Removal of Arsenic (III) from synthetic wastewater by using immobilized banana peels (*Musa paradisiaca* L.) as a biofilm on silica gel

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***ABSTRACT*: The biosorption of arsenic (III) by using immobilized biomass of banana peels (*Musa paradisiaca* L.). Biosorbent were prepared by immobilizing biomass on silica gel. Immobilization enhance sorption chromium ion and repetitive use of sorbent could be achieved. The influence of several operating experimental parameters such as solution pH, biosorbent dose concentration, initial arsenic (III) concentration, contact time, temperature and agitation rate determined in the experiment were effective in determining the efficiency of arsenic (III) onto banana peels (*Musa paradisiaca* L.). Langmuir adsorption isotherm, Frenudlich adsorption isotherm, Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm and Temkin adsorption isotherm were tested in batch equilibrium studies. For kinetics studies, Pseudo-first-order model, Pseudo-second-order model, Elovich model and Weber and Morris intra-particle diffusion model were applied to the experimental data and followed by thermodynamic study. The results showed that immobilized waste biosorbent was a low-cost promising sorbent for sequester of arsenic (III) ions from wastewater.**

***Keywords*: arsenic (III), immobilization, banana peels (*Musa paradisiaca* L.), silica gel, adsorption isotherm, adsorption kinetics, thermodynamic study.**

INTRODUCTION:

Environmental pollution and its harmful effect on ecology have been studied intensively during last decade years. Problems of the pollutants removal from wastewater were increased with fast industrialization. These waste waters are produced large volumes and must be absolutely treated before discharge. Heavy metals are very harmful for humans, animals and plants. Global and local agencies have therefore established certain limits on the quantities of heavy metals being discharged into environment.

Arsenic is a metalloid, a known poison element, and exists as oxide or anion and known to be 20th most abundant element in the earth [1]. The presence of arsenic in water is due to natural weathering process, geochemical reactions, biological activity, combustion of fossil fuels, volcanic eruptions, gold mining, leaching of man-made arsenic compounds, smelting of metals ores, desiccants, wood preservatives, agricultural pesticides and many other anthropogenic activities [1–3]. Arsenic generally occurs as arsenic (V) and (III), depending on pH and redox conditions [1, 4, 5]. Arsenic (III) is more toxic than arsenic (V), because arsenic (III) binds to single but with higher affinity to vicinal sulfhydryl groups that reacts with a variety of proteins and inhibits their activity [6]. Arsenic (III) is more stable than As (V) because of electronic configuration. Long term ingestion of arsenic contaminated drinking water causes skin lungs and kidney cancer, gastrointestinal disease, bone marrow disorder, cardiovascular diseases and other diseases [7]. Due to extreme toxicity of arsenic in drinking water, World Health Organization (WHO, Geneva, Switzerland), Environmental Protection Agency (US-EPA, United States), the European Commission (EU) [8, 9] and Central Pollution Control Board (CPCB, India) [10,11] has set 0.01 mg L^{-1} and 0.05 mg L^{-1} as maximum permissible limit of arsenic in drinking water.

Traditional / conventional treatment techniques for water purification need very expansive and continuous input of chemicals becomes impracticable and uneconomical which causes further damage to the environment. Therefore, it is required to produce an easy, effective, economic and eco-friendly technique for wastewater treatment [12, 13]. Biosorption is a cost-effective and eco-friendly technique for removal of heavy metals. Biosorption may be defined as removal of substances from solution by biological material [14, 15].

In the present research work, banana peels (*Musa paradisiaca* L.) is an agro-industrial based waste material belongs to the family Scitaminaceae and sub-family Musaceae and these materials have the potential to sequester heavy metals from solutions. The present research describes the increased utilization and efficiency of banana peels (*Musa paradisiaca* L.) biomass when immobilized as a bio-film on silica gel for the biosorption of arsenic (III) from wastewater. The study was extend with the objective for estimation and calculation of various parameters affecting the biosorption such as solution pH, biosorbent dose concentration, initial concentration of heavy metals, contact time, temperature and agitation rate. Adsorption isotherms model and kinetics models was employed to understand the probable biosorption mechanism. Thermodynamic studies were also carrying out to estimate the standard free change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0).

MATERIALS AND METHODS

Chemical and reagent:

All the chemicals and reagents were of analytical reagent (AR) grade. Double distilled water was used for all experimental work including the preparation of arsenic (III) solution. The arsenic (III) solution was prepared by using their respective compounds. The desired pH of the metal ion solution was adjusted with the help of dilute hydrochloric acid and sodium hydroxide.

Preparation of arsenic (III) solution:
The stock solution of 1000 ppm of arsenic (III) was prepared by dissolving 0.132 g of arsenic trioxide (As_2O_3) in 100 ml of double distilled water and further desired test solutions of arsenic (III) were prepared using appropriate subsequent dilutions of the stock solution.

Preparation of biosorbent:
Fresh banana peels (*Musa paradisiaca* L.) was collected from domestic wastes, as its availability and transportation was easy. The peels was washed several times with tap water and followed by distilled water. The washed material then cut in to small pieces and banana peels was first dried, in sun light for 10 days and then in an oven at 50^0C.The moisture content was lost from it and the color change was observed from yellow to brownish black. The dried material was finely ground and screened through the sieves of cut size of 100-200µm. The dried biosorbent powder was stored in air tight glass bottles to protect it from moisture.

Immobilization of biosorbent:
0.5g banana peels powder was dissolved in appropriate amount of acetone to make slurry of peels. Weight silica gel (2.0 g) was mixed in slurry in the way that each of silica gel should have the uniform coating of slurry. This mixture was allowed to dry completely. After it dried, it was wash to remove excess of banana peels powder which was not coated on silica gel. Those excess of banana peels powder was collected, dried and weight to know the actual weight of banana peels coated on silica gel. The prepared biosorbent was allowed to dry up completely before using it during the experiments.

Instrumentation:

The concentration of arsenic (III) in the solutions before and after equilibrium was determined by measuring absorbance using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode.

Experimental procedure:

The static (batch) method was employed at temperature (30^0C) to examine the biosorption of arsenic (III) by biosorbent. The method was used to determine the adsorption capacity, stability of biosorbent and optimum biosorption conditions. The parameters were studied by combining biosorbent with arsenic (III) solution in 250 ml separate reagent bottles. The reagent bottles were placed on a shaker with a constant speed and left to equilibrate. The samples were collected at predefined time intervals, centrifuged, the content was separated from the adsorbent by filtration, using Whatmann filter paper and amount of arsenic (III) in the supernatant/filtrate solutions was determined by ICP-AES. The following equation was used to compute the percent removal (% Adsorption) of arsenic (III) by the biosorbent,

$$\%\ \mathbf{Adsorption} = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (1)$$

where C_i and C_e are the initial concentrations and equilibrium concentrations of the arsenic (III) in mg/L.
The equilibrium adsorptive quantity (q_e) was determined by the following equation,

$$q_e = \frac{(C_i - C_e)}{w} \times V \qquad (2)$$

where q_e (mg metal per g dry biosorbent) is the amount of arsenic (III) biosorbed, V (in liter) is the solution volume and w (in gram) is the amount of dry biosorbent used.

Biosorption-desorption study:
To evaluate desorption efficiency, arsenic (III) loaded biosorbent was dried after equilibrium sorption experiments. The dried biosorbent was contacted with 0.1 M nitric acid (HNO_3), 0.1 M hydrochloric acid (HCl) and 0.1 sulphuric acid (H_2SO_4) separately for 3 hours to allow arsenic (III) to be release from biosorbent. The samples were separated from the biosorbents by filtration, using Whitman filter paper and amount of and arsenic (III) in the supernatant/filtrate solutions was determined by ICP-AES to find out desorption efficiency. Desorption efficiency was calculated from the amount of metal adsorbed on the biosorbent and the final metal concentration in the biosorption medium (equation 3).

$$\textit{Desorption efficiency}\ (\%) = \frac{\text{released metal ions in mg/L}}{\text{initially adsorbed metal ions in mg/L}} \times 100 \qquad (3)$$

RESULTS AND DISCUSSION:
Characterization of biosorbent by Fourier Transform Infrared (FTIR) spectroscopy:
FTIR offers excellent information on the functional groups present on the surface of the biosorbent and also presents three main advantages as an analytical technique: it is fast, nondestructive and requires only small sample quantities. Silica gel immobilized banana peels (*Musa paradisiaca* L.), as seen in the figure unloaded biosorbent displays a number of absorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3439 cm^{-1} is the indicator of -OH and -NH groups. The peaks located at 1641 cm^{-1} are characteristics of carbonyl group. The presence of -OH group along with carbonyl group confirms the presence of carboxyl acid groups in the biosorbent. The peaks observed at 1087 cm^{-1} are due to C-H and C-O bonds. The –OH, NH, carbonyl and carboxyl groups are important sorption sites. As compared to simple biosorbent, biosorbent loaded with Arsenic (III), the broadening of -OH peak at 3439 cm^{-1} and carbonyl group peak at 1641 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of arsenic (III) ions.

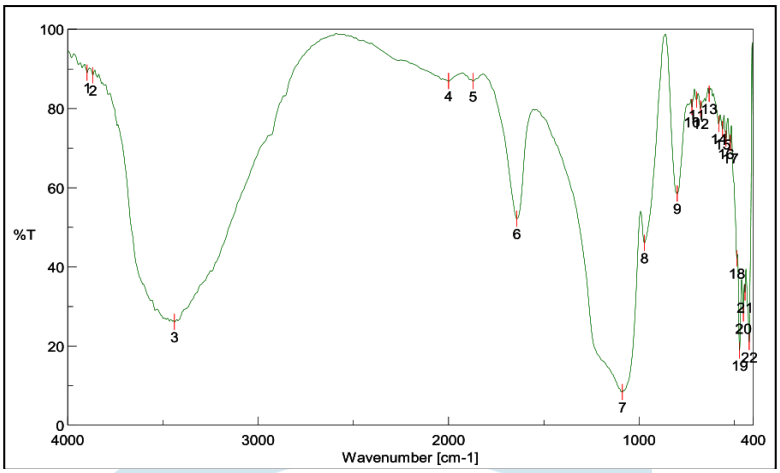


Figure 1 (a): Fourier Transform Infrared (FTIR) spectra of Silica gel immobilized banana peels (*Musa paradisiaca* L.) unloaded with arsenic (III)

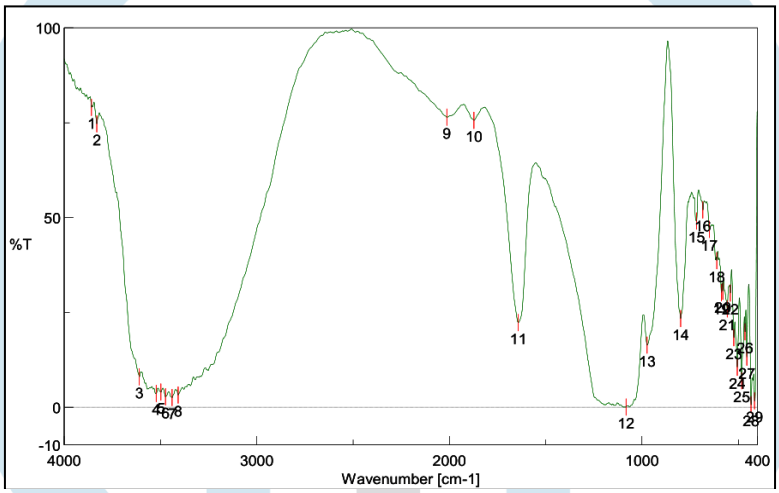


Figure 1 (b): Fourier Transform Infrared (FTIR) spectra of Silica gel immobilized banana peels (*Musa paradisiaca* L.) loaded with arsenic (III)

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis:

The SEM analysis of banana peel confirmed that they have large number of pores on the surface with cracks and crevices. The SEM clearly demonstrated that there is more uniformity after biosorption on metal ions in comparison to before biosorption. It was evident from the micrographs that the biosorbents presents an unequal structure before metal adsorbed. The number of canals in the biosorbents was higher in the initial case. The metal ions adsorbed on the cell wall matrix and created stronger cross linking and uniformity on the surface of biosorbent.

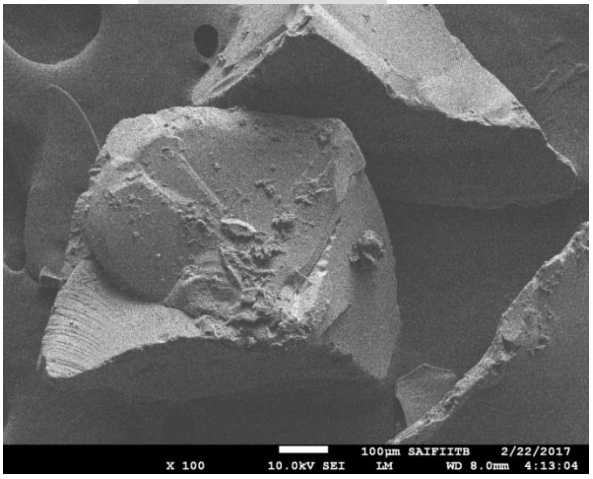


Figure 2 (a): Scanning electron micrograph (SEM) of Silica gel immobilized banana peels (*Musa paradisiaca* L.) before biosorption of arsenic (III) magnification ×100, bar represents 100µm

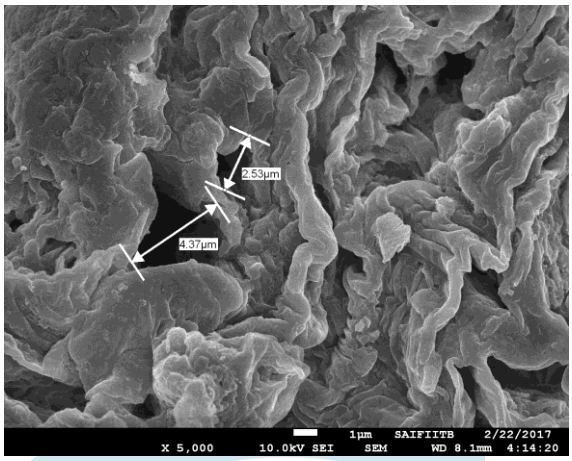


Figure 2 (b): Scanning electron micrograph (SEM) of Silica gel immobilized banana peels (*Musa paradisiaca* L.) after biosorption of arsenic (III) magnification ×5000, bar represents 1µm

Characterization of biosorbent by *X-ray diffraction analysis (XR-D) analysis:*

X-ray diffraction is a non-destructive technique used to provide detailed information on the crystallographic structure of materials. The XRD profile of the unloaded silica gel immobilized banana peels (*Musa paradisiaca* L.) shows typical diffraction peaks. Broad peaks were obtained instead of sharp peaks indicating the sample was poorly crystalline. The XRD spectra of loaded arsenic (III) exhibit strong peaks at 2θ value 22.02º, 27.12º and 45.90º corresponding to 276.836, 296.293 and 167.3756, planes, respectively for silica gel immobilized banana peels (*Musa paradisiaca* L.).

In addition, several other low intensity peaks corresponding to other crystalline phases have also been observed. After biosorption of arsenic (III), the porous structures of the biosorbents decreased. These causes low intensity XRD peaks. Hence crystalline phases should have been reduced. XRD pattern of arsenic ions loaded plant materials shows the presence of phases of $AlAsO_4$, As_2O_3, and As $(OH)_3$ which indicates that arsenite are converted into the above species and finally get adsorbed over the surface of plant materials.

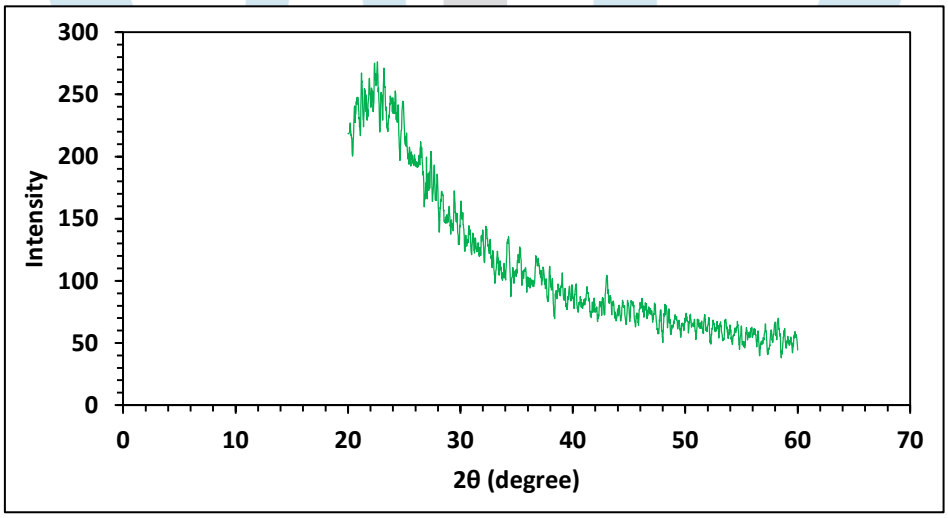


Figure 3 (a): X-ray diffraction (XRD) image of silica gel immobilized banana peels (*Musa paradisiaca* L.) unloaded with arsenic (III)

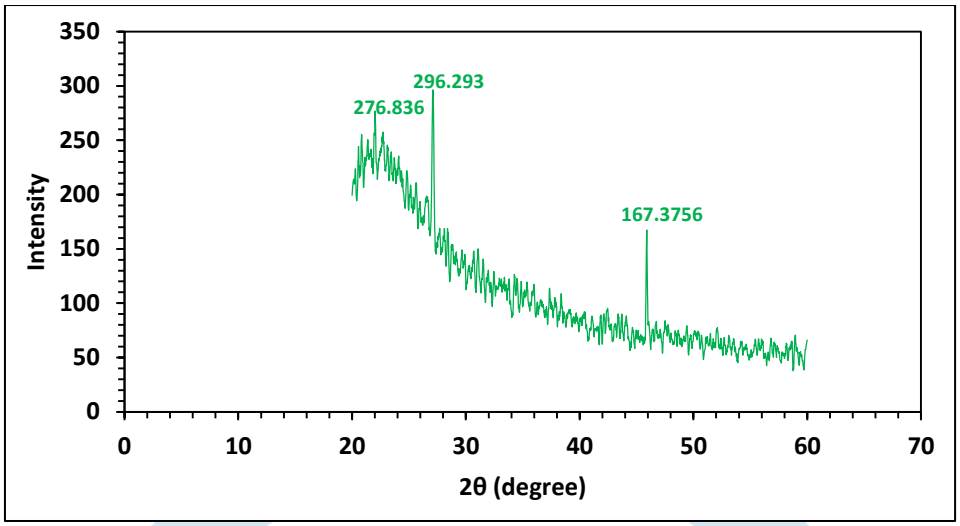


Figure 3 (b): X-ray diffraction (XRD) image of silica gel immobilized banana peels (*Musa paradisiaca* L.) loaded with arsenic (III)

Effect of pH:

The biosorption capacity of the biosorbent and speciation of metals in the solution is pH dependent. The optimization of pH was done by varying the pH in the range of 1-8 for bisorption of arsenic (III) and pH trend observed in this case is shown in Figure 1. It was found that at pH 6.0 the biosorption process was maximum with 84.39 % and after increasing pH, biosorption was decreases. At low pH (2.0-6.0), the surface of banana peels biomass is highly protonated and as a result, a strong attraction exists between oxyanion and positively charged surface of the biomass. The further decreases in arsenic (III) uptake with increase in pH (6.0 – 8.0) may be due to the fact that at higher pH, the substrate may be negatively charged by adsorbing hydroxyl ions on the surface or by ionization of very weak acidic functional groups of the banana peels biomass. A repulsive force may develop between the negatively charged surface and the anions. At lower pH, the process of regeneration predominates over the process of removal. The process of conversion of biosorbent into its H^+ form plays an important role leaving behind arsenic (III) ions in the aqueous solution [16].

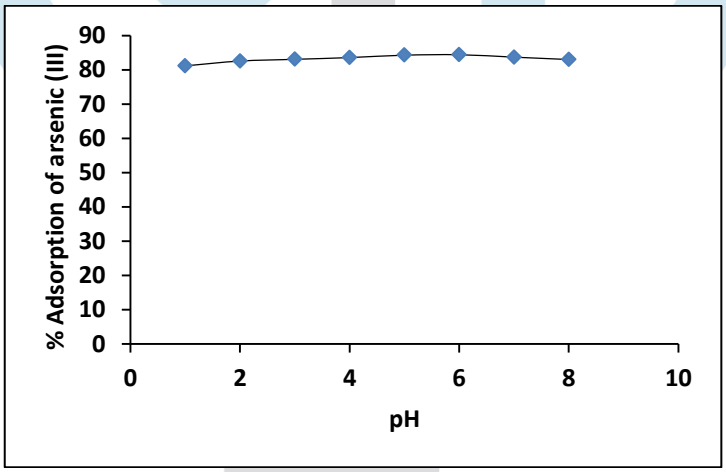


Figure 3: Effect of pH on arsenic (III) biosorption by silica gel immobilized banana peels (*Musa paradisiaca* L.) (biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Effect of biosorbent dose concentration:

Biosorbent dosage is an important parameter studied while conducting batch mode studies. The sorption capacity of silica gel immobilized banana peels (*Musa paradisiaca* L.) on to arsenic (III) ions by varying its dosage from 1 g/L to 15 g/L as shown in Figure 2. From the results it was found that biosorption of arsenic (III) ions increases with increase in biosorbent dosage and is highly dependent on biosorbent concentration. Increase in biosorption by increase in biosorbent dose is because of increase of ion exchange site ability, surface areas and the number of available biosorption sites [17]. The point of saturation for silica gel immobilized banana peels (*Musa paradisiaca* L.) was found at 5 g/L of biosorbent dose with 84.40% of removal efficiency. The biosorbent dose 5 g/L was chosen for all further studies.

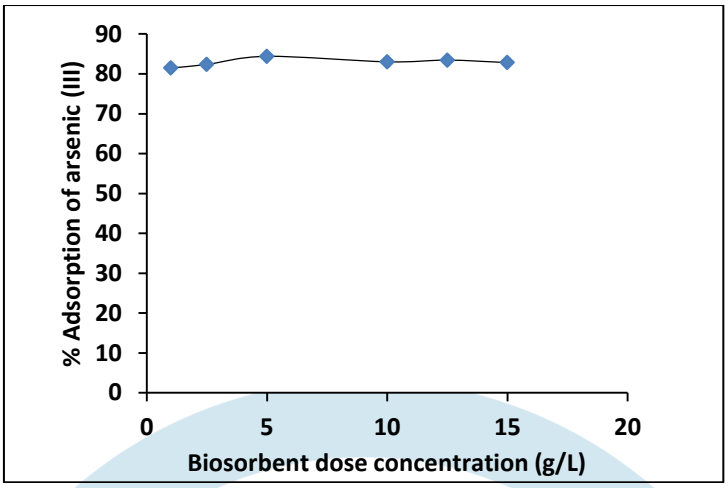


Figure 4: Effect of biosorbent dose concentration on arsenic (III) biosorption by silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH: 6.0, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Effect of initial arsenic (III) concentration:

The effect of initial arsenic (III) concentration from 10mg/L-250mg/L on the removal of arsenic (III) from aqueous solutions at biosorbent dose 5 g/L and at optimum pH 6.0 at 30^{0}C was studied. On increasing the initial arsenic (III) ions concentration, the total arsenic (III) ions uptake decreased slightly at arsenic (III) ions concentration ranges from 10 mg/L- 250 mg/L.

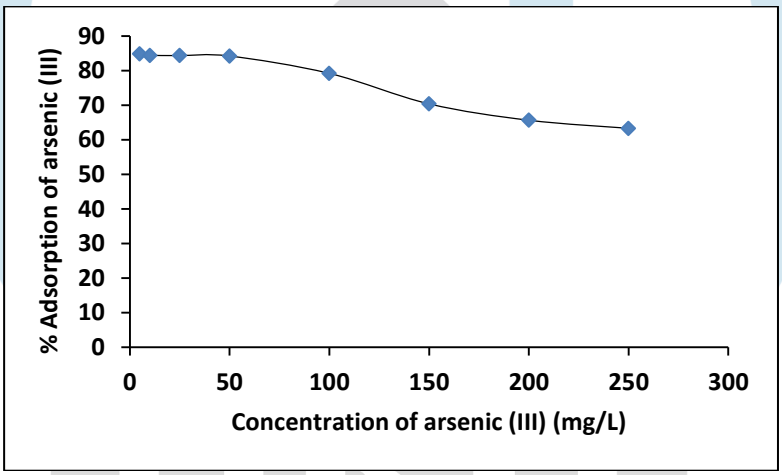


Figure 5: Effect of arsenic (III) concentration on arsenic (III) biosorption by silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, contact time: 150 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Effect of contact time:

In order to optimize the contact time for the maximum uptake of metals ions, contact time was varied between 10 minute-180 minute on the removal of arsenic (III) from aqueous solutions in the concentration of arsenic (III) 10 mg/L and biosorbent dose 5g/L at optimum pH 6.0 at 30^{0}C. The results obtained from the biosorption capacity of arsenic (III) ions onto silica gel immobilized banana peels (*Musa paradisiaca* L.) showed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of arsenic (III) ions onto silica gel immobilized banana peels (*Musa paradisiaca* L.) was 150 minutes with 84.24 % removal. The rapid uptake of arsenic (III) is due to the availability of ample active sites for biosorption. A further increase in the contact time has a negligible effect on the biosorption capacity of arsenic (III) biosorption. So a contact time of 150 minutes was fixed for further experiments.

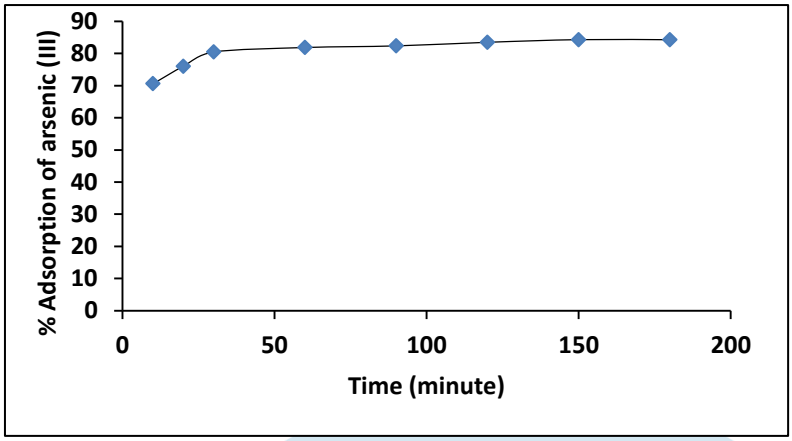


Figure 6: Effect of contact time on arsenic (III) biosorption by silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, temperature: 30^{0}C, agitation rate: 120 rpm)

Effect of temperature:

The effect of temperature on removal of arsenic (III) ions from aqueous solutions using silica gel immobilized banana peels (*Musa paradisiaca* L.) was studied at different temperatures from 20^{0}C-40^{0}C. The influence of temperature is depicted in Figure 5. Maximum sorption was seen at 30^{0}C with percentage removal 84.39%.

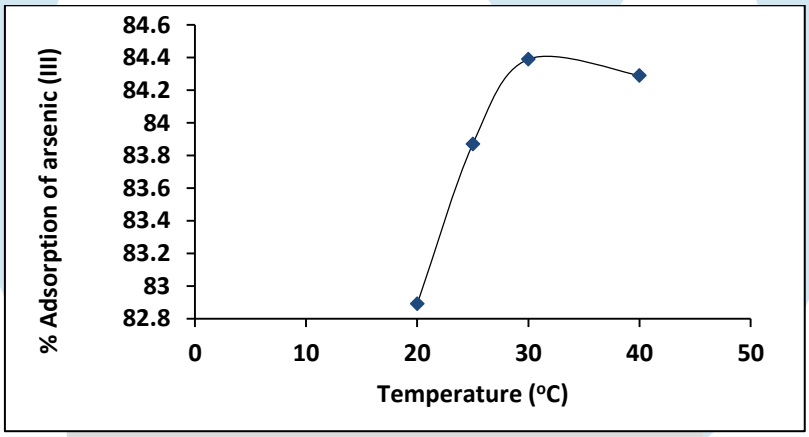


Figure 7: Effect of temperature on arsenic (III) biosorption removal using silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH 6.0, biosorbent dose concentration: 5 g/L, initial arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, agitation rate: 120 rpm)

Effect of agitation rate:

The effect of agitation rate on removal of arsenic (III) from aqueous solutions at biosorbent dose 5 g/L and at optimum pH 6.0 was studied at different rpm such as 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200 rpm. The efficiency was highest at 120 rpm with percentage removal 84.39%. So, 120 rpm was chosen for all further biosorption studies.

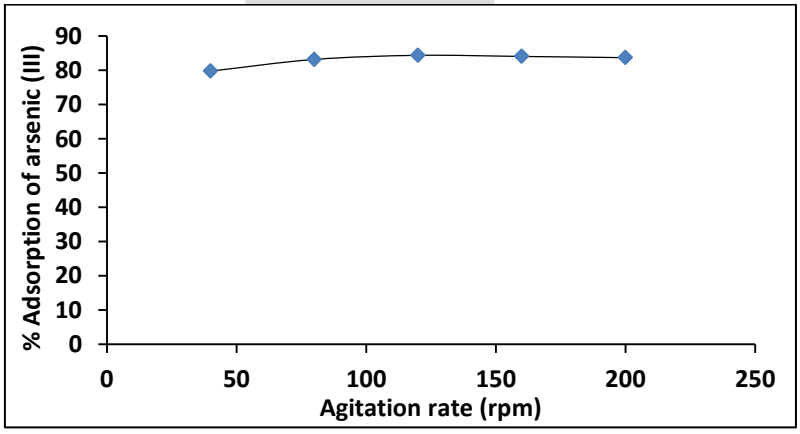


Figure 8: Effect of agitation rate on arsenic (III) removal using silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH 6.0, biosorbent dose concentration: 5 g/L, initial arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature 30 ^{o}C)

Biosorption-desorption study:

In application of real wastewater, desorption of heavy metal ions in the biosorbent is important process. Banana peels (*Musa paradisiaca* L.)was the most effective waste biosorbent with desorption efficiency 50.40% (0.1 M hydrochloric acid), 50.13% (0.1 M nitric acid) and 66.53% (0.1 M sulphuric acid).

Sulphuric acid has shown highest desorbed capacity of arsenic (III) followed by hydrochloric acid and nitric acid from banana peels (*Musa paradisiaca* L.).

Adsorption isotherm models:

The analysis of the adsorption isotherms data by fitting them into different isotherm models is an important step to find the suitable model that can be used for design process. The experimental data were applied to the two-parameter isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin.

Langmuir adsorption isotherm [18]:

The Langmuir equation, which is valid for monolayer sorption onto a surface of finite number of identical sites, is given by:

$$q = \frac{q_m b C_e}{1+bC_e} \qquad (4)$$

Where q_m is the maximum biosorption capacity of adsorbent (mg g^{-1}). b is the Langmuir biosorption constant (L mg^{-1}) related to the affinity between the biosorbent and sorbate.

Maximum biosorption capacity of biosorbents (q_m) is found to be 49.504 mg g^{-1} of silica gel immobilized banana peels (*Musa paradisiaca* L.).

Linearized Langmuir isotherm allows the calculation of adsorprtion capacities and Langmuir constants and is represented as:

$$\frac{1}{q} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \qquad (5)$$

The linear plots of $1/q$ vs $1/c_e$ is shown in Figure 7 (a). The two constants b and q_m are calculated from the slope ($1/q_m \cdot b$) and intercept ($1/q_m$) of the line. The values of q_m, b and regression coefficient (R^2) are listed in Table 1.

Frenudlich adsorption isotherm [19]:

Freundlich equation is represented by:

$$q = KC_e^{1/n} \qquad (6)$$

where K and n are empirical constants incorporating all parameters affecting the adsorption process such as, sorption capacity and sorption intensity respectively.

Linearized Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\log q = \log K + \frac{1}{n}\log C_e \qquad (7)$$

Equilibrium data for the adsorption is plotted as log q vs log C_e, as shown in Figure 7 (b). The two constants n and K are calculated from the slope ($1/n$) and intercept (log K) of the line, respectively. The values of K, $1/n$ and regression coefficient (R^2) are listed in Table 1.

Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm [20]:

Linearized Dubinin-Kaganer-Radushkevich (DKR) adsorption isotherm equation is represented as:

$$lnq_e = \ln q_m - \beta\, \varepsilon^2 \qquad (8)$$

where q_m is the maximum sorption capacity, β is the activity coefficient related to mean sorption energy and ε is the polanyi potential, which is calculated from the following relation:

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \qquad (9)$$

Equilibrium data for the adsorption is plotted as $\ln q_e$ vs ε^2, as shown in Figure 7 (c). The two constants β and q_m are calculated from the slope (β) and intercept (lnq_m) of the line, respectively. The values of adsorption energy E was obtained by the following relationship.

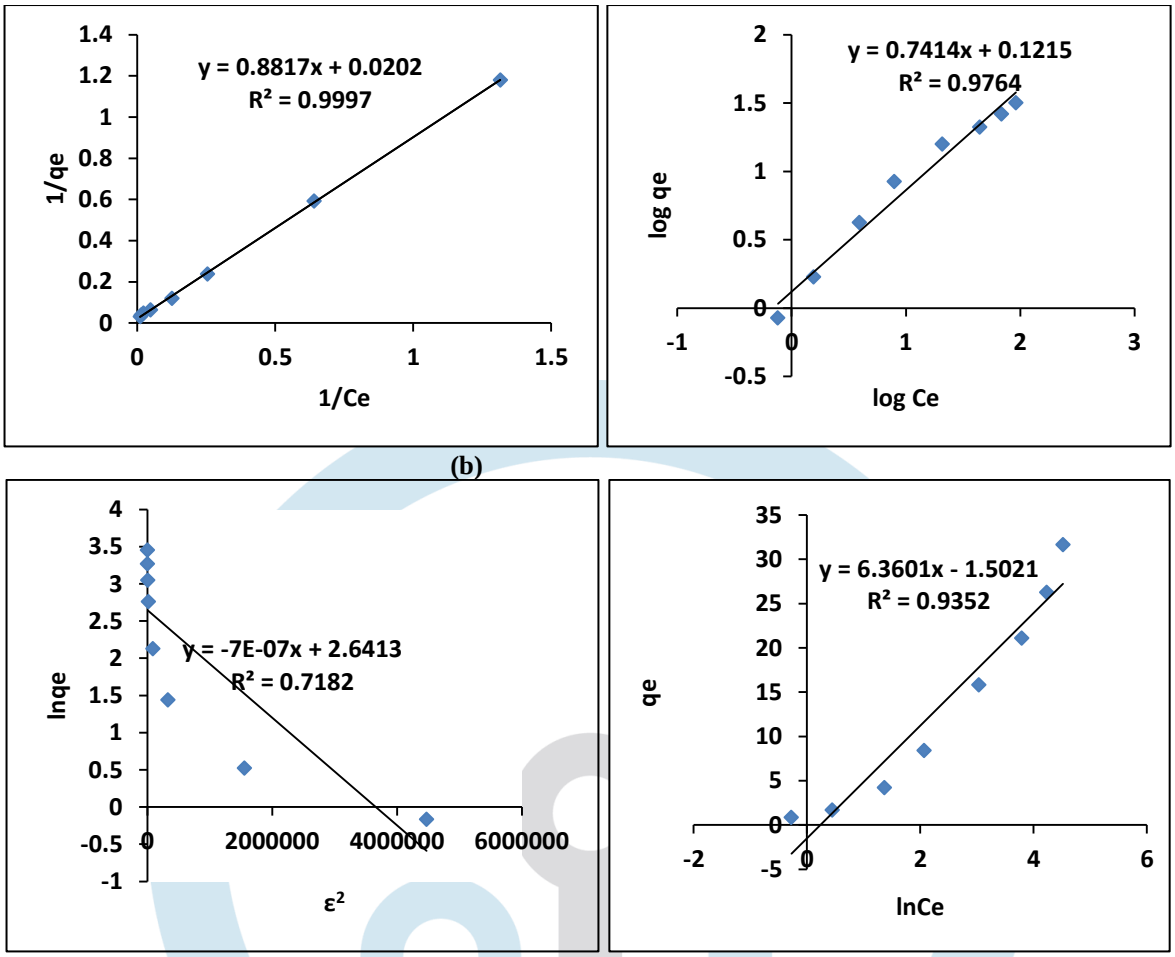
$$E = \frac{1}{\sqrt{-2\beta}} \qquad (10)$$

Temkin adsorption isotherm [21]:

Linearized Temkin adsorption isotherm is given by the equation:

$$q_e = \frac{RT}{b_T}\ln(A_T\, C_e) \qquad (11)$$

Where b_T is the Temkin constant related to heat of sorption (J/mol) and A_T is the Temkin isotherm constant (L/g).Equilibrium data for the adsorption is plotted as q_e vs $\ln C_e$, as shown in Figure 7(d). The two constants b_T and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot lnA_T$) of the line.



(a) (b) (c) (d)

Figure 9: Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for bisorption of arsenic (III) silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, contact time: 150 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Langmuir parameters			Freundlich parameters			DKR parameters				Temkin parameters		
q_m	b	R^2	K	$1/n$	R^2	β	q_m	E	R^2	A_T	b_T	R^2
49.504	0.0229	0.9997	5.5131	8.2304	0.9764	-7E-07	3.5064	0.8451	0.7182	68.999	396.085	0.9351

Table 1: Adsorption isotherm constants for biosorption of arsenic (III) by silica gel immobilized banana peels (*Musa paradisiaca* L.)

Adsorption kinetics:

As aforementioned, a lumped analysis of adsorption rate is sufficient to practical operation from a system design point of view. The commonly employed lumped kinetic models, namely (a) the pseudo-first-order equation [22] (b) the pseudo-second-order equation [23] (c) Elovich equation [24] (d) Weber & Morris intra-particle diffusion model [25] are presented below:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (12)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (13)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (14)$$

$$q_t = k_i t^{0.5} + c \quad (15)$$

where q_e (mg g^{-1}) is the solid phase concentration at equilibrium, q_t (mg g^{-1}) is the average solid phase concentration at time t (min), k_1 (min^{-1}) and k_2 (g mg^{-1} min^{-1}) are the pseudo-first-order and pseudo-second-order rate constants, respectively. The symbols of α (mg g^{-1} min^{-1}) and β (g mg^{-1}) are Elovich coefficients representing initial sorption rate and desorption constants, respectively. k_i (mg g^{-1} min$^{-1/2}$) is the intra-particle diffusion rate constant, c is intercept.

If the biosorption follows the pseudo-first-order model, a plot of ln $(q_e$-$q_t)$ against time t should be a straight line. Similarly, t/q_t should change lineally with time t if the adsorption process obeys the pseudo-second order model. If the adsorption process obeys Elovich model, a plot of q_t against ln t should be a straight line. Also a plot of q_t against $t^{0.5}$ changes lineally the adsorption process obeys the Weber and Morris intra-particle diffusion model.

Biosorption of arsenic (III) onto biosorbent was monitored at different specific time interval. The arsenic (III) uptake was calculated from the data obtained. From the arsenic (III) uptake was plotted against time to determine a suitable kinetic model, the adsorption data was fitted into pseudo-first-order model, pseudo-second-order model, Elovich models and the Weber & Morris intra-particle diffusion model.

The pseudo-first-order model was plotted for $ln\ (q_e\text{-}q_t)$ against t (Figure 11 (a)). The values of k_1 and q_e values were calculated from the slope (k_1) and intercept ($ln\ q_e$) of the plot and shown in Table 2. Kinetic adsorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions adsorbed onto it [26].

The pseudo-second-order model was plotted for t/q_t against t (Figure 11 (b)). The values of q_e and k_2 are calculated from the slope ($1/q_e$) and intercept ($1/k_2\ q_e^2$) of the plot and values are shown in Table 2.

The Elovich model was plotted for q_t against $ln\ t$ (Figure 11 (c)). The values of β and α are calculated from the slope ($1/\beta$) and the intercept ($ln\ (\alpha\ \beta)/\beta$) of the plot and values are shown in Table 2. The Elovich model has been used with the assumption that the actual adsorption surface is energetically heterogeneous [27].

The Weber & Morris intra-particle diffusion model was plotted for q_t against $t^{0.5}$ (Figure 11 (d)). The value of k_i and c are calculated from the slope (k_i) and intercept (c) of the plot and values are shown in Table 2. The pseudo-second-order model showed a strongest correlation value (R^2 = 0.9989) being higher than the correlation coefficient for the pseudo-first-order model, Elovich model and Weber & Morris intra-particle diffusion model. The intercept of the plot does not pass through the origin, this is indicative of some degree of boundary layer control and intra-particle pore diffusion is not only rate-limiting step [25].

The plot of intra-particle diffusion model showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of biosorbent or the boundary layer diffusion of solute molecules. The second portion describes ion stage, where intra-particle diffusion is a rate limiting. The third portion is attributed to the final equilibrium stage. However the intercept of the line fails to pass through the origin which may attribute to the difference in the rate of mass transfer in the initial and final stages of biosorption [28].

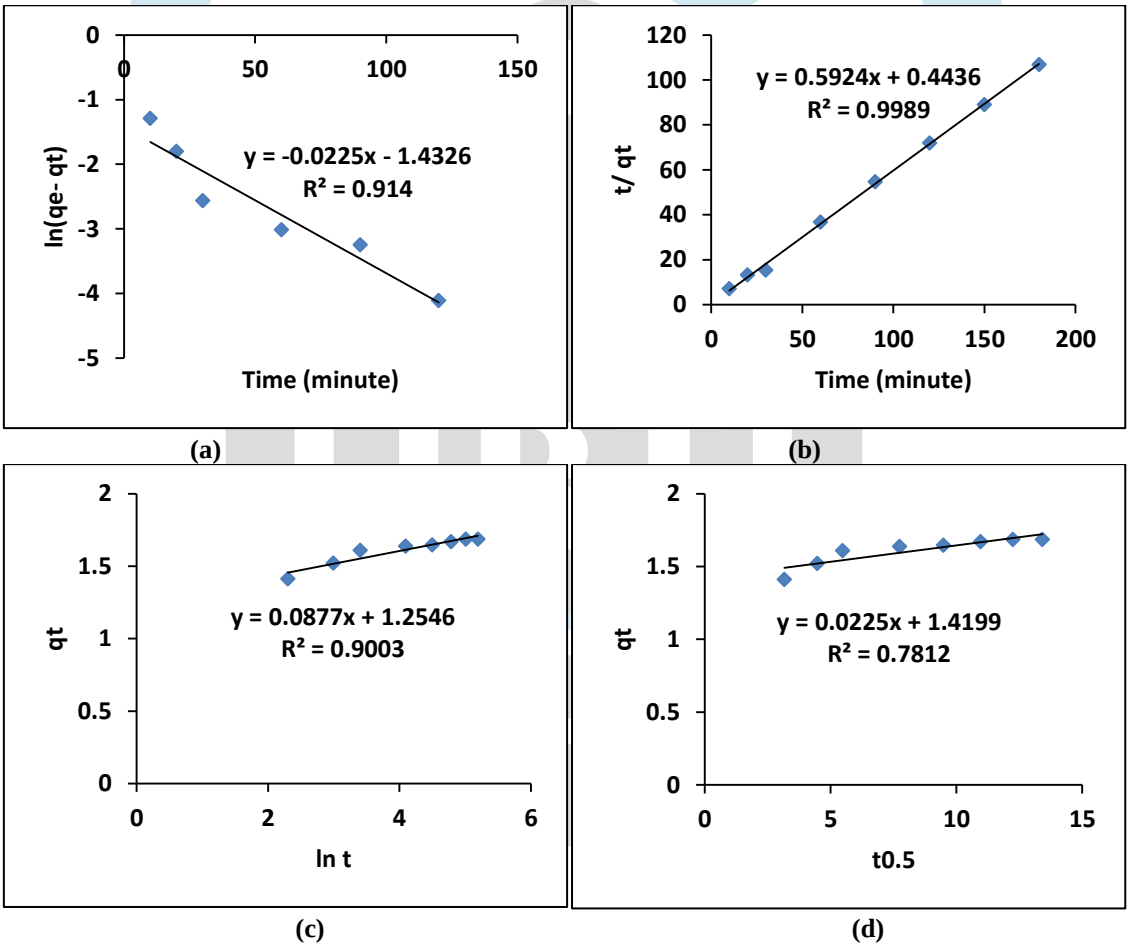


Figure 10: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffussion equation, for biosorption of arsenic (III) by silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, temperature: 30^{0}C, agitation rate: 120 rpm)

Pseudo-first-order model			Pseudo-second-order model			Elovich model			Intra-particle diffusion model		
q_e	k_1	R^2	q_e	k_2	R^2	α	β	R^2	Ki	c	R^2
4.1895	0.0077	0.9140	1.6880	0.7912	0.9989	1.430×10^5	11.402	0.9003	0.0225	1.4109	0.7812

Table 2: Adsorption kinetic data for biosorption of arsenic (III) by silica gel immobilized banana peels (*Musa paradisiaca* L.)

Determination of thermodynamic parameters:

The effect of temperature on removal of arsenic (III) from aqueous solutions in the concentration of arsenic (III) 10 mg/L and biosorbent dose 5 g/L with optimum pH 6.0 was studied. Experiments were carried out at different temperatures from 20^0C-40^0C. The samples were allowed to attain equilibrium. The equilibrium constant [29] at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations:

$$K_c = \frac{C_{Ae}}{C_e} \quad \textbf{(16)}$$

$$\Delta G^0 = -RT \ln K_c \quad \textbf{(17)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \textbf{(18)}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad \textbf{(19)}$$

where K_c is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L) and C_{Ae} is the amount of Arsenic (III) ions biosorbed on the biosorbent per liter of solution at equilibrium (mg/L). ΔG^0, ΔH^0 and ΔS^0 are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol K), respectively. R is the gas constant (8.314 J/mol K) and T is the temperature (K).

The values of ΔH^0 and ΔS^0 were determined from the slope and the intercept from the plot of *lnKc* versus *1/T* (Figure 9). The values of equilibrium constant (*Kc*), Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0) and the entropy change (ΔS^0) calculated in this work were presented in Table 3.

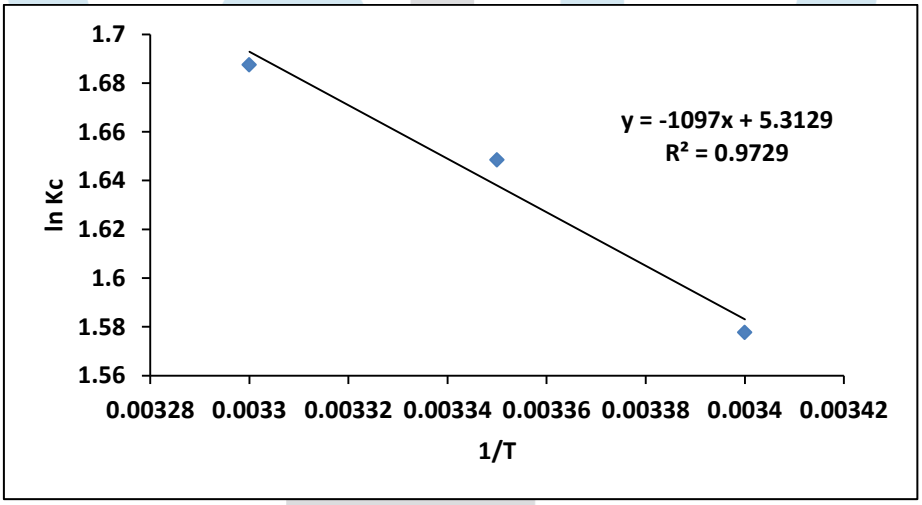


Figure 11: Plot of *lnKc* against *1/T* for determination of thermodynamic parameters for biosorption of arsenic (III) by silica gel immobilized banana peels (*Musa paradisiaca* L.) (pH 6.0, biosorbent dose concentration: 5 g/L, initial arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, agitation rate: 120 rpm)

Sr. No.	Temperature (^{0}C)	Temperature (K)	*Kc*	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	20^0C	293	4.8445	3.8435	9.1204	44.171
2	25^0C	298	5.1996	4.0842		
3	30^0C	303	5.4061	4.2510		
4	40^0C	313	5.3656	4.3718		

Table 3: Thermodynamic parameters of biosorption of arsenic (III) by silica gel immobilized banana peels (*Musa paradisiaca* L.)

CONCLUSIONS

The present investigation revealed that silica gel immobilized banana peels (*Musa paradisiaca* L.) used as inexpensive, excellent biosorbent for the removal of arsenic (III) from aqueous solutions. The optimal parameters such as solution pH, biosorbent dose, agitation rate, initial arsenic (III) concentration, contact time and temperature determined in the experiment were effective in determining the efficiency of arsenic (III) onto silica gel immobilized banana peels (*Musa paradisiaca* L.). Sorption equilibrium exhibited better fit to Langmuir isotherm than Freundlich isotherm, Temkin isotherm and Dubinin-Kaganer-Redushkevich (DKR) isotherm. The maximum arsenic (III) loading capacity (q_e) of silica gel immobilized banana peels (*Musa paradisiaca* L.) determined from Langmuir adsorption isotherm was found to be 49.504 mg g^{-1}. The second-pseudo-order model was found to be correlate the experimental data strongest than other three kinetic models. The thermodynamic study confirmed that reaction of biosorption of arsenic (III) was spontaneous, endothermic and increasing randomness of the solid solution interfaces. From these observations it can be concluded that silica gel immobilized banana peels (*Musa paradisiaca* L.) has considerable biosorption capacity, available in abundant, non-hazardous can be used as an effective indigenous material for treatment of wastewater stream containing arsenic (III).

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