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Biosorption of Arsenite and Arsenate from Aqueous Medium Using *Dalbergia Sissoo* Stem Powder: Kinetics, Thermodynamic and Mechanistic Aspects

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Abstract
The adsorption characteristics of arsenic on stem powder of Dalbergia sissoo, a low-cost, natural and indigenous biosorbent, were investigated at laboratory scale using the synthetically contaminated water sample. The experiments were done through batch mode procedure. DBS stem powder was found to be an effective biosorbent to remove bothAs(III) and As(V) from water. Under optimized conditions of biosorbent dosage, contact time, pH, temperature and initial concentration, removal efficiencies from contaminated water were found to be 96% for As(III) and 94.3 for As(V). Experimental data were modeled by Langmuir, Freundlich, Temkin and D-R adsorption isotherms. It was observed that arsenic biosorption was best fitted with Freundlich and Temkin adsorption isotherms. The adsorption free mean energy (E) calculated from D-R isotherm was 0.585 kJmol^{-1} for As(III) and 0.286 kJmole^{-1} for As(V) which indicates physiosorption nature. The pseudo-second-order and intra-particle diffusion model described better than pseudo-first-order kinetics adsorption kinetics data for both As(III) and As(V). The thermodynamic parameter revealed that the process was exothermic, spontaneous/feasible nature of physisorption. Desorption/reuse was also undertaken for four cycles to restore the biosorbent inits original state. The stem powder of DBS can be used as a natural low-cost biosorbent for removal of arsenic from contaminated water.
Keywords: *arsenic: Dalbergia sissoo, biosorption, adsorption isotherm, thermodynamic parameters.*

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I. INTRODUCTION

Arsenic (As) is a toxic element and their contamination in water has been a great challenge for the worldwide scientific communities [1-3]. Its toxicity greatly depends upon itschemical speciation (oxidation state and its organic or inorganic forms). Arsenic contamination of surface water can be through both anthropogenic as well as natural sources. Major anthropogenic sources are agricultural waste (via use of pesticide, herbicide, fertilizer etc.), industrial effluents, coal fired thermal power plants, and discharge from petroleum refineries [4-5]. In the environment, inorganic arsenic can occuras As(V) (arsenate, AsO_4^{3-}), As(III) (arsenite, AsO_2^-) and As(0) (metalloids of arsenic). In water, mostly As(III) and As(V) states of arsenic are predominant. Among different oxidation states of arsenic,As(III) is sixty times more toxic than As(V), which is due to the fact that As(III) has more cellular uptake [6]. In humans, arsenic is a proven carcinogen. Consumption of high level of arsenic contaminated water has been found to increase the risk of tumors in liver, lungs, kidneys and also cause skin cancer,damages the mucous membrane and the nervous, respiratory and circulatory systems [7]. Exposure to high levels of arsenic contaminated water either for long or short period of time may cause health complications, *e.g.*, dislocation and thickening of the skin, pain or cramping of muscles, numbness in feet and hands, and other kinds of health problems.

Thus, development of low cost technology for arsenic decontamination from drinking water is of utmost importance. Different methods for arsenic treatment that have been studied are at various stagesof development. They are based on the principles of adsorption, surface complexation [8], reverse osmosis, co-precipitation and membrane separation [9]. Most of these techniques have some advantages but the major disadvantages are thehigh capital investment cost, the operational complexity, the maintenance and generation of toxic metal sludge, and the lack of suitability for backward/rural areas where such problems predominantly exists [10-12]. In third world countries that are at risk, bioremediation is analternative technologyand green methodology to remove metal pollution from water [13]. Bioremediation of arsenic from contaminated water

have many advantages, like eco-friendly, show excellent performance, has possibility for regeneration, is cost effective, hassludge free operation and is very simple to operate [14].

The present study involves the use of stem powder of*Dalbergia sissoo* to investigate its potential for removal of arsenic from water. *Dalbergia sissoo*, family fabaceae, is a timber tree, indigenous to India, Pakistan and Nepal. DBS is commonly known as Indian rose wood and shesham. A number of researchers reported that its bark and wood are bitter in taste, it is abortifacient, astringent and expectorant and also profitable in the treatment of skin related disease like eczema, leprosy, scabies andleucorrhea [15-20]. The leaves of *Dalbergia sissoo* have shown antipyretic, analgesic and anti-inflammatory action [21].In the present investigation the unexploited characteristics of the stem powder of the ubiquitous plant DBS as a biosorbent for removal of two predominant oxidation state of As(III) and As(V) from water. To prove the reusability of the biosorbent, the desorption efficiency of loaded biomaterial also examined.Several parameters such as temperature, contact time, biosorbent dosage, different concentration of adsorbate and pH were investigated to optimize favorable conditions.

II. MATERIALS AND METHODS

Preparation of biosorbent

The stem powder of DBSwas collected in the form of waste material from a saw mill (near B.I.T More, Ranchi Jharkhand, India). It was washed with distilled water several times to remove color, dust and other adhering impurities. After washing, it was dried in an oven at 80°C overnight. The dried biomass was sieved to find out particle size (0.6 mm-1.0 mm).The obtained dried biomass was stored in airtight plastic bottle for future use without any chemical treatment.

Reagents andsolution preparation

Throughout the experiment plastic ware was used to avoid contamination of other metals. It was cleaned with HCl(25% v/v) followed by HNO_3 (25%, v/v) (Merk, Darmstadt,Germany) and thoroughly rinsed with deionizedwater. All other reagents and standards used were of analytical grade.As(III)stock solution was prepared by dissolving 1.734 g of sodium arsenite ($NaAsO_2$, Sigma-Aldrich)and diluted to 1000 mL to get 1000 mgL^{-1} As(III) stock solution. As(V) stock solution (1000 mgL^{-1}) was prepared by adding 4.164 g of sodium arsenate ($Na_2HAsO_4.7H_2O$; Loba chemicals) in ultrapure water (UPW, Millipore, 18Ω). Working stock solutionswere prepared by diluting the stock solution at the time of requirement by proper dilution.

Characterization and instrumentation

The functional groups present in the biosorbent was identified using a Fourier transform infrared spectrophotometer (FTIR) (Make and model: Shimadzu, Japan; IR Prestige21). Spectra of the biosorbent before and after arsenic sorption were recorded. Surface morphology of the biosorbent was examined by scanning electron microscope (SEM) (Make and Model: Jeol, Japan; JSM-6390LV) before and after treatment with As(III) and As(V). The distribution of elements on the biosorbent surface was also analyzed before and after treatment with arsenic using energy dispersive X-ray spectrometer (EDS). As concentration in water sample was examined using inductively coupled plasma optical emission spectrometer (Perkin Elmer, USA; Optical 2100DV ICP-OES). The pH value was examined by using Orion 720 A^+ ion analyzer equipped with combined fluoride ion selective electrode (Orion 9609 BN fluoride combined electrode) and the other physiochemical parameters of water were analyzed by standard methods.

Batch experiment study of arsenic removal

Biosorbent prepared from stem powder of DBS, was studied for its potential for removal of arsenic from the contaminated water at different concentrations (0.1-0.3 mgL^{-1}). The experiments were done through batch procedure, where 100 mL of arsenic solutions of desired concentration were taken in a conical flask in which optimum amount of biosorbent was added. The conical flask was shaken for 30 min for As(III) and 40 min for As(V) using horizontal rotary shaker (shaking speed 150 rpm), until equilibrium is established. Initial arsenic concentration was maintained at 0.3 mgL^{-1} for both As(III) and As(V) for every experiment except for those where arsenic concentration was optimized. Whereas the biomass stem powder of DBS was removed using Whatman filter paper. The residual arsenic concentration was preliminarily analyzed by semi-quantitative arsenic test kit (Quantofix Arsen 10, Germany) and finally using ICP-OES. All experiments were performed at 20 ± 2°C for As (III) and 40 ± 2°C in case of As (V) except for the case where temperature is optimized. The pH of the solution was adjusted by using either NaOH or HCl. All the experiments of various physical parameters were conducted twice and the mean values were used as optimum values.

The percentage removal of arsenic (R %) and the amount of arsenic adsorbed (q_e) per unit weight of adsorbent (mg g^{-1}) at equilibrium were calculated from the following equation:

$$\boldsymbol{R}\% = \frac{(\boldsymbol{C_o} - \boldsymbol{C_e})}{\boldsymbol{C_o}}\mathbf{100} \qquad (1)$$

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

Where C_o and C_e (mgL^{-1}) are the initial and equilibrium arsenic concentrations in the solution respectively, V is volume of solution (L) and m is the mass (g) of adsorbentused [22-25].

III. RESULTS AND DISCUSSION

SEM and EDS analysis of biosorbent

The surface morphologies of biosorbent and distribution of elements on the adsorbent surface were analyzed by scanning electron microscope (SEM) and corresponding EDS spectrum along with percentage atomic and molecular weight were embedded on the EDS spectra respectively which is shown in (Fig.1). The image obtained before treatment has several voids, which were occupied by As(III) or As(V) and after treatment with As(III) and As(V) separately. The prime constituents of biosorbent like C, O, Ca, and Fe along with Cu aggregated onto biosorbent before treatment and its distribution is presented in the EDS analysis (Fig.1).The EDS analysis after treatment clearly shows the peak of arsenic, other than the prime element. This concludes that arsenic is adsorbed over the surface of stem powder of DBS.

FT-IR spectroscopy analysis of biosorbent

FTIR spectra analysis was performed to determine the functional groups present in biosorbent which was conducted in the range of a wave number of 4000-500 cm^{-1}. The FTIR spectra of stem powder of DBS before and after treatment with As(III) and As(V) is shown in Fig.2. The analysis of FTIR spectra of biosorbent surfaces, showed a broad peak at ~3263 cm^{-1} whichis due to the streaching vibration of O-H of carboxylic acid. The shoulder peak at 2893 cm^{-1} shows a presence of C-H streach of alkane.The peak appeared at 2129 cm^{-1} >C≡C< can be assigned to stretching of alkynes. The peak found at ~1735 cm^{-1}exemplify the carbonyl (>C=O) stretch from carboxylic acid. The absorption peak at ~1651 cm^{-1} shows the streaching vibration of >C=O group. The peak at 1323 cm^{-1}shows C-N structure of aromatic amine where a peak at 1060 cm^{-1} indicated the presence of C-N structure of aliphatic amine.

Fig.1

After biosorption studied with the As(III) and As(V) on stem powder of DBS the absorbance peak at 3263 cm^{-1} of $(OH)_{str}$ shifts to 3278 and 3475 cm^{-1}, showing strong intraction with the substrate As(III) and As(V). The peaks 2893cm^{-1} shows an interaction with As(III) but not interacting with As(V). Absorbance peak of ~ 2129 cm^{-1}(-C≡C-) show no interaction with the arsenic substrate it may be due to the absence of coordinating site. The peak observed at 1732.08 cm^{-1} (>C=O) in untreated stem powder of DBS was shifted to 1735.93 $cm^{-1}$and 1743.65 cm^{-1} after absorptionwith sodiumarsenite and sodium arsenate respectively.Furthermore, as shown in Fig 2, the IR spectrum measured before 1319 and 1041 cm^{-1} as aromatic and aliphatic C-N stretching of the amine group and after arsenite and arsenate absorption on stem powder of DBS of the group shifts to a broad spectrum of 1323 in both arsenite and arsenate whereas, in case of aliphatic C-N streching shifted to 1064 and 1060 cm^{-1} these indicate that such functional groups interact with As(III) and As(V) ion in liquid phase.

Analytical studies

Effect ofcontact time

The percentage removal of arsenic bystem powder of DBS, at different contact times(10-50 min),biosorbent dosage of 35 gL^{-1}, initialconcentration 0.3mgL^{-1}, temperature 20^oC for As(III) and for As(V) biosorbent dosage 40 gL^{-1}, initial concentration 0.3 mgL^{-1}, at temperature 40^oC and pH 7.0 remained the same for both states of arsenic. The removal efficiency of arsenic increased with variation of contact time in both states. Equilibrium was achieved after 40 min and 35 min accounting for removal of 87.15% As(III) and 85.86 %As(V). After thatany furtherincrease in contact time (Fig.3) did not show any significant changein percent removal of arsenic. This may be due to the fact that initially high solute concentration gradientand maximum active sites of adsorption were available for adsorbate.Thus, 40min and35minfor As(III) and As(V) respectively, were chosen as an optimum value for further investigation.

Fig.2

The adsorption kinetics was interpreted by pursuing several mathematical models such as pseudo-first-order, pseudo-second-order and intra-particle diffusion model. The theoretical concept leads to understand the different models.

The pseudo-first-order kinetics

The pseudo-first-order kinetics was developed for irreversible sorption onto solid/liquid phase. The Lagergren pseudo-first-order rate equation is expressed as [26].

$$\boldsymbol{log(q_e - q_t) = log\ q_e - \frac{K1}{2.303}\ t} \qquad (3)$$

Fig.3

Where q_t and q_e are the amount of solute adsorbed (mg g^{-1}) at time t and at equilibrium whereas K_1 (min^{-1})is the rate constant for pseudo-first order kinetics. Linear plot of log (q_e - q_t) *vs* t gives a straight line from where q_e and K_1 can be determined from the intercept and slope respectively. The correlation coefficient R^2 was 0.756 and $q_{e,\ cal}$ (calculated adsorption capacity) value was 1.17 mg g^{-1} forAs(III) whereas, the respective values for As(V) were 0.928 and 0.059 mg g^{-1}. This revealed that the data did not follow pseudo-first-order kinetics. The various constant values of the kinetics are summarized in Table 2.

The pseudo-second order kinetics

The pseudo-second order kinetics reaction model is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_s\ (q_e)^2} + \frac{t}{q_e} \qquad (4)$$

where K_s is rate constant for pseudo second order kinetics (g mg^{-1} min^{-1}); q_t and q_e are the amount of solute adsorbed at time t and at equilibrium (mg g^{-1}) respectively. A linear plot of t/q_t*vs* t may give straight line (Fig.4) and the values of K_s and q_e are obtained from the slope and intercept respectively. The results confirm that the rate of reaction follows pseudo-second order kinetics, with good correlation coefficient (R^2). The R^2 and $q_{e,cal}$ values were 0.998, and 9.09 mg g^{-1} for As(III) and 0.999, and 4.40 mg g^{-1} for As(V), respectively, indicating that adsorption follows pseudo-second order kinetics. Various constant values of this kinetic model are presented in Table 2.

Fig.4

The intra-particle diffusion model

The intra-particle diffusion model is represented as:

$$\boldsymbol{q_t = K_i\sqrt{t} + I} \qquad (5)$$

Where K_i is the constant for the intra-particle diffusion model (mg g^{-1} $min^{-1/2}$) and I is the intercept. A plot of q_t *vs* $t^{1/2}$ may give a straight line, whose intercept gives the value of I which provides information regarding the thickness of boundary layer. The K_i determined from the slope value and the correlation coefficient (R^2) were found to be 1.0 for As(III) and 0.988 for As(V). All other constant values are reported in Table 2.

Table 2

Effect ofarsenic concentration

The relationship between the variation of initial arsenic concentration and percentage removal of arsenic, as well as the adsorption capacity (q_e) were investigated by varying the arsenic concentration within the range of 0.1-0.5 mgL^{-1}. For such experiments, optimum condition of other physical parameters such as biosorbent dosage, contact time period, pH, and temperature remained the same as previously mentioned for both As(III) and As(V). Initially, with increasing concentration of arsenic, the percent removal of arsenic increased (Fig.5) for both oxidation states of arsenic and reached a maximum at 0.3 mgL^{-1}, both for As(III) and As(V). This may be due to the fact that after reaching equilibrium state, the available co-ordination site gets saturated, thereby resulting in a decreased trend in adsorption capacity (q_e) as well as observed percent arsenic removal.

To explain the adsorption efficiency of stem powder of DBS, four different adsorption isotherm models, that is, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich(D-R) were tested.

The fundamental assumptions of Langmuir isotherm model are that the uptake of adsorbate occurs on a homogenous surface forming a monolayer, without any interaction between adsorbate and adsorbent molecule[10, 27]. Freundlich adsorption isotherm is the most acceptable mathematical model used for aqueous systems for multilayer adsorption. The linear form of Freundlich adsorption isotherm widely applies for heterogeneous systems[27]. Temkin adsorption isotherm model is based upon the interaction between adsorbent - adsorbate that is

Fig.5

linear in nature and the adsorption is characterized by uniform distribution of binding energies. D-R isotherm model helps us to find out the free energy of adsorption and explain the adsorption mechanism.

Langmuir isotherm model:

$$\frac{1}{q_e} = \frac{1}{K_L\, q_m C_e} + \frac{1}{q_m} \qquad (6)$$

Where q_m is the amount of adsorbate that can be absorbed per unit weight of biosorbent (mg g^{-1}), K_L (L mg^{-1}) is the adsorption constant which represents the enthalpy of adsorption and C_e (mgL^{-1}) is the concentration of arsenic at equilibrium. The value of q_m and K_L can be calculated from the slope and intercept of the plot $1/q_e$ *vs* $1/C_e$ (Fig.6) respectively. Good correlation coefficients R^2 were found *i.e.* 0.864 for As(III) and 0.981 for As(V) values are reported inTable 4.

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In order to predict the absorption process is favorable or unfavorable for the Langmuir type adsorption isotherm, the separating factor R_L, was calculated based on the following equation:

$$R_L = \frac{1}{1 + K_L C_o} \qquad (7)$$

Fig.6

Where K_L is Langmuir isotherm constant and C_o is the initial concentration of adsorbate. The process of Langmuir isotherm is favorable if the magnitude lies in the range $0 < R_L < 1$, if $R_L = 1$, it is linear, if $R_L = 0$, it is irreversible, and if $R_L > 1$ the isotherm process is unfavorable [28]. The value of $R_L$was calculated for the entire range of concentration (Table 2), and was found between 0 and 1, confirming favorable condition of adsorption.

Freundlich adsorption isotherm:

$$\log\ q_e = \log K_F + \frac{1}{n} \log C_e \qquad (8)$$

Where n represents adsorption intensity and K_F is constant representing adsorption capacity. The constants n and K_F were calculated from the slope and intercept respectively by plotting log q_e *vs* log C_e (Fig.7) respectively.Whereas, Freundlich constant (n) is in the range of 0–10 indicating, adsorption is the favorable[29]. The value of n, $K_L$and correlation coefficient (R^2) has been reported in Table 3.

Temkin isotherm model

Temkin isotherm model is based upon the interaction between adsorbent - adsorbate. The linear form of Temkin isotherm is written as:

$$q_e = B_1 \ln A + B_1 \ln C_e \qquad (9)$$

Fig.7

WhereB_1 is constant related to the heat of adsorption and A is equilibrium constant (L g^{-1}) related to the maximum binding energy[30]. The value of B_1 and A was obtained by plot of q_e *vs* ln C_e from the intercept and slope respectively (Fig.8). The values of B_1, A and correlation coefficient are listed in Table 3.

Fig.8

Langmuir and Freundlich adsorption isotherms are unable to explain the mechanism of adsorption.In order to get an idea about the nature of adsorption the data were also applied to Dubinin-Radushkevich (D-R) adsorption isotherm[31, 32]. Thelinear form of D-R isothermcan be expressed as:

$$\ln q_e = \ln X_m - \beta\varepsilon^2 \qquad (1$$

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (11)$$

Where q_e is amount of adsorbate adsorbed per unit of adsorbent by stem powder of DBS, ε is Polanyi potential, C_e is equilibrium concentration, X_m is theoretical saturation capacity, β is the constant related to adsorption energy ($mol^2\ kJ^{-2}$), R is the universal gas constant (8.314 $Jmol^{-1}\ K^{-1}$), T is temperature (K).). The constant (β) and (X_m) were obtained from slope and intercept of the plot of lnq_e*vs* ε^2 respectively (Fig.9). The adsorption free

mean energy [E], which is defined as free energy change when one mole of ions transferred from infinite to the surface of the absorbent, was calculated from β-value using given equation:

$$\boldsymbol{E} = \frac{1}{\sqrt{-2\beta}} \qquad (12)$$

From the magnitude of E we can estimate the type of adsorption if the value between 8-18 $kJmol^{-1}$,the adsorption type ischemisorption[33]whereasfor values of E < 8$kJmol^{-1}$the kinds of absorption is physisorption (due to weak van der Wall forces). In thisinvestigative value of E was found to be 5.85 $kJmol^{-1}$ for As(III) and 2.86$kJmol^{-1}$ for As(V), which indicate the absorption are physical in nature. All the constants values are summarized in Table 3.

The plot between $q_{e,\ exp}$ and $q_{e,\ cal}$ for all the four adsorption isotherm models is shown in Fig.10. The Temkin and Freundlich adsorption isotherm showed the best fitting with the obtained results for As(III) and As(V) respectively. The theoretically predicted isotherm data were determined using the Origin 8.1 professional for the linear analysis of As(III) and As(V).

Fig.9

Table 3

Fig.10

However, in order to determinate the most appropriate adsorption isotherm model for the biosorption of As(III) and As(V) on stem powder of DBS, the error function analysis was attempted. The error function analysis was performed by the use of linear least square method using Microsoft excel and SPSS 13.0statical software. Five different frequently used error functions were applied to evaluate the error deviation between the experimental and predicted equilibrium data using linear analysis. The mathematical equation of different error functions applied in this investigation is given below[34]:

(a) The average relative errorsdeviation (ARED):

$$\boldsymbol{ARED} = \frac{1}{N}\sum_{k=0}^{n}\left|\frac{q_{e,cal}-q_{e,exp}}{q_{e,exp}}\right| \mathbf{100} \qquad (13)$$

Where N is number of experimental data point, $q_{e,\ cal.}$ is calculated equilibrium adsorption capacity (mg g^{-1}) and$q_{e,\ exp}$is experimental equilibrium adsorption capacity (mg g^{-1}).

(b) The sum of square of the errors (SSE):

$$\boldsymbol{SSE} = \sum(q_{e,cal} - q_{e,exp})^2 \qquad (14)$$

(c) The Marquardt's percent standard deviation (MPSD):

$$\boldsymbol{MPSD} = \sqrt[100]{\frac{1}{N-P}\sum_{i=1}^{n}\left(\frac{q_{e,exp}-q_{e,cal}}{q_{e,cal}}\right)_i^2} \qquad (15)$$

(d) The hybrid fractional error function (HYBRID)

$$\boldsymbol{HYBRID} = \frac{1}{N-P}\sum\left|\frac{q_{e,exp}-q_{e,cal}}{q_{e,exp}}\right| \mathbf{100} \qquad (16)$$

(e) The sum of absolute errors (SAE):

$$\mathbf{SAE} = \sum_{i=1}^{n}\left|q_{e,cal} - q_{e,exp}\right| \qquad (17)$$

The calculated values of above mentioned error functions are reported in Table 4. By analysis of data, it may concluded that the Temkin model for As(III) and for As(V) Freundlich model are most perfect model to satisfactorily explain the biosorption on stem powder of DBS and such conclusion based on maximum R^2 values and minimum ARED, SSE,SAE, MPSD, HYBRID values of error function analysis.

Table 4

Effect of variation of pH

The pH is an important parameter that determines the ability to control the sorption of arsenic on adsorbent surfaces. During the current investigation, the sorption efficiency of arsenic by stem powder of DBS was examined under an optimum conditions as biosorbent dosage 35 gL^{-1}, initial concentration 0.3 mgL^{-1}, contact time 40 minutes, temperature 20°C for As(III) and biosorbent dosage 40 gL^{-1}, contact time 35 minutes, initial concentration 0.3 mgL^{-1}, temperature 40°C pH range of 3.0-11.0 for As(V) (Fig.10). Maximum removal for As(III) and As(V) was found to be 96 % and 94.3% respectively at pH 7.0 which were chosen as optimum value in present investigation. Result shows that stem powder of DBS has been potential to remove arsenic from contaminated water at neutral pH and can be used as an efficient biosorbent.

Based on the relevant literature [35] and our experimental data, we can develop a mechanism for arsenic binding to the stem-powder of DBS. Which contains amino acids (glycine, alanine, threonine, isoleucine, phenylalanine)[36], 4-phenyl chromene, dalbergichromene[37], dalbergin[38], dalbergenone[24]. The amino-acid has several structurally related pH- dependent characteristics of generating either negatively or positively charged sites for attracting cationic or anionic species respectively.

In the pH range 7-9,As(III) exists in anionic ($H_2AsO_3^-$and $HAsO_3^{2-}$) state whereasAs(V) exists as monovalent and divalent ($H_2 AsO_4^-$ and $HAsO_4^{2-}$). However,the pH range 2-7the nonionic state $NaAsO_2$ can be easily understood to the availability of negative site while interacting with positive site of amino acids[39]. In the pH range 4-8mostof the amino acid have an isoelectric point.Carboxylic acid group (-COOH) of amino acid is deprotonated with increase for pH whereas, at the same time amino ($-NH_2$) group of amino acid is protonated as $-NH_3^+$ ions which canfacilitate the arsenic binding with adsorbent.

Fig.11

Effect of biosorbent dosage

In order to find out the optimum biosorbent dosage for removal of arsenic, the experiment were performed at optimal conditions of temperature, contact time, pH and initial metal ion concentration with varying biosorbent dosage the range of 10-50 gL^{-1}. The observations showed that removal efficiency of arsenic increased with an increase in biosorbent dosage (Fig.11) and became maximum (94.5%) at the dosage of 35 gL^{-1} for As(III) whereas maximum (85%) at the dosage of 40 gL^{-1} for As(V). Thereafter, not any significant changes were observed with increase the biosorbent dosage. Thus the biosorbent dosage 35 gL^{-1} for As(III) and 40 gL^{-1} for As(V) were chosen as an optimum value for the further investigation, whereas absorption capacity of biosorbent showing negative trend that has it decreased with increasing biosorbent dosage for As(III) and As(V). The reason could be decreased the concentration differences of arsenic between initial and equilibrium state per unit mass of biosorbent.Jain et al. Reviewed the effect of adsorbent dosage and concluded that the adsorption increases with the increase in adsorbent dosage due to availability of greater surface area and binding sites[40].Similar results were observed in the present study.

Effect of temperature

The effect of temperature for percentage removal ofAs(III) and As(V),was studied in range of 10-50^oC (Fig.12) at an optimum condition of pH 7.0, biosorbent dosage 35gL^{-1}, contact time40 minutes and initial concentration 0.3$mgL^{-1}$for As(III) and contact time 35 minutes, biosorbent dosage 40 gL^{-1}, initial concentration 0.3 mgL^{-1} and pH 7.0 for As(V). From Fig.12it was clear that the percentageAs(III) and As(V) removal efficiencies curves wereincreased smoothly and leading towards saturation.At later stages the removal efficiency decreased with temperature. The increase in temperature generally enhanced the process of biosorption of metal ions which mightbe due to enhancement in the surface activity and kinetic energy of dissolved metal ions.At higher temperatures physical structure of biosorbent surface changes which might bedecreased adsorption efficiency of biosorbent[8].

Fig.11

In the present investigation, the optimum values of temperaturewas selectedas 20^oC for As(III) and 40^oC for As(V).For this purpose, the experiments were performed in horizontal incubator shaker, and lower temperature was maintained by placing conical flask containing test sample in an ice bath.

Fig. 12

To identify the feasibility of the adsorption process using stem powder of DBS as an adsorbent, temperature variation for the process of adsorption was done. Thus the relationship between thermodynamic properties was expressed by Van't Hoff equation as:

$$\Delta G^o = -RT \ln K_c \qquad (18)$$

Where R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), ΔG^o are the standard free energy change and K_c is the distribution coefficient. The calculated value of ΔG^o was found to be negative in the entire temperature range (Table 5). The value of ΔG^o indicated that the adsorption is spontaneous in nature, meaning thereby the adsorptive forces have the ability to overcome the potential barrier and the less negative

values show that the sorption is not favored at higher temperatures. Further, from the relationship between K_c versus standard entropy (ΔS^o) and standard enthalpy (ΔH^o) thermodynamic factor written as:

$$\boldsymbol{ln\ K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}} \quad (19)$$

The value of ΔH^o and ΔS^o was calculated from the plot of ln K_c *vs* 1/T, intercept and slope of the plot gave the value of ΔS^o and ΔH^o respectively. The negative values of ΔH^o for As(III) and As(V) implies that the adsorption is exothermic in nature, leading to the decrease of adsorption efficiency with temperature. The negative values for ΔS^o again reveals that the randomness of sorption decreases at the solid / liquid interface during As(III) and As(V) sorption process on the stem powder of DBS.

The sticking probability (S^*) is a function of the adsorbate/adsorbent systems and always depends upon temperature. It is the measure of the potential of adsorbate to remain on the adsorbent surface indefinitely[41]. The equation is expressed as:

$$\boldsymbol{S^* = (1-\theta)e^{-\frac{E_a}{RT}}} \quad (20)$$

Where, ɵ is surface coverage area and *E*a is activation energy.

$$\boldsymbol{\theta = (1-\frac{C_e}{C_o})} \quad (21)$$

Where, C_e and C_o are equilibrium and initial concentration of arsenic respectively. From the plot of log (1-ɵ) *vs* 1/T, the slope E_a/R and intercept log S^* gave the value of *E*aand S^*respectively. The result is shown in Table 5 reveals that such high value of S^* for As (III) and As (V) adsorbed on stem powder of DBS confirm that the adsorption process is physical. The negative values of activation energy *E*a further confirm exothermic nature sorption process for As(III) and As(V) both.

Desorption/Reuse

To investigate the probability of the repeated use of biosorbent, desorption and reuse experiment were also conducted. Effective reuse of biosorbent directly affects the cost factor. In real life adsorbent has practical application, which can be reused.Desorption of both As(III) and As(V) species from loaded stem powder of DBS has also been attempted.Fig.13 explainsdesorption activity after treating with HCl and HNO_3. In general, with increasing the concentration of acid from 0.01 to 0.1 M, extent of desorption increases. The maximum desorption was 94.2 % for As(III) and 97.2% for As(V) when the strength of HNO_3 was 0.1M. However, use of0.1M HCl asdesorbent gave better result of 97.1% for As(III) and 98.2% for As(V). The percentage of As(III) and As(V) adsorption by stem powder of DBS was found to be reduced from 92 to 88% for As(III) and 96 to 91% for As(V) following sequence of 1st to 4th cycle of operation shown in Fig.14.

Table 5

IV. CONCLUSIONS

In our present investigation, arsenic removal from contaminated water was achieved using stem powder of DBS.Under optimized conditions of temperature, metal ion concentration, pH, contact time and biosorbent dosage, the removal efficiency was found to be96% for As(III) and 94.3% for As(V). The kinetic data were best fitted with pseudo-second-order kinetics with the good correlation coefficients (R^2), 1.0for As(III) and 0.999 for As(V). Experimental data also were modeled by Langmuir, Freundlich, Temkin and D-R adsorption isotherms. The result revealed to be best fitted with Langmuir and Freundlich adsorption isotherms. The thermodynamic parameters indicate thatadsorption process is spontaneous or feasible and exothermic in nature and kinds of adsorption is physisorption. The separating factor (R_L) values lying between 0 to1both for As(III) and As(V), confirmed sorption condition favorable. The experimental observation showed that stem powder of DBS is an appropriate biosorbent for arsenic removal from contaminated water.This biosorbent can be recycled and hence can be reused up to 4th cycle,which makes it an efficient biosorbent for the removal of arsenic from contaminated water. This is also natural, low-cost, and a valuable alternative as compared to commercially availablebiosorbent even for a common man.

Fig. 13 Fig. 14

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