fitting with other isotherm models in the order of Tempkin > Generalized form > Freundlich. Equilibrium relationship is required in designing of fixed-bed adsorption column which yields the difference in liquid-phase concentration and equilibrium solid-phase concentration (driving force). This driving force is required to evaluate the amount of As(V) accumulated on solid surface which is needed to obtain the liquid-phase concentration of As(V) at any given time. Adsorption isotherm also

Fig. 5 Langmuir-1 (a) and Langmuir-2 (b) isotherm models of As(V) adsorbed onto *R. stricta*



characterizes the shape of the breakthrough curve which is a dominant design parameter in designing of fixed-bed adsorption column. If the isotherm is favourable, the breakthrough curve becomes steeper which results in a decrease in the length of unused bed and higher percentage removal of As(V) of the fixed-bed adsorption column.

Adsorption kinetics

The knowledge of the kinetics of any adsorption process is crucial in order to be able to design industrial-scale separation processes. The study of adsorption dynamics describes the solute uptake rate, and evidently this rate controls the residence time of adsorbate uptake at solid–solution interface. Batch experiments were conducted to explore the rate of As(V) adsorption by *R. stricta* at pH=5 and plant biomass of 1, 1.5, 2, 2.5 and 3 g. l⁻¹ and initial metal concentrations of 25–125 mg.l⁻¹. The process of metal removal from aqueous phase by certain adsorbent may be investigated by several models to examine the rate-controlling of the adsorption process such as chemical reaction, diffusion control and mass transfer. Since the kinetic parameters are used to predict the adsorption

rate and give important information for designing and modeling of the adsorption processes, the kinetics of the adsorption of As(V) onto *R. stricta* was investigated for selecting optimum operating conditions for full-scale batch process. Pseudo first-order (Lagergren 1898) and Elovich (Sparks 1986) kinetic models were applied for the adsorption of As(V), and the conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2).

Pseudo first-order equation

The Lagergren pseudo first-order model (Lagergren 1898) is the earliest known equation describing the adsorption rate based on the adsorption capacity. The differential equation is commonly expresses as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{10}$$

Where q_e and q_t refer to the amount of As(V) adsorbed (milligrams per gram) at equilibrium and at any time, t (minute), respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption (liters per minute). Integrating Eq. (14)

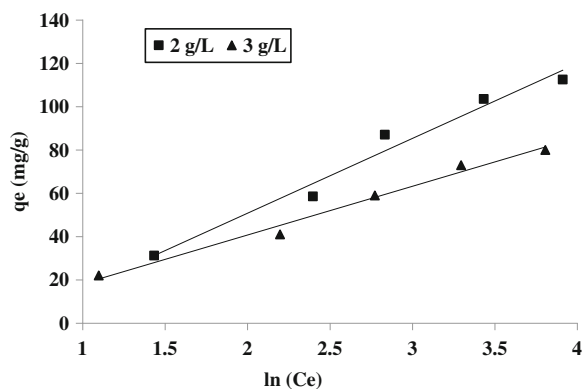


Fig. 6 Temptkin equilibrium isotherm model for the adsorption of As(V) onto *R. stricta*

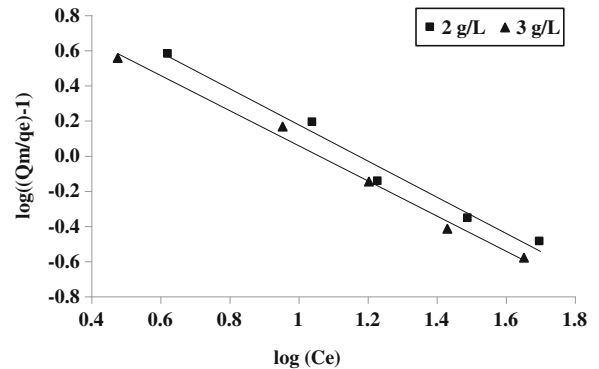


Fig. 7 Generalized isotherm model

for the boundary conditions $t=0$ to t and $q_t=0$ to q_t gives:

$$\log\left(\frac{q_e}{q_e - q_t}\right) = \frac{k_1}{2.303}t \tag{11}$$

Which is the integrated rate law for a pseudo first-order reaction.

Equation (11) can be rearranged to obtain the linear form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \tag{12}$$

Values of the rate constant, k_1 , equilibrium adsorption capacity, q_e , and the correlation coefficient, R^2 , were calculated from the plots of $\log(q_e - q_t)$ versus t (Fig. 8). Although the correlation coefficients obtained from pseudo first-order model are found to be not high, the calculated q_e agree with experimental values (Table 4). This indicates that adsorption of As(V) onto *R. stricta* is ideal pseudo first-order reaction (Crini et al. 2007).

Elovich kinetic equation

Elovich equation is a rate equation based on the adsorption capacity commonly expressed as following Eq. (13) (Sparks 1986):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{13}$$

Where α is the initial adsorption rate (milligrams per gram per minute) and β the desorption constant (grams per milligram) related to the extent of surface coverage and activation energy for chemisorptions.

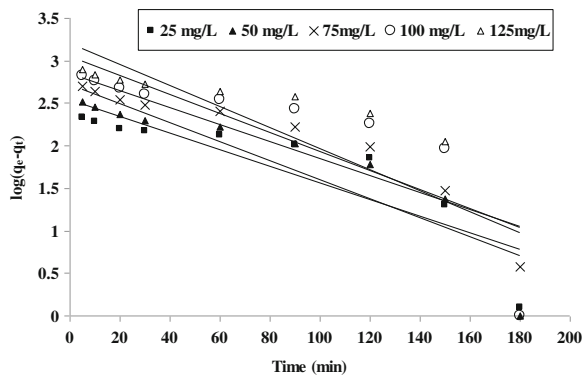


Fig. 8 Pseudo first-order kinetics for As(V) adsorption onto *R. stricta*. Conditions: adsorbent dose, pH 5.0, temperature 25±2 °C

Table 4 Comparison of the first-order adsorption rate constant and calculated and experimental q_e values for different initial As(V) and biomass of *R. stricta*

Parameter	First-order kinetic model					
	Biomass dose	As(V), mg l ⁻¹	q_e (exp)	$K_1 \times 10^3$	q_e (calc.)	R^2
1.0	25	25	34.1	4.47	33.5	0.87
	50	50	36.9	4.32	34.1	0.86
	75	75	41.2	4.13	39.5	0.86
	100	100	46.7	3.67	43.1	0.85
	125	125	50.1	3.79	47.5	0.87
1.5	25	25	35.2	4.19	33.9	0.89
	50	50	38.7	4.06	37.5	0.88
	75	75	40.2	3.94	38.2	0.88
	100	100	42.2	3.75	40.4	0.89
	125	125	48.5	3.69	46.9	0.89
2.0	25	25	31.1	4.29	30.1	0.88
	50	50	32.7	4.17	31.2	0.88
	75	75	32.2	3.91	31.9	0.87
	100	100	35.9	3.69	33.4	0.89
	125	125	36.5	3.34	34.1	0.88
2.5	25	25	30.1	4.21	28.9	0.89
	50	50	31.5	4.02	29.4	0.88
	75	75	32.9	3.95	31.1	0.88
	100	100	33.9	3.78	32.6	0.89
	125	125	37.1	3.56	35.5	0.89
3.0	25	25	28.7	4.29	27.5	0.90
	50	50	29.8	4.21	28.1	0.89
	75	75	31.1	4.09	29.0	0.89
	100	100	32.4	3.96	30.1	0.90
	125	125	35.3	3.73	33.2	0.90

Equation (13) is simplified by assuming $\alpha\beta \gg t$ and by applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$ becomes:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \tag{14}$$

Figure 9 depicts plot of q_t versus $\ln(t)$, and the Elovich constants α and β were obtained from the intercept and the slope, respectively, and reported in Table 5. The correlation coefficients R^2 are higher than 0.94, which is comparable to correlation coefficients obtained for pseudo first-order model. This reflects the applicability of this model to the experimental data obtained for the adsorption of As(V) onto *R. stricta*.

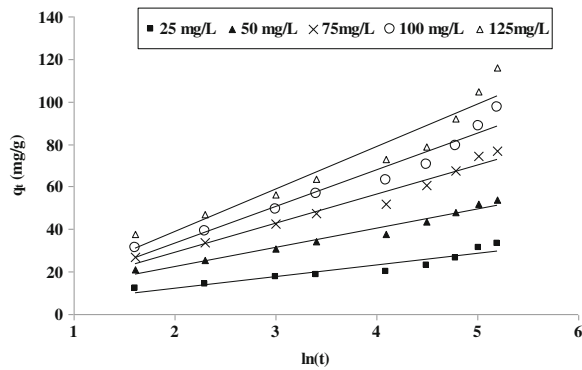


Fig. 9 Elovich model plot for the adsorption of As(V) onto *R. stricta* (3 g l⁻¹) at different initial As(V) concentrations (25, 50, 75, 100, 125 mg l⁻¹)

Table 5 The parameters obtained from Elovich kinetics model using different initial As(V) concentrations and biomass doses

Parameter		Elovich kinetic model		
Biomass doses	As(V), mg l ⁻¹	β	α	R^2
1.0	25	0.18	2.18	0.953
	50	0.16	2.09	0.951
	75	0.15	2.01	0.949
	100	0.12	1.99	0.952
	125	0.11	1.87	0.942
1.5	25	0.21	2.11	0.956
	50	0.19	2.31	0.954
	75	0.17	2.59	0.960
	100	0.15	2.87	0.960
	125	0.14	2.99	0.952
2.0	25	0.25	2.09	0.946
	50	0.23	2.22	0.945
	75	0.20	2.41	0.940
	100	0.18	2.52	0.946
	125	0.16	2.69	0.942
2.5	25	0.32	1.99	0.943
	50	0.29	2.15	0.942
	75	0.23	2.31	0.941
	100	0.19	2.43	0.942
	125	0.17	2.47	0.942
3.0	25	0.51	2.11	0.944
	50	0.46	2.32	0.942
	75	0.32	2.53	0.945
	100	0.26	2.71	0.941
	125	0.21	2.82	0.942

The biosorption of As(V) from aqueous solutions by pine sawdust chemically modified with iron in batch systems was investigated by Lopez Leal et al. (2012). 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.

Biosorption studies using industrial wastewater

To study the effect of other ions on the As(V) removal by *R. stricta*, real wastewater was collected from an outfall of second industrial area in Riyadh City, KSA. The physico-chemical characteristics of industrial wastewater are given in Table 6. The As(V) concentration in the industrial wastewater was 27 mg l⁻¹. pH of this wastewater was adjusted to 5 with HCl after filtration, and adsorbent dose was maintained at 3.0 g l⁻¹ for 3 h. Percent removal was found to be 52 % for industrial wastewater which was much lower as compared to the simulated sample (as mentioned in Fig 2). The difference between the As(V) uptake from the simulated sample and the effluent may be attributed to the presence of other ions and impurities like Mn, Fe, Cd, Zn and Ni as indicated in the Table 6 which may compete with As(V) for binding sites thus leading to lesser As(V) removal in the effluent making the metal unavailable for the adsorption by the adsorbents. While in the

Table 6 Physico-chemical analysis of industrial wastewater

Parameter	Characteristics
Color	Dark brown
pH	6.4
Total solids (mg l ⁻¹)	14,000
Suspended solids (mg l ⁻¹)	1,600
Dissolved solids (mg l ⁻¹)	12,300
BOD (mg l ⁻¹)	<2.0
COD (mg l ⁻¹)	<2.0
Chromium as Cr(VI) (mg l ⁻¹)	16
Cadmium ad Cd (mg l ⁻¹)	1.8
Iron as Fe (mg l ⁻¹)	42
Zinc as Zn (mg l ⁻¹)	12.8
Nickel as Ni (mg l ⁻¹)	6.1
Copper as Cu (mg l ⁻¹)	2.1

aqueous solution, only As(V) metal ions are present, so the binding sites were occupied by only As(V) ions, thus leading to higher percent removal from synthetic wastewater.

Conclusion

Utilization of plant biomass such as *R. stricta* for the removal of As(V) from the industrial wastewater stream is investigated. The percentage removal was found to be dependent on pH, the quantity of adsorbent, time and initial concentration of the sorbate. The process of uptake was maximum at pH 5. The removal of As(V) increased with time and attained the maximum value at about 150 min. Also, more than 65 % removal of As(V) in its lower initial concentration (25 mg l⁻¹) occurred in the first 60 min. The results showed that As(V) removal percentage reached almost 90 % at lower initial concentration (25 mg.l⁻¹) as dose increased from 0.5 to 2.5 g/l. The equilibrium adsorption data are tested with various isotherm models. The data are found to be fitted well with the Langmuir (1 and 2) isotherm model which indicates the monomolecular adsorption of As(V) onto *R. stricta*. It is also fitting with other isotherm models in the order of Tempkin>Generalized form>Freundlich. With respect to the suitability of the pseudo first-order and the Elovich models, it has been found that the adsorption of As(V) preferably obeys Elovich model which provides good correlation coefficients, higher than 0.94. This reflects the applicability of this model to the experimental data obtained for the adsorption of As(V) onto *R. stricta*. Also, the calculated q_e from pseudo first-order agrees well with the experimental data. The data thus obtained may be helpful for designing and establishing a continuous treatment plant water and wastewater enriched in As(V). The cost of removal is expected to be quite low as the adsorbent is cheap and easily available in large quantities.

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