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Arsenic removal from the aqueous system using plant biomass: a bioremedial approach

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Abstract Metal species released into the environment by technological activities tend to persist indefinitely, circulating and eventually accumulating throughout the food chain, thus becoming a serious threat to the environment. Environment pollution by toxic metals occurs globally through military, industrial, and agricultural processes and waste disposal. Bioremediation processes are the target of recent research and are considered low-cost, ecofriendly methods to alleviate the current problems of water decontamination, particularly for remote and rural areas. The present piece of work reports the unexploited sorption properties of the powdered seed of the plant *Moringa oleifera* (SMOS) for the removal of Arsenic [As(III) and As(V)] from aqueous solutions. Sorption studies, using standard practices, result in the standardization of optimum conditions such as biomass dosages (2.0 g), metal concentrations (25 ppm), contact time (60 min) and volume of the test solutions (200 ml) at pH 7.5, for As(III) and pH 2.5 for As(V). Maximum sorption for As(III) and As(V) species is 60.21 and 85.6%, respectively. Protein/Amino acid–Arsenic interactions are found to play an important role in the biosorption process using plant biomass SMOS.

Keywords Arsenic removal · Biosorption · *Moringa oleifera* · Amino acid–arsenic interaction · Domestic water treatment

Introduction

The water resources of the world are being polluted through various anthropogenic activities. Arsenic is one such toxic metalloid commonly occurring in the natural

ecosystem. The health hazards associated with even low levels of Arsenic in natural underground water have attracted the attention of the scientific community. Arsenic, the king of poisons, is known to be detrimental to human beings and animals, causing several neurological [6], dermatological [22], gastro-intestinal [11], and cardio renal diseases [16], besides the fact that it is considered to be carcinogenic [8]. It is currently under watch by different countries for a reduction in its maximum contaminant level (MCL). The U.S. Environment Protection Agency has revised the maximum contaminant limit of Arsenic from 0.05 to 0.01 mg/l [10]. The environmentally important oxidation states of Arsenic are the pentavalent Arsenate (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} and AsO_4^{3-}) and trivalent Arsenite (H_3AsO_3 , H_2AsO_3^- , HASO_3^{2-} and AsO_3^{3-}) species. The trivalent form of Arsenic is more toxic and has also been found more difficult to be removed.

A large number of physico-chemical methods based on coagulation, ion-exchange, reverse osmosis and flocculation (with various synthetic coagulants such as aluminum, ferric salts, soda ash, polymers, etc.) have been developed for Arsenic removal [3, 23]. However, these methods are associated with several disadvantages such as unpredictable metal ion removal, high material costs and the generation of toxic sludge that is often more difficult to manage. Research findings have raised strong doubts and explored several drawbacks in the synthetic coagulants based removal processes like Alzheimer's disease [18], the carcinogenic effects of alum and other health problems associated with residual Iron salts [17].

An increasing awareness has been developed for the importance of renewable natural resources. Newly emerging terms like Come Back to Nature, Grey to Green chemistry and various ecofriendly techniques are the new principles guiding the development of products and processes of the next generation. Sorption using plant biomass has emerged as the potential alternative to chemical techniques for the removal and recovery of metal ions from aqueous solutions. Research attention has been paid towards the use of natural coagulants

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[15, 19] and biosorption processes [1, 20] for the decontamination of water.

Moringa oleifera (Saihjan or drumstick), a cosmopolitan tropical, drought tolerant tree, available throughout the year, has been well documented for its various pharmacological importances, viz. its analgesic [13], antihypertensive [5] and anti-inflammatory effects [7]. The powdered seed of the plant *M. oleifera* has coagulating properties [14, 24] that have been used for various aspects of water treatment such as turbidity, alkalinity, total dissolved solids and hardness. However, its biosorption behavior for the removal of toxic metals from water bodies has not been given adequate attention. The present piece of work reports the unexploited properties of the powdered seed of this multi-dimensional plant (*M. oleifera*) as a bioremedial approach for the removal of Arsenic from aqueous solution.

Materials and methods

Biosorbent preparation

Moringa oleifera seeds were collected in February–March 2004. The seeds were washed thoroughly with double distilled water to remove adhering dirt, dried at 65°C for 24 h, crushed and finally sieved through (105, 210 and 420 µm) mesh copper sieve. For the shelled seeds, the husk enveloping each seed was removed and the kernel ground to a fine powder, using a blender. No other chemical or physical treatments were used prior to the adsorption experiments.

Biosorption studies

Sorption studies using standard practices were carried out in batch experiments (triplicates) as functions of biomass dosage (0.5–6.0 g), contact time (20–100 min), metal concentration (10–100 µg/ml), pH (2–9), and particle size (105–420 µm). The solutions of As(III) (sodium arsenite; NaAsO₂) and As(V) (sodium hydrogen arsenate; Na₂HAsO₄·7H₂O) were taken in separate Erlenmeyer flasks. After pH adjustments, a known quantity of dried biosorbent was added and the metal bearing suspensions were kept under magnetic stirring until the equilibrium conditions were reached. After shaking, the suspension was allowed to settle down. The residual biomass sorbed with the metal ion was filtered using a Whatman 42 filter paper (Whatman International Ltd., Maidstone, England). The filtrate was collected and subjected for metal ion estimation using Flameless Atomic Absorption Spectroscopy (Perkin Elmer 2380). The metal concentrations before and after adsorption were recorded. The percent metal sorption by the sorbent was computed using the equation: Percent Sorption = $C_o - C_e / C_o \times 100$, where C_o and C_e are the initial and final concentration of metal ions in the solution.

IR analyses on solid samples

The IR analyses of native and exhausted (after metal sorption) SMOS samples were performed using a FT-IR Spectrophotometer (FTIR-8400, Shimadzu).

Results

The soluble metal fractions of As(III) and As(V) ions after SMOS biosorption under different experimental conditions have been recorded and presented (Tables 1, 2). A perusal of the tables, in general, shows the following trends of sorption.

Effect of metal concentration

The sorption behavior of the two oxidation states of Arsenic [As(III) and As(V)] species was carried out in the metal concentration range 10–100 µg/ml at pH 7.5. In general, the sorption of As(III) and As(V) on shelled *M. oleifera* seeds increased with the increasing concentration of the metal ions reaching the optimum level 60.21 and 85.6%; respectively at the metal concentration (25 µg/ml) after which the percentage sorption remained constant. Interestingly, a decreasing trend in the metal sorption was observed in concentration range (50–100 µg/ml).

Effect of sorption time

The effect of contact time on the biosorption of both the Arsenic [As(III) and As(V)] species on the plant biomass was studied in the duration of 20–100 min at pH 7.5. The percent sorption of metal ions as a function of time indicated a biphasic pattern with a rapid initial uptake up to 60 min, which gradually reached an equilibrium after a period of 60 min.

Effect of biomass dosage

While observing the influence of the dry weight of plant biomass on the sorption potential at pH 7.5, it was noted that the sorption potential of both the Arsenic [As(III) and As(V)] species increased with increased biomass dosages (0.5–2.0 g). No significant increment in the sorption tendency was observed on further raising the biomass dosages from 2.0 g onwards.

Effect of volume on sorption

The percentage sorption of the two Arsenic [As(III) and As(V)] species on the target biomass was recorded under similar experimental conditions in a different set of

Table 1 Soluble As(V) ion concentration after maximum biosorption at optimum time (60 min) at pH 7.5, on unmodified SMOS as a function of metal concentration, biomass dosage and volume of the test solution

Initial concentration $\mu\text{g/ml}$ (μM)	Soluble metal species (μM) at different biomass dosages			
	0.5 g	2.0 g	4.0 g	6.0 g
Volume of the test solution (100 ml)				
10 (13.35)	8.25 \pm 0.18	7.16 \pm 0.11	6.86 \pm 0.16	6.81 \pm 0.21
25 (33.38)	12.77 \pm 0.21	9.93 \pm 0.12	9.22 \pm 0.21	8.81 \pm 0.11
50 (66.76)	26.78 \pm 0.13	20.02 \pm 0.11	19.07 \pm 0.11	18.67 \pm 0.11
100 (133.51)	56.96 \pm 0.12	42.54 \pm 0.12	39.79 \pm 0.11	39.60 \pm 0.09
Volume of the test solution (200 ml)				
10 (26.70)	10.60 \pm 0.20	8.39 \pm 0.11	8.19 \pm 0.11	7.78 \pm 0.14
25 (66.75)	19.93 \pm 0.11	9.61 \pm 0.21	9.43 \pm 0.11	9.33 \pm 0.21
50 (133.51)	43.63 \pm 0.11	24.81 \pm 0.10	23.82 \pm 0.12	20.91 \pm 0.20
100 (267.0)	101.09 \pm 0.11	63.04 \pm 0.13	60.85 \pm 0.15	58.69 \pm 0.12
Volume of test solution (300 ml)				
10 (40.05)	15.68 \pm 0.10	12.24 \pm 0.21	11.66 \pm 0.21	11.52 \pm 0.21
25 (100.13)	29.36 \pm 0.11	13.88 \pm 0.13	13.39 \pm 0.14	12.88 \pm 0.13
50 (200.27)	63.93 \pm 0.21	36.29 \pm 0.11	33.16 \pm 0.13	31.60 \pm 0.10
100(400.53)	143.43 \pm 0.11	91.56 \pm 0.11	79.47 \pm 0.12	75.06 \pm 0.12

volumes (100–300 ml) of the test solution. Maximum sorption was found in the volume 200 ml of the test solution.

Effect of particle size

Different sizes of the particle (105, 210 and 420 μm) of the plant biomass were used to observe the pattern of the biosorption behavior of [As(III) and As(V)] species. A decrease in particle size in the range (420–105 μm) had a favorable effect on the biosorption of the metal.

Effect of the pH

Figure 1 represents the percentage removal as a function of the pH at optimum concentration (25 $\mu\text{g/ml}$) of As(V) and As(III). The optimum sorption (85.6%) of the

Arsenic(V) species by the plant biomass was obtained in the pH range of 2.5–6.5. The percentage sorption of the As(III) ion, by the same target biomass, enhanced as the pH of the test solution was increased from 2.0 to 7.5, and attained the optimum value of 60.21%. However, there was no significant increase in the biosorption with a further increase in the pH from 7.5 to 9.0.

Adsorption isotherm

The Langmuir isotherm was applied for the adsorption equilibrium of both As(III) and As(V), using following equation:

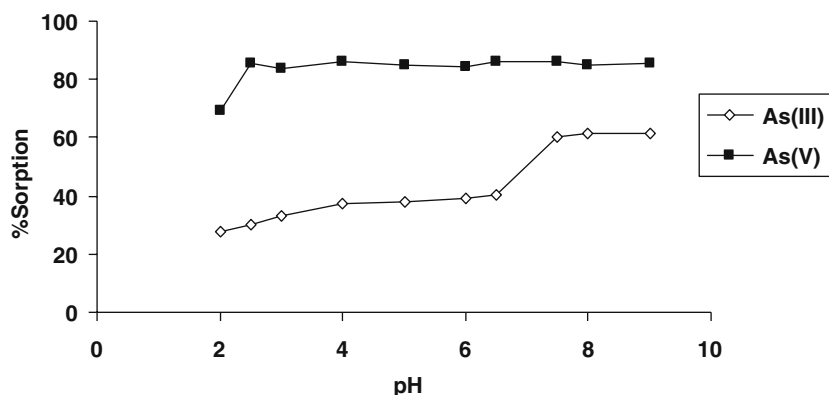
$$C_e/q_e = (1/Q_o b) + (C_e/Q_o), \quad (1)$$

where C_e represents the equilibrium concentration ($\mu\text{g ml}^{-1}$), q_e the amount of As(III) and As(V) adsorbed

Table 2 Soluble As(III) ion concentration after maximum biosorption at optimum time (60 min) at pH 7.5, on unmodified SMOS as a function of metal concentration, biomass dosage and volume of the test solution

Initial Concentration $\mu\text{g/ml}$ (μM)	Soluble metal species (μM) at different Biomass dosages			
	0.5 g	2.0 g	4.0 g	6.0 g
Volume of the test solution (100 ml)				
10 (13.35)	10.62 \pm 0.12	9.94 \pm 0.10	9.88 \pm 0.11	9.77 \pm 0.12
25 (33.38)	20.86 \pm 0.12	19.22 \pm 0.12	19.03 \pm 0.21	19.02 \pm 0.11
50 (66.76)	43.47 \pm 0.13	40.67 \pm 0.11	39.47 \pm 0.10	38.64 \pm 0.11
100 (133.51)	92.02 \pm 0.12	83.20 \pm 0.12	82.72 \pm 0.11	80.53 \pm 0.11
Volume of the test solution (200 ml)				
10 (26.70)	16.29 \pm 0.21	14.36 \pm 0.21	13.83 \pm 0.21	13.60 \pm 0.14
25 (66.75)	31.24 \pm 0.11	26.56 \pm 0.21	26.45 \pm 0.13	26.00 \pm 0.20
50 (133.51)	66.92 \pm 0.10	65.41 \pm 0.13	65.26 \pm 0.11	61.17 \pm 0.12
100 (267.0)	159.35 \pm 0.13	155.76 \pm 0.12	154.75 \pm 0.13	147.83 \pm 0.11
Volume of test solution (300 ml)				
10 (40.05)	23.80 \pm 0.11	21.27 \pm 0.12	21.16 \pm 0.21	20.29 \pm 0.21
25 (100.13)	44.69 \pm 0.10	39.67 \pm 0.11	39.14 \pm 0.14	38.93 \pm 0.13
50 (200.27)	103.76 \pm 0.21	93.69 \pm 0.11	91.20 \pm 0.13	88.10 \pm 0.10
100 (400.53)	223.02 \pm 0.10	210.92 \pm 0.11	202.91 \pm 0.11	194.98 \pm 0.12

Fig. 1 Effect of pH on As(III) and As(V) biosorption



at equilibrium ($\mu\text{g g}^{-1}$). Q_o and b are the Langmuir constants related to adsorption capacity and the energy of adsorption, respectively. Q_o and b were determined from the slope and intercept of the plot and found to be Q_o 3.13 and 8.33 and b 0.32 and 0.42, respectively (Fig. 2).

The Freundlich isotherm is represented by the equation:

$$\log q_e = \log K_f + 1/n \log C_e, \quad (2)$$

where q_e is the uptake of the metal per unit weight of the biosorbent, C_e the equilibrium (residual) concentration of the metal ion in solution ($\mu\text{g ml}^{-1}$), K_f and n are the characteristic constants. The Freundlich constants K_f and n were found to be K_f 0.12 and 0.34 and n 1.09 and 0.90, respectively (Fig. 3).

The above set of experiments standardize the optimum conditions for the biosorption of the trivalent and

pentavalent species using target plant biomass shelled *M. oleifera* seeds (SMOS) as: biomass dosage (2.0 g), metal concentration (25 $\mu\text{g/ml}$), contact time (60 min) and volume of the test solution (200 ml) at pH 7.5 (Fig. 4).

Discussion

A study of the isotherm provides the extent of the adsorption capacity of the sorbent for the removal of the target species from the solution at standardized conditions. The sorption capacity of the target plant biomass for both the oxidation states of Arsenic has been mathematically examined. The high degree of linearity obtained in both the isotherms show that the data are best fitted into these models (Figs. 2, 3), thus indicating the easy separation of target metal ions from water bodies.

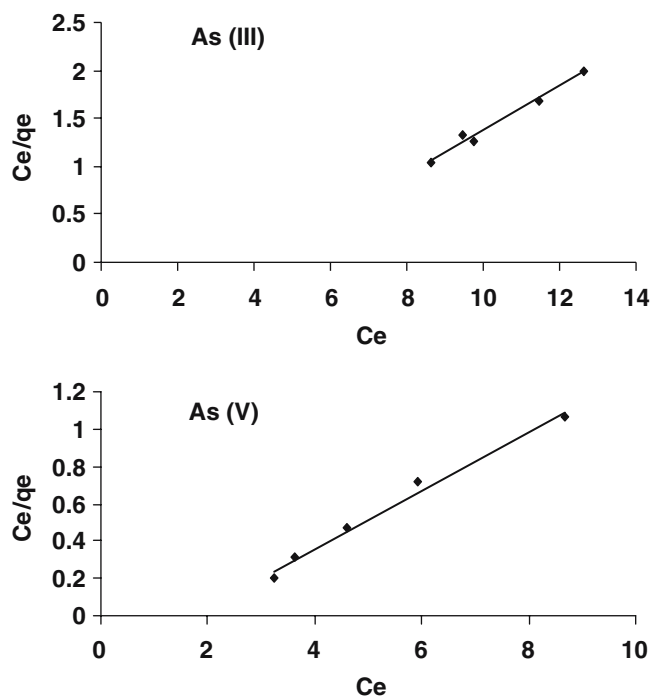


Fig. 2 Langmuir isotherms of As(III) and As(V)

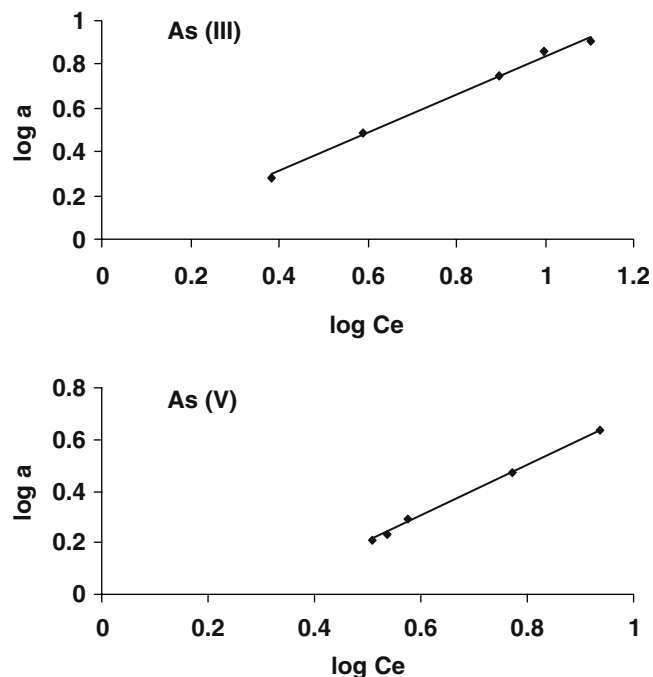
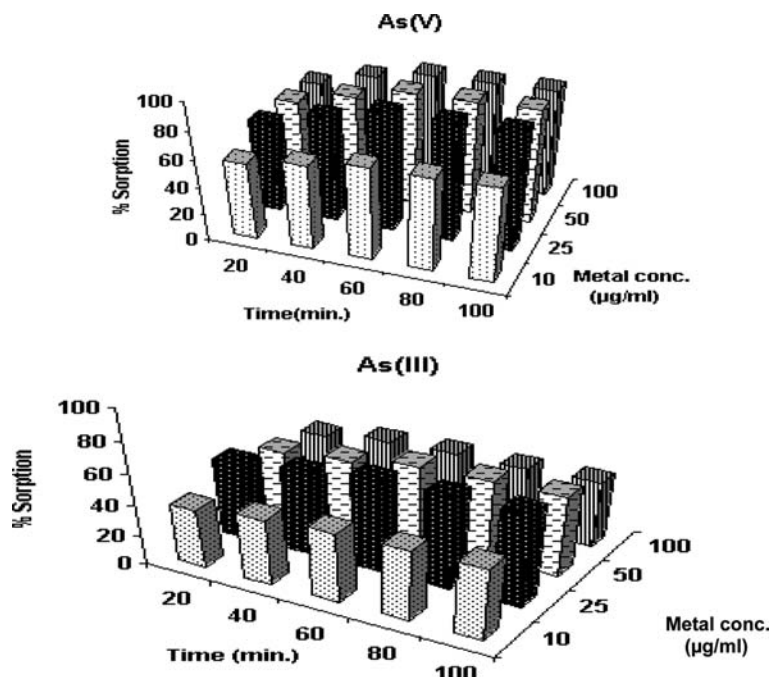


Fig. 3 Freundlich isotherms of As(III) and As(V)

Fig. 4 Percentage removal of As(V) and As(III) species, as a function of metal concentration, and contact time using optimum biomass dose (2.0 g) at pH 7.5



The present piece of work has embodied the tremendous potential that exists in shelled *M. oleifera* seed as a biosorbent for removal of toxic metals (Arsenic) from the aqueous system. It becomes imperative to understand the mechanistic aspects of interactions of constituents of seed with metal ions, thus, highlighting the nature of chemical species playing the pivotal role in efficient biosorption, as obtained in present experiments. A possible explanation has been synthesized based on our experimental findings and pertinent information is available on the relevant topic. The pH profile and the concentration of the metal ions employed in our experiments provide an insight to the biosorption process involving the interaction of cellular constituents of *M. oleifera* seeds with metal ions. It is reported that an aqueous solution of the Moringa seed is a heterogeneous complex mixture, having cationic polypeptides with various functional groups, especially low molecular weight amino acids [9, 12]. Amino acids have been reported as efficient phytochelators that work at even at low concentrations and having the tendency to interact with metal ions and significantly enhance their mobility. The proteinacious amino acids, depending upon the pH, possess both the negatively and positively charged ends and are, thus, capable of generating the appropriate atmosphere for attracting the anionic or cationic species of the metal ions.

Arsenic in the pentavalent oxidation state shows optimum sorption (85.6%) by plant biomass (SMOS) in the pH range 2.5–9.0. The pentavalent Arsenic species exists in the monovalent (H_3AsO_4^-), and divalent anion ($\text{H}_2\text{AsO}_4^{2-}$) in the pH range 2.0–9.0 [8]. The majority of amino acids present in the target biomass

have isoelectric points in the range 4.0–8.0 [21]. In this range of pH, over 90% of the amino acid molecules are in the ionized state. The negatively charged monovalent arsenate species may be held by the positively charged group of amino acids. The percentage sorption of trivalent Arsenic species, on the same target biomass, increased as the pH of the test solution was enhanced from 2.0 to 7.5, had optimum sorption (60.21%) at pH 7.5 and no increase occurred in the percent sorption at any higher pH (7.5–9.0). The trivalent Arsenic species exists in a non-ionic form in the pH range 2.0–7.0 and in the anionic form [8] in the pH range 7.5–9.0. Optimum biosorption (60.21%) in the pH range 7.5–9.0 can be easily assigned to the availability of the negatively charged Arsenic(III) species, which interacts with the positively charged ends of amino acids. With the increase in pH range, the carboxylic group of the amino acids would progressively be deprotonated as carboxyl-

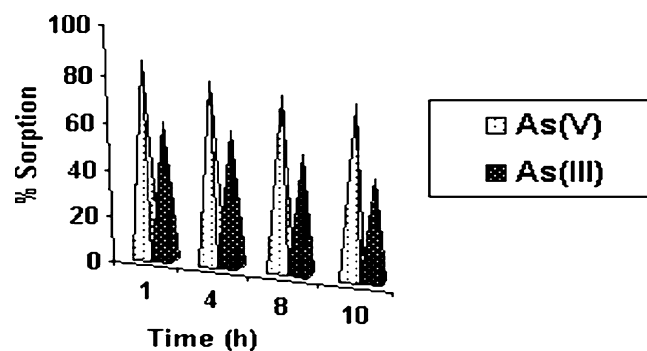


Fig. 5 Phytotoxicity of Arsenic at 100 µg/ml to SMOS, in terms of decreasing % sorption as a function of time

ate ligands, simultaneously protonating the amino group. Such positively charged amino groups (NH_3^+) facilitate the SMOS-Arsenic binding. SMOS contains proteins and has a net positive charge at pH below 8.5 ($\text{pK}_a > 8.6$). These positively charged proteins are also considered to be active moieties for binding metal ions.

The observation that Protein/Amino acid–Arsenic interactions appear to be an ion exchange process, contributing a significant role in the biosorption of Arsenic using SMOS, finds further support by the decreasing trend in sorption at high metal concentration (50–100 $\mu\text{g/ml}$). Arsenic induced loss in protein content has been reported in several plant biomasses [2]. Such Arsenic induced decrease in protein content might be due to an increase in the breakdown of amino acid [4] of SMOS at higher Arsenic concentrations. This fact is confirmed by separate experiments on the percentage sorption in the metal concentration range (50–100 $\mu\text{g/ml}$), as a function of prolonged time period from 1 to 10 h. A significant reduction in the range (13 to 17%) was observed in the presence of Arsenic concentration (100 $\mu\text{g/ml}$) during 10 h of contact time (Fig. 5).

The protein/amino acid–Arsenic interactions can be further highlighted on the basis of records of the IR spectrum of native and exhausted (after metal sorption) SMOS. The shifting of the NH_3^+ stretching band (2854.2 and 2925.2 cm^{-1} to 2924.6 and 3005.3 cm^{-1}), the NH_3^+ asymmetric stretching (1656.4 cm^{-1} to 1658.6 cm^{-1}), and the symmetric NH_3^+ bending band (1544.4 cm^{-1} to 1545.9 cm^{-1}) have been observed. The absence of the characteristic peak of the carboxylate ion (1600–1590 cm^{-1}) further confirms the cationic nature of polypeptides present in SMOS. Experiments on the characterization of the bioactive principle of SMOS and desorption studies of metal contaminated shelled *M. oleifera* seeds, using various acidic eluting agents for its subsequent reuse, are in progress.

The present piece of work represents a simple physico-chemical scheme for the removal of appreciable amounts of Arsenic [As(III) and As(V)] species, using SMOS from water bodies. This method largely depends on the metal concentration, biomass dosage, size of the particle, contact time and the pH. Isotherm studies support the suitability of the proposed method and explain the easy separation of heavy metal ions from wastewater and a high biosorption capacity. Shelled *M. oleifera* seeds provide an exciting opportunity under the domain of Green Processes for domestic, environment friendly, low-cost methods for the decontamination of toxic metals from aqueous systems. It is believed that, in the near future, SMOS could be a potential challenger of synthetic coagulants for the treatment of contaminated water.

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