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# Morus alba- A Potential Sorbent for the Removal of Arsenic: Equilibrium, Kinetic and Thermodynamic Study

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#### Abstract

In present study, arsenic (As) uptake potential of an eco-friendly *Morus alba* (mulberry) leave biomass was analyzed. Surface properties of the sorbent and its affinities for arsenic ions with respect to temperature were studied. Freundlich, D-R, Florry-Huggins and Halsey isotherms were found to be similar with recorded experimental data. Maximum sorption capacities 2.82 mg/g and 4.93 mg/g were calculated for As(III) and As(V) at pH-6 and pH-4, respectively. The energy values of the sorption 3.31-5.89 (<8) kJ/mole indicated the physisorption. The applicability of Halsey isotherm supported the heteroporosity of the biomass. Mechanism of the reaction was best explained by pseudo first order rate, Morris-Weber and Richenberg equations. Intra-particle diffusion as well as surface sorption was noticed during the study. Equilibrium was achieved up to 120 minutes. Thermodynamically, sorption reaction was endothermic and spontaneous in nature. Maximum recoveries of As(III) and As(V) were 83.3% and 95.52%, respectively observed with 1 M H<sub>2</sub>SO<sub>4</sub>.

Keywords: Morus alba, Arsenic, Sorption, Isotherm

#### Introduction

For centuries, arsenic (As) has been considered as contaminant [1]. It is non-biodegradable and detrimental to the flora and fauna. As contamination of drinking water can be found in earth's outer layer, marine and ground water. More than 300 species of As bearing minerals exist in nature [2]. As is mobilized through biological activities, volcanic emissions. weathering reactions, anthropogenic activities such as gold mining, copper smelting, petroleum refining, arsenical pigments, combustion of fossil fuels in power plants, arsenical pesticides and herbicides [3].

In 1999, WHO ranked As contamination as "major public health issue". USEPA (1997) and IARC (2004) classified As category 1 (group A) carcinogen [4]. It has mutagenic and tetratogenic capacity to human health (ASTDR 1990). From the various oxidation states (-3, 0, +3, +5), As(III) and As(V) are widespread in water [5]. Water contains both organic and inorganic As species. Organic arsenicals have much lower toxicities than inorganic compounds [6]. Inorganic As compounds of As(V) are dominant and stable in oxygen rich surface water environment while As(III) are in reasonable anaerobic ground water [7]. As(III) is more mobile and more toxic (25-60 times) than As(V) and many times more toxic as compared to organic As species [8]. As(III) is quite difficult to remove as contrast to As(V), which also exists mostly as deprotonated oxyanions (HAs $O_4^{2-}$ ). As disturbs the regular metabolic activity of living organisms. In mammals its toxicity is due to reaction with groups sulfhydryl of enzymes [9]. Bioaccumulation of As in food chain even in relatively low concentration (greater than 10 ppb) threatens to human, animal and plant life [10]. As poisoning causes heart disease, anemia, keratosis, hyper pigmentation, gangrene of toes, solid swelling of legs, burning sensation of eyes, neuropathy, liver fibrosis and cancer in lungs, skin, kidney, liver, prostate and bladder [11]. Severe As poisoning causes human even to death.

Keeping in view this potential threat, scientists have employed various techniques for the removal of As from aqueous solution, such as chemical precipitation. solvent extraction. chelating and ion exchange, adsorption, membrane separation and electrochemical methods. However, most of these methods could not be used in fullscale applications due to their high operational cost or potential secondary pollution [12]. It has been observed that in last two decades adsorption technique has received lot of consideration due to the availability of variety of adsorbents. Adsorption is a very economical, simple, effective, highly versatile process for removing harmful pollutants from wastewater [13]. Morus alba leave biomass is locally available and cost effective. It cannot contaminate drinking water during the sorption process. This plant can easily grow in most areas of Pakistan. Further, this plant also bears sweet fruit as well. In comparison to other metal removal techniques, adsorption has numerous advantages such as short operational time, enhanced selectivity for specific metal ions of interest, reusability of biomass, high metal binding efficiency, no production of secondary toxic compounds etc [14]. Methods other than adsorption are not appropriate for small level industries.

The objective of the present work is to investigate the sorption potentials of *Morus alba* for the removal of As(III) and As(V) from real sample solutions. Further, the applicability of the developed method was also analyzed with As contaminated real samples.

# Materials and Methods Chemicals

In the present experimental work all reagents used were of analytical grade. Stock solutions (1000 mg/L) of As(III) and As(V) were prepared by dissolving calculated amounts of arsenic oxide arsenous (As<sub>2</sub>O<sub>3</sub>) (Poole, England) and sodium arsenate (Na<sub>3</sub>AsO<sub>4</sub>) (Merck, Germany) in de-ionized water respectively. Required working solutions for experiment were freshly prepared from the stock solutions. pH of solutions were maintained by the various buffers (acetic sodium acetate, potassium chloride, acid. hydrochloric acid and sodium hydroxide). The mixture of 0.2% w/v sodium borohydride (NaBH<sub>4</sub>) (Darmstadt company, Merck, Germany) in 0.05 % w/v sodium hydroxide (NaOH) (Fisher scientific UK) was used for the reduction of As.

## **Instrumentation**

pH meter (Thermo Scientific Orion 5 Star, 8102BNUWP; USA), Shaking Incubator 1-40000 Irmeco GmbH (Germany), Atomic Absorption Spectrometer Analyst 800 (Perkin Elmer, Singapore) connected with Flow Injection System for hydride generation (FIAS 100 Perkin Elmer, Singapore) equipped with a hallow cathode lamp having current 18 mA, wavelength 193.7 nm, energy 40, bandwidth 0.7 nm and Quartz Tube Atomizer (Universal QAT, part number B300-0350, Singapore) were used during the sorption experiments.

## Sample preparation

The green *Morus alba* leaves were collected from the fruit farm of Shoukat Ali Khaskheli, Hussainabad, Kotdiji district Khairpur Mir's, Sindh, Pakistan. Sample leaves were washed many times with water and then with deionized water in order to remove dust and extraneous. Thereafter, leaves were dried in an oven at 60 °C for one day. The dried biomass was subsequently grounded and sieved into uniform particle size (0.125-0.42 mm) for the sorption experiments.

## General method

10 mL of test solution was taken in 100 mL stoppered conical flask. Suitable amount of sorbent was added and then agitated for the stipulated contact time at 200 rpm. The experiments were performed at 20, 30 and 40 °C. The equilibrium time was estimated by drawing the samples from shaker at regular intervals. The samples were filtered out using filter paper and filtrate was analyzed by using FAAS connected to FIAS system. The stated experimental procedure was repeated for the optimization of different parameters- biomass dosage (0.05-0.3 g), contact time (0-1440 min), metal concentration (0.01-50 mg/L) and pH (1-10).

# Results and Discussion FT-IR characterization of Morus alba sorbent

The FT-IR spectroscopy is a power tool for the direct investigation of the sorption mechanism before and after the loading of metal ions on surface of sorbent. Spectra of sorbent were recorded in range of  $500 - 4000 \text{ cm}^{-1}$  and are presented in Fig. 1. The band ranged from  $3280 - 3334 \text{ cm}^{-1}$  represented O-H (hydrogen bonding) stretching vibration of alcohols or phenols.

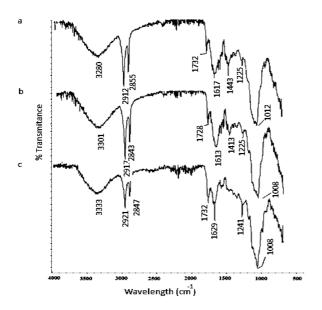


Figure 1. (a) FT-IR specta of Morus alba leaves, (b) Morus alba leaves loaded with As(III) and (c) Morus alba leaves loaded with As(V)

The peaks from 2843 - 2922 cm<sup>-1</sup> and 1723 - 1728 cm<sup>-1</sup> were assigned to the stretching vibrations of C-H (alkane) and -C=O (carboxylic group). Peaks at 1613 - 1629 cm<sup>-1</sup> and 1413 cm<sup>-1</sup> are attributed to bending vibrations of C=C (aromatic) and -O-H (carboxylic acid) groups, respectively. The bands at 1008 - 1012 cm<sup>-1</sup> were assigned to the C-O stretching of alcohols.

The stretching vibrations at 1413 cm<sup>-1</sup> and 2921 cm<sup>-1</sup> remained same for As(III) and As(V) loaded sorbent, respectively. The peaks of O-H (phenol or alcohol) at 3280.82 cm<sup>-1</sup> and C-H (aldehvde) 2855.85 cm<sup>-1</sup> were shifted for As(III)loaded sorbent and As(V)-loaded Morus alba leaves peak at 1413 cm<sup>-1</sup> (-O-H of carboxylic acid) was disappeared in the As(V) loaded sorbent. The shifts of peaks at 1617 cm<sup>-1</sup> and 1012 cm<sup>-1</sup> were also observed for As(III) and As(V) loaded sorbent. Results demonstrate that the carboxyl (-COOH), C=C (aromatic) and O-H (alcohol or phenol) groups mainly participate in the sorption of As(III) and As(V) onto Morus alba sorbent. The sorption process may be attributed to the ion exchange, physical adsorption, complexation, chemical reaction with surface sites and surface precipitations.

## Effect of pH

The pH plays one of the important role in the sorption of As ions on the *Morus alba* biomass. The pH effect on the removal of As(III) and As(V) on sorbent (*Morus alba* leaves) was studied in the pH 1-10 range, results are presented in Fig. 2. In case of As(III) in the range of pH 1-5 and 7-10 sorption is nearly constant. Maximum sorption of As(III) and As(V) were 49.3% and 78% observed at pH-6 and 4 respectively. Therefore, further studies were carried out at pH-6 for As(III) and pH-4 As(V) respectively. Same trend of pH with As(III) and As(V) was observed in literature [15].

In the above mentioned range of pH, the predominant mono-anionic  $(H_2AsO_3^-)$  is considered to be responsible for the sorption of As(III), substituting water molecules or hydroxyl ions.  $H_3AsO_4$ ,  $H_2AsO_4^-$ ,  $HAsO_4^{2-}$  and  $AsO_4^{3-}$  are the dominant As(V) species in pH ranges of <2.26, 2.26-6.76, 6.76-11.29 and >11.29, respectively.

According to Fig. 2 in alkaline pH both species of As showed decrease in sorption. This can be recognized as the repulsive forces produced between the negatively charge sorbent and anionic species of As [16].

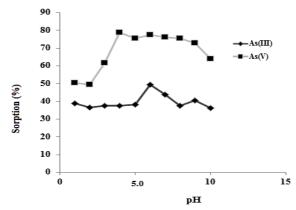


Figure 2. Effect of pH on removal of  $\mbox{As}(\mbox{III})$  and  $\mbox{As}(\mbox{V})$  through Morus alba leaves

#### Effect of biomass concentration

Sorption efficiency in terms of amount of biomass was investigated 0.05 - 0.30 g with an interval of 0.05 g by maintaining all the other parameters at their optimal values such as metal ion concentration 5 mg /L, volume 10 mL, temperature 30 °C, agitation time 30 min, shaking speed 250 rpm, pH-6 for As(III) and pH-4 As(V). Generally, it has been observed that there was slight increase in sorption as amount of biomass was increased. The increase in sorption can be caused due to the surface area and creation of electrostatic force of attraction between metal and functional group present in *Morus alba* biomass.

## Effect of contact time

In batch experiments, time play very important role for the optimization of rate of sorption. Therefore, the effect of contact time was studied in the range between 0-1440 min at pH-6 for As(III) and pH-4 for As(V). Results from the Fig. 3 showed that equilibrium was achieved after 120 min. Similar trend of equilibrium time was also seemed for the removal of As(V) on modified sawdust of *spruce* [17]. Then decrease in sorption was observed. This decrease may be due to autodesorption of metal ions.

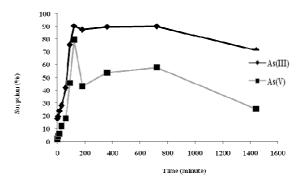


Figure 3. Uptake of As(III) and As(V) on Morus alba leaves as a function of time

#### Sorption isotherm study

Isotherm study deals sorbent surface properties and its affinities for ions at fixed temperature and pressure. Experimental sorption data was also applied to the following adsorption isotherm models.

## Freundlich adsorption isotherm model

Like other isotherm models, Freundlich Model is also widely used for the adsorption of variety of organic and in-organic compounds on the surface of various adsorbents (natural and synthetic). The experimental data was applied to the following linear form of the equation 1.

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

Where q<sub>e</sub> is amount of metal adsorbed per unit mass of adsorbent, while Ce is amount of metal in the liquid phase at equilibrium, K<sub>F</sub> (Freundlich Constant) relative adsorption capacity and n is adsorption intensity. 1/n < 1 suggest presence of convex isotherm while 1/n > 1 concave isotherm [18]. Fit of the experimental data indicates that multilayer of the metal ions are formed on heterogeneous surface (non-equivalent binding sites) of sorbent. The values of n and K<sub>f</sub> are calculated from intercept and slope respectively from the plot Log  $q_e$  versus Log  $C_e$ . Here the calculated values of n are greater than 1 (1/n < 1) support the convex isotherm and favorable nature of sorption. Table 1 shows that as temperature increases, K<sub>F</sub> and n values decreases and vice versa.

*Table 1.* Regression parameters for the Fruendlich, D-R adsorption, Florry-Huggins and Halsey isotherms by using *Morus alba* leaves as sorbent at different temperatures.

| Metals                 | As(III) |        |        | As(V)  |        |        |  |
|------------------------|---------|--------|--------|--------|--------|--------|--|
| Temperature (°C)       | 20      | 30     | 40     | 20     | 30     | 40     |  |
| Freundlich             |         |        |        |        |        |        |  |
| $K_F(mg/g)$            | 2.82    | 2.53   | 1.99   | 4.93   | 4.49   | 3.74   |  |
| n                      | 1.100   | 1.080  | 1.050  | 1.050  | 1.100  | 1.050  |  |
| r                      | 0.9666  | 0.9787 | 0.9761 | 0.9829 | 0.9969 | 0.9770 |  |
| D-R                    |         |        |        |        |        |        |  |
| Xm (mg/g)              | 2.63    | 1.68   | 1.61   | 5.86   | 5.02   | 4.48   |  |
| $B (kJ^2/mol^2)$       | 0.0455  | 0.040  | 0.0472 | 0.0498 | 0.0415 | 0.0473 |  |
| E (kJ/mol)             | 3.310   | 3.540  | 3.250  | 3.170  | 3.470  | 5.890  |  |
| r                      | 0.9843  | 0.9822 | 0.9860 | 0.9932 | 0.9933 | 0.9764 |  |
| Flory-Huggins          |         |        |        |        |        |        |  |
| n <sub>FH</sub>        | 2.090   | 2.100  | 2.680  | 1.480  | 1.620  | 1.250  |  |
| $K_{FH} (10^6)$        | 9.050   | 7.460  | 7.760  | 6.450  | 10.17  | 2.890  |  |
| $\Delta G (kJ/mol)$    | -39.02  | -38.55 | -38.65 | -38.19 | -40.65 | -38.72 |  |
| r                      | 0.9440  | 0.9390 | 0.9617 | 0.9771 | 0.9775 | 0.9514 |  |
| Halsey                 |         |        |        |        |        |        |  |
| n <sub>H</sub>         | -0.476  | -0.458 | -0.456 | -1.122 | -1.176 | -1.137 |  |
| $K_{\rm H}({\rm L/g})$ | 1.530   | 1.440  | 1.270  | 6.042  | 6.042  | 4.810  |  |
| r                      | 0.9739  | 0.9772 | 0.9780 | 0.9909 | 0.9959 | 0.9971 |  |

#### **D-R** isotherm

In order to evaluate the nature of adsorption (chemical or physical) the data was tested by D-R isotherm (equation 2).

$$Lnq_e = lnK_{D-R} - \beta\epsilon^2$$
<sup>(2)</sup>

Where  $\varepsilon$  is Polanyi potential ( $\varepsilon$  = RTln(1+1/C<sub>e</sub>), R general gas constant (kJ/mol), K adsorption capacity, T absolute temperature (Kelvin) and  $\beta$  constant used to calculate energy (mol<sup>2</sup>/kJ<sup>2</sup>).

$$\mathbf{E} = -\frac{1}{\sqrt{2\beta}}$$

Fitting of the data to the equation demonstrates that filling of uniform pores of the sorbent by metal ions rather than layer by layer surface coverage of sorbate. Sorption may be attributed to the Vander Waal's forces. Energy values of sorption (Table 1) calculated for As(III) and As(V) were in range of 3.25-5.89 (<8)

showing the physical nature of sorption [19]. It means there was no any chemical bonding between the arsenic ions and the sorbent.

#### Flory-Huggins isotherm

This isotherm is used for the estimation of the degree of surface coverage on sorbent and to measure the apparent Gibbs free energy of change [20]. Flory-Huggins equation (equation 3) is given below.

$$\log \frac{\theta}{C_{i}} = \log K_{FH} + n_{FH} \log(1 - \theta)$$

$$\theta = 1 - \frac{C_{e}}{C_{i}}$$
(3)

Whereas  $\theta$  is degree of surface coverage,  $n_{FH}$  is the Flory-Huggins model exponent represents the number of metal ions of solute occupy active sites of sorbent, K<sub>FH</sub> is the Flory-Huggins model equilibrium constant and Ce equilibrium metal ion concentration. The values of  $K_{\text{FH}}$  and  $n_{\text{FH}}$  were determined from slope and intercept respectively from the plot  $\log\theta/C_i$  versus  $\log(1-\theta)$ . High values of correlation coefficient of As(III) and As(V) show the excellent applicability of the isotherm. Table 1 shows that as temperature increases number of metal occupying sorption sites increases for As(III) and decreases for As(V). This causes the increase sorption reaction. K<sub>FH</sub> was also used to determine the Gibbs free energy of spontaneity ( $\Delta G^{\circ}$ ) by following relationship.

$$\Delta G^{\circ} = - RT ln K_{FH}$$

#### Halsey isotherm

According to this isotherm, multilayer on the surface of sorbent can be composed of three regions: non-cooperative sorption on a strongly heterogeneous surface; cooperative multilayer sorption induced by small Vander Waal's perturbation at some distance from the surface and cooperative sorption on a still heterogeneous surface. The linear form of Halsey (Halsey, 1948) adsorption isotherm (equation 4) is given below.

$$\ln q_{e} = \frac{1}{n_{H}} \ln K_{H} - \frac{1}{n_{H} \ln C_{e}}$$
(4)

Where  $K_H$  and  $n_H$  are Halsey isotherm constants. This equation is used for the multilayer adsorption [21]. Table 1 shows high value of correlation coefficient (r=9739) which attests the heteropososity (i.e. macropore and micropore) nature of the sorbent. The heteroporous nature favors the different intensities of surface sorption at various sites of the *Morus alba* sorbent.

#### Kinetic study

Kinetic study describes the pathway of reaction along time to reach equilibrium. Kinetics depends on the chemical and physical composition of sorbent.

#### Pseudo first order rate equation

The sorption of As(III) and As(V) onto *Morus alba* was analyzed by applying observed experimental data to the following linear form of Legregren equation (equation 5).

$$Ln(q_e - q_t) = lnq_e - kt$$
(5)

Where k is first-order rate constant (describe the transportation of metal ions from bulk aqueous solution to sorbent),  $q_e$  is amount of metal sorbed at equilibrium and  $q_t$  is amount of As(III) and As(V) metal ions sorbed at time t. The rate of sorption of metal ions onto the sorbent surface is proportional to the amount of metal ions sorbed from the solution phase.  $ln(q_e-q_t)$  was plotted against t. The values of  $q_e$  and k were calculated from the slope and intercept. The graph was linear up to 120 min (Fig. 4). This indicates that sorption is first order. Beyond 120 min data did not follow the lagergren equation.

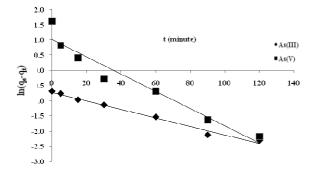


Figure 4. Pseudo-first order plot for the sorption of As(III) and As(V) on Morus alba leaves

#### Intra particle diffusion (Morris-Weber equation)

Intra-particle diffusion model (equation 6) is used to confirm the influence of mass transfer resistance on binding of metal ions to adsorbent.

$$q_t = k_{id\sqrt{t}} + C \tag{6}$$

Where q<sub>t</sub> is adsorption capacity of metal on adsorbent at time t (mg/g), k<sub>id</sub> intra-particle diffusion rate constant  $(mg/g.min^{1/2})$  and C intercept which gives idea of thickness of boundary layer. The graph was plotted qt versus  $t^{1/2}$ . According to Fig. 5 and Table 2, As(III) and As(V) experimental data follow equation up to 360 minutes with  $k_{id}$  values 1.34 mg/g min<sup>1/2</sup> and 1.01 mg/g min<sup>1/2</sup> respectively and then deviated. Linear portion of the plot is not passing through origin indicated that the intra-particle diffusion was not only the rate limiting step [22]. It supports that sorption mechanism is complex; Intra-particle diffusion as well as surface sorption occurs. Same trend was also observed for adsorption of As on bone char.

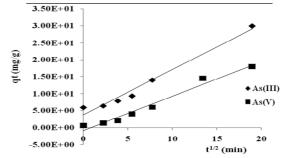


Figure 5. Morris-Weber plot for the sorption of As(III) and As(V) on *Morus alba* leaves

*Table 2.* Kinetics parameters for the sorption of As(III) and As(V) on *Morus alba* leaves at various temperatures.

| Metals  | Firs                      | st order 1               | Intra-particle<br>Diffusion      |        |   |        |
|---------|---------------------------|--------------------------|----------------------------------|--------|---|--------|
|         | k<br>(min <sup>-1</sup> ) | q <sub>e</sub><br>(mg/g) | h<br>(mg/g.<br><sup>-</sup> min) | r      | k <sub>id</sub><br>(mg/g.<br>min <sup>1/2</sup> ) | r      |
| As(III) | 0.014                     | 0.48                     | 0.003                            | 0.9931 | 1.34  | 0.9884 |
| As(V)   | 0.028                     | 2.77                     | 0.220                            | 0.9697 | 1.01  | 0.9861 |

#### **Richenberg** equation

The mechanism of sorption of arsenic ions on *Morus alba* through film diffusion or intra particle diffusion was described by Richenberg model (equation 7).

$$Q = \frac{1 - 6\pi^{-Bt}}{\pi^2}$$
(7)

Where Q = qt/qm,  $Bt = \pi^2 Di/s^2$ , qt is sorption capacity of metal at time t, qm is maximum sorption capacity of the sorbent, Di is an effective diffusion co-efficient of ions exchanging inside the sorbent particle. The value of Bt can be calculated for the each value of Q using following equation 8.

$$Bt = -0.4977 - \ln(1 - Q) \tag{8}$$

The plots of Bt versus t of As(III) and As(V) are linear from 0 to 60 minutes with a regression coefficient of 0.9922 and 0.9931. Fig. 6 shows that regression lines of plot of As(III) and As(V) are not passing through origin it means that the thin metal film is formed on the surface of *Morus alba* sorbent [23].

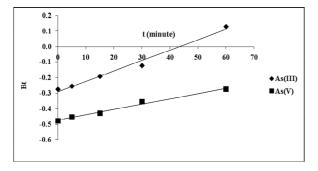


Figure 6. Richenberg plot for the sorption of  $\mathrm{As}(\mathrm{III})$  and  $\mathrm{As}(\mathrm{V})$  on Morus alba leaves

## Thermodynamic study

Thermodynamic study helps in estimating the possibility and nature of adsorption process. Thermodynamic parameter Gibbs free energy was calculated by using the following equation 9 [24].  $\Delta G = - RT ln K_C$  (9)

Where  $\Delta G$  is Gibbs free energy, R general gas constant (8.3143 J/mol.K), K<sub>c</sub> is equilibrium constant and T solution temperature (K). K<sub>c</sub> is determined by following equation 10.

$$K_{\rm C} = \frac{C_{\rm a}}{C_{\rm e}} \tag{10}$$

Where  $C_a$  is equilibrium concentration of the As ions sorbed on mulberry (mg/L) and  $C_e$  is equilibrium concentration of arsenic ions in solution (mg/L).

Enthalpy change ( $\Delta$ H) and entropy change ( $\Delta$ S) were calculated by plotting lnK<sub>c</sub> versus 1/T. Table 1 (Flory-Huggins Isotherm) and Table 3 show that Gibbs free energy values of both As(III) and As(V) are negative means the sorption reaction of As ions on *Morus alba* leave was feasible and spontaneous (i.e adsorption forces are strong to overcome potential barrier). Decrease of negative value with the increase of temperature shows that an increase of the temperature does not favor sorption process. Result shows that the sorption of As(V) was more feasible than As(III). Other two thermodynamic parameters (entropy change and enthalpy change) were calculated by using following equation 11 [25].

$$\ln K_{\rm C} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

The values of  $\Delta H$  and  $\Delta S$  were determined from slope and intercept from the plot lnK<sub>c</sub> versus 1/T. In Table 3 negative values of  $\Delta S$  for As(III) and As(V) show that there was orderliness (immobilization or fixation) of sorbate ions on surface of sorbent during the process. Positive values of enthalpy change ( $\Delta H$ ) for both species of As indicates that sorption process is an endothermic.

Table 3. Thermodynamic constants for the sorption of As(III) and As(V) on the Morus alba leaves at different temperatures.

| Metals  | Temp.<br>(K) | ΔG<br>(KJ/mol) | ΔH<br>(KJ/mol) | ΔS<br>(J mol/K) |
|---------|--------------|----------------|----------------|-----------------|
| As(III) | 293          | -5.87          | 15.01          | 0.041           |
|         | 303          | -5.47          | 17.91          | -0.041          |
|         | 313          | -5.05          |                |                 |
| As(V)   | 293          | -6.68          |                |                 |
|         | 303          | -5.64          | 29.41          | -0.078          |
|         | 313          | -5.13          |                |                 |

#### Desorption/ regeneration study

To make sorption method more economical, therefore, it is necessary to desorb the metals and metalloids sorbed. Desorption process yields metal ions in concerted form, facilitate their disposal and restore sorbent for effective reuse [26]. 0.1 g of As (10 mg/L) loaded biomass was added to 5 mL of leaching agent (desorbent) in a stoppered conical flask. Various leaching agents (acids and bases of varying concentrations) were used. The contents of flask were agitated at 250

60

rpm for 30 min maintaining the temperature at 25  $^{\circ}$ C. The mixture was filtered by filter paper. After the washing of *Morus alba* sorbent, filtrate was analyzed by atomic absorption spectrometer connected with FIA system. Maximum 83.3% and 95.52% recoveries of As(III) and As(V), respectively were obtained with 1 M H<sub>2</sub>SO<sub>4</sub>.

#### Interference study

Before applying the developed method in real samples, it is important to investigate the effect of electrolytes on the removal efficiency of Morus alba leave sorbent because real samples contain various electrolytes. Effect of some common electrolytes in the ratios of 1:10 and 1:100 were examined on the removal efficiency of As(III) and As(V) by Morus alba leaves. In 1:10 ratio 7.5 mL of As (10 mg /L) and 0.075 mL of an electrolyte (10000 mg/ L) were taken in 15 mL volumetric flask. In case of 1:100 ratio 7.5 mL of As (10 mg /L) and 0.75 mL of an electrolyte (10000 mg/L) were taken in 15 mL volumetric flask. After maintaining optimum pH, volumes of both flasks were made up to 20 mL. According to histogram Fig. 7 and Fig. 8 As(III) and As(V), respectively with Iron(III) show maximum removal of As ions.

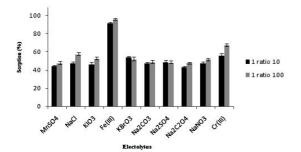


Figure 7. Electrolytic effect on the sorption of As(III) ions on Morus alba leaves

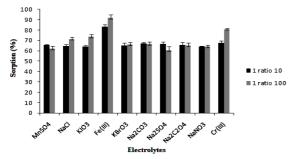


Figure 8. Electrolytic effect on the sorption of As(V) ions on Morus alba leaves

## **Applications**

The developed method was applied to remove the As metal ions from the contaminated water samples. Sample (S1) Industrial effluents of Kotri Site area, District Jamshoro, Pakistan was collected from the draining point in Karachi Wah. The sample (S2) tube well water near United Etanol Industry Sadiqabad, District Rahimyar Khan, Pakistan. Up to 89.84% of As was successfully removed from the As contaminated water samples (Table 4).

Table 4. Removal of Arsenic from real water samples.

| Sample | Original<br>Arsenic<br>Concentration<br>in Sample<br>(µgL <sup>-1</sup> ) | Amount of<br>Arsenic<br>Added<br>(µgL <sup>-1</sup> ) | Recovery<br>(%) | Residual<br>Concentration<br>(µgL <sup>-1</sup> ) |
|--------|---|---|-----------------|---|
| 1      | 40  |   | 75.28           | 9.89  |
|        | 40  | 50  | 89.84           | 9.14  |
| 2      | 0.68  | 50  | 74.13           | 10.14   |

Table 5. Comparative capacities of different sorbents and Morus alba.

|                                     |                    | Optimized conditions |               |              | Capacity<br>(mg.g <sup>-1</sup> ) |            |
|-------------------------------------|--------------------|----------------------|---------------|--------------|-----------------------------------|------------|
| Adsorbents                          | Metals             | pН                   | Time<br>(min) | Temp<br>(°C) |                                   | Reference  |
| Aspergillus                         | As (III)           | 6                    | 420           | 30           | 0.086                             | [10]       |
| niger biomass                       | As (V)             | 6                    | 420           | 30           | 0.1                               |            |
| Grape fruit peel waste              | As (V)             | 4                    | 120           | 45           | 37.76                             | [12]       |
| Cod fish scale                      | As (III)           | 4                    | -             | -            | 0.025                             | [15]       |
| Lamarck seed                        | As (V)<br>As (III) | 4<br>7.5             | -<br>60       | -            | 0.027<br>1.5                      | [27]       |
| powder                              | As (V)             | 2.5                  | 60            | -            | 2.16                              |            |
| Hematite                            | As (V)             | 4.2                  | -             | 30           | 0.2                               | [28]       |
| Feldspar                            | As (V)             | 4.2                  |               | 30           | 0.18                              |            |
| Bauxol<br>(Neutralized<br>red mud)  | As (V)             | 4.5                  | -             | 23           | 1.081                             | [29]       |
| Dry water<br>hyacinth plant<br>leaf | As (V)             |                      | -             | -            | 0.34                              | [30]       |
| Oliver soil                         | As(V)              | 5-6                  | -             | 25           | 0.42                              | [31]       |
| Sharkey soil                        | As (V)             | 5-6                  | -             | 25           | 0.74                              |            |
| Winder soil                         | As (V)             | 5-6                  | -             | 25           | 0.55                              |            |
| Orange peel<br>waste                | As (V)             | 7                    | 120           | 45           | 132                               | [32]       |
| Morus alba                          | As (III)           | 6                    | 120           | 20           | 2.82                              | This study |
|                                     | AS (V)             | 4                    | 120           | 20           | 4.93                              |            |

# Conclusion

The proposed method demonstrate that Morus alba leaves has great potential as a sorbent for the removal of As(III) and As(V) simultaneously. The results reveal that Morus alba leaves has better As removal efficiency as compared to many sorbents as mentioned in Table 5. At pH-6 and pH-4, As(III) and As(V), respectively showed maximum sorption capacity 2.82 mg/g and 4.93 mg/g on Morus alba leaves sorbent. Kinetically, experimental data follow the Pseudo first order rate equation. Furthermore, thermodynamic parameters Gibbs free energy and enthalpy change values indicate the sorption reaction is spontaneous and endothermic in nature. proposed method was applied on The contaminated water samples which show that up to 89.84% of As was successfully removed.

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