Sorption Capacity of Banana Peels (Musa Paradisiaca L.) To Remove Arsenic (III) In Aqueous Solution

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Abstract- *Arsenic pollution of water is a major problem faced worldwide. The availability of arsenic in ground water and potable water accounts many toxic effects on human health because of its high toxicity level.Therefore, it is essential to remove it from wastewater before disposal. The endeavor of this research work is to remove arsenic (III) using banana peels (Musa paradisiaca L.) in batch studies. The batch studies were carried out by varying 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 banana peels (Musa paradisiaca L.) as biosorbent was a low-cost promising sorbent for sequester of arsenic (III) from wastewater.*

Keywords- Arsenic (III), banana peels (Musa paradisiaca L.), adsorption isotherm, adsorption kinetics, thermodynamic study.

I. INTRODUCTION

The use of heavy metals and their compounds has increased the comfort of human being in great way. They are used in different processes [1]. The excessive use of heavy metals and metalloids causes to increase their concentration in aquatic systems. Arsenic, a common element in nature, is a naturally occurring contaminant of drinking water and can be found in the earth's crust, ground, and marine water and in the organic world as well. It is mobilized through a combination of natural processes such as weathering reactions, biological activity, and volcanic emissions [1, 2] as well as through a range of anthropogenic activities such as gold mining, nonferrous smelting, petroleum refining, combustion of fossil fuel in power plants, and the use of arsenical pesticides and herbicides [3, 4]. Contaminated groundwater by arsenic is a well-known environmental problem that can have severe human health implications. Chronic exposure to arsenic concentrations above 100 ppb can cause vascular disorders, such as dermal pigments (Blackfoot disease) and skin, liver, and lung cancer [5, 6]. An arsenic concentration of 10μg/L has been recommended by World Health Organization as a guideline value for drinking water [7].

Researchers in many countries are studying the removal of arsenic from contaminated water using several techniques, namely oxidation/precipitation, electrocoagulation/ co-precipitation, lime softening, metal-oxide adsorption, reverse osmosis and nanofiltration, ion-exchange resin, coagulation-microfiltration, etc [8, 9, and 10]. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries [11]. 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 aqueous solution. The present research he emphasis has been laid to know the efficiency of banana peels (*Musa paradisiaca* L.) biomass in removing the arsenic (III) from wastewater. Optimum biosorption conditions were determined as a function of solution pH, biosorbent dose concentration, initial concentration of arsenic (III), contact time, temperature andagitation rate. Adsorption isotherms model and kinetics models were employed to understand the probable biosorption mechanism. Thermodynamic studies were also carrying out to estimate thestandard free change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0).

II. MATERIALS AND METHODS

Proposed study will be carried out in the following steps:

Chemical and reagent:

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

Preparation of arsenic (III) standard 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.) were collected from domestic wastes, as its availability and transportation was easy. The peels were 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.

- **Instrumentation:**

The pH of the solution was measured by digital pH meter (EQUIP-TRONICS, model no. Eq-610) using a combined glass electrode. The concentration of arsenic (III) in the solution before and after equilibrium was determined by measuring absorbance using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) technique. Biosorbent was characterized by Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) and X-ray diffraction (XRD).

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis: The Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups present in the biosorbent. The biomass samples were examined using FTIR spectrometer (model:FT/IR-4100typeA) within range of 400-4000 cm^{-1}. All analysis was performed using KBr as back ground material. In order to form pellets, 0.02 g of biomass was mixed with 0.3 g KBr and pressed by applying pressure.

Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis: The Scanning Electron Microscope (SEM) was used to see the porosity of the biosorbent. The samples were covered with a thin layer of gold and an electron acceleration voltage of 10 KV was applied and then Scanning Electron Micrograph was recorded.

Characterization of biosorbent by X-ray diffraction analysis (XRD) analysis:

X-ray diffraction (XRD) was used for the qualitative and quantitative determination of solid samples of biosorbent. It works on the principle that X-ray diffraction pattern is unique for each sample. This pattern from XR-D was compared with a known compound and the chemical compound was identified.

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 biosorption 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 biosorbent by filtration, using Whatmann filter paper and amount of arsenic (III) in the supernatant/filtrate solutions was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The following equation was used to compute the percent removal (% Adsorption) of arsenic (III) by the biosorbent,

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

whereC_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,

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

whereq_e (mgmetal 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.

Desorption study:

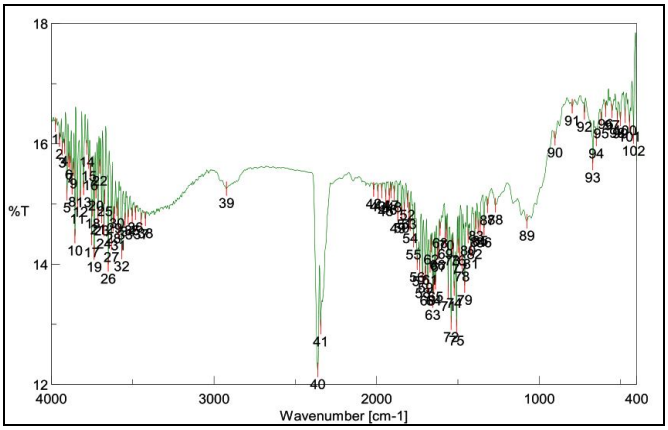
To evaluate desorption efficiency, arsenic (III) loaded biosorbent was dried after equilibrium sorption experiments. The dried biosorbent was contacted with 0.1 M nitric acid (HNO_3), 0.1 M hydrochloric acid (HCl) and 0.1 sulphuric acid (H_2SO_4) separately for 3 hours to allow arsenic (III) to be release 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).

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

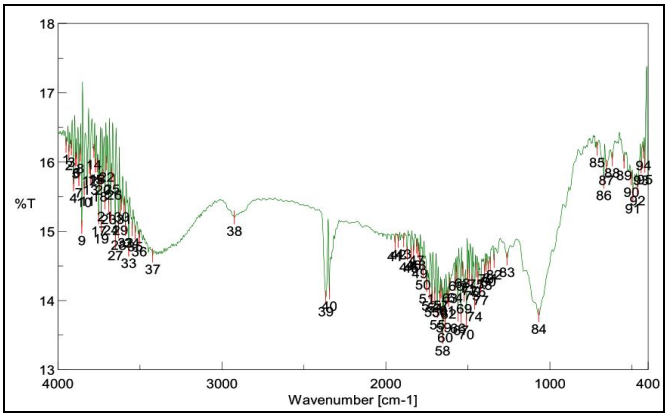
III. RESULTS AND DISCUSSION

Characterization of biosorbent by Fourier Transform Infrared (FTIR) analysis:

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. As seen in the figure biosorbent displays a number of biosorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3422 cm^{-1} is the indicator of -OH and -NH groups. The stretching of the –OH groups bound to methyl groups presented in the signal at 2924 cm^{-1}. The peaks at 2366 cm^{-1} and 2345 cm^{-1} are stretching peaks. The peaks located at 1735 cm^{-1} and 1637 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 peak at 1508 cm^{-1} is associated with the stretching in aromatic rings. The peaks observed at 1066 cm^{-1} are due to C-H and C-O bonds. The –OH, NH, carbonyl and carboxyl groups are important sorption sites. Biosorbent loaded with arsenic (III), the broadening of -OH peak at 3422 cm^{-1} and carbonyl group peak at 1637 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of arsenic (III).



(a)

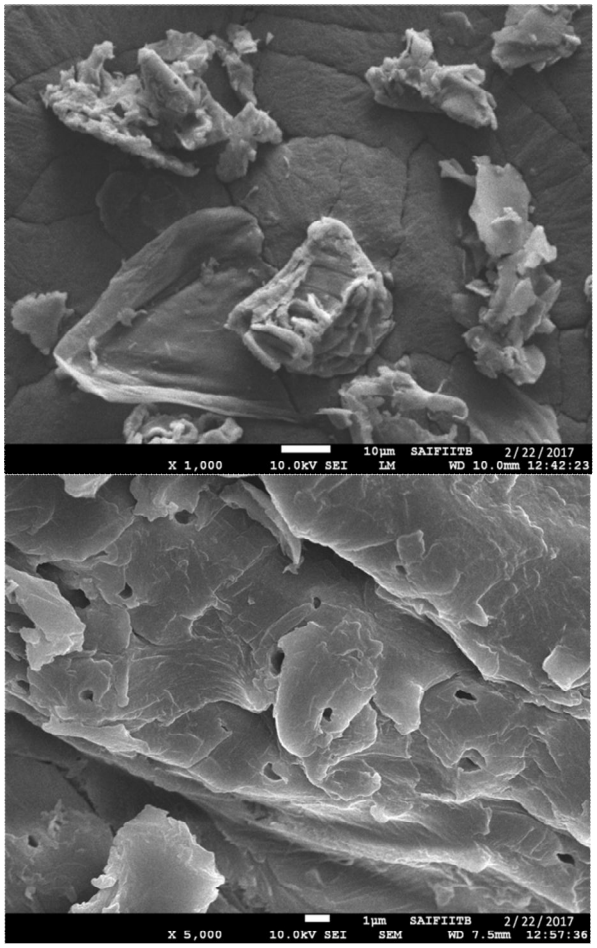


(b)

Figure 1: FTIR spectra (a) Biosorbent banana peels (*Musa paradisiaca* L.) (b) Biosorbent 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.



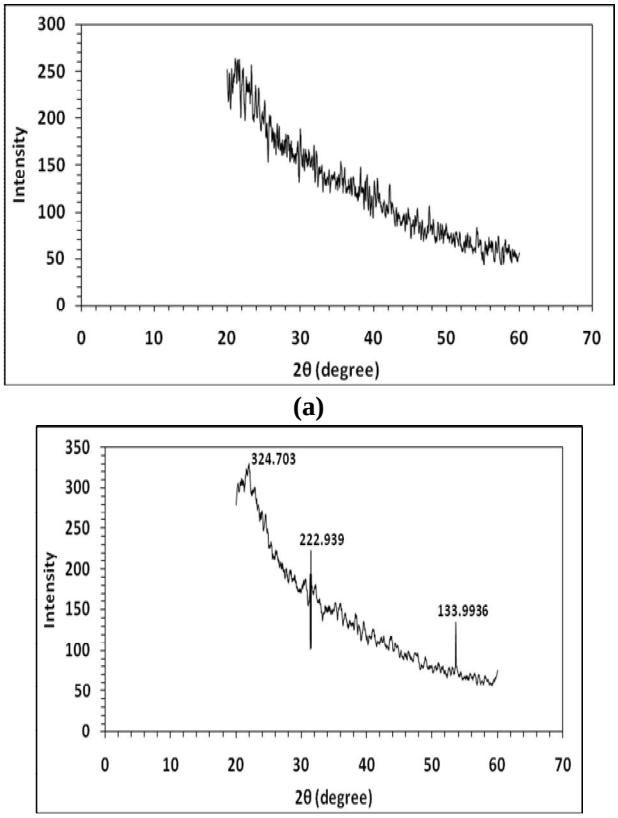
(a) (b)

Figure 2:Scanning Electron Microscope (SEM) analysis (a) Biosorbent banana peels (*Musa paradisiaca* L.) (b) Biosorbent banana peels (*Musa paradisiaca* L.)loaded with arsenic (III)

Characterization of biosorbent by X-ray diffraction analysis (XRD) analysis:

X-ray diffraction (XRD) is a non-destructive technique used to provide detailed information on the crystallographic structure of materials. The XRD profile of the unloaded 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 21.52º, 31.42º and 53.6º corresponding to 324.703, 222.939 and 133.9936 planes, respectively for 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 biosorbent decreased. These causes low intensity XRD peaks. Hence crystalline phases should have been reduced. XRD pattern of arsenic ions loaded biosorbent 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 biosorbent.



(a)

(b)

Figure 3:X-ray diffraction analysis (XRD) study (a) Biosorbent banana peels (*Musa paradisiaca* L.) (b) Biosorbent banana peels (*Musa paradisiaca* L.) loaded with arsenic (III)

Effect of pH:

The pH of the solution is one of the most critical parameters in the biosorption of pollutants from aqueous solutions. In order to determine the preferred pH for biosorption of arsenic (III) over banana peels (*Musa paradisiaca* L.), the uptake of arsenic (III) as a function of hydrogen ion concentration was studied. Figure 4depicts the effect of pH on biosorption of arsenic (III) onto the banana peels (*Musa paradisiaca* L.)(30°C). Both biosorption efficiency and capacity have the same trend. The maximum biosorption capacity of banana peels (*Musa paradisiaca* L.)forarsenic (III) occurred at pH 6. Nevertheless, highest biosorption has taken place at pH 6.0 (62.11%) which was chosen as an optimum pH condition for further experiments. pH parameter is very important since it strictly depends upon

the nature of biosorbate and biosorbent. Also, it is an established fact that arsenic (III) is more strongly biosorbed than arsenic (V) where pH is acidic or near neutral [16]. In addition, after biosorption, the pH of solution was slightly relevated. One reason for the change of pH may be the ion exchange process.

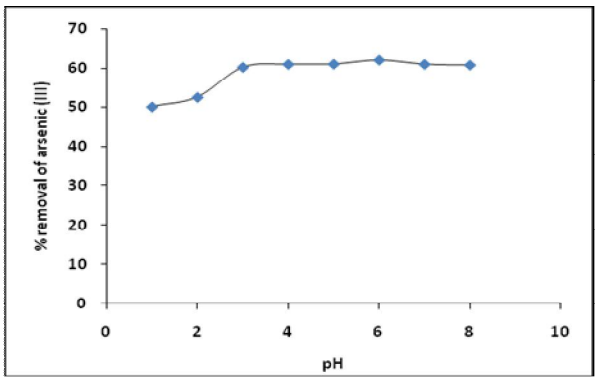


Figure 4: Effect of pH on arsenic (III) biosorption by banana peels (*Musa paradisiaca* L.) (Biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Effect of biosorbent dose concentration:

Effect of biosorbent dose of biosorption of metal ions which is an important parameter used to determine the capacity of biosorbent a given concentration of the biosorbate.Various biosorbent dose concentrations of banana peels (*Musa paradisiaca* L.) in the range of 1.0, 2.5, 5.0, 10.0, 12.5 and 15.0 g/L were used to study the biosorption of arsenic (III).From the results it was found that biosorption of arsenic (III) increases with increase in biosorbent dose and is highly dependent on biosorbent concentration.The point of saturation for banana peels (*Musa paradisiaca* L.)was found at 5 g/L of biosorbent dose with maximum removal efficiency 62.71%.The decrease in efficiency at higher biosorbent dose concentration could be explained as a consequence of partial aggregation of biosorbent which results in a decrease in effective surface area for metal uptake. The biosorbent dose 5 g/L was chosen for all further studies.

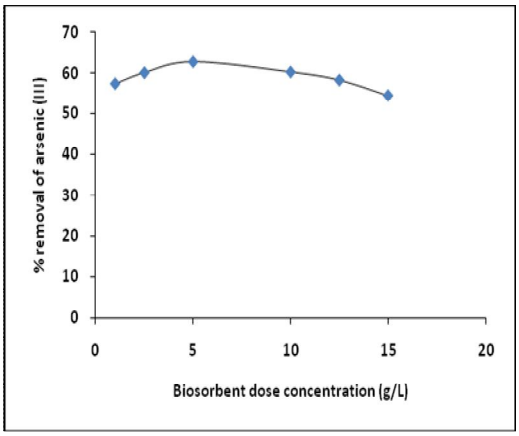


Figure 5: Effect of biosorbent dose concentration on arsenic (III) biosorption by banana peels (*Musa paradisiaca* L.) (pH: 6.0, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Effect of initial arsenic (III) concentration:

It is evident from initial arsenic (III) concentration is decreased from 05 mg/L to 250 mg/L and the corresponding removal gradually decreases from 63.84% to 51.92 % at optimum pH 6.0 at 30^{0}C was studied. It is clear from the results that more than 60-90 % sorption of arsenic (III) took place in first 30 min and equilibrium is established 30 min. At higher concentrations, metals need to diffuse to the biosorbent surface by intra-particle diffusion and highly hydrolyzed ions will diffuse at a slower rate. This indicates the possible monolayer formation of arsenic (III) on the outer surface.

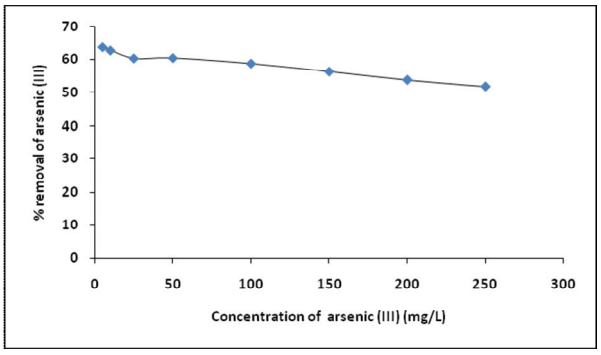


Figure 6: Effect of arsenic (III) concentration on arsenic (III) biosorption by banana peels (*Musa paradisiaca* L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, contact time: 150 minutes, temperature: 30^{0}C, agitation rate: 120 rpm)

Effect of contact time:

In order to optimize the contact time for the maximum uptake of metal, 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 10g/L at optimum pH 6.0 at 30^0C. The results obtained from the biosorption capacity of arsenic (III) onto 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) onto banana peels (*Musa paradisiaca* L.)was150 minutes with 61.76% removal. The rapid uptake of arsenic (III) is due to the availability of ample active sites for sorption. 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.

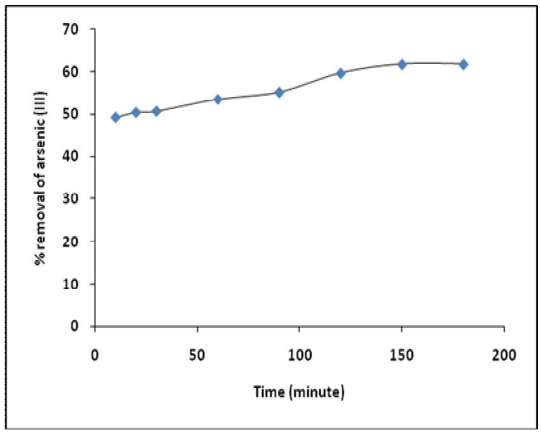


Figure 7: Effect of contact time on arsenic (III) biosorption by banana peels (*Musa paradisiaca* L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, temperature: 30^0C, agitation rate: 120 rpm)

Effect of temperature:

The effect of temperature on removal of arsenic (III) from aqueous solutions using banana peels (*Musa paradisiaca* L.) was studied at different temperatures from 20^0C – 40^0C. The influence of temperature is depicted in Figure 8. Maximum sorption was seen at 30^0C with percentage removal 61.14%.

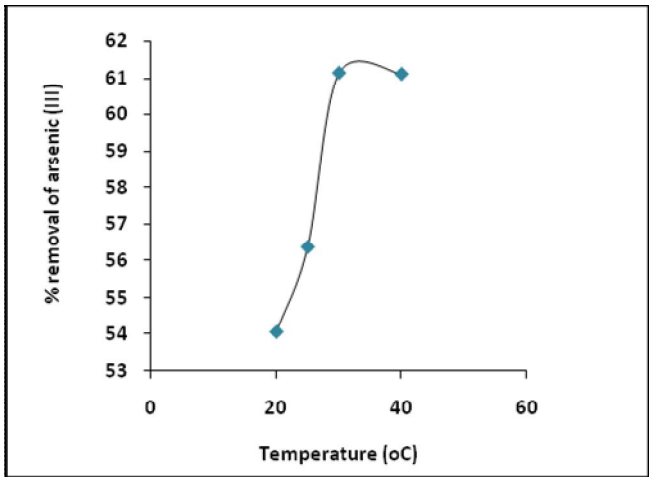


Figure 8: Effect of temperature on arsenic (III) biosorption removal using banana peels (*Musa paradisiaca* L.) (pH 6.0, biosorbent dose concentration: 5 g/L, initial arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, agitation rate: 120 rpm)

Effect of agitation rate:

The effect of agitation rate on removal of arsenic (III) from aqueous solutions at biosorbent dose 10 mg/ml and at optimum pH 6.0 at 30^0C was studied at different rpm such as 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200rpm. The efficiency was highest at 120rpm with percentage removal 61.11%. So, 120 rpm was chosen for all further biosorption studies.

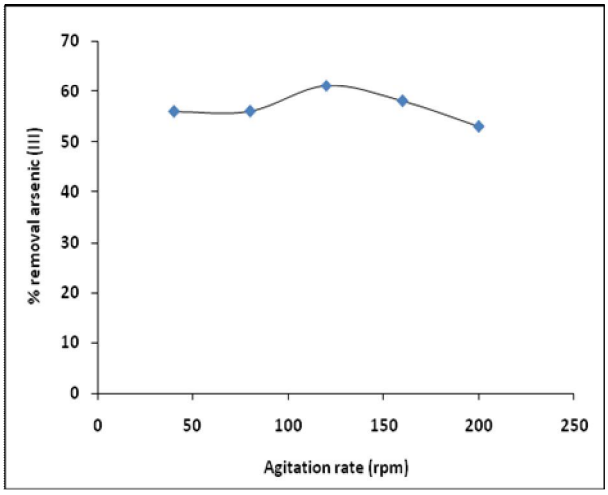


Figure 9: Effect of agitation rate on arsenic (III) ions removal using banana peels (*Musa paradisiaca* L.) (pH 6.0, biosorbent dose concentration: 5 g/L, initial arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^0C)

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 adsorption 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 adsorption isotherm models: Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin. Adsorption isotherms results for biosorption of arsenic (III) by banana peels (*Musa paradisiaca* L.) is shown below;

Langmuir adsorption isotherm [17]:

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

$$q = \frac{q_m b C_e}{1+b C_e} \quad \textbf{(4)}$$

whereq_m is the maximum biosorption capacity of biosorbent (mg g^{-1}). *b* is the Langmuir biosorption constant (L mg^{-1}) related to the affinity between the biosorbent and biosorbate.

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

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

The linear plots of $1/q$ vs $1/c_e$ is shown in Figure 10 (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.

Maximum biosorption capacity of biosorbents (q_m) is found to be 43.290 mg g^{-1} of banana peels(*Musa paradisiaca*L.).

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the biosorbate and biosorbent which is calculated using following equation;

$$R_L = \frac{1}{1+b C_i} \quad \textbf{(6)}$$

where b is the Langmuir constant and C_i is the maximum initial concentration of arsenic (III). The value of separation parameters R_L provides important information about the nature of adsorption. The value of R_L indicated the type of Langmuir isotherm separation factor or dimensionless equilibrium parameters, R_L expressed as in the following equation: to be irreversible (R_L = 0), favorable (0 <R_L< 1), linear (R_L = 1) or unfavorable (R_L>1). The R_L was found to 0.3278-0.9606 for concentration of 10 mg/L-250 mg/L of arsenic (III). They are in the range of 0-1 which indicates favorable biosorption [18].

Frenudlich adsorption isotherm [19]:

Freundlich equation is represented by:

$$q = K C_e^{1/n} \quad \textbf{(7)}$$

where*K* and *n* are empirical constants incorporating all parameters affecting the biosorption process such as, biosorption capacity and biosorption intensity respectively.
Linearized Freundlich adsorption isotherm was used to evaluate the biosorption data and is represented as:

$$\log q = \log K + \frac{1}{n} \log C_e \quad \textbf{(8)}$$

Equilibrium data for the adsorption is plotted as log *q* vs log C_e, as shown in Figure 10 (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.

The *n* value indicates the degree of non-linearity between solution concentration and adsorption as follows: if n = 1, then adsorption is linear; if *n* <1, then adsorption is chemical process; if *n*>1, then biosorption is a physical process. A relatively slight slope and a small value of 1/ *n* indicate that, the biosorption is good over entire range of concentration. The *n* value in Freundlich equation was found to be 0.4065. Since*n*<1, this indicates that biosorption is a chemical process biosorption of arsenic (III) onto banana peels (*Musa paradisiaca* L.). The higher value of *K* (7.8236)

indicates the higher biosorption capacity for the banana peels (*Musa paradisiaca* L.).

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

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

$$lnq_e = \ln q_m - \beta \varepsilon^2 \quad (9)$$

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

$$\varepsilon = RTln\left(1 + \frac{1}{C_e}\right) \quad (10)$$

Equilibrium data for the adsorption is plotted as lnq_e vs ε^2, as shown in Figure 10 (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,

$$E = \frac{1}{\sqrt{-2\beta}} \quad (11)$$

The E value was found to be0.4082 KJ mol^{-1}.The mean free energy gives information about biosorption mechanism whether it is physical or chemical biosorption. If E value lies between 8 KJ mol^{-1} and 16 KJ mol^{-1}, the biosorption process take place chemically and E> 8 KJ mol^{-1}, the biosorption process of the physical in nature (Olivieri and Brittenham, 1997). In the present work, E value (0.4082 KJ mol^{-1}) which is less than 8 KJ mol^{-1}, the biosorption of arsenic (III) ions onto banana peels (*Musa paradisiaca* L.) is of physical in nature [21].

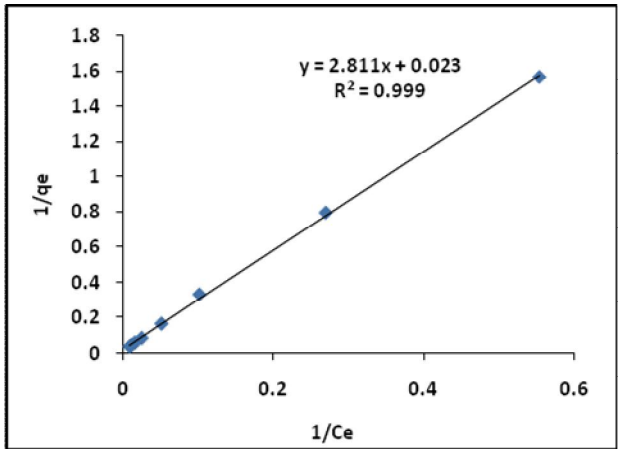
Temkin adsorption isotherm [22]:

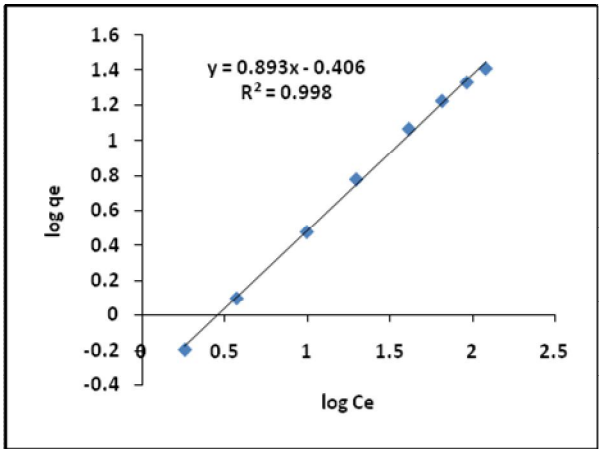
Linearized Temkin adsorption isotherm is given by the equation;

$$q_e = \frac{RT}{b_T} ln\, A_T + \frac{RT}{b_T} ln\, C_e \quad (12)$$

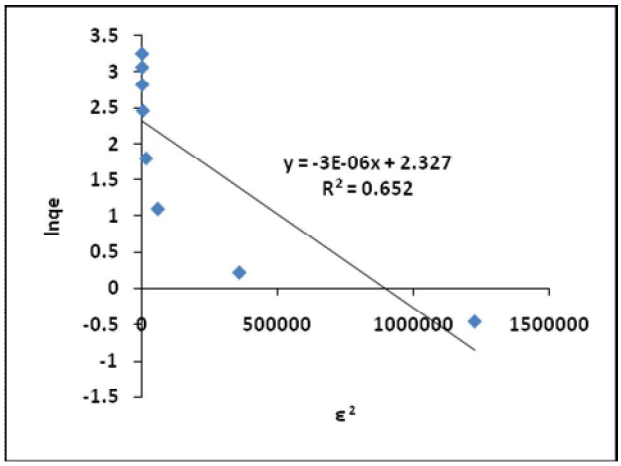
where$b_T$is the Temkin constant related to heat of biosorption (J/mol) and A_T is the Temkin isotherm constant (L/g).Equilibrium data for the adsorption is plotted as q_e vs lnC_e, as shown in Figure 10(d). The two constants $b_T$and A_T are calculated from the slope (RT/b_T) and intercept ($RT/b_T \cdot lnA_T$) of the line. The values of A_T,b_T and regression coefficient (R^2) are listed in Table 1.

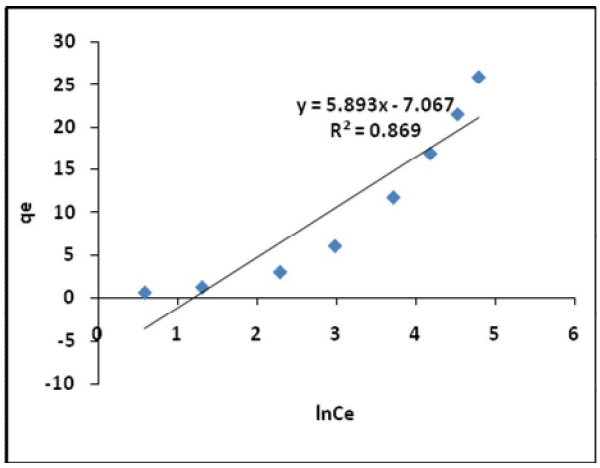
The various constants and regression coefficient R^2obtained from adsorption isotherms (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) are summarized in Table 1.





(a) **(b)**





(c) **(d)**

Figure 10: Adsorption isotherms (a) Langmuir, (b) Freundlich (c) DKR and (d) Temkin for bisorption of arsenic (III) 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)

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

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
43.2900	0.00082	0.9994	7.82376	2.46000	0.9983	-3E-06	2.07001	0.40822	0.65233	2.30118	427.480	0.86922

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 [23] (b) the pseudo-second-order equation [24](c) Elovich equation [25] (d) Weber & Morris intra-particle diffusion equation[26] are presented below;

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (13)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (14)$$

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln t \quad (15)$$

$$q_t = k_i t^{0.5} + c \quad (16)$$

whereq_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 biosorption 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 adsorption 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-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 [27].

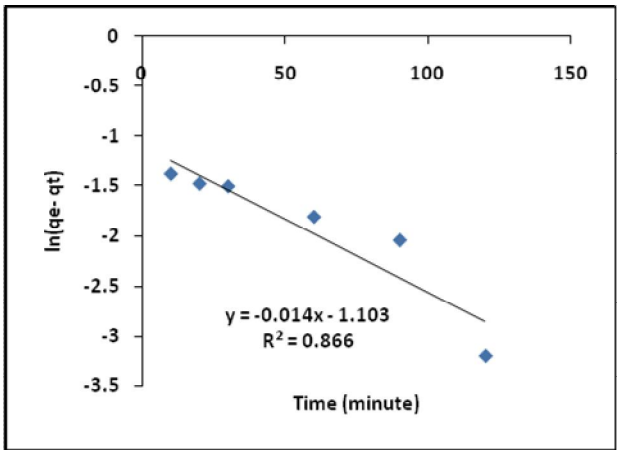
The pseudo-second-order model was plotted for t/q_t against t (Figure 11 (b)). The values of q_e and k_2 are calculated from the slope ($1/q_e$) and intercept ($1/k_2$ q_e^2) of the plot and values are shown in Table 2.

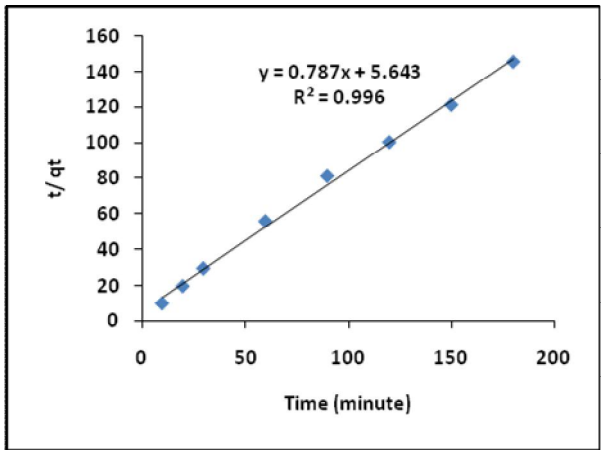
The Elovich model was plotted for q_t against ln t (Figure 11 (c)). The values of β and α are calculated from the slope ($1/\beta$) and the intercept (ln $(\alpha\beta)/\beta$) of the plot and values are shown in Table 2. The Elovich model has been used with the assumption that the actual adsorption surface is energetically heterogeneous [28].

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 = 0.9968) 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 [26].

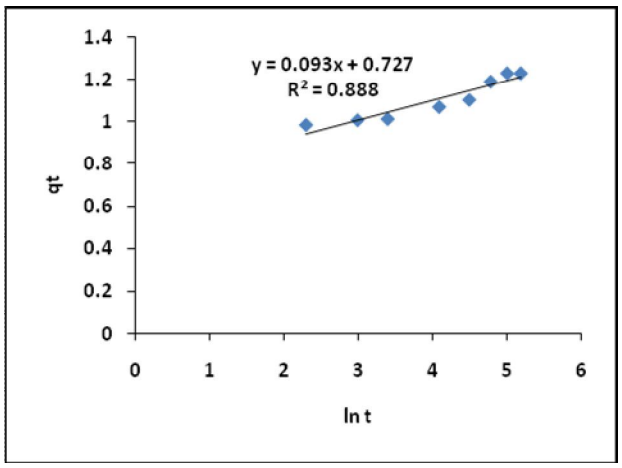
The plot of intra-particle diffusion model showed multilinearity, indicating that three steps take place. The first, sharper portion is attributed to the diffusion of adsorbate through the solution to the external surface of biosorbent or the boundary layer diffusion of solute molecules. The second portion 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 [29].

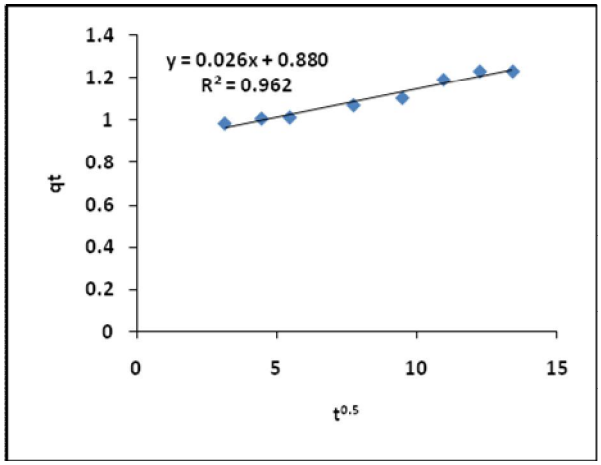




(a)

(b)





(c)

(d)

Figure 11: Adsorption kinetic models (a) pseudo-first-order, (b) pseudo-second-order (c) Elovich and (d) Weber and Morris intra-particle diffusion equation, for biosorption of arsenic (III) 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)

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

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
0.0986	0.0146	0.8666	1.2704	0.1097	0.9968	3.643×10^2	10.660	0.8882	0.0269	0.8808	0.9625

Determination of thermodynamic:

The effect of temperature on removal of arsenic (III) from aqueous solutions in the concentration of arsenic (III) 10 mg/L and biosorbent dose concentration5 mg/ml 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. Sorption slightly increases from. The equilibrium constant [30] at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations;

$$K_c = \frac{C_{Ae}}{C_e} \quad (17)$$

$$\Delta G^0 = -RT ln K_c \quad (18)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (19)$$

$$ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (20)$$

whereK_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 $\Delta S^0$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 $\Delta H^0$and ΔS^0 were determined from the slope and the intercept from the plot of *lnKc* versus *1/T* (Figure 12). The values of equilibrium constant (*Kc*), standard Gibbs free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) calculated in this work were presented in Table 3. The equilibrium constant (*Kc*) increases with increase in temperature, which may be attributed to the increase in the pore size and enhanced rate of intra-particle diffusion. The value of standard Gibbs free energy change (ΔG^0) is small and negative and indicates the spontaneous nature of the biosorption. The values of ΔG^0 were found to decreases as the temperature increases, indicating more driving force and hence resulting in higher biosorption capacity. The value of ΔH^0 was positive, indicating the endothermic nature of the biosorption of arsenic (III) onto banana peels (*Musa paradisiaca* L.). The positive values of ΔS^0 shows an affinity of biosorbent and the increasing randomness at the solid solution interface during the biosorption process.

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

Sr. No.	Temperature (^{0}C)	Temperature (K)	*Kc*	$-\Delta G^0$ (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	20^0C	293	1.1777	0.3982	23.9775	82.732
2	25^0C	298	1.2925	0.6280		
3	30^0C	303	1.5713	1.1384		
4	40^0C	313	1.5733	1.1759		

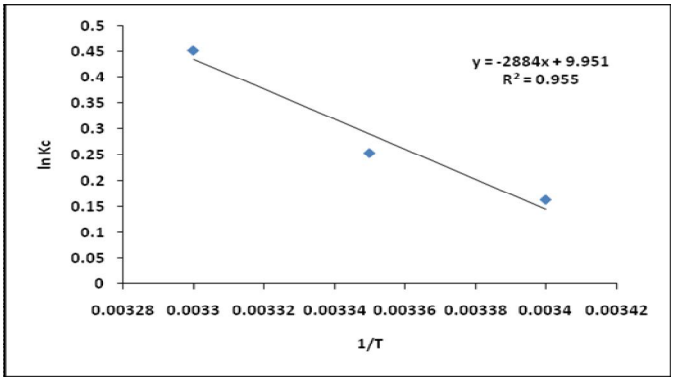


Figure 12: Plot of lnKc against 1/T for determination of thermodynamic parameters for biosorption of arsenic (III) by banana peels (*Musa paradisiaca* L.) (pH: 6.0, biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, agitation rate: 120 rpm)

IV. CONCLUSIONS

The present investigation revealed that 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, initial arsenic (III) concentration, contact time temperature and agitation rate determined in the experiment were effective in determining the efficiency of arsenic (III) biosorption onto banana peels (*Musa paradisiaca* L.). Biosorption 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 banana peels (*Musa paradisiaca* L.) determined from Langmuir adsorption isotherm was found to be 43.290 mg g^{-1}. The Pseudo-second-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 banana peels (*Musa paradisiaca* L.) has considerable biosorption capacity, available in abundant, non-hazardous agro material can be used as an effective indigenous

material for treatment of wastewater stream containing arsenic (III).

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