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Adsorptive uptake of arsenic (V) from water by aquatic fern *Salvinia natans*

Somnath Mukherjee and Sunil Kumar

ABSTRACT

The sorption potential of the As (V) ion from aqueous solution has been studied using the water fern *Salvinia natans* as a scavenging candidate for aquatic arsenic. Sodium arsenate was used to prepare the stock solution of As (V). The diluted stocks with nutrient as sample solutions with As-free pond water were kept in different Perspex cells of a multiple chamber and for each concentration a varying amount of dry mass of the plants were nourished under adequate lighting for supporting the growth of the plants. The samples were drawn from each chamber at 24 h intervals up to 5 days and for each sample the residual As (V) was estimated by the silver diethyl dithio carbonate (SDDC) method.

Test results indicate that the plant could effectively uptake As (V) between 0.25 and 2 mg l^{-1} to the extent of 74.8 to 54%, respectively, after 120 h contact time for a plant mass of 20 g l^{-1} at neutral pH. The experimental data were fitted well to both Langmuir and Freundlich isotherms. The effect of pH and biomass quantities on sorption rate have been also investigated along with some metabolic parameters.

Key words | arsenic (V), isotherm, kinetics, pH effect, *Salvinia natans*, sorption

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INTRODUCTION

Freshwater resources around the world are being contaminated through various anthropogenic activities over time. Arsenic is a commonly occurring toxic metalloid which finds its way into the hydrosphere through natural means or through the wastewater discharges of industries such as glassware, pesticides, ceramics, paint and dye, metallurgical and fertilizers. A variety of arsenic poisoning symptoms have been recorded. Such symptoms include dermatological lesions, muscular and neurological disorders, impairment of bone marrow function, damage of liver function and skin cancer. Usually, arsenic is found in trivalent and pentavalent forms. The trivalent from is more toxic than the pentavalent form, though under oxidative conditions arsenate in As (V) predominates (Prasad and Dubey 1995). Furthermore, As (III) can be easily oxidised to As (V) by peroxide.

Chemical precipitation and sedimentation are two common separation processes to convert arsenic compounds into insoluble forms (Tokunaga *et al.* 1997). These conventional methods have certain limitations owing to the production of leachate from sludge disposal. Among the various potential reduction methods, adsorption technology has been recommended as a promising method to reduce arsenic concentration in the aqueous environment (Tokunaga *et al.* 1997; Manju and Anirudhan 2000; Nagarnaik *et al.* 2002).

Aquatic macrophytes and other smaller floating plants have been used in recent years to treat wastewater successfully. This aquatic treatment system works through the direct uptake of the substance by the plant's root system under favourable environmental conditions. The encouraging results for the metal uptake capacity of aquatic plants from several researchers (Lakshman 1979; Walter and O'Brien 1981; Chigbo *et al.* 1982; O'Keefe *et al.* 1984; De *et al.* 1985; Selvapathy and Sreedhar 1991; Sen and Bhattacharyya 1993; Low *et al.* 1994; Alam *et al.* 1995;

Panda 1996; Ingole and Bhole 2002) gained the attention of local and state agencies in different parts of world for treating such wastewater. *Salvinia natans* is an easily available free-floating plant that grows abundantly in ponds and lakes in India and can also be handled easily and economically. Previously *Salvinia* was used for Hg (II) removal (Sen and Mondal 1987) and also for uptake of copper (II) (Sen and Mondal 1990). The authors have attempted in the present work to study the adsorption of As (V) from aqueous solution using the water fern *Salvinia*. This investigation aimed to observe As (V) uptake potential with kinetics of water fern (*Salvinia natans*) with some of its metabolic stress effect in a laboratory environment.

MATERIALS AND METHODS

Materials

The investigation was carried out in a muticells aquarium in the Environmental Engineering Laboratory, Department of Civil Engineering, Jadavpur University, Kolkata (India). Young wild plants of *Salvinia natans* were collected from a local, uncontaminated fresh water pond. Several tests on pond water and sediment samples were done to analyse background As (V) level. The test results showed no detectable As (V) concentration in the pond water. The collected plants were grown in an earthen flat jar in a glasshouse for more than a month (35–40 days) before their use for the experiment. Only mature plants were used during this study. Mature plants were harvested from this jar and washed thoroughly in deionised water, 0.01 (M) NH_4-EDTA solution and finally again in deionised water in order to grow them hydroponically in aquaria cells. Each test cell was filled with 3 l of sample solution and a mixture of culturing nutrients. The culturing medium with pH 7.0 ± 0.2 was prepared according to Hoagland and Arnon (1950).

Culturing the plants with As (V)

Stock As (V) solution of 100 mg l^{-1} was prepared by dissolving 0.416 g of sodium arsenate (Na_2 HAs O_4, $7H_2O$) in 1 l of double distilled water. The stock solution was diluted proportionately with the nutrient solution to obtain different desired initial concentrations of As (V).

Matured *Salvinia* plants (total fresh weight 60 g) were placed in different cells of aquaria in floating conditions with sample solutions of varied initial concentration of As (V). The plants were grown at 25 ± 5°C for a photoperiod of approximately 10 h under a source of light intensity 10,000 lux. Analysis of uptake of As (V) was made in the culture medium after 1, 2, 3, 4 and 5 days of contact. The plants were harvested after 120 h. Biochemical parameters such as chlorophyll and soluble protein were also analysed in the treated plants after different contact periods.

Estimation of As (V) and other parameters

As (V) in the culture medium was estimated using UV-VIS spectrophotometer (Shimatzu 2100) by the silver diethyl dithio carbonate (SDDC) method as outlined in *Standard Methods* (1989). The pH of the solution was tested using a digital pH meter (Phillips). Total chlorophyll was measured spectrophotometrically using the UV-VIS spectrophotometer after extracting it from 1 g fresh leaf tissue of exposed plant with 80% acetone. The absorbance value of the sample was measured at 652 nm wavelength following the procedure suggested by Yoshida *et al*. (1976). Soluble protein was extracted from 19 samples of plants (root zone) by grinding in a cold solution of phosphate buffer (0.1 M sodium phosphate) at pH 7.5. The buffer sample ratio was maintained at 10:1 (volume:weight). This extraction method followed the technique described by Lazen *et al*. (1983). Then the protein content was measured by UV-VIS spectrophotometer with Bradford reagent prepared with: (i) 20 mg of commasic brilliant blue G 250; (ii) 9.6 ml of 99% dehydrated alcohol; (iii) 9.3 ml 88% orthophosphoric acid and deionised water added to make the volume 200 ml.

RESULTS AND DISCUSSION

Uptake of As (V) by *Salvinia*

Salvinia plants, water and sediment samples collected from a selected pond on the university campus were

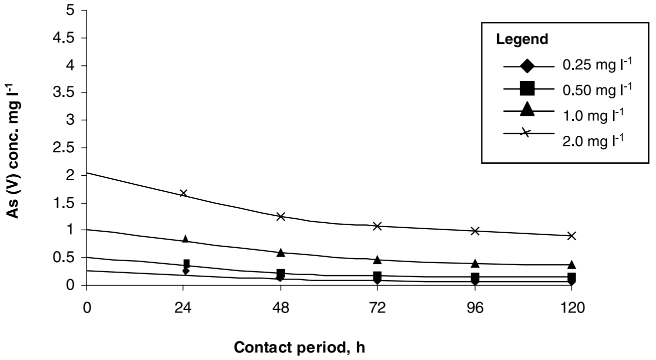

Figure 1 | Uptake of As (V) by *Salvinia* with time.

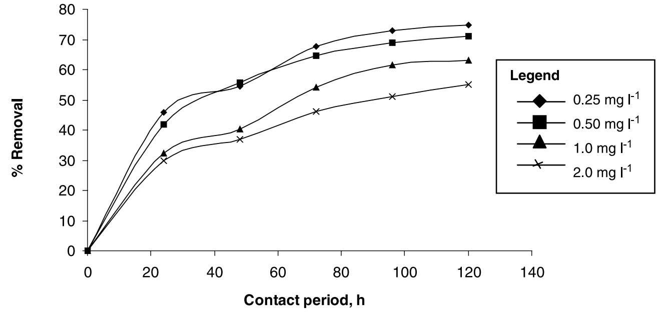

Figure 2 | Removal kinetics of As (V) with time.

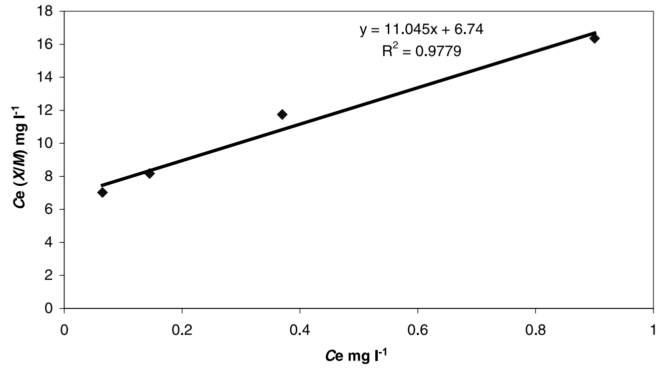

Figure 3 | Langmuir isotherm plot for As (V) sorption by *Salvinia*.

analysed for As (V). No As (V) was detected in these samples since the SDDC method has a detection limit of 0.1 mg l^{-1}. During the course of the experiment, the residual As (V) concentration was estimated from the culture solution at 24-hour intervals up to 120-hour contact period against different initial As (V) concentrations. From the residual arsenic concentration in the aqueous media after treatment with the test plant, the removal percentage was calculated at specified time intervals. The studies were undertaken for up to 5 days with 0.25, 0.50, 1.00 and 2.00 mg l^{-1} of initial As (V) concentration. The results of As (V) uptake by *Salvinia* roots during the course of the experiment at various initial concentrations are shown in Figure 1. The trend of removal reveals a biphasic nature of uptake with rapid sorption up to a period of 48 hours reaching equilibrium after 120 hours. The reduced rate of removal beyond 48 hours as exhibited in Figure 2 may be indicative of a rapid attainment of saturation state in the plants. A similar uptake model was identified by Selvapathy and Sreedhar (1991) for cadmium removal using water lettuce and water hyacinth.

It was also observed that the sorption by *Salvinia* reached a maximum at 0.25 mg l^{-1} of initial As (V) concentration and declined progressively with each increment of initial As (V) concentration. After a contact period of 120 h with an initial As (V) concentration of 0.25 mg l^{-1}, about 74.8% removal was achieved, whereas 55% As (V) removal was observed with an initial As (V) concentration of 2.0 mg l^{-1}, as shown in Figure 2. The declining rate of As (V) adsorption by *Salvinia* may be due to an increase of toxic effects on the plant metabolism crossing a threshold limit that promotes senescence (Jana and Chaudhury 1982).

Sorption isotherm

The sorption equilibrium was reached after a period of 120 h and the residual As (V) concentration after this period was taken as the equilibrium arsenic concentration. Equilibrium data were tested for fitting to different standard isotherm models and the parameter values were calculated along with the standard errors and regression coefficient. Figures 3 and 4 illustrate the plot of Langmuir and Freundlich isotherms, respectively, which were found to fit the data well.

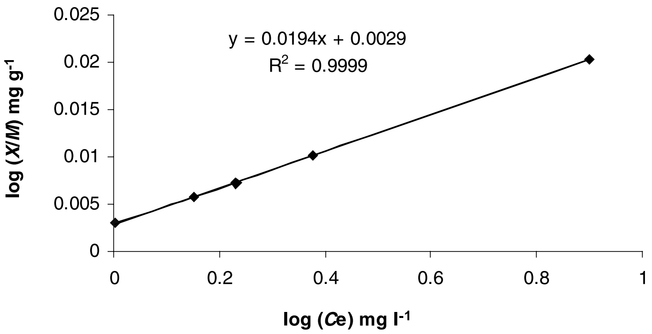

Figure 4 | Freundlich's isotherm plot for As (V) sorption by *Salvinia*.

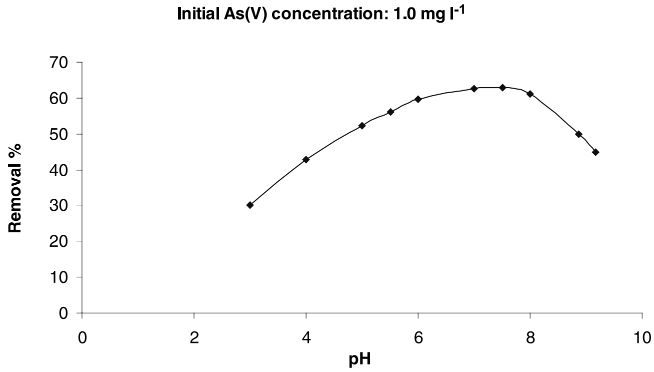

Figure 5 | Effect of pH on As (V) removal.

The linear form of the Langmuir isotherm model can be expressed as:

$$\frac{Ce}{\frac{X}{M}} = \frac{1}{X_m}(Ce) + \frac{K}{X_m}$$

where, Ce = equilibrium concentration

$\frac{X}{M}$ = mass of sorbate adsorbed per unit quantity of the sorbent

X_m = sorption capacity

K = Langmuir constant.

From Figure 3, the following relationship was obtained:

$$\frac{Ce}{\frac{X}{M}} = 11.045\,Ce + 6.74$$

Regarding Freundlich's isotherm model, the linear form can be presented as:

$$\log\left(\frac{X}{M}\right) = \log \mathrm{K} + \frac{1}{\mathrm{n}}\log Ce$$

where $\frac{1}{n}$ is known as Freundlich's isotherm parameter constant corresponding to sorption intensity.

From Figure 4, the equation corresponding to Freundlich's isotherm model can be written as:

$$\log\left(\frac{X}{M}\right) = 0.0029 + 0.0194\log Ce$$

The data indicating the adsorption phenomenon is favoured in the present study.

Effect of pH

In the process of sorptive uptake, pH has a direct influence on the chemical and physical properties of both the sorbent and the sorbate. To estimate the As (V) uptake capacity of *Salvinia natans* at different pH, removal percentage after 120 h was determined at various pH values from acidic to alkaline, with initial As (V) concentration of 1.00 mg l^{-1} and taking the mass of absorbent at 60 g in 3 l of culture solution. The effect of pH on the uptake of As (V) by *Salvinia* is illustrated in Figure 5. A maximum of 63% removal was observed at pH 7.5. It was also found that the uptake rate progressively reduced with the lowering of the pH of the medium. However, the removal percentage dropped further beyond pH 8.0. At lower pH values, sorption was unfavourable perhaps because the H + ion is competing for sorption sites on the root making the H^+–As^- exchange unattractive. A similar trend was also observed by Lee and Low (1989) during their investigation into copper removal from solution using moss as adsorbent medium.

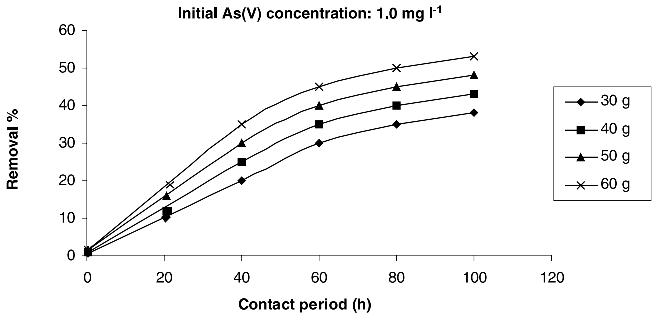

Figure 6 | Effect of biomass quantity on removal of AS (V) by *Salvinia* roots.

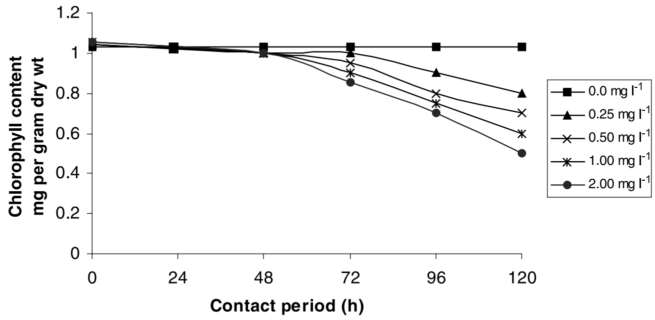

Figure 7 | Effect on chlorophyll with different initial As (V) concentration.

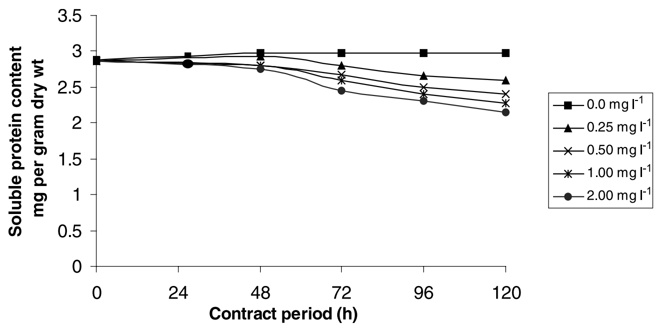

Figure 8 | Effect on soluble protein in plants with different initial As (V) concentration.

Effect of biomass quantity

It is obvious that the sorbate adsorption rate depends on the amount of available sites on the sorbents. A study was performed with a view to exploring the influence of biomass quantity on a dry weight basis on As (V) uptake rate by plant roots. Different biomass quantities of 30, 40, 50 and 60 g were used in the study in 3-l working volumes in aquaria. The initial concentration of As (V) was 1.00 mg l^{-1}. The sample was withdrawn at 24-h intervals and the residual level of As (V) was measured in each set. The pattern of removal was found to be identical independent of biomass quantity (Figure 6). It is evident from the figure that, because more sites were available, maximum removal was achieved with 60 g biomass. The removal rate was faster during initial period, then became almost asymptotic in nature after a contact period of 5 days.

Effect on chlorophyll content

Total chlorophyll was estimated for *Salvinia* plants with time of exposure to observe the change in biochemical constituents of *Salvinia*. Figure 7 shows the effect of varied initial As (V) dosages on chlorophyll content for *Salvinia* at different time periods. It is evident that, during the initial contact hours (i.e. up to 48 h), there were no significant toxic effects on chlorophyll content of the plant irrespective of initial As (V) concentration. But a definite toxic effect on chlorophyll content resulting in a 60% loss was noticed after 5 days' contact for an initial As (V) concentration of 2.0 mg l^{-1}. This result suggests the possible disorderliness of the chloroplast membrane and inactivation of electron transport of the photosystem at 2.0 mg l^{-1} of As (V). Similar toxic effects on chlorophyll content for *Salvinia* plants were noted by Sen and Bhattacharyya (1993) where lead (Pb^{2+}) was treated with *Salvinia*. Sen and Mondal (1987) demonstrated that biochemical parameters such as chlorophyll, protein and hill activity were unaffected for *Pistia* plants below Cr (VI) concentration 5 mg l^{-1}.

Effect on soluble protein content

A significant reduction of soluble protein content was observed in the plants as both the initial As (V) concentration and the contact period increased. The declining pattern, as evident in Figure 8, indicates that inhibition occurred promoting senescence of *Salvinia* plants by decreasing the protein content of the plant. A maximum reduction of 20% was noted at an initial As (V) concentration of 2 mg l^{-1} for a time period of 120 h. The loss of protein content in plants due to accumulation of heavy metals has been reported by various researchers (Cooley and Martin 1979; O'Keefe *et al*. 1984; Sen and Bhattacharyya 1993). Such a stress-induced decrease could be due to the reduction of denovo synthesis of protein, or may be due to immediate breaking down of amino acids at a higher rate as explained by Dugger and Ting (1970).

CONCLUSION

The roots of the water fern (*Salvinia natans*), an easily available wild aquatic macrophyte commonly found in India, have been shown to have the potential to remove arsenic (V) from aqueous solution. The test results indicate that the plant was able to adsorb As (V) to the extent of 74.8 to 54% for initial As (V) concentrations of 0.25 to 2 mg l^{-1}, respectively, after 5 days' contact period. The toxic effect related to destruction of chlorophyll content and soluble protein reduction was observed for an initial As (V) concentration equal to or more than 2.0 mg l^{-1}. At lower pH (<6.0) and also at higher pH (>8.0) the removal rate was decreased. The equilibrium data fitted well to both Langmuir and Freundlich's isotherm models. The results of the present study indicate the need for experiments to observe hill activity, peroxides activity, pyrophosphatase activity, enzymatic activity and so on, in order to ascertain the toxic effects of As (V) on *Salvinia natans*.

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