King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Equilibrium and thermodynamic studies for the removal of As(V) ions from aqueous solution using dried plants as adsorbents

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Abstract This paper reports the feasibility of using dried plants to remove As(V) from aqueous solution under different experimental conditions. For this purpose, micro-particles of both *Calami rhizoma* and *Withania frutescens* plants, have been separately used without pre-treatment as natural adsorbents. Effect of various process parameters, namely adsorbent dose, contact time, initial As(V) concentration, temperature, and pH has been studied. The experimental data were analyzed using Freundlich, Langmuir, and Temkin isotherm models to determine the mechanistic parameters related to the adsorption process. It was found that the Langmuir and Freundlich models fitted well. Thermodynamic parameters, viz, free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0), were also determined. The negative values of free energy change indicated the spontaneous nature of the adsorption and the positive values of enthalpy change suggested the endothermic nature of the adsorption process. The presence of some competing ions like Cl^-, NO_3^-, Mg^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} did not affect the arsenate uptake or removal, whereas HPO_4^{2-} strongly interfered negatively.

1. Introduction

Heavy metal pollution of surface water and wastewater is a common environmental threat, since the toxic element ions dissolved can eventually reach the top of the food chain and thus become a risk factor for human health. Arsenic is one of the most toxic metal ions and possesses a serious health risk in many countries of the world, which could increase the risk of skin, lung, and kidney cancer (Chen et al., 1992). The major source of arsenic pollution in the environment is the smelting of ores such as those of gold, silver, copper, and others.

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Arsenic from these sources is distributed in the air, water, and soil and finds its way into the human system by way of direct inhalation or through contamination of food and consumer products. The World Health Organisation (WHO) recommended that many authorities reduce their regulatory limits and it has established a provisional guideline value of 10 μg/l for arsenic in drinking water. For example in Europe (Directive 98/83/CE), and in the USA (United States Environmental Protection Agency, 2001), where they were lowered from 50 to 10 μg As/l (0.13 μM) (WHO, 2004). Processes to remove excess arsenic from drinking water and wastewater are therefore urgently required. Arsenic exists in both organic and inorganic forms in nature; inorganic arsenic is mostly found in natural water systems. Generally, inorganic arsenic has two different oxidation states, that is, trivalent and pentavalent, in natural aqueous systems (Elizalde-Gonzalez et al., 2001; Chutia et al., 2009). The mobility of arsenical forms in water is very dependent on pH, Eh conditions and the presence of different chemical species (Smedley et al., 2002). Pentavalent arsenic (As(V), arsenate) is stable in oxidative condition and exists as a monovalent ($H2AsO_4^-$) or divalent ($HAsO_4^{2-}$) anion, while trivalent arsenic (As(III), arsenite) is stable in reductive conditions (Grossl et al., 1997) and exists as an uncharged ($H_3AsO_3^0$) or anionic species ($H_2AsO_3^-$). Generally, inorganic arsenic is more toxic than organic arsenic, and As(III) is approximately 10 times more toxic than As(V) (Pontius et al., 1994).

Many various physicochemical techniques have been developed to remove arsenic from both water and wastewater. The conventional methods used to remove arsenic are membrane techniques (reverse osmosis, nanofiltration, etc.), oxidation/precipitation (hydroxides, sulfides, etc.), coagulation and flocculation, ion-exchange, adsorption by activated carbon (Nguyen et al., 2009; Choonga et al., 2007; Fierro et al., 2009; Hossain, 2006; Mohan and Pittman, 2007; Atkinson, 2006; Mondal et al., 2006; Sun et al., 2006), etc. However, these methods have several disadvantages, which include incomplete metal removal, high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries. Adsorption processes are effective techniques and they have long been used in water and wastewater industries to remove inorganic and organic pollution for easy handling, minimal sludge production and its regeneration capability. Liquid-phase adsorption is one of the most efficient

methods for the removal of toxic pollutants from industrial effluents. Granular or powdered activated carbon is the most widely used adsorbent (Fierro et al., 2009) but its use is usually limited due to high cost. That is why increasing attention and this problem have led many workers to search for cheaper adsorption substitutes including natural raw materials (chitosan, alginate, biomass, etc.), clays (clinoptilolite, montmorillonite, kaolinite, etc.), and agricultural or industrial wastes (red mud, fly ash, lignite, peat, bone char, rice polish, etc.) (Mohan and Pittman, 2007; Ranjan et al., 2009; Carja et al., 2008; Chen et al., 2008; Genc-Fuhrman et al., 2004; Mohan et al., 2007), due to their local abundance and low cost. There are large numbers of studies in the literature in which various adsorbents are used for the removal of arsenic from aqueous solution. Two recent reviews reported by Mohan et al. (2007) and Hossain (2006) can be referred for the other possible adsorbents for the removal of arsenic oxyanions. Although these materials are regarded as cheap and effective adsorbents, there are several problems (their impurities, unknown stability and regeneration, low adsorption capacity and slow kinetics) associated with their use (Ranjan et al., 2009; Chen et al., 2008; Rahaman et al., 2008; Gimenez et al., 2007). For the past few years, the focus of the research is to use cheap materials as potential adsorbents and the processes developed so far are based on exploring those natural adsorbents, which can prove economic and bring cost effectiveness (Benhima et al., 2008).

Removal of heavy metals by these materials might be attributed to their protein, carbohydrates, and phenolic compound contents, which have metal-binding functional groups such as carboxyl, hydroxyl, sulfate, phosphate, and amino groups (Shin et al., 2007). Mohan and Pittman (2007) observed that the loss of metal ions from their solutions in the presence of natural materials may be due to the adsorption on surface and pores, and to complexation by these materials.

In our previous works, we have investigated the biochemical composition of some inert plants (Chiban et al., 2007) and also the adsorption of phosphate, nitrate, cadmium, and lead from aqueous solutions onto micro-particles of dry plants (Benhima et al., 2008; Chiban et al., 2005, 2011a). In this paper, we have tested the removal of arsenate on two dried plants as low cost adsorbents collected from two different regions; *Calami rhizoma* as Romanian plant and *Withania frutescens*

as Moroccan plant, in order to compare the uptake capacities of these materials as well as with the one obtained by different authors in the literature. In this meaning, the kinetics of adsorption, the adsorption isotherms as well as the influence of several parameters such as: contact time, initial concentration, pH, temperature on the adsorption of arsenate by both dried plants individually was studied. The effect of some anions and cations on the adsorption of arsenate onto both dried plants was also presented.

2. Materials and methods

2.1. Adsorbent preparation

The low-cost materials used in the present work were obtained from dried plants such as *C. rhizoma as* Romanian plant and *W. frutescens* as Moroccan plant. A recent screening (Chiban et al., 2007, 2011b) for chemical composition and surface characterization has shown that the major functional groups on *W. frutescens* plant are polar hydroxyl, aldehydic, and carboxylic groups. These groups have made these plants to have great potential as adsorbents for cations and anions ions in aqueous solutions. In addition, the micro-particles of these plants are also known to be non-toxic (Ahmad et al., 1990) and their selection was made in relation to their relative abundance in all the zones where they are considered as a worthless matter. The plant parts (leaves and stems) were dried under permanent air-conditioning during 1 week. These organs were chopped into small fragments, then washed several times with double distilled water and again dried in an oven at 35 °C during 24 h. After drying, the organs were pulverized with an electric grinder to get fine powders. The micro-particles of these dried plants are used as adsorbent materials in batch experiments without any pre-treatment to avoid extra expenditure.

2.2. Solution preparation

Stock solution of arsenate (1 g/l) was prepared by dissolving 4.164 g of sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$, Sigma, product of USA) in double distilled water to make a solution volume of 1 l. The aqueous solution was diluted with double distilled water to obtain the As(V) synthetic solution of desired concentration. Other agents used, such as KNO_3, NaCl, $Na_2HPO_4 \cdot 12H_2O$, $Na_2SO_4 \cdot 10H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ were all of analytical grade and without further purification. All experiments employed double distilled water.

2.3. Instrumentation

A UV–Vis Spectrophotometer (Jasco, model V-550, Japan) was employed to measure residual arsenate ion concentrations. The pH of the solutions was measured with Titroline (SCHOTT instruments) pH meter with a glass electrode. A mechanical shaker model Labotec was used for shaking the adsorption batches. The centrifuge HETTICH model EBA 21 was used to separate the micro-particles of plants from the solutions after complete adsorption experiments. An analytical balance Precisa model XT 220A was used for weighting the dried plants and salts samples.

2.4. Experimental procedure

2.4.1. Adsorption studies

Adsorption experiments were made by a batch technique at room temperature (except when the effect of temperature was studied). The batch mode was selected because of its simplicity and reliability. Known amounts of dried plant were placed in different stoppered Erlenmeyer glass flasks of 100 ml capacity containing 40 ml of As(V) anion solution of known concentration and pH. The solutions were shaken vigorously for a given time period to reach equilibrium. The agitation speed was kept constant for each run to ensure equal mixing. After contact time t (T_c, min), the Erlenmeyer containing the sample was withdrawn from the shaker, the suspensions were centrifuged at 5000 rpm for 10 min and the supernatant was filtered through a Whatman filter paper. The filtrates were then prepared for analysis according to the molybdate blue method (Lenoble et al., 2003). The concentration of unadsorbed As(V) in the filtrate was analyzed by the UV spectrophotometer at a wavelength of 842 nm. The concentration of As(V) removed (C_r) from aqueous solutions was calculated by the difference of initial concentration, C_i, and the concentration at time t ($C_r = C_i - C_t$). The removal percentage of arsenate from aqueous solutions (%) on micro-particles of both plants was calculated from:

$$\% \text{ Removal} = \frac{C_i - C_t}{C_i} \times 100$$

The amount of arsenate adsorbed on a given adsorbent (Q_t, mg/g) is calculated by the following equation:

$$Q_t = \frac{C_i - C_t}{m} \times v$$

where C_i is the initial concentration of arsenate in the feed solution (mg/l), C_t is the concentration of arsenate in solution at a given time t (mg/l), v is the total volume of the feed solution (ml); and m is the weight of the adsorbent (g).

At adsorption equilibrium, arsenate concentration in the feed C_t becomes the equilibrium concentration C_e and adsorbed amount Q_t becomes Q_{max}.

Adsorption experiments for the effect of solution pH were conducted as follows: 1 g of dried plant was suspended in 40 ml of arsenate solutions containing 100 mg/l for both dried plants separately. The pH of the solution was adjusted to 2–12 by adding dilute solution of hydrochloric acid or sodium hydroxide (0.5 M NaOH or 0.5 M HCl), the agitation time was fixed to 12 h and the temperature was 22 ± 2 °C.

Adsorption isotherm studies were conducted by adding 1 g of both dried plants individually in the solution containing 40 ml with various initial concentrations of As(V) at different temperatures. The initial arsenate concentrations ranged between 200 and 1000 mg/l and the temperature of the solutions ranged from 25 to 40 °C.

The effect of competing ions (cations and anions) on the removal of arsenate was tested at room temperature. Arsenate solutions containing different competing ions individually (i.e., Cl^-, NO_3^-, SO_4^{2-}, HPO_4^{2-}, Mg^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+}) were prepared by dissolving various amounts of their salts in arsenate solutions (100 mg/l). The initial concentrations of coexisting ions are the same as initial As(V) concentration at pH 6. at pH 6. 1 g, different concentrations were then added to each of the solutions in 100 ml Erlenmeyer and the

suspensions were stirred for 12 h. After filtering the suspensions through membrane filters, the concentrations of arsenate in the filtrates were determined as before.

2.4.2. Desorption studies

Desorption of As(V) was carried out as follows: a series of an Erlenmeyer that contained 1 g of adsorbent were treated with 40 ml As(V) solution (100 mg/l). The arsenate-loaded adsorbents were filtered after 12 h of contact time and washed gently several times with double distilled water to remove any excess of unadsorbed As(V). It was then treated with 20 ml of hydroxide solution at different concentrations (0.01–0.07 M) for a period equal to the adsorption time and then filtered. The volumes used for adsorption and for desorption were, respectively, V_a = 40 ml and V_d = 20 ml and the ratio V_d/V_a equaled 0.5 (Elizalde-Gonzalez et al., 2001; Lenoble et al., 2002). The filtrates were analyzed for As(V) desorbed. The amounts desorbed of arsenate are calculated by the following equation:

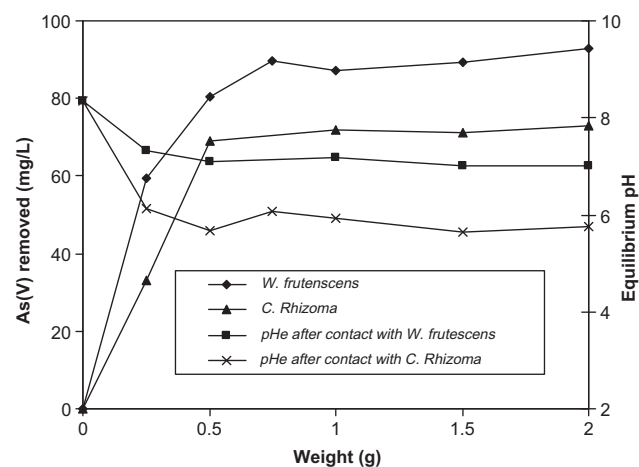$$\% \text{ Desorption} = \frac{\text{released As(V)(mg/l)}}{\text{initially As(V)adsorbed(mg/l)}} \times 100$$

2.4.3. Regeneration studies

One gram of adsorbent was treated with 40 ml As(V) solution (100 mg/l) in an Erlenmeyer and after equilibrium time (12 h) was filtered. The adsorbent was then treated with 20 ml NaOH solution (0.07 M) for a period equal to the adsorption time. It was filtered and the filtrate was then analyzed for As(V) desorbed. The adsorbent was washed several times with double distilled water in order to remove any excess of NaOH. It was again treated with 40 ml of As(V) solution at 100 mg/l.

3. Results and discussion

3.1. Effect of adsorbent mass

Fig. 1 shows the arsenate ions removal and pH final of medium as a function of adsorbent mass using batch adsorption technique. These graphs show the increase of As(V) ions removal against the increase in the weight of both dried plants up to a weight of 1 g for 100 mg/l of arsenate initial concentration. The arsenate adsorption for an agitation time of 12 h increased from 59% (2.36 mg/g) to 91% (3.64 mg/g) and 33% (1.32 mg/g) to 72% (2.88 mg/g) when the adsorbent amount was increased from 0.25 to 1 g for C. rhizoma and W. frutescens, respectively. Increasing the amount of the adsorbent makes a large number of sites available leading to an increase in adsorption. There are many factors that can contribute to this adsorbent concentration effect. The most important factor is that adsorption sites remain unsaturated during the adsorption reaction. This is due to the fact that as the mass of adsorbent is increased, there is a less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent. It is also seen from Fig. 1 that pH of solution after contact with both dried plants decreased and remained nearly constant at about 6 for C. rhizoma and 7 for W. frutescens. This difference can be explained by the difference in the chemical composition of these plants. In order to achieve experiments for maximum retention of the As(V) ions, the plant weight has been chosen to be 1 g in all experiments.

3.2. Effect of contact time and initial concentration

The contact time of adsorbate and adsorbent has a great importance in adsorption, because it depends on the nature of the system used. Figs. 2 and 3 show the effect of contact time on batch adsorption of different initial arsenate concentrations ranging between 0.1 and 1 g/l at ambient temperature for W. frutescens and C. rhizoma, respectively. The pH of the solutions was not fixed but measured before and after each experiment. The amount of As(V) adsorbed increases very rapidly up to about 120 min and slowly reaches saturation at about 180 min. The adsorption of As(V) remained constant after 180 min implying that equilibrium had been reached. The plots also show that the time of equilibrium as well as time required to achieve a definite fraction of equilibrium adsorption is independent of the initial concentration. With the increase in the initial concentration of As(V) from 0.1 to 1 g/l, the amount adsorbed increased from 3.04 mg/g (73%) to 16.88 mg/g (42%) for W. frutescens and from 3.64 mg/g
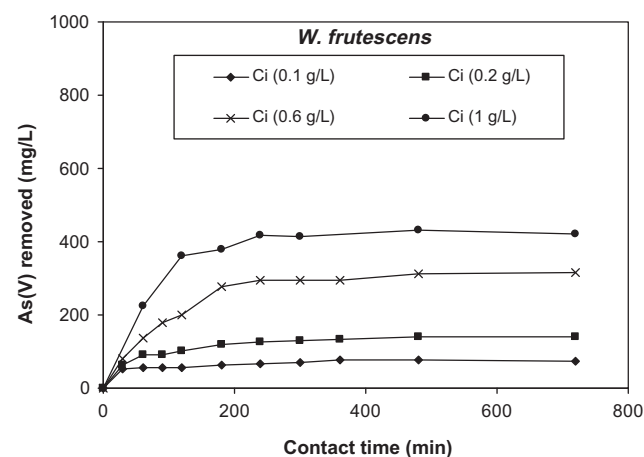

Figure 1 Effect of amount of both dried plants individually on the adsorption of As(V) at initial As(V) concentration, 100 mg/l; temperature, 22 °C; contact time, 12 h; and initial pH_i = 8.3.
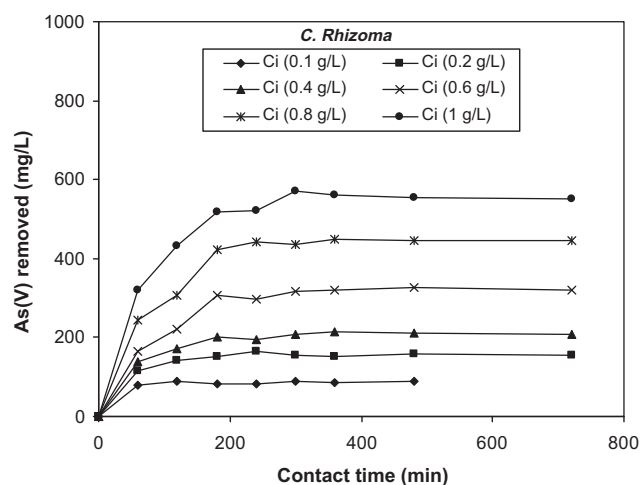

Figure 2 Effect of contact time and initial arsenate ion concentration on the removal of As(V) by W. frutescens: m/v = 25 g/l, pH_i = 8.3, and temperature ~22 °C.

(91%) to 22.04 mg/g (55%) for *C. rhizoma*. At higher initial concentration the available sites of adsorption become fewer and hence the percentage adsorption depends on the initial concentration. These values depend to some extent on the type of plant. For a fixed adsorbent dose, the total available adsorption sites are limited, there by adsorbing almost the same amount of the adsorbate, thus resulting in a decrease in percentage adsorption corresponding to an increase in initial adsorbate concentration. The increase of loading capacities of adsorbents with the increase of arsenate ion concentration is probably due to higher interaction between arsenate ions and adsorbent. The fast adsorption kinetics observed for both adsorbents represents a key advantage for designing water treatment systems based on this principle. In comparison, the equilibrium time for the adsorption of As(V) by some other adsorbents in the literature is acceptable. For example, Ranjan et al. (2009), using agricultural residue 'rice polish' for biosorption of arsenic from aqueous solution, found that the equilibrium time needed for As(III) and As(V) sorption on rice polish was 60 and 40 min, respectively. Gimenez et al. (2007) using different natural iron oxides for the removal of both As(III) and As(V) oxyanions, found that equilibrium was reached in less than 2 days and the kinetics of sorption seems to be faster for goethite and magnetite than for hematite. However, the results from Jeon et al. (2009) were similar to those found in this investigation.

3.3. Effect of solution pH

One of the most critical parameters in the adsorption process of arsenic ions from aqueous solutions is the pH of the medium (Gimenez et al., 2007). The initial pH of adsorption medium is related to the adsorption mechanisms onto the adsorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the adsorptive sites of adsorbents (Sari and Tuzen, 2009). The standard range of pH in drinking water varies from 6.5 to 8.5 (Menhage-Bena et al., 2004) and therefore the investigation of the effect of a wide range of pH on arsenate removal is needed. Hence, the effect of initial pH on the uptake capacities
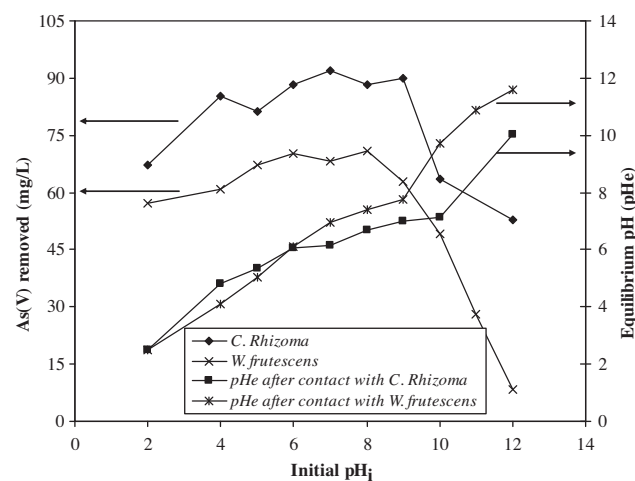
of As(V) on both dried plants was studied at room temperature. The pH range studied was between 2.0 and 12.0 for 100 mg/l of initial As(V) concentration. Equilibrium pH (pH_{final}) values as well as the retained arsenate concentration, C_r (mg/l), are measured and the results are presented in Fig. 4. It is clear that the pH of the medium affected the adsorption of arsenate by the adsorbents and the micro-particles of the plants used as adsorbents shown to be effective for the quantitative removal of As(V) at pH ranging from 6 to 9. It was found that in the lower pH range (below 9.0) the adsorption of arsenate was good, but above pH 9.0, the adsorptivity decreases sharply. This can be due to the fact that at the higher pH range there is a competition between the hydroxyl ions present at higher pH and arsenic species, for the adsorption sites. In addition, the carboxyl, hydroxyl, and amide groups of the plants will be negatively charged in alkaline conditions. Therefore, there exists a repulsive force between the negatively charged adsorbent and anionic species of arsenic, resulting in reduced adsorption efficiency (Rahaman et al., 2008). For both adsorbents, the pH_{final} increases smoothly with the increase of $pH_{initial}$ (Fig. 4). However, in case of *C. rhizome* adsorbent, a plateau is found up to pH 6 and then again starts to increase with initial pH (Fig. 4). In both cases, arsenate uptakes increase up to near pH 6 and afterward decrease with the increase of pH. At pH 6, maximum arsenate removal percent of 70% and 89% is obtained for *W. frutescens* and *C. rhizoma*, respectively. As(V) speciation is affected by the solution pH through the following equilibrium (Yusof and Malek, 2009):

$$H_3AsO_4 \leftrightarrow H_2AsO_4^- + H^+, \qquad pK_{a1} = 2.3 \qquad (1)$$

$$H_2AsO_4^- \leftrightarrow HAsO_4^{2-} + H^+, \qquad pK_{a2} = 6.8 \qquad (2)$$

$$HAsO_4^{2-} \leftrightarrow AsO_4^{3-} + H^+, \qquad pK_{a3} = 11.6 \qquad (3)$$

From Eqs. (1)–(3), the As(V) species occurs mainly in the form of $H_2AsO_4^-$ in the pH range between 3 and 6, while a divalent anion $HAsO_4^{2-}$ dominates at higher pH values (such as between pH 8 and 11). In the intermediate region which is in the pH range between 6 and 8, both species coexist with one another (Kim et al., 2004). Thus, it is evident that the adsorption of As(V) by dried plants is pH dependent.

Figure 3 Effect of contact time and initial arsenate ion concentration on the removal of As(V) by *C. rhizoma*: $m/v = 25$ g/l, $pH_i = 8.3$, and temperature ∼22 °C.

Figure 4 The effect of initial pH_i on adsorption of As(V) onto *C. rhizoma* and *W. frutescens*: initial concentration of As(V) was 100 mg/l, temperature was 22 °C, dose of dried plants was 25 g/l, and mixing time was 12 h.
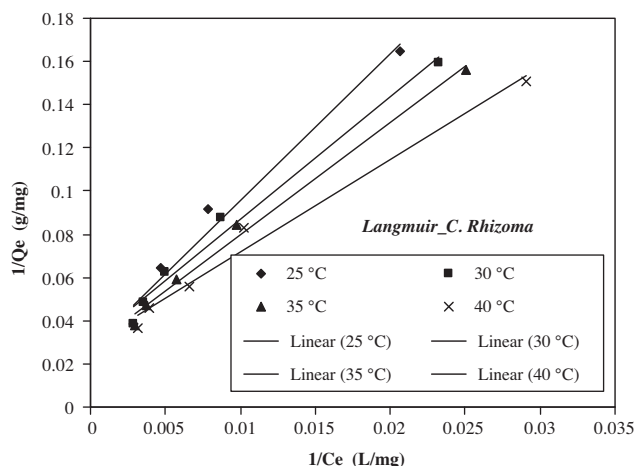
Figure 5 Langmuir adsorption isotherm for As(V) on *C. rhizoma* at various temperatures: $m/v = 25$ g/l, $pH_i = 8.3$, $T_c = 12$ h.

Figure 6 Freundlich adsorption isotherm for As(V) on *C. rhizoma* at various temperatures: $m/v = 25$ g/l, $pH_i = 8.3$, $T_c = 12$ h.

3.4. Adsorption isotherms

Adsorption isotherms are mathematical models that describe the distribution of the adsorbate species among the solid and liquid phases, and are important data to understand the mechanism of adsorption. Several models have been published in the literature to describe experimental data of adsorption isotherms. The Langmuir, Freundlich and Temkin models are the most frequently employed models. In this study, these three models were used to describe the relationship between the adsorbed amount of arsenate on dried plants and its equilibrium concentration in solution.

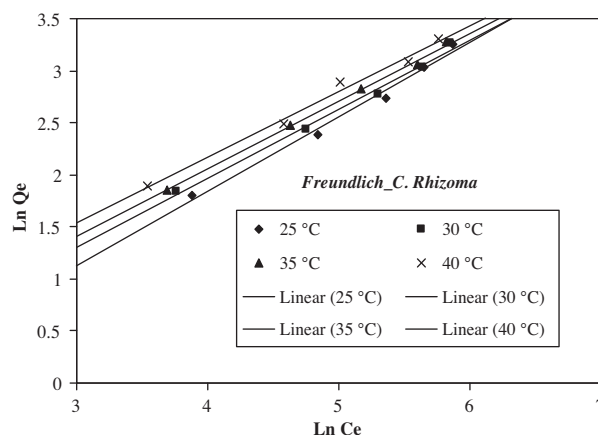#### 3.4.1. Langmuir adsorption isotherm
The data obtained were then fitted to the Langmuir adsorption isotherm applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is expressed by the following equation (Langmuir, 1918):

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \qquad (4)$$

It can be expressed in the linear form in Eq. (5)

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} K_L C_e} \qquad (5)$$

where q_e is the equilibrium arsenate concentration on the adsorbent (mg/g), C_e is the equilibrium As(V) concentration in the solution (mg/l), q_{max} is the maximum adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir adsorption constant (l/mg) and is related to the free energy of adsorption (Chen et al., 2008). The plot of $1/q_e$ versus $1/C_e$ for both dried plants gives a straight line of slope $1/q_{max} K_L$ and intercepts $1/q_{max}$ (Figs. 5 and 6). The values of the adsorption capacity (q_{max}), the Langmuir constant (K_L), and the coefficient of determination (r^2) were presented in Table 1. The values of the coefficient of determination for both dried plants were 99% and 98% for *W. frutescens* and *C. rhizoma*, respectively, indicating a good fit of the Langmuir model to the adsorption of arsenate on the two plants. The

Langmuir model is an indication of surface homogeneity of the adsorbent. The basic assumption of Langmuir adsorption isotherm is also based on monolayer coverage of the adsorbate on the surface of adsorbent. The adsorption capacity of the adsorbent increased on increasing the temperature. The highest value of q_{max} obtained at 40 °C was 29.06 mg/g for *W. frutescens* and 34.72 mg/g for *C. rhizoma*. It appears to be the highest in comparison with the uptake obtained at the other temperatures (Table 1). The essential feature of the Langmuir isotherm can be expressed by means of 'R_L', a dimensionless constant referred to as separation factor or equilibrium parameter to predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the following equation (Weber and Chakkravorti, 1974):

$$R_L = \frac{1}{1 + K_L C_i} \qquad (6)$$

where C_i is the initial As(V) concentration (mg/l). The parameter R_L indicates the shape of the isotherm and nature of the adsorption process. According to the value of R_L the isotherm shape may be interpreted as follows (Bulut et al., 2007) (Table 2):

In this study, the values of R_L calculated from Eq. (6) were incorporated in Table 1. Further, for C_0 from 0.2 to 1 g/l used in the present study, the values of R_L at all temperatures studied range from 0.079 to 0.553 for *W. frutescens* and 0.129 to 0.553 for *C. rhizoma*, therefore, the adsorption is favorable.

3.4.2. Freundlich adsorption isotherm
The adsorption data obtained were then fitted to the Freundlich adsorption isotherm (Freundlich, 1906), which is the earliest relationship known describing the adsorption equilibrium and is expressed by Eq. (7) and its linear form in Eq. (8):

$$q_e = K_f C_e^{1/n} \qquad (7)$$

$$\text{Ln } q_e = \text{Ln } K_f + \frac{1}{n} \text{Ln } C_e \qquad (8)$$

The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The con-

Table 1 Isotherm constants for As(V) adsorption onto both dried plants at different temperatures: $m/v = 25$ g/l, $pH_i = 8.4$, $T_c = 12$ h.

	C. rhizoma				W. frutescens			
	25 °C	30 °C	35 °C	40 °C	25 °C	30 °C	35 °C	40 °C
Langmuir								
Q_{max}	35.97	33.33	35.97	34.72	23.53	21.98	28.57	29.07
K_L	0.004	0.005	0.005	0.007	0.004	0.005	0.007	0.011
r^2	0.979	0.981	0.992	0.983	0.992	0.990	0.982	0.997
R_L	0.198–0.553	0.159–0.486	0.157–0.482	0.13–0.427	0.198–0.553	0.158–0.484	0.123–0.413	0.079–0.300
Freundlich								
$1/n_f$	0.71	0.66	0.65	0.63	0.57	0.55	0.58	0.53
K_f	0.36	0.50	0.58	0.70	0.47	0.58	0.73	1.19
r^2	0.988	0.991	0.997	0.990	0.981	0.987	0.997	0.988
Temkin								
B	9.33	8.86	8.91	8.95	5.70	5.71	7.65	7.60
K_T	0.032	0.039	0.044	0.051	0.033	0.038	0.048	0.07
r^2	0.900	0.910	0.948	0.944	0.963	0.961	0.946	0.911

Table 2 Type of isotherm for different values of R_L.

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

stants K_f and n were calculated from Eq. (8) and Freundlich plots (Figs. 7 and 8). The amount of absorbent required to reduce any initial concentration to predetermined final concentration can be calculated. The values for Freundlich constants and correlation coefficients (r^2) for the two adsorbents used during the study are also presented in Table 1. The values of n between 1 and 10 (i.e., $1/n$ less than 1) represent a favorable adsorption (Faust and Aly, 1987). The values of n, reflects the intensity of adsorption. The numerical values of n at all temperatures lies between 1.792 and 2.177 and is greater than unity, indicating that arsenate ions are favorably ad-

sorbed by both dried plants at all the temperatures studied. In general, both Freundlich and Langmuir models had a good agreement with the data for arsenate adsorption, evidenced by the high r^2 values (all greater than 0.97) (Table 1). These experiments confirm the efficiency of the micro-particles of dried plants to remove As(V) from aqueous solution.
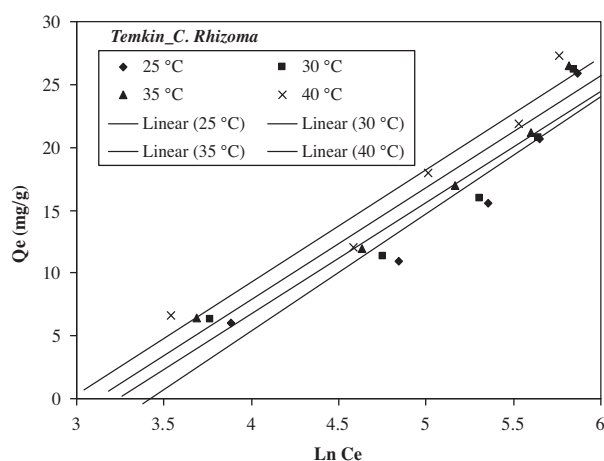
3.4.3. Temkin Isotherm
The Temkin adsorption isotherm model based on the heat of adsorption of the ions, which is due to the adsorbate and adsorbent interactions taken (Temkin and Pyzhev, 1940). The Temkin isotherm equation is given as:

$$q_e = \frac{RT}{b}\mathrm{Ln}(K_T \cdot C_e) \quad \text{where } RT/b = B \tag{9}$$

A linear form of the Temkin isotherm can be expressed as:

$$q_e = B\mathrm{Ln}(K_T) + B\mathrm{Ln}(C_e) \tag{10}$$

where T is absolute temperature in Kelvin and R the universal gas constant, 8.314 J/(mol K). b (J/mol) is Temkin isotherm

Figure 7 Temkin adsorption isotherm for As(V) on *C. rhizoma* at various temperatures: $m/v = 25$ g/l, $pH_i = 8.3$, $T_c = 12$ h.
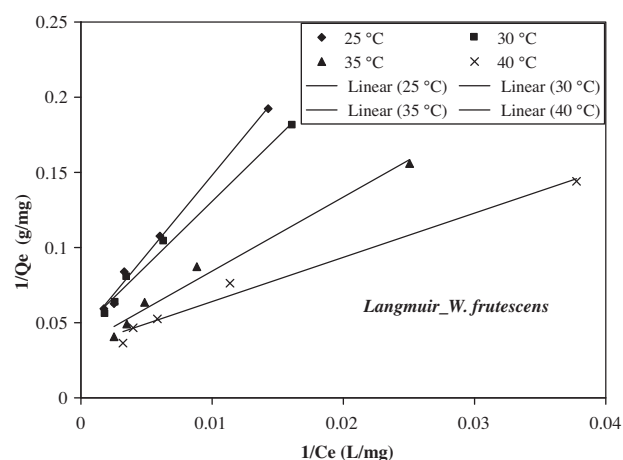
Figure 8 Langmuir adsorption isotherm for As(V) on *W. frutescens* at various temperatures: $m/v = 25$ g/l, $pH_i = 8.3$, $T_c = 12$ h.

constant and constant B (dimensionless) is related to the heat of adsorption (Bulut et al., 2008). K_T (l/mg) is the equilibrium binding constant (l/g) corresponding to the maximum binding energy. The Temkin isotherm plot for both plants at four temperatures are presented in Figs. 9 and 10 and the isotherm parameters are given in Table 1. The Temkin constant (B) related to the heat of adsorption for the two dried plants was between 5.7 and 7.6 kJ/mol for *W. frutescens* and from 8.86 to 9.33 kJ/mol at studied temperature ranges. It has been reported (Ho et al., 1996) that the typical range of bonding energy for ion-exchange mechanism is 8–16 kJ/mol. The low values in this study in case of *W. frutescens* indicate a weak interaction between adsorbate and adsorbent, supporting an ion-exchange mechanism for the present study. From linear regression of the data points, the r^2 values range from 0.91 to 0.96 for *W. frutescens* and 0.90 to 0.94 for *C. rhizoma*, respectively, are rather low indicating that the adsorption of As(V) did not follow the Temkin isotherm closely.
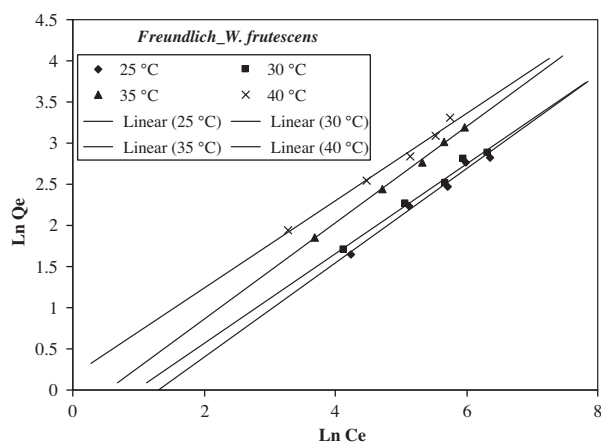
Figure 9 Freundlich adsorption isotherm for As(V) on *W. frutescens* at various temperatures: $m/v = 25$ g/l, pH$_i$ = 8.3, $T_c = 12$ h.
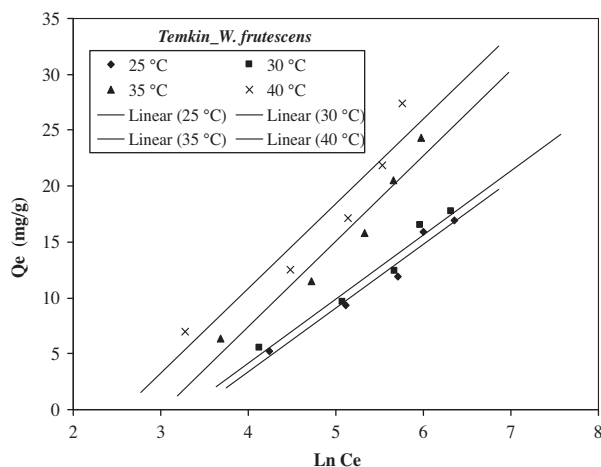
Figure 10 Temkin adsorption isotherm for As(V) *W. frutescens* at various temperatures: $m/v = 25$ g/l, pH$_i$ = 8.3, $T_c = 12$ h.

3.5. Thermodynamic studies

The thermodynamic parameters such as standard Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0) were estimated to evaluate the feasibility and nature of the adsorption process. The values of standard Gibbs free energy change for the adsorption process were evaluated by using K_L values obtained from the Langmuir model at different temperatures and thermodynamic parameters are presented in Table 3. The Gibbs free energy change, of the process is related to equilibrium constant by following the equation (Parfitt and Rochester, 1983; Bulut and Tez, 2007):

$$\Delta G^0 = -RT \operatorname{Ln} k_L \tag{11}$$

where T is temperature in Kelvin, R is the gas constant having a value of 8.314×10^{-3} kJ/(mol K), and K_L is the equilibrium constant obtained from the Langmuir model.

According to thermodynamics, the Gibbs free energy change is also related to the enthalpy change (ΔH^0) and entropy change (ΔS^0) at constant temperature by the following equation,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{12}$$

Now using Eqs. (12) and (11) can be transformed to Eq. (13).

$$\operatorname{Ln} K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{13}$$

The values of enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the slope and intercept of the plot of $\operatorname{Ln} K_L$ versus $1/T$ (Fig. 11) (Bulut and Tez, 2007). The calculated values of these parameters are given in Table 3. It can be seen in Table 3 that ΔG^0 values were found to be negative for all temperature conditions studied, verifying that the adsorption process was spontaneous in nature (Bulut and Tez, 2007). However, the decreasing value of ΔG^0 with increasing temperature implies that the spontaneity degree of the adsorption process increases with increasing of the temperature. The results for ΔH^0 and ΔS^0 were found to be 53.67 and 227.19 kJ/mol of *W. frutescens* and 23.27 and 125.91 for *C. rhizoma*, respectively. Unlu and Ersoz (2006) stated that although there are no certain criteria that are related to the ΔH^0 values defining the adsorption, heats of adsorption between 20.9 and 418.4 kJ/mol, which are heats of chemical reactions, are frequently assumed to be comparable to those associated with the chemisorption processes. Based on the result of ΔH^0 value, this study suggests that the adsorption of As(V) onto dried plants proceeded via chemisorption and that the adsorption process was endothermic in nature. This result is also supported by the increase in the value of uptake capacity of adsorbents with the rise in temperature. Han et al. (2006) stated that the increasing sorption capacity of the sorbent with temperature is attributable to the enlargement of pores and/or the activation of the sorbent surface. In addition to that, the positive value of entropy (ΔS^0) revealed that the degrees of free active sites increased at the solid–liquid interface during the adsorption of As(V) onto dried plants.
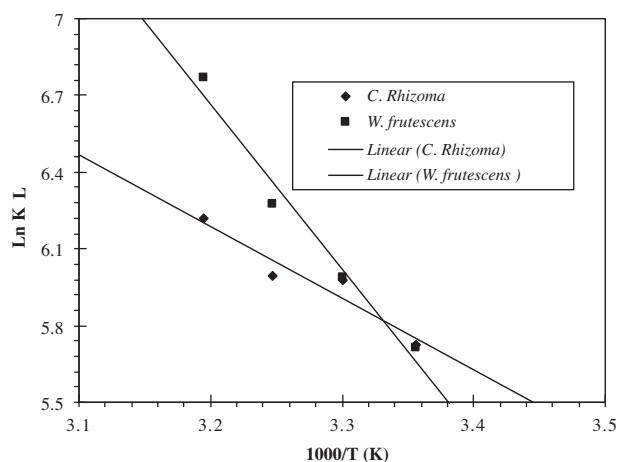
3.6. Desorption and readsorption capacity

Desorption studies will help to elucidate the nature of adsorption process and to recover the As(V) from both
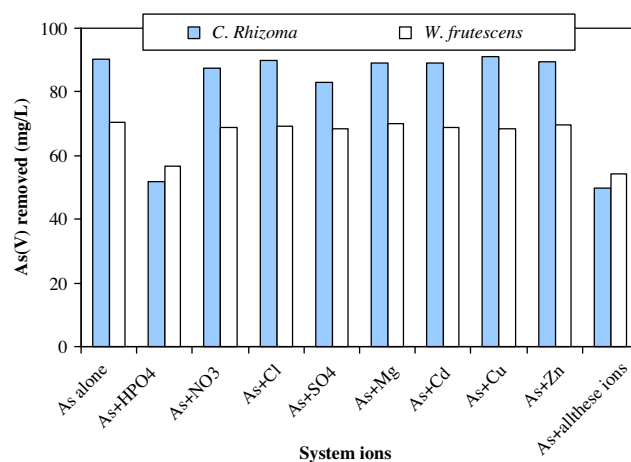
Table 3 The thermodynamic parameters at various temperatures for As(V) adsorption by both dried plants separately.

Adsorbent	T (°C)	K_L (l/mol)	Ln K_L	$-\Delta G^0$ (kJ/mol)	ΔH^0 (J/mol)	ΔS^0 (J/(mol K))
C. rhizoma	25	306.15	5.72	14.18	23.27	125.91
	30	395.27	5.98	15.06		
	35	401.35	5.99	15.35		
	40	502.13	6.22	16.18		
W. frutescens	25	302.38	5.71	14.15	53.67	227.19
	30	399.16	5.99	15.09		
	35	532.04	6.27	16.07		
	40	873.08	6.77	17.62		

Figure 11 Plot of ln K_L vs. $(1/T)$ for estimation of thermodynamic parameters for both dried plants.

Figure 12 Effect on the removal of As(v) on *C. rhizoma* and *W. frutescens* with coexisting ions at initial concentration for each ion was 100 mg/l; temperature was 22 °C; contact time was 12 h; and initial pH$_i$ was 6.

adsorbents individually. Moreover, it also will help to regenerate the adsorbents so that it can be used again to adsorb arsenate ions, and to develop the successful adsorption process. The desorption experiments were carried out at 25 °C by using various NaOH solutions and the effect of initial concentration of NaOH on desorption of As(V) from the adsorbents is shown in Table 4. It was expected that increased concentration of OH⁻ ions should compete greatly with the already adsorbed arsenate on both dried plants, hence sodium hydroxide solution was used to desorb arsenic from the adsorbent. Generally, desorption of the arsenate ions was more favored in strong alkaline solution. With 0.03 M NaOH solution, 78% of the adsorbed As(V) from *W. frutescens* plant was desorbed, and desorption percent could arrive at 91% if the concentration of NaOH was higher than 0.07 M. With regard to *C. rhizoma* plant, satisfactory desorption (40%) of the arsenate adsorbed ions achieved with relatively higher concentration of NaOH (0.07 M NaOH)

(Table 4). A noticeable amount of arsenate can be readsorbed in a second procedure by *W. frutescens* plant treated with 0.7 M of NaOH at 12 h, although it does not reach the amounts retained in the first contact, it is probably due to a residual adsorption level. The readsorption percentage of arsenate onto both dried plants was found to be 52% (2.08 mg/g) for *W. frutescens* and 30% (1.2 mg/g) for *C. rhizoma* plant.

3.7. Effect of the coexisting ions

Till now all the adsorption results discussed above were obtained by taking the arsenate anions as adsorbate (As(V) alone). However, in reality the contaminated water contains several other ions (both cations and anions) which can affect the adsorption of arsenate. In a representative test, the effects

Table 4 Desorption data for As(V) adsorbed on both adsorbents using different concentrations of NaOH by batch process.

Adsorbent	Concentration initial of As(V) (mg/l)	Removal efficiency (%)	Desorption (%) with NaOH				
			0.01 M	0.02 M	0.03 M	0.05 M	0.07 M
C. rhizoma	100	92.21	21.28	27.66	34.52	39.70	39.53
W. frutescens	100	73.6	40.01	43.98	78.36	90.81	91.69

Table 5 Maximum dried plants adsorption capacities (Q_{max}, mg/g) of As(V) compared with other adsorbents (in mg per g of solid material).

Adsorbent	Initial pH	Concentration range	Q_{max} (mg/g)	References
Raw mixed (hydr)oxide	8	5–500 mg/l	26.8	Escudero et al. (2009)
Inonotus hispidus biomass	2	10–500 mg/l	59.6	Sari and Tuzen (2009)
Rice polish	4	100–1000 µg/l	0.14	Ranjan et al. (2009)
Modified zeolite	6	10–50 mg/l	1.34	Yusof and Malek (2009)
Maghemite nanoparticles	3	1–11 mg/l	50.0	Tuutijärvi et al. (2009)
Fish scale	4	0.2–1 mg/l	0.03	Rahaman et al. (2008)
Lassonia nigrescens	2.5	50–600 mg/l	45.2	Hossain (2006)
Tea fungal biomass	7.2	0.9 mg/l	4.95	Hossain (2006)
Bone char	10	0.5–1.5 mg/l	1.43	Chen et al. (2008)
Leather waste	1	10–100 mg/l	26	Oliveira et al. (2008)
Calcium alginate	5 to 6	6 mg/l	6.75	Lim and Chen (2007)
Orange juice residue	10	–	67.43	Ghimire et al. (2002)
Red mud	3.5	10 mg/l	0.52	Altundogan et al. (2002)
Red mud	2.3	2.5–30 mg/l	0.51	Altundogan et al. (2000)
Coconut coir pith	7	5–100 mg/l	13.57	Anirudhan and Unnithan (2007)
Chitosan	4	400 mg/l	58	Mcafee et al. (2001)
Chitosan	3,5	0–10 mg/l	14.16	Kwok et al. (2009)
C. rhizoma	8	1000 mg/l	22.04	This study
W. frutescens	8	1000 mg/l	16.88	This study

of the presence of individual and simultaneous anions and cations such as: sulfate, chloride, nitrate, phosphate, magnesium, cadmium, copper, and zinc on the adsorption capacity of both crushed dried plants for As(V) were investigated. The amount of arsenate removal values in the absence and the presence of these anions and cations are given in Fig. 12. Generally, no interference was observed between arsenate and studied cations. The adsorption capacity of arsenate on *C. rhizoma* decreased by 42.6% and 8.1% in the presence of phosphate and sulfate anions separately; while no evidently competitive effects on the adsorption of As(V) onto the two plants separately were observed with other coexisting anions such as chloride and nitrate (Fig. 12). The significant interference on As(V) adsorption by phosphate is due to the similar chemical properties of arsenate with phosphate in aqueous solution at pH 6.0 (Hughes, 2002). Similar results were reported by Rahman et al. (2008) and Mkandawire et al. (2004) about the removal of arsenic by *Spirodela polyrhiza* L. and *Lemna gibba* L., respectively. These results probably meant that these dried plants had also high adsorption ability to phosphate or sulfate under some conditions that we had in our experiment. The results also show that the arsenate uptakes by both dried plants were not affected by the presence of simultaneous bivalent cations, nitrate, and chloride.

3.8. Comparison of adsorption capacity with different adsorbents reported in literature

In order to justify the validity of dried plants as adsorbents for adsorption, its adsorption potential must be compared with other various adsorbents used for this purpose. The values of maximum adsorption capacity of the adsorbents for the removal of As(V) reported in the literature are given in Table 5. The direct comparison of the adsorbent capacity of studied adsorbents with other adsorbents capacity reported in the literature is difficult due to the varying experimental conditions

employed in those studies; however, both dried plants in this study possess reasonable adsorption capacity in comparison with other adsorbents. The adsorption capacity differences of arsenate ions uptake are ascribed to the properties of each adsorbent such as adsorbent structure, functional groups and surface areas (Ozsoy and Kumbur, 2006).

4. Conclusion

This study indicates that micro-particles obtained from dried plants such as *C. rhizoma* and *W. frutescens* can be used as adsorbents for the treatment of wastewater contaminated with arsenate. The adsorption process has been shown to be affected from experimental conditions such as pH, initial arsenate ion concentration and contact time. Batch adsorption studies under varying experimental conditions showed that the adsorption of arsenate ions is fairly rapid in the first 60 min and thereafter increases slowly to reach equilibrium in about 3 h. The maximum arsenate removal was observed at about pH 8.0. The percentage removal of arsenate from aqueous solutions by both dried plants was 91% (3.64 mg/g) for *C. rhizoma* and 72% (2.88 mg/g) for *W. frutescens* at an initial arsenate concentration of 100 mg/l. The equilibrium data fitted well to Langmuir, Freundlich, and Temkin isotherm models, in the studied concentration range at all temperatures studied. The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic parameters such as ΔG^0, ΔH^0, and ΔS^0 of adsorption. A positive value of the standard enthalpy change suggests that the interaction of As(V) adsorbed by both plants is of endothermic nature. The negative adsorption standard free energy changes indicate that the adsorption reaction is a spontaneous process. The natural materials used in this work are suitable candidates as adsorbents in As(V) removal techniques, considering that these adsorbents are naturally abundant and relatively low-cost materials.

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