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An assessment on removal performance of Arsenic with treated Turbinaria vulgaris as an adsorbent: characterization, optimization, isotherm and kinetics study

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Highlights

- Surface characteristic of Treated *T. vulgaris* evidenced as a better As removal biosorbent
- Maximum As metal uptake has been attained to 26.54 mg/g with removal efficiency of 92.12%
- *T. vulgaris* could be a suitable biosorbent over wide range of pH and As concentration
- Five various kinetic model and four isotherm study has been completed during removal study
- Kinetics and isotherm study shows that *T. vulgaris* could be an efficient biosorbent

An assessment on removal performance of Arsenic with treated *Turbinaria vulgaris* as an adsorbent: characterization, optimization, isotherm and kinetics study

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Abstract

In this current research, batch experiments were performed towards the characterization and optimization of arsenic removal by *Turbinaria vulgaris (T.vulgaris)*. The four process parameters i.e. initial solution pH (3–5), initial arsenic ion concentration (20–100 mg/l), *T.vulgaris* dosage (0.1–0.5 g/L) and temperature (293-313K) were considered for the process optimization through response surface methodology (RSM) via central composite design (CCD) approach. According to CCD methodologya set of 30 experimental runs were conducted and the results were analysed, suggested quadratic model has well matched to the experimental results which might be used to design space according to ANOVA study.The highest removal efficiency of 92.12% was attained, retaining the process conditions viz. pH 4.41, biomass dosage 0.3 g/L and initial arsenic concentration 21.33 mg/L and temperature 298.32 K. Biosorbent morphology and chemical properties were characterized by means of FT-IR and SEM analysis. The presence of metal ions in the *T.vulgaris* biomass after biosorption was confirmed from SEM result. These results are significant towards the assessment and optimization of removal of arsenic ions by *T.vulgaris* biomass. To estimatethe solute interaction and bio-sorption nature, the experimental data were verified with different isotherms and kinetic models. The results discovered that *T.vulgaris* could be a cost-effective and eco-friendly bio-sorbent for removal of arsenic ions.

Keywords: Bio-sorption; RSM; Arsenic; *T.vulgaris;* Isotherms; Kinetics.

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1. Introduction

Gradual escalation of heavy metal pollution in aqueous environment experienced animmense concern in the second half of 20th century, since the occurence of many industrial and environmental accidents, warned the world for the sake of harmful environmental consequences. A huge attention of researchers and authorities has been motivated towards arsenic (As), as it has been projected as an influential element towards the impact on environmental pollution related to heavy metal throughout the world since last few decades. Arsenic is a metalloid, having properties of metals and non-metals; known to be carcinogenic to humans, is persisting in environment through various industrial activities and anthropogenic sources [1]. Researchers have been focused on the potential research on heavy metal pollution as well as the influence on human health and environment through inspection of arsenic abundance, behaviour and remediation. The World Health Organization (WHO) has established the guidelines of permissible limit of arsenic in drinking water as 10µg/l, since 2006 [2]. This has become the motivation for removal of arsenic during last few decades using various technologies, amongst them biosorption turn out to be a popular one due tohigh adsorption capacities, low costs and regeneration characteristics. Due to its efficient sorption of many contaminants and the detoxification property of heavy metals in human body, algae have been introduced and were in useto remove heavy metals from industrial wastewaters.This have been themajor reason behind the use of various strains of algae for wastewater treatment since last few years [3, 4, 5, 6]. *Turbinaria vulgaris* has been considered as one of the potential algae that could be used to remove the heavy metal contamination from wastewater.

The biosorption mechanism has become more complex and non-linear due to the presence of various biological components in metal removal. Optimization of process parameters is essential

to maximize the biosorption efficiency and to make the process as economically viable. The classical method of optimization has certain disadvantages like ignorance of interaction effect, requirement of more experimental runs, etc. Therefore, the use of classical "one factor at a time" method is not advisable for the optimization of non-linearprocesses. In order to overcome the problem of multivariate optimization, various statistical tools have been employed to find out the optimum combination and interaction of process parameters. Factorial design and RSM were considered as the most popular designs used for the optimization of multivariable processes [7]. In the present study, the pretreated *T.vulgaris.* (brown algae) was used as biosorbent for efficient removal of arsenic from an aqueous solution.The objective of the present investigation focuses on the optimization of process variables for optimum arsenic removal, isotherm studies and estimation of biosorption kinetics of arsenic with possible mechanism.

2. Materials and Methods

2.1. Preparation of biomass

The biosorbent, *T.vulgaris* used in the present study was gathered from the Gulf of Mannar, Tamil Nadu, India.The collected algae was washed with deionized water several times to get rid of unwanted material. The washing procedure was kept till the wash water contains no dirt. The washed *T.vulgaris* was completely dried and scorching it for about 3-4 weeks.The dried leaves then crushed into small pieces and make in powdered form using domestic mixer. The prepared *T.vulgaris* was pre-treated using 0.1 M $CaCl_2$ which increases the active sites and surface firmness of dry adsorbent. In order to modify algae, 20 g of dried algae was shed in 200 ml $CaCl_2$ 0.1 M solution and stirred for 24 h with a stirring agitator at a speed of 200 rpm. Afterward, the solution was filtered using Whatman filter paper and algae were washed with

doubled distilled water and kept in the oven at 343.14 K for 48 h. In the present study, the powdered materials have an average particle size range of 75-212 μm.

2.2. Preparation of stock solution

Arsenate solution was prepared by dissolving solid $Na_2HAsO_47H_2O$ in distilled water. The ionic strength of solutions was adjusted by addition of (0.1N) HNO_3 and (0.1N) NaOH.

2.3. Bio-sorption Experiments:

Arsenic removal capacity of *T.vulgaris* was investigated by varying the pH, initial concentration of arsenic ions, biomass dosage and temperature at a constant volume of reaction mixture, 30 ml designed from CCD. The samples were agitated at 180 rpm for a pre determined contact time of 60 min (not discussed here) and filtered using Whatman 40 filter paper. The Atomic Absorption Spectroscopy (Shimadzu AA 6300) was used to evaluate the presence of residual arsenic in solution. To ensure the presence of the arsenic in the solution blank and triplicate experiments were conducted and the mean values have been recorded.

The metal uptake of arsenic onto *T.vulgaris* was determined from the accompanying mathematical expression.

$$q = \frac{V(C_i - C_f)}{1000w} \quad (1)$$

Where q signifies the amount of arsenic biosorbed by *T.vulgaris* (mg/g), C_i is the initial concentration of solute in the solution before biosorption (mg/l), C_f indicates the final concentration of solute in the solution after adsorption (mg/l), V is the volume of the metal solution and *w* is the mass of *T.vulgaris.*

2.4. Central composite design (CCD)

In order to develop the empirical relation between the process variables and response, a standard experimental design of RSM called the Central composite design (CCD) is used. The experimental design matrix for four variables and each with three levels (–1, 0, +1) is designed by CCD in order to find out the optimum values of pH, metal ion concentration, biomass dosage and temperature. The ranges and levels of independent process parameters are given in Table.1. The mathematical equation relating four independent process variables and the response function i.e., percentage removal of metal ions has been expressed by the following quadratic model.

$$Y = \beta_o + \beta_1 A + \beta_2 B + \beta_3 C + \beta_4 D + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{44} D^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{14} AD + \beta_{24} BD + \beta_{34} CD \quad (2)$$

Where, Y indicates predicted response, β_0 the intercept term, β_i the linear effect, β_{ii} the standard effect and β_{ij} the interaction effect.

2.5. Equilibrium models

2.5.1. Langmuir &Freundlich Isotherms

In order to predict maximum arsenic removal by *T.vulgaris*, the equilibrium studies are performed. Experiments were conducted at 20mg/l by fixing other parameters as constant. Langmuir and Freundlich models were used in establishing equilibrium relation between the biosorbed arsenic ions by *T.vulgaris* (q_e) and residual arsenic ions in solution (c_e). Langmuir isotherm has been extensively used for dilute solutions in following linear form[8].

$$\frac{C_e}{q_e} = \left(\frac{C_e}{a}\right) + \frac{1}{ab} \quad (3)$$

where, 'a' represents maximum metal uptake per unit mass of adsorbent to form complete monolayer and 'b' represents the affinity of binding sites. The plot of (c_e/q_e) against (c_e) indicates the applicability of this model. From the graph, it has seen that, the equilibrium data was well fitted by Langmuir model.

Freundlich model can be described by the below mentioned equation [9]

$$q_e = K_f C_e^{1/n} \quad (4)$$

where, the value of k_f and n are indicators of biosorption capacity and intensity respectively. The linear plot of log (q_e) against log (c_e) describes the fitness of this model.

2.5.2. Dubinin–Radushkevich (D-R) isotherm

D–R isotherm model is used to determine the nature of biosorption as physical or chemical process. The linear form of this model is expressed as [10]

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (5)$$

Where q_e and q_m are equilibrium and maximum metal uptake (mol/g) respectively, β is the activity coefficient which represents mean biosorption energy (mol^2/J^2) and ε is the Polanyi potential which is estimated from the following equation

$$\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right) \quad (6)$$

The mean biosorption energy (E, kJ/mol) is calculated from

$$E = \frac{1}{\sqrt{-2\beta}} \quad (7)$$

If E value is between 8 and 16 kJ/mol, the biosorption process follows chemically and if E < 8 kJ/mol, the biosorption process is a physical process. The mean biosorption energy was calculated as 5.79 kJ/mol for the biosorption of arsenic ions.

2.5.3. Temkin isotherm

The Temkin isotherm model takes into account the interactions between biosorbate and biosorbent species [11]. Temkin isotherm assumes that the heat of biosorption decreases linearly on a surface and the molecules biosorbed over the surface are epitomized with consistent binding energies up to a notable maximum value. Consequently, Temkin and Pyzhev suggested that due to the effect of indirect interaction of sorbate molecules, there is a significant reduction in heat of biosorption of the sorbate on the surface of the biosorbent. The linearized Temkin isotherm is presented as follows:

$$q_e = \frac{RT}{b} \ln A_T + \frac{RT}{b} \ln C_e \tag{8}$$

$$q_e = B \ln K_T + B \ln C_e \tag{9}$$

where B = RT/b, b stands for Temkin constant related to heat of sorption (J/mol); A indicates Temkin isotherm constant (L/mg), R signifies the universal gas constant (8.314 J/mol K), and T the absolute temperature (K). A plot of q_{eq} versus lnC_{eq} enables the determination of the isotherm constants K_T and b.

2.6. Kinetic models

2.6.1. Pseudo-first & second order models

The equilibrium and kinetic studies were conducted in order to find out biosorption mechanism as well as several parametric determination such as; initial adsorption rate, order of metal uptake kinetics, rate constant, rate controlling mechanism, diffusion coefficient, etc. Equation 10 denoted as an experimental correlation for first order kinetics [12]

$$\ln(q_e - q_t) = \ln q_e - k_{p1} t \quad (10)$$

Pseudo second order equation is given by [13]

$$\frac{t}{q_t} = \frac{1}{k_{p2} q_e^2} + \frac{t}{q_e} \quad (11)$$

where k_{p1} and k_{p2} signifies the pseudo first order and second order rate constants respectively. q_e and q_t symbolized for metal uptake at equilibrium and uptake at time t respectively for both models.

2.6.2. Intra-particle diffusion model

The influence of metal ion diffusion through the adsorbent pores on rate of biosorption was detected and characterized by the below mentioned equation [14]

$$q_t = K_{ip} t^{0.5} + I \quad (12)$$

Where k_{ip} indicates rate constant and *I* specifies intercept value which determine the boundary layer thickness. The linearity plot between q_t and $t^{0.5}$ shows the acceptability of proposed model.

2.6.3. Boyd model

This proposed model is used to predict the slowest rate controlling of biosorption process. Equation (13) represents the kinetic rate data which were investigated by Boyd model [12]

$$F = \left(1 - \frac{6}{\pi^2}\right) \exp(-\beta_t) \quad (13)$$

Where F indicates the metal uptake relative to equilibrium uptake and β_t signifies a mathematical character calculated from below mentioned equation (14).

$$\beta_t = -0.4977 - \left(\ln - F\right) \quad (14)$$

From the experimental data vs. Time plot, β_t value was determined, from which the rate controlling step was also established.

2.6.4. Elovich model

Elovich equation was widely used by many researchers to demonstrate second order reaction kinetics of heterogeneous reactions. This was first employed to illustrate the kinetics of chemisorption mechanism of gas molecules onto a solid surface [15]. In recent years it had been successfully utilized by the investigators headed for chemisorption behavior of biosorption. The Elovich equation can be represented as:

$$q_t = \left(\frac{1}{b}\right)\ln(ab) + \frac{1}{b}\ln t \quad (15)$$

Where 'a' and 'b' suggests the initial sorption rate and the constant associated with the magnitude of surface coverage and required activation energy for chemisorption respectively.

3. Results and Discussions

The functional groups like hydroxyl, carboxyl, amine, sulphate and phosphate composing the algal cell wall plays a major role in metal binding [16]. The FTIR spectra of *T.vulgaris* algae were documented at the frequency range of 4000 to 500 cm^{-1}considering before and after arsenic biosorption which shown in Fig 1. Several peaks (Fig. (1a)) were observed indicating the presence of various functional groups which are responsible for binding of arsenic. The broad peak at 3334.92cm^{-1} specifies O-H stretching vibration which indicates alcohols and phenols

existence on biosorbent surface. The peaks within a strech of 2924.09 -2852 cm^{-1} revealed O-H,C-H and N-H bonds, which imply carboxylic and amino groups [16]. In most of the brown algae, 70% of cell wall functional groups are carboxylic and amino groups, these groups play vital role in metal binding [17]. The peaks at wave numbers of 1616.35, 1317.38, 1246.02, 1066.64, 1037.7, 781.17 and the peaks below 500 cm^{-1}significantly indicates the presence of N-H, C-O, C-N, C=C,C-F, C-Cl and C-I groups respectively [16]. Therefore, the surface functional groups of a cell wall like carboxylic acids, amino, alkenes and alkyl groups are responsible for biosorption of arsenic. Comparison of FTIR spectra of *T.vulgaris* with arsenic (Fig. (1b)) revealed the significant changes. One indication of chemical reaction between metal ions and surface functional groups concluded from apeak appearance at 3365.78 cm^{-1} and disappearance at 3334.92 cm^{-1}. The absorption peaks of C-H &O-H stretching vibrations marginally moved from 2924.09 to 2926.01 cm^{-1}. The shift of C-O stretch from 1317.38 to 1319.31 cm^{-1} point out the strong association of carboxylic acids, esters and aldehydes through biosorption process[18]. The swing of peak from 1157.28 to 1103.28 cm^{-1}shows the contribution of more alcoholic groups in biosorption process. On comparision of the IR spectra of *T. vulgaris* before and after biosorption, it is seen that bisorption bands shifted to higher values due to carboxylate and hydroxylate anions.

In order to study the surface texture and porosity of biosorbent the SEM analysis of *T.vulgaris* was performed. The result obtained is shown in Fig.(2a). It clearly illustrates that the surface area of *T. vulgaris* is highly heterogeneous and uneven with porous structure. The SEM micrograph of *T. vulgaris* showed that the biosorbent is highly heterogeneous and the surface morphology of biosorbent is rough. SEM micro graphs of biosorbent T.*vulgaris* after biosorption of arsenic is shown in Fig.(2b). The surface of metal loaded biosorbent clearly shows that the surface of

biosorbent dosage was covered with metal ions. The pores was completely filled with the metal ions after the biosorption of arsenic metal and the pores appear to be smooth which indicates that the metal was biosorbed to the functional groups present in the pores. The surface of the biosorbent became smooth after the biosorption of arsenic metal.

3.2. Optimization of process parameters

3.2.1. Response surface methodology

A quadratic model has been established via CCD approach considering the process variables viz. pH (A), initial concentration (B), biosorbent dosage (C) and temperature. Overall 30 experimental runs was planned which comprises of 16 factorial, eight axial and six centre points were performedalong with analysis of obtained results. A design matrix created using CCD with implicit variables, response reported from experiments and predicted response for biosorption of arsenic onto *T.vulgaris* is given in Table 2.

3.2.2. Regression analysis

The following reduced quadratic model equation represents an empirical correlation between the response (sorption percentage of arsenic) and input variables in coded terms established by RSM software:

$$(Y) = 86.63 + 6.11\ A - 4.6\ B + 1.7\ C - 1.09D - 21.24A^2 - 0.49\ B^2 - 0.41C^2 - 0.54D^2 - 0.93AB - 1.67AC + 8.125 \times 10^{-3}AD + 1.3BC + 0.49BD + 0.18CD \quad (16)$$

The influence of individual variables on the biosorptionof arsenic from an aqueous solution represented by equation (16) and noted that factors A and C had a proportional impact, whereas

B and D gave a negative effect on biosorption of arsenic. Similar trends of results were specified for biosorption of chromium onto chitosan and carbonized rice husk [18].

3.2.3. Fitting the quadratic model

The statistical significance of the quadratic model was evaluated by the analysis of variance (ANOVA) as presented in table 3. The results showed that this regression was statistically significant at F-value of 352.88 and lack of fit tests clearly specifies the model and insignificance of lack of fit confirms the model suitability.

Besides significant "model P-value" (< 0.0001), large "lack of fit P-value" (0.2071) and higher determination coefficient (0.997) also confirms the significance of model. Effect of individual parameters and their interaction was examined using P-values of respective factor i.e. A, B, C, D, AB, AC, BD, A^2 [18]. Collaborative effect of pH and initial concentration, pH and biosorbent dosage, initial concentration and biosorbent dosage have more significant influence as compared to individual variable such as pH, initial concentration, biosorbent dosage and temperature. Square effect of pH had also indicates moderate significance on biosorption. Entire ANOVA studies point out, the model acceptability of biosorption process through simulation of arsenic removal by means of *T. vulgaris.*

3.2.4. Optimization of process variables and authentication

After the development of the mathematical model for the biosorption of arsenic onto *T. vulgaris*, optimization was carried out to predict the maximum metal uptake by *T. vulgaris*. Predicted solution by RSM is shown as contour plot in Fig.3. Through RSM model, at a fixed optimum conditions of pH 4.1, initial concentration of 22.81 mg/l, biosorbent dosage of 0.49 mg/l and temperature 298.32 K, projected a maximum 92.12% removal of arsenic via biosorption. A new

experiment was conducted to assess the validity of optimization of process using RSM, considering the optimum parametric condition. 92.02% arsenic removal is attained thru the current study which is extremely well likened to RSM model predicted value. Therefore the model projected conditions specified by RSM were selected as optimum removal parameters of arsenic via biosorption through *T.vulgaris*.

3.2.5. Interactive effects of two variables

The combined effects of process variables on biosorption were analyzed with the help of 3D (three dimensional) surface diagram. Fig. (4a) illustrates the combined influence of initial metal ion concentration and initial pH of the solution and noticeably point out the supremacy of pH over initial concentration. An increase in initial concentration experienced a rise in sorption percentage instead of decline result. In overall the effect of initial metal ion concentration was decreased by the effect of pH. Fig. (4b) represents the interactive impact of pH and bio sorbent dosage on arsenic removal and clearly shows the superiority of pH over biosorbent dosage. The sorption percentage of arsenic was greater at higher biosorbent dosage because of more binding sites, increase in negative charge on biosorbent surface along with an increase of pH, both collectively provided increase of biosorption percentage. The interactive effects of temperature and pH is shown if Fig. (4c) and observed that increase in tendency of sorption percentage initially and then decreased with increasing temperature. The interactive effects of the biosorbent dosage and initial metal ions concentration canbe inferred from the response plot of Fig. (5a) holding pH at central values. From the figure it could be observed that percentage biosorption was increased with increase in dosage and percentage biosorption was increased with decrease in initial concentration, which concludes the significant impact of both the variables. The interactive effects of temperature and initial concentration are shown in Fig. (5b) and clearly

shows the percentage biosorption was increased with increase in temperature. Considering overall effect, percentage biosorption was decreased with increasing concentration. The interactive effects of temperature and dosage are shown in Fig. (5c). It clearly indicates that with increase in dosage the percentage biosorption increased and sorption percentage was decreased with increasing temperature. Similar results were obtained for lead removal by a novel super paramagnetic nanocomposite [19]. It can be verified from ANOVA study that, the p-value of the factor AD, BD, CD is very high, which indicates the insignificant effect of those factor. From the experimental and graphical analysis concludes that, collaborative impact of pH and temperature, initial concentration and temperature, biosorbent dosage and temperature had no such significant influence on arsenic biosorption.

3.3. Isotherm studies

The equilibrium sorption data was tested by fitting the experimental data on the Langmuir, Freundlich, D-R, Temkin models towards knowing the sorption isotherm. The Langmuir mathematical model is used to estimate the maximum adsorption capacity conforming to the complete monolayer scope on the biosorbent surface. Thereby, the Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases. In Fig. (6a), C_{eq}/q_{eq} was plotted against C_{eq} yielding a straight line with R^2 = 0.996 for arsenic signifies that sorption data were well matched with Langmuir model. From slope of the linear plot, (Q_{max} =25.64 mg/g) value for arsenic was determined, where as K_L =0.1029 value was derived from the intercept.

3.3.1. Freundlich isotherm

Logarithmic plot of adsorbed and equilibrium concentration provides a straight line with coefficient of determination close to unity (0.984 for arsenic). The values of $1/n$ (0.493 for arsenic) and K_f (3.724 for arsenic) are originated from the slope and intercept of the straight line for arsenic and chromium respectively which is shown in Fig. (6b) and tabulated in Table 4.

The magnitude of K_f and n indicates an easy separation of arsenic ions from an aqueous solutions with high biosorptive capacity of the *T. vulgaris*, especially at 303±1 K and pH = 4 respectively.

3.3.2. Dubinin–Radushkevich Isotherm

Mean free energy of biosorption is used to describe the nature of biosorption and its mechanisim. This mean free energy of biosorption is estimated from the correlation coefficient of Dubinin–Radushkevich isotherm. The D–R isotherm model was well fitted to the equilibrium data since R^2 values were found to be 0.998 for arsenic (Fig. (6c). From the intercept of the plot, the q_m value was found to be 18.919×10^{-2} mg/g for arsenic. The mean biosorption energy was measured as 5.79 kJ/mol for arsenic. This result suggests that the bio-sorption of arsenic onto *T. vulgaris* might takes place via chemical reaction involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

3.3.3. Temkin isotherm

Temkin and Pyzhev revealed the effects of indirect adsorbate/adsorbate interactions on biosorption isotherms. Due to adsorbate/adsorbate interactions the heat of biosorption of all the molecules in the layer would decreases linearly with coverage [20].

The biosorption data of arsenic onto *T.vulgaris* was investigated according to the linear form of the Temkin isotherm and the resultant graph represented in Fig. (6d). The examined data shows that the Temkin isotherm provides a close fit to the arsenic biosorption onto *T.vulgaris*. The linear isotherm constants and coefficients of determination are shown in Table 4.

The equilibrium sorption data of arsenic onto *T. vulgaris* was fitted well to all four equilibrium models and estimated isotherm constants are displayed in Table 4. Based on the linear regression correlation coefficient (R^2), best fitted equilibrium model was established. The corresponding Table 4 displays that sorption data of arsenic were extremely well classified by Langmuir isotherm with higher correlation coefficient of 0.999, followed by Dubinin–Radushkevich, Temkin and Freundlich isotherm with a value of 0.998, 0.996 and 0.971 respectively. The higher biosorption capacity Q_{max} indicates the strong electrostatic force of attraction.

3.4. Kinetic studies

Biosorption kinetics study illustrates the solute uptake rate, which in turn governs the residence time of biosorption. Hence, kinetic study of removal of arsenic using biosorbent was carried out with different initial arsenic concentrations ranging from 20–100 mg/l at an initial pH of 4 and temperature of 303 K. The suitability of kinetic data to pseudo first and second order rate equations is described in Figs. (7a) and (7b) and corresponding rate constants, predicted arsenic uptake and R^2 values are reported in Table 5. In case of pseudo first order model R_1^2 values were found in the range of 0.958–0.982 which shows the significance of model, but the predicted maximum metal uptake values were expressively differed with the experimental values. According to Sinha et al. [21], if the predicted metal uptake is not equal to experimental value the kinetic equation is not appropriate, even if the plot has a high regression coefficient. Hence

pseudo first order rate equation is not suitable for kinetics determination. In case of pseudo second order, high correlation coefficients and nearer predicted and experimental metal uptake values indicates the model significance of biosorption kinetics of arsenic. Therefore biosorption of arsenic onto *T.vulgaris* follows pseudo second order model along with chemisorption as a rate determining step [22]. Further kinetic data were fitted to Elovich model to confirm the chemisorption. As shown in Fig. (8c) the plots are linear with good correlation coefficient (R^2 in the range of 0.985). So the suitability of data to Elovich model suggests the biosorption of arsenic follows chemisorption, involving valence forces through sharing or exchange of electrons between biosorbent and biosorbate [23]. The rate constant (k_2) values were decreased from 0.052 to 0.006 1/ g min with an increase in initial arsenic ion concentration where as the initial sorption rate increased from 1.186 to 4.201 mg/g min which shown in Table 5. This can be interpreted as with an increase in initial metal concentration, concentration gradient increases between bulk solution and biosorbent surface, results the driving force for metal uptake. However at higher concentrations, greater probability of metal ion collisions makes metal ions diffusion towards the surface ligands or micro pores difficult and hence reduces the overall rate of kinetics.The intra-pore diffusion of arsenic ion is investigated by fitting the kinetic data to intra particle diffusion model. Fig. (8a) shows the fitness of kinetic data to the intraparticle diffusion model. If the intra-particle diffusion is the only rate-controlling step then the plot should pass through the origin, else the boundary layer diffusion affects the biosorption to some degree. From Fig. (8a) it was clear that the linear curves are not passing through the origin which indicates the existence of external pore diffusion in biosorption. Similar trend was reported by Jafari et al. [24] for biosorption of arsenic onto brown seaweed and by Ofomaja [25] for removal of lead using mansonia wood sawdust. Further investigation was performed towards the kinetic data matching

with Boyd model to observe an exact rate limiting step and calculated B_t values then plotted against contact time. From the linear trend the rate controlling step of biosorption can be obtained. If the plot is linear and passes through the origin, the pore diffusion is the rate controlling step otherwise surface (film) diffusion indicates the rate limiting stage. Fig. (8b) represents the plot of B_t vs contact time which was linear with correlation coefficient (R^2 = 0.696), but it was not passed through the origin, indicates the external mass transport controlled process, where particle diffusion is rate determining step.

4. Conclusion

The chemically modified biosorbent prepared from the biomass of *T.vulgaris* towards the removal of arsenic (As) from aqueous metal solutions was investigated and the biosorption potential of prepared bio-sorbent was optimized with the help of RSM software. The surface functional groups responsible for biosorption of arsenic onto *T. vulgaris* were identified using FTIR and found that carboxylic acids, amino, alkenes and alkyl groups are involved in metal binding. The surface texture and porosity of the biosorbent was analyzed by SEM analysis and found that the biosorbent surface is highly heterogeneous and uneven with porous structure.The maximum theoretical arsenic biosorption potential was estimated to be 26.54 mg/g, which is fairly high compared to previous reports. Further behaviour of arsenic biosorption onto *T. vulgaris* was investigated through kinetic studies and results illustrated chemisorption with surface ions exchange. The present study concludes that bio-sorbent produced from *T.vulgaris* could be a potential sorbent towards the removal of metal arsenic.

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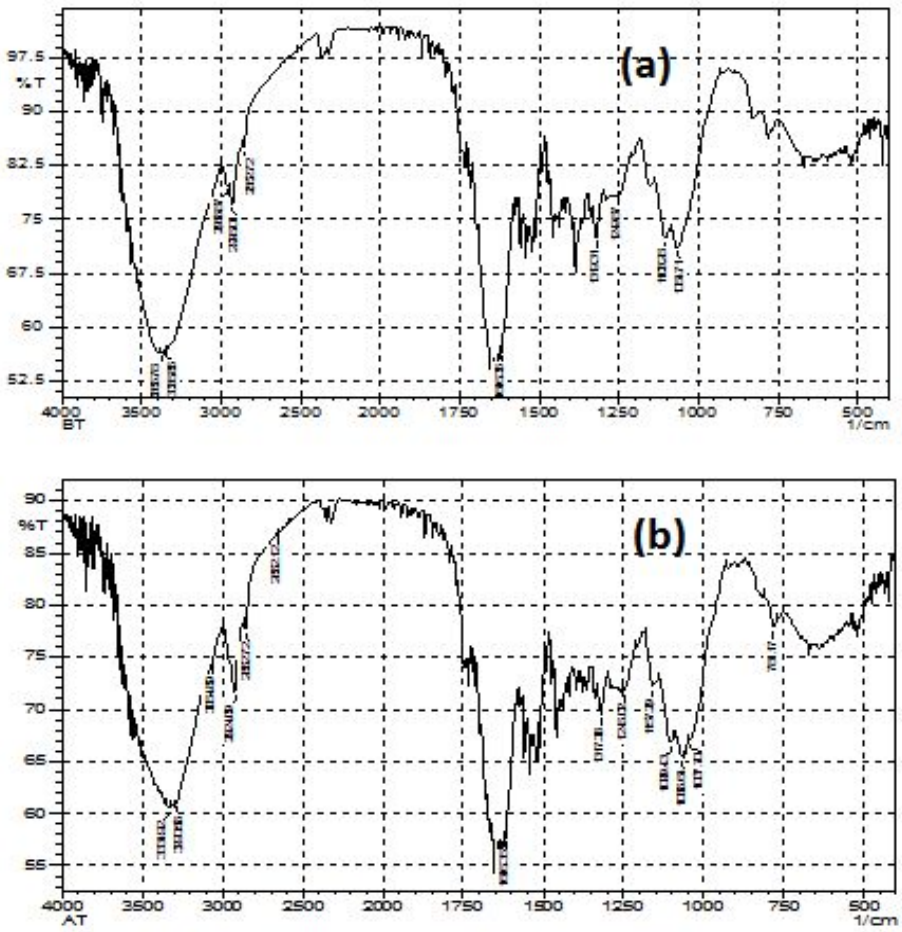

Fig 1 FTIR spectra of *T.vulgaris* a) before biosorption b) after biosorption

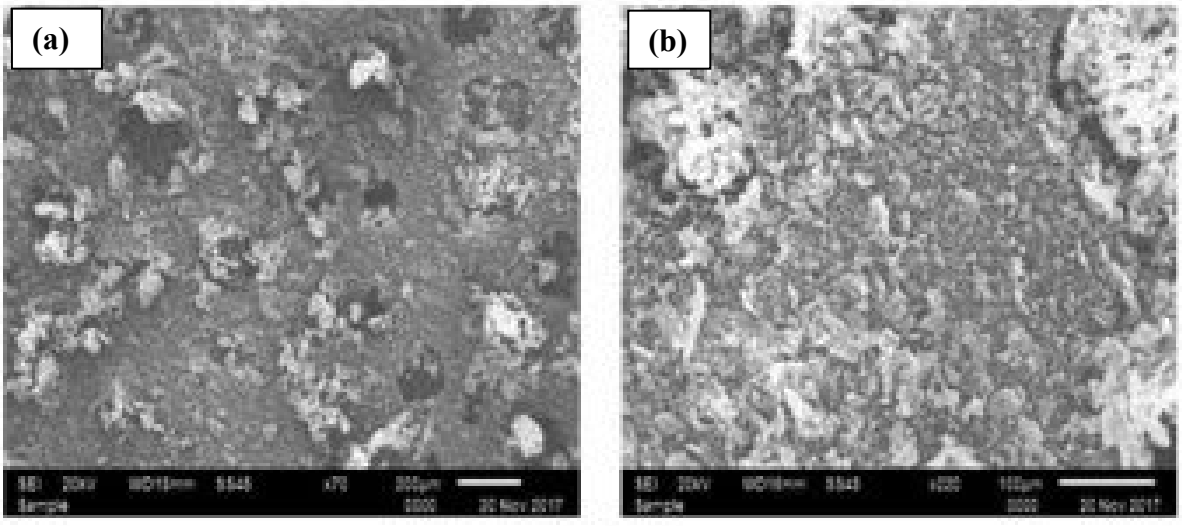

Fig. 2 SEM analysis for biosorption of arsenic using *T. vulgaris* a) before and b) after biosorption

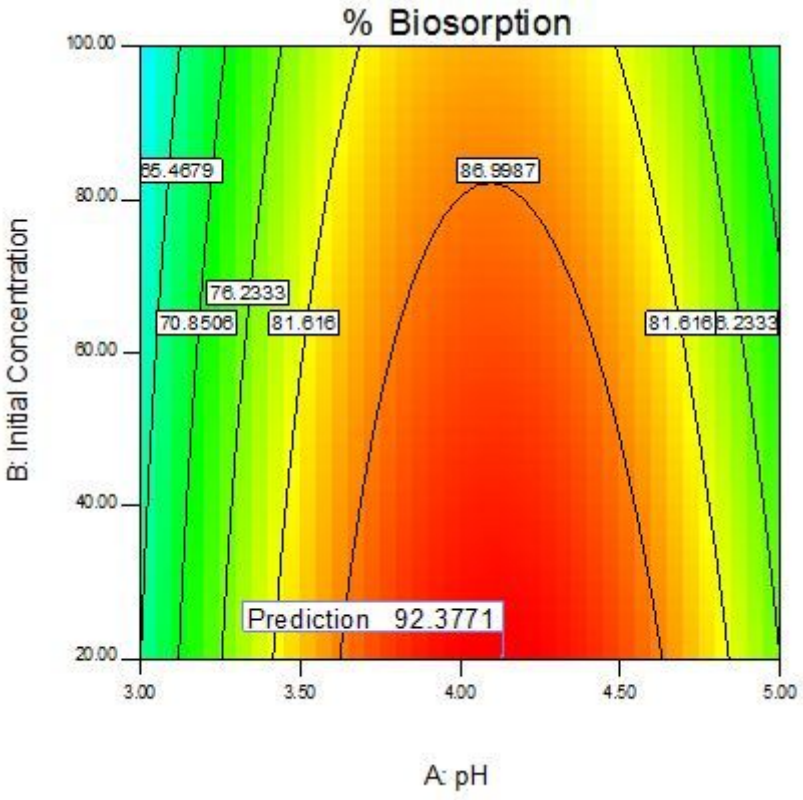

Fig 3 Contour plot of optimization of biosorption of arsenic onto *T. Vulgaris.*

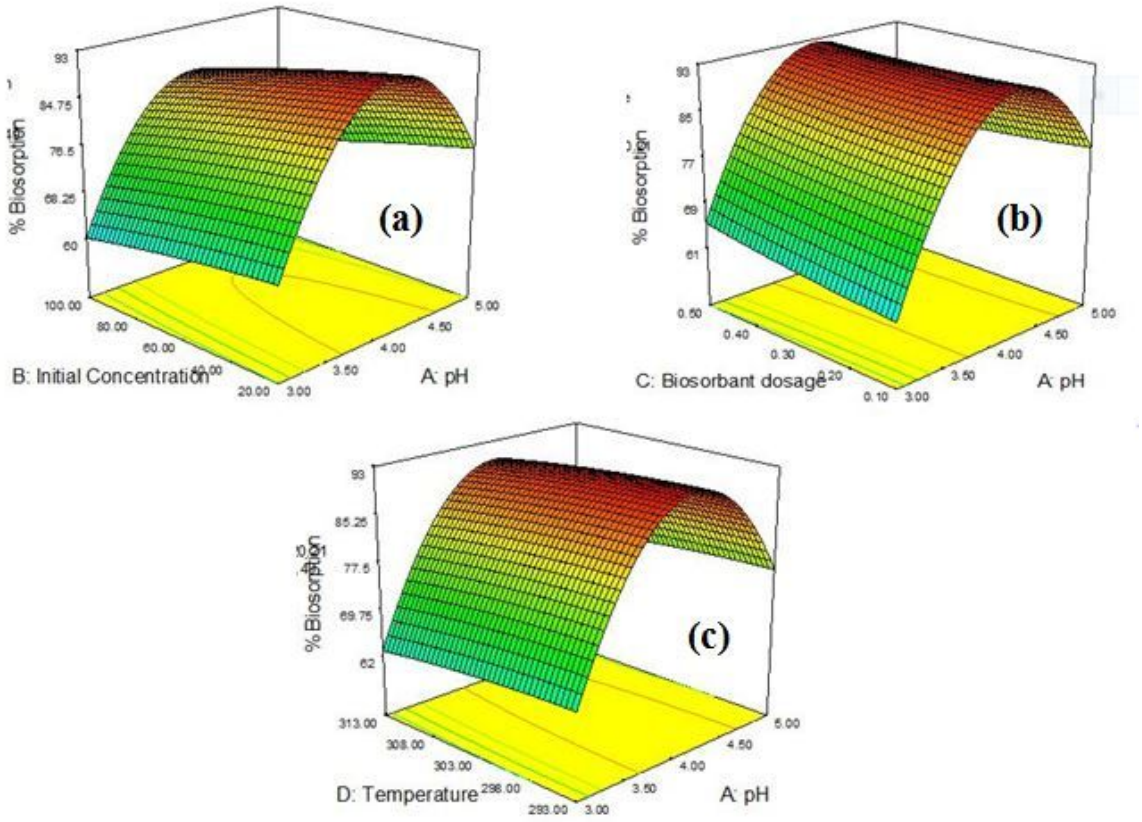

Fig. 4 Response surface plot for interactive effects of (a) initial concentration and pH, (b) biosorbent dosage and pH, (c) temperature and pH on biosorption of arsenic using modified *T. vulgaris*.as biosorbent.

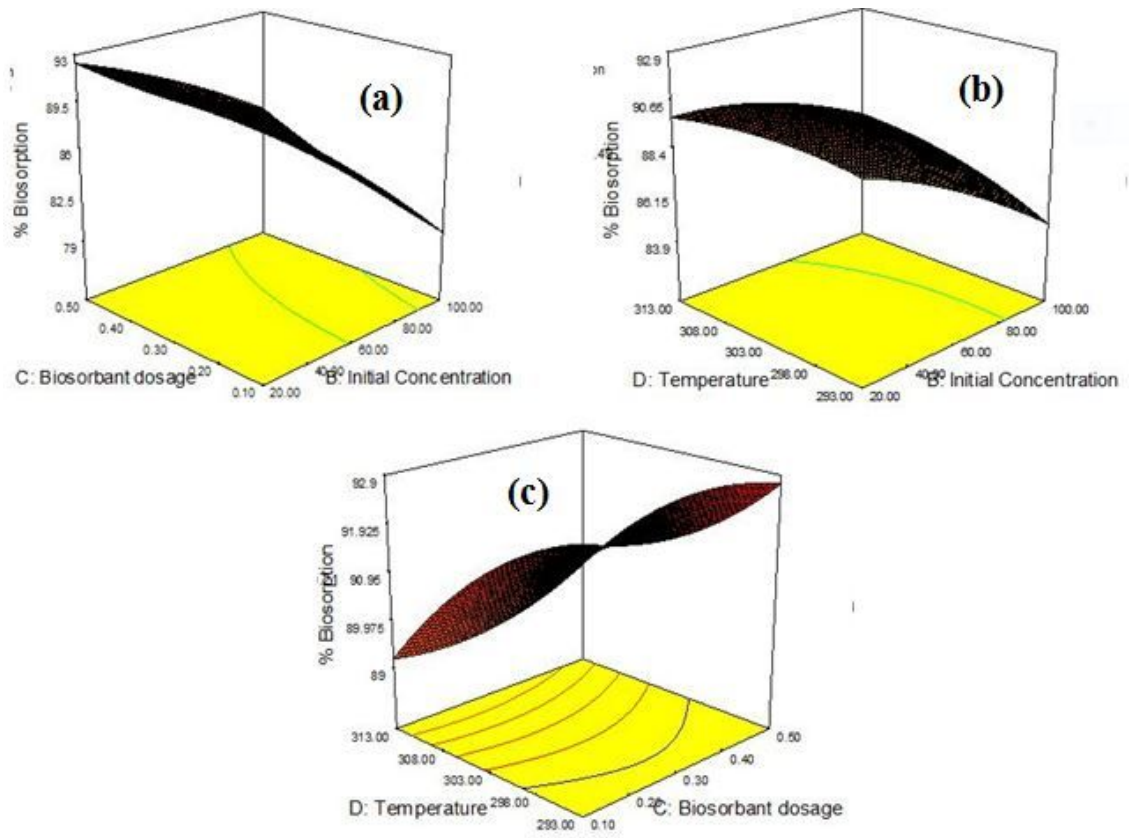

Fig. 5 Response surface plot for interactive effects of (a) biosorbent dosage and initial concentration, (b) temperature and initial concentration, (c) temperature and biosorbent dosage on biosorption of arsenic using modified *T. vulgaris*.as biosorbent.

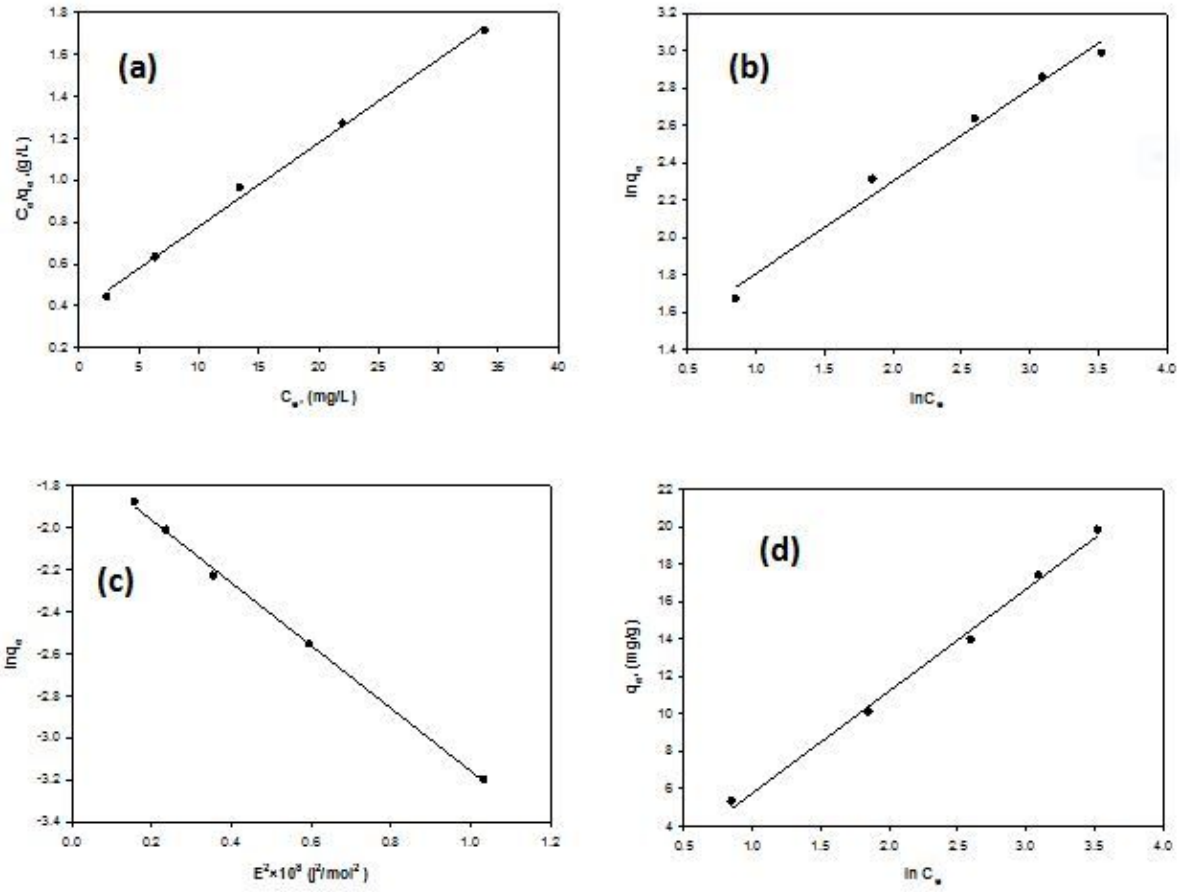

Fig. 6 a) Langmuir b) Freundlich c) D-R d) Temkin isotherm models for biosorption of arsenic using T. vulgaris as biosorbent.

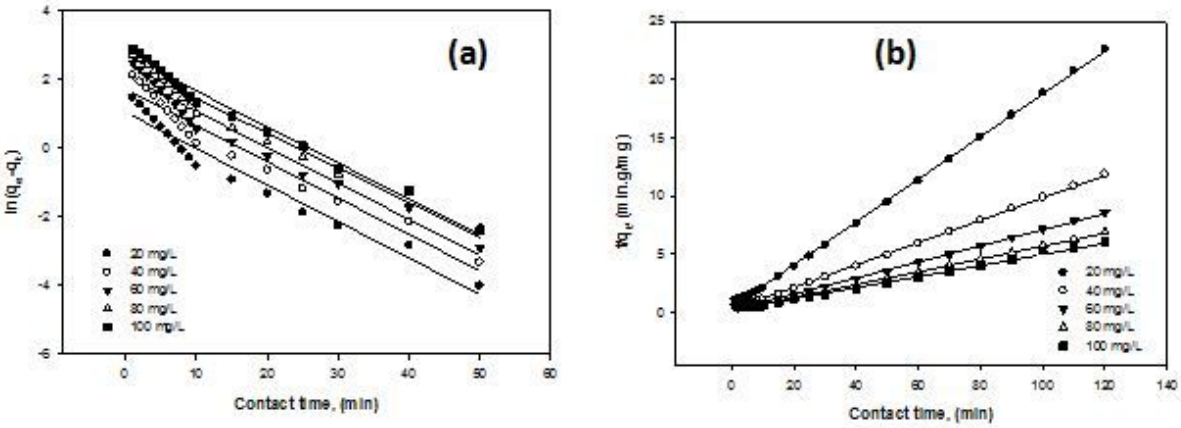

Fig: 7 a) Pseudo first order b) Pseudo second order models for biosorption of arsenic using *T. vulgaris* as biosorbent.

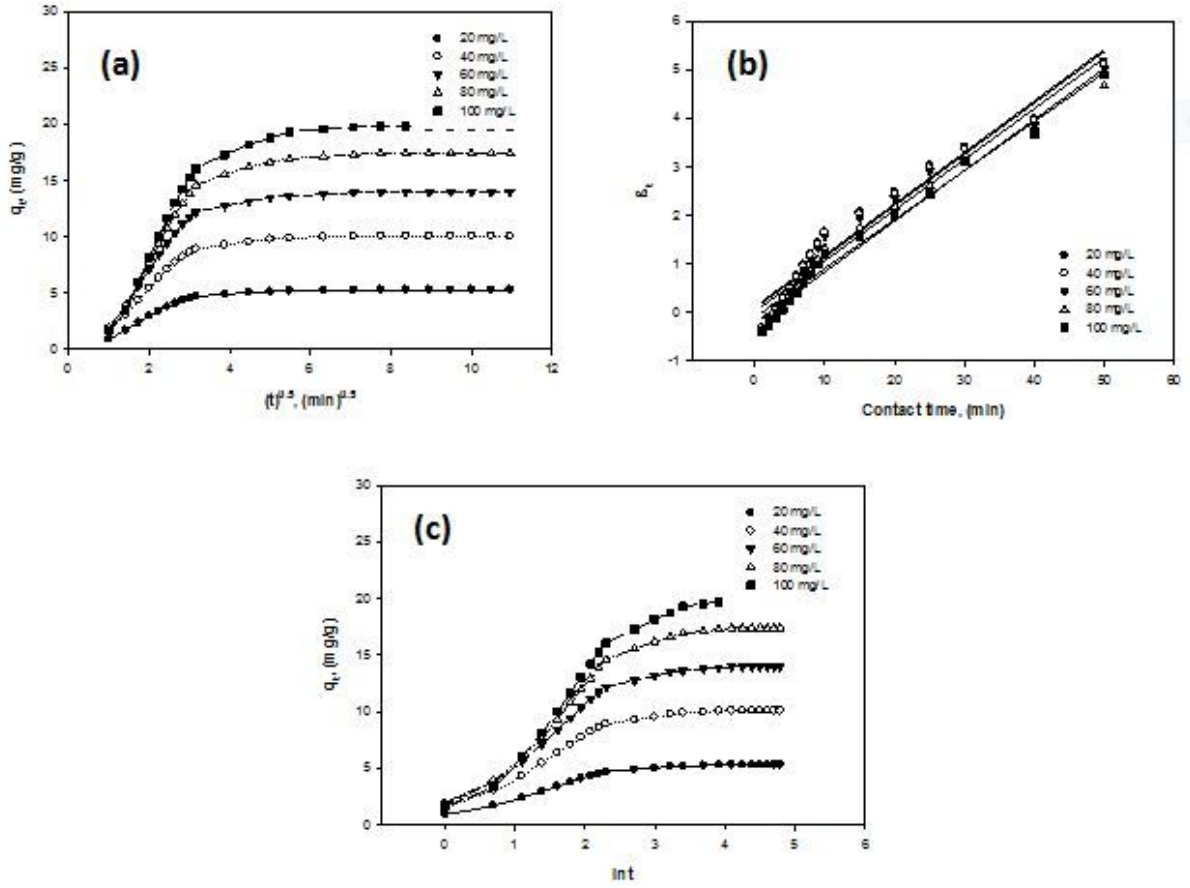

Fig: 8 a) Intra-particle diffusion b) Boyd c) Elovich models for bio-sorption of arsenic using *T. vulgaris* as biosorbent.

Table 1 Levels of different process variables used in CCD for bio-sorption of arsenic onto *T. vulgaris.*

Factor	Name	Units	Symbol &levels		
			-1	0	1
A	pH	--	3.00	4.000	5.00
B	Initial arsenic concentration	mg/l	20.00	60.000	100.00
C	*T. vulgaris* dosage	G	0.100	0.300	0.50
D	Temperature	K	293.00	303.000	313.00

Table 2 Experimental design (CCD) observed and predicted response for biosorption of arsenic onto *T. vulgaris.*

Standard order	pH	Initial concentration	Biosorbent dosage	Temperature	Experimental % biosorption	Predicted % biosorption
1	3.00	20.00	0.10	293.00	61.64	62.03
2	5.00	20.00	0.10	293.00	80.28	79.42
3	3.00	100.00	0.10	293.00	51.58	51.11
4	5.00	100.00	0.10	293.00	64.51	64.79
5	3.00	20.00	0.50	293.00	65.23	65.82
6	5.00	20.00	0.50	293.00	76.19	76.53
7	3.00	100.00	0.50	293.00	60.37	60.10
8	5.00	100.00	0.50	293.00	67.62	67.10
9	3.00	20.00	0.10	313.00	58.24	58.49
10	5.00	20.00	0.10	313.00	75.41	75.92
11	3.00	100.00	0.10	313.00	49.64	49.53
12	5.00	100.00	0.10	313.00	64.1	63.24
13	3.00	20.00	0.50	313.00	63.04	62.99
14	5.00	20.00	0.50	313.00	73.54	73.74
15	3.00	100.00	0.50	313.00	58.64	59.23
16	5.00	100.00	0.50	313.00	66.42	66.26
17	3.00	60.00	0.30	303.00	60.22	59.29
18	5.00	60.00	0.30	303.00	70.43	71.50
19	4.00	20.00	0.30	303.00	92.12	90.74
20	4.00	100.00	0.30	303.00	80.03	81.54
21	4.00	60.00	0.10	303.00	84.49	85.34
22	4.00	60.00	0.50	303.00	89.45	88.74
23	4.00	60.00	0.30	293.00	86.67	87.18
24	4.00	60.00	0.30	313.00	85.37	84.99
25	4.00	60.00	0.30	303.00	87.95	86.63
26	4.00	60.00	0.30	303.00	86.28	86.63
27	4.00	60.00	0.30	303.00	85.94	86.63
28	4.00	60.00	0.30	303.00	87.04	86.63
29	4.00	60.00	0.30	303.00	86.24	86.63
30	4.00	60.00	0.30	303.00	86.73	86.63

Table 3 ANOVA for quadratic surface model for biosorption of arsenic onto *T. vulgaris*.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	
Model	4603.30	14	328.81	352.88	< 0.0001	Significant
A-pH	*671.00*	*1*	*671.00*	*720.12*	*< 0.0001*	
B-Initial Concentration	*380.70*	*1*	*380.70*	*408.57*	*< 0.0001*	
C-Biosorbant dosage	*52.05*	*1*	*52.05*	*55.86*	*< 0.0001*	
D-Temperature	*21.54*	*1*	*21.54*	*23.12*	*0.0002*	
AB	*13.78*	*1*	*13.78*	*14.79*	*0.0016*	
AC	*44.59*	*1*	*44.59*	*47.85*	*< 0.0001*	
AD	*1.056E-003*	*1*	*1.056E-003*	*1.134E-003*	*0.9736*	
BC	*27.01*	*1*	*27.01*	*28.99*	*< 0.0001*	
BD	*3.83*	*1*	*3.83*	*4.11*	*0.0607*	
CD	*0.51*	*1*	*0.51*	*0.54*	*0.4718*	
A^2	*1168.58*	*1*	*1168.58*	*1254.12*	*< 0.0001*	
B^2	*0.62*	*1*	*0.62*	*0.66*	*0.4290*	
C^2	*0.43*	*1*	*0.43*	*0.46*	*0.5071*	
D^2	*0.76*	*1*	*0.76*	*0.82*	*0.3800*	
Residual	13.98	15	0.93			
Lack of Fit	*11.33*	*10*	*1.13*	*2.14*	*0.2071*	*not significant*
Pure Error	*2.64*	*5*	*0.53*			
Cor Total	4617.28	29				

Table 4 Equilibrium constants for biosorption of arsenic onto *T. vulgaris*

Isotherm	**Constants**	**Arsenic**
Langmuir	$Q_{max}(mg/g)$	25.64
	$K_L(L/mg)$	0.102
	R^2	0.996
Freundlich	$K_f(mg/g)$	3.724
	$1/n\ (L/g)$	0.493
	R^2	0.984

Temkin	$A_T\ (L/mg)$	4.845
	b_T	0.057
	R^2	0.995
Dubinin–Radushkevich	$Q_{\max}(mg/g)$	18.919X10^{-2}
	β	1.491X10^{-8}
	$E(kJ/mol)$	5.79
	R^2	0.998

Table 5 Pseudo first & second order kinetic constants for biosorption of arsenic onto *T. vulgaris*

Initial concentration, mg/L	**First order**			**Second order**		
	Rate constant, $k_1\ (1/\min)$	**Amount of arsenic biosorbed onto T. *vulgaris*,** q_{eq} **(mg/g)**	**Correlation coefficient ,** R_1^2	**Rate constant,** $k_2\ (g/mg\ \min)$	**Amount of arsenic biosorbed onto *T. vulgaris*,** q_{eq} **(mg/g)**	**Correlation coefficient,** R_2^2
20	0.106	2.880	0.958	0.0715	5.464	0.999
40	0.105	5.663	0.958	0.0349	10.4166	0.999
60	0.122	9.355	0.974	0.022	14.4927	0.998
80	0.101	11.763	0.967	0.013	18.5185	0.998
100	0.104	15.256	0.982	0.0091	21.2765	0.994

Table 6 Comparison of the arsenic biosorption capacity of present work with those reported in the literature

Adsorbent/Biosorbent	q_{max} (mg/g)	Reference
Lessonia nigrescens	4.2	26
Activated Moringa oleifera	6.23	27
shelled Moringa oleifera Lamarck seedpowder	2.16	28
powder of stem of Acacia nilotica	5.8	29
untreated powdered eggshell	2.14	30
Use of fl y ash and fl y ash agglomerates	5.7	31
Coagulant Of Plant Origin With Ferric Chloride	1.38	32
AC (olive pulp)	1.39	33
Turbinaria vulgaris sp.	25.64	**Present study**