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Sequestration of trivalent arsenic from aqueous solution by using banana peels (*Musa paradisiaca* L.) modified in calcium alginate beads

Amit S. Sharma[1], Prof. (Dr.) Satish A. Bhalerao[2]
[1, 2] Environmental Sciences Research Laboratory, Department of Botany, Wilson College, Mumbai-400007, affiliated to University of Mumbai, M.S., India

Abstract: Banana peels (Musa paradisiaca L.) was modified into calcium alginate beads via entrapment, were used as biosorbent for the removal of arsenic (III) in aqueous solution. The extent of arsenic (III) removal capacity was tested by the material by varying the solution parameters such as effect of pH, biosorbent dose concentration, initial arsenic (III) concentration, contact time, temperature and agitation rate. Desorption efficiency of banana peels modified into calcium alginate beads was highest for sulphuric acid followed by hydrochloric acid and nitric acid. The biosorption process followed pseudo-second-order kinetics and biosorption data were best fitted to linearly transformed Langmuir isotherm with correlation coefficient of R^2= 0.9951. Maximum biosorption capacity calculated from Langmuir isotherm was found to be 52.083 mg g^{-1}. The thermodynamic study confirmed that reaction of biosorption of arsenic (III) was spontaneous, endothermic and increasing randomness of the solid solution interfaces. The results indicating that calcium alginate beads have better biosorption properties than other naturally-occurring materials like algae, flower wastes and minerals like zeolite and bentonite. This study demonstrated that alginate beads are good candidates for a fast and efficient removal of arsenic (III) from aqueous solution.

Keywords: Arsenic (III), banana peels (Musa paradisiaca L.), calcium alginate beads, adsorption isotherm, adsorption kinetics, thermodynamic study.

I. INTRODUCTION

One of the most challenging environmental problems today is the removal of heavy metals and other toxic contaminants from industrial wastewater. Many aquatic environments face metal concentrations that exceed water quality limits designed to protect the environment, animals, and humans [1]. Metals hazardous to humans include lead, cadmium, mercury, arsenic, copper, zinc, and chromium. Arsenic is carcinogenic metal. Cadmium can cause bone and kidney damage. Copper and lead can cause brain and bone damage [2].

Arsenic (As) is a component of many industrial raw materials, products and wastes. Elevated levels of arsenic in drinking water have been implicated in human diseases and mortality [3]. Chronic exposure to arsenic causes neurological and haematological toxicity [4]. Arsenic impacts the major organs and is a potential carcinogen [5-7]. The most common arsenic species observed in the environment are the trivalent form arsenite As (III) and pentavalent form arsenate As (V) in which As (III) is more toxic than As (V) [8]. Because arsenic readily changes valence state and reacts to form species with varying toxicity and mobility, effective treatment of arsenic can be challenging.

Removal of arsenic (III) contaminated water has thus become a major environmental issue. Several approaches for metal-treatment wastewater have been described including chemical and surface chemistry processes. Sensitive operating conditions, low efficiency, and production of secondary sludge demanding additional expensive disposal are inherent limitations in the application of these methods [9-11]. These short comings, together with the need for more economical and efficient technique for removal of metal from wastewater, have focused interest towards other techniques. One such option is biosorption that is based binding ability of certain types of biomass with metals even from very dilute aqueous solution [12]. The adsorption technique can operate over wide range of pH and temperature exhibiting high efficiency, economic feasibility along with less chemical and biological sludge, therefore find niche in potential metal treatment technologies [13].

The Powdered form provides some difficulties associated with separation of biomass after biosorption, mass loss after regeneration and small particle size which make it difficult to use in column applications. Therefore, modification of raw biomass can improve the sorption capacity. The modification can be achieved by physical processes, chemical processes, and chemical entrapment of the biomass to form membranes, beads, pellets or granular biosorbents [14]. Alginate has been applied in preparation of beads for biosorption. The idea is entrap the biomass and prevent its loss while substrates and products are allowed to pass through the support material [15]. Alginate is a polyelectrolyte material commonly present in gel form. It possesses properties such as a relatively inert aqueous environment, encapsulation process free of solvents, ability to control the porosity with single coating, procedures to make a favorable matrix for entrapment of organic and inorganic compounds.

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 modified into calcium alginate beads for the biosorption of 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 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).

II. MATERIALS AND METHODS

Proposed study will be carried out in following steps:

A. 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.

B. 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.

C. 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 100-200 µm. The dried biosorbent powder was stored in air tight glass bottles to protect it from moisture.

D. Modification of biosorbent

2% solution of calcium chloride was prepared by dissolving 2.0 g anhydrous calcium chloride in 100ml distilled water. 0.5 g banana peels powder was mixed with 0.5 g sodium alginate powder and slurry was prepared by adding appropriate amount of distilled water with constant stirring to avoid the formation of lumps. This mixture was extruded as droplet in 2% solution of calcium chloride through a glass nozzle (1.0 cm length and 2.5-3 mm internal diameter) and the solution was stirred to avoid clumping of immobilized beads. Beads were formed of approximately 3-3.5 mm diameter. The beads were allow curing for 1 hour at 4^oC in the same solution and then washed thoroughly with distilled water. After that it was stored in refrigerator for further use as biosorbent.

E. 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).

1) *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-4100 type A) 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.

2) *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.
3) *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.

F. *Experimental procedure*

The static (batch) method was employed at temperature (30^{0}C) 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,

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

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.

G. *Desorption study*

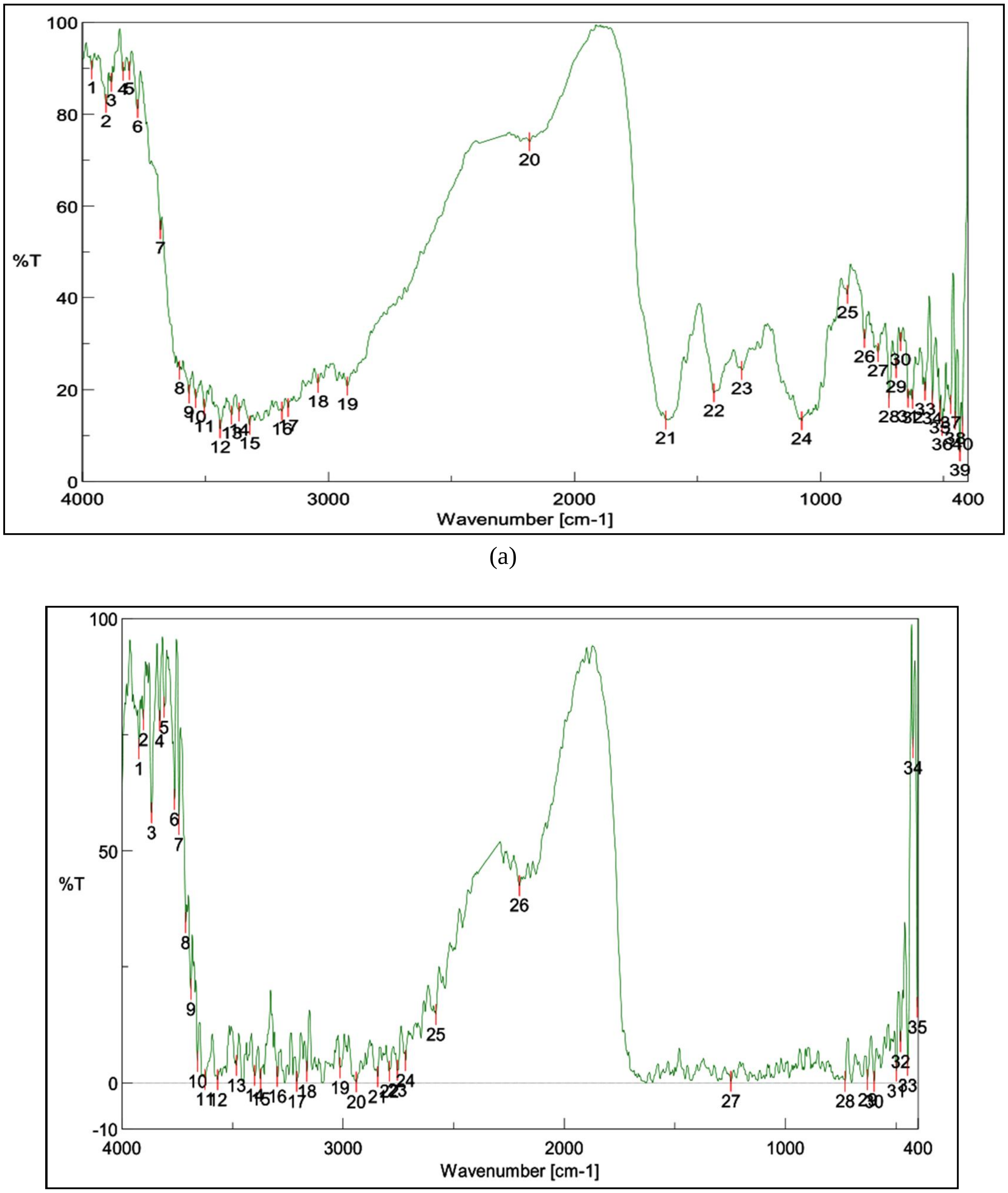
To evaluate desorption efficiency, arsenic (III) loaded biosorbent was dried after equilibrium sorption experiments. The dried biosorbent was contacted with 0.1 M nitric acid (HNO_3), 0.1 M hydrochloric acid (HCl) and 0.1 sulphuric acid (H_2SO_4) separately for 3 hours to allow arsenic (III) to be release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

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

III. RESULTS AND DISCUSSION

A. *Characterization of biosorbent by Fourier Transform Infrared (FTIR) spectroscopy*

FTIR spectra of banana peels modified with calcium alginate, as seen in the figure unloaded biosorbent displays a number of biosorption peaks, reflecting the complex nature of biosorbent. The broad peak at 3440 cm^{-1} is the indicator of -OH and -NH groups. The peaks located at 1628 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 1076 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 3440 cm^{-1} and carbonyl group peak at 1628 cm^{-1} was observed. This indicates the involvement of hydroxyl and carbonyl groups in the biosorption of arsenic (III) ions.



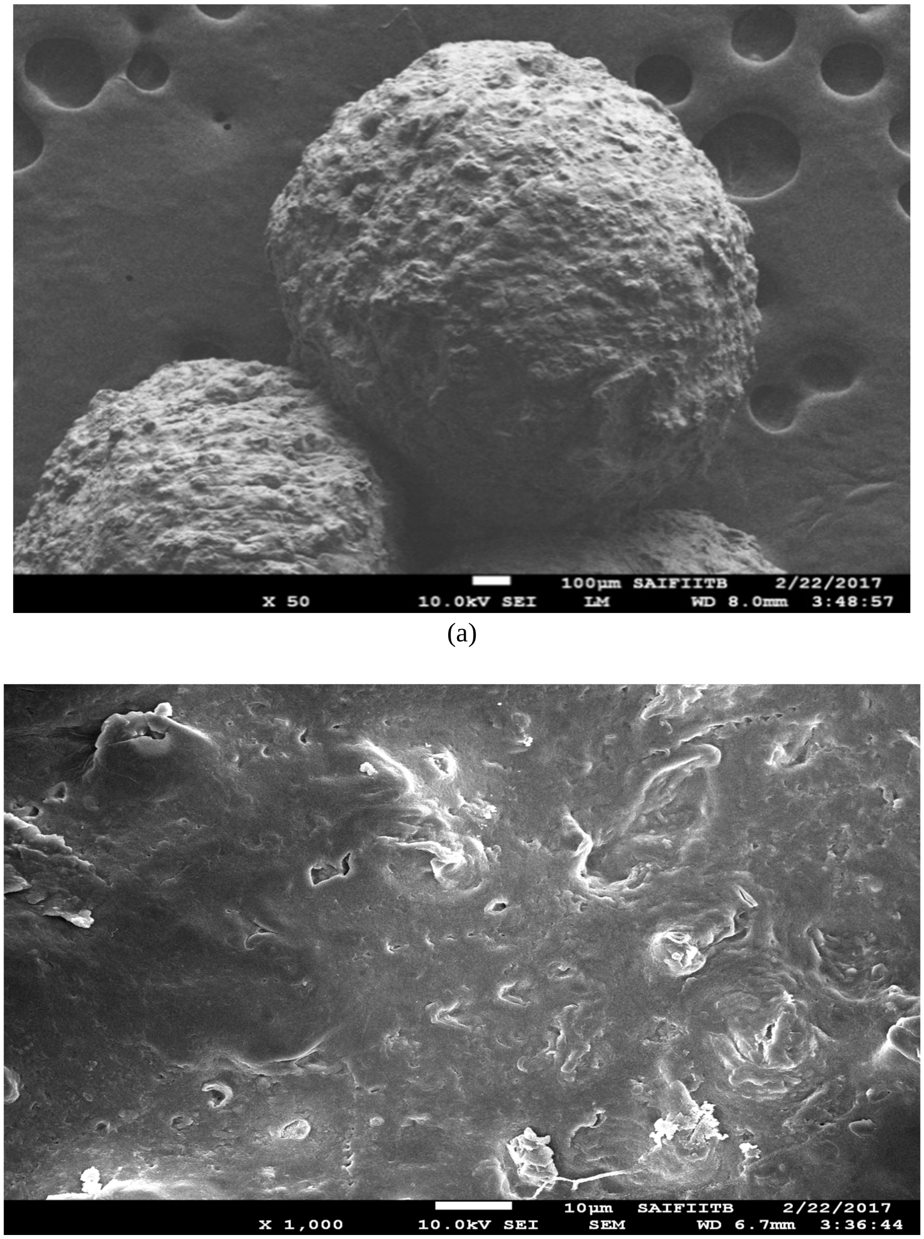
(a)

(b)

Figure 1: FTIR spectra (a) Biosorbent banana peels modified with calcium alginate (b) Biosorbent banana peels modified with calcium alginate loaded with arsenic (III)

B. Characterization of biosorbent by Scanning Electron Microscope (SEM) analysis

The surface characteristics, structure and particle size distribution of banana peels modified with calcium alginate before and after biosorption was examined using Scanning Electron Microscope (SEM). Banana peels modified with calcium alginate 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 biosorbents.



(a)

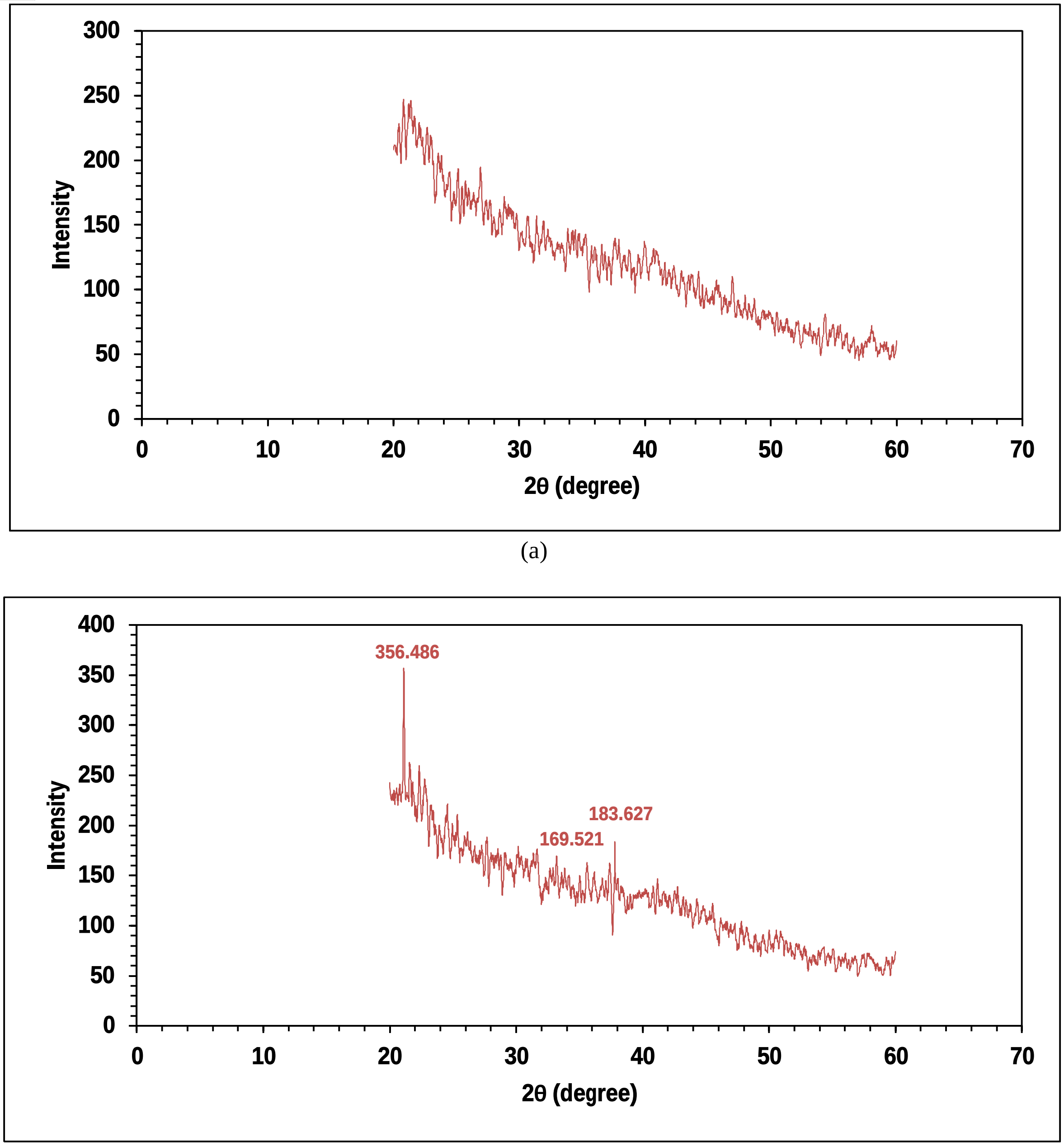
(b)

Figure 2:Scanning Electron Microscope (SEM) analysis (a) Biosorbent banana peels modified with calcium alginate (b) Biosorbent banana peels modified with calcium alginate loaded with arsenic (III)

C. X-ray diffraction analysis (XRD) analysis

X-ray diffraction is a non-destructive technique used to provide detailed information on the crystallographic structure of materials. This method offers several advantages e.g., non-destructive, high accuracy, capability to detect single crystals, polycrystalline or amorphous materials.The XRD profile of the banana peels modified with calcium alginate 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 21.10º, 37.80º and 35.60º corresponding to 356.486, 183.627 and 169.521, respectively.

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.



(a)

(b)

Figure 3:X-ray diffraction analysis (XR-D) study (a) Biosorbent banana peels modified with calcium alginate (b) Biosorbent banana peels modified with calcium alginateloaded with arsenic (III)

D. Effect of pH

Solution pH is an important monitoring parameter influencing the biosorption behaviour of biosorbate onto biosorbent surface due to its impact on both the surface binding-sites of the biosorbent and the metal ion solution.The amount of metal ion removed at equilibrium increases with increasing pH, up to pH 6.0. With further increase in pH, there is no significant increase in the amount of metal ion removed. Maximum removal is observed at pH 6.0 with percentage removal as shown in Figure 4. Hence, all further experiments were carried out at pH 6.0. But adsorption decreases when pH increases further. The minimum biosorption at low pH (< 2) may be due to the higher concentration and high mobility of H^+. The H^+ ions are preferentially adsorbed over metal ions. Solution pH would affect both aqueous chemistry and surface binding-sites of the banana peels. The amount of biosorption increases with increasing pH up to the point (>6) where the metals precipitate.

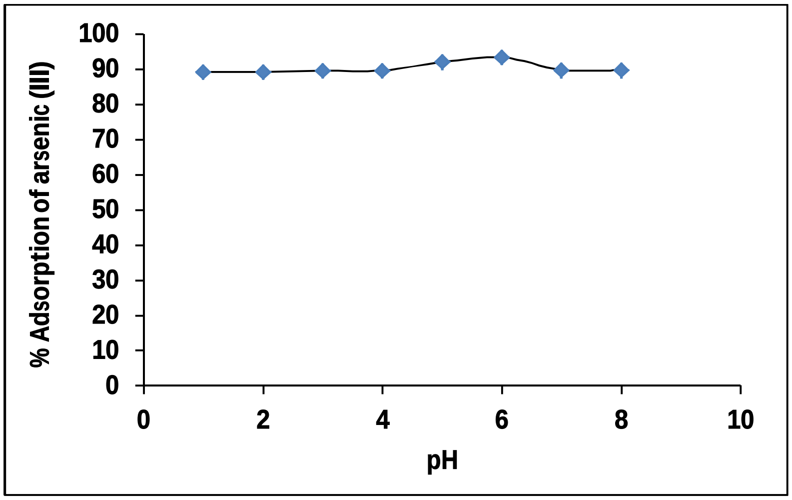


Figure 4:Effect of pH on arsenic (III) biosorption by banana peels modified with calcium alginate (Biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^0C, agitation rate: 120 rpm)

E. 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. The biosorption capacity of arsenic (III) onto banana peels modified with calcium alginate by varying biosorbent dose from 1.0 g/L to 15 g/L. Data obtained from the experiment in Figure 5. With increase in biosorbent dose from 1.0g/L to 5 g/L, the arsenic (III) removal efficiency increases from 88.86 to 93.32%. 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. Further, increase in biosorbent dose did not significantly change the biosorption yield. This is due to the binding of almost all metal ions to the biosorbent surface and establishment of equilibrium between the metal ions on the biosorbent and in the solution.The biosorbent dose 5 g/L was chosen for all further studies [16].

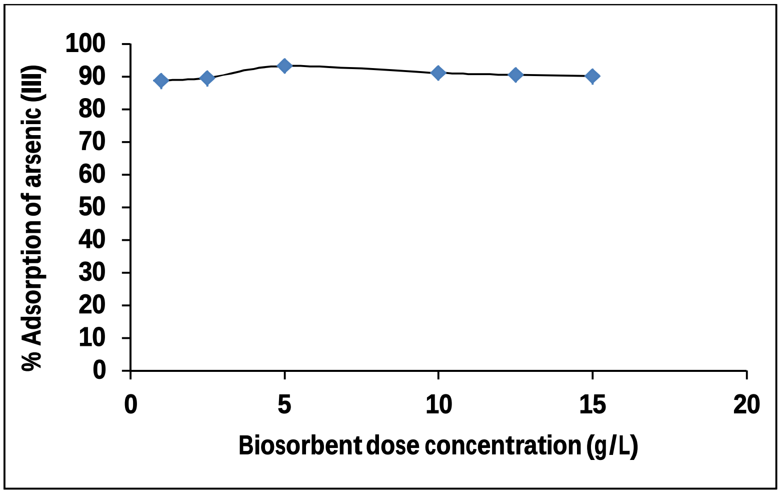


Figure 5: Effect of biosorbent dose concentration on arsenic (III) biosorption by banana peels modified with calcium alginate (pH: 6.0, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature: 30^0C, agitation rate: 120 rpm)

F. Effect of initial arsenic (III) concentration

The effect of initial arsenic (III) concentration from 5 mg/L-250 mg/L on the removal of arsenic (III) from aqueous solutions at biosorbent dose 5 g/L and at optimum pH 6 at 30^0C was studied. The percentage removal of metal ion decreases with increase in initial metal concentration and shows little decrease at higher concentrations from 92.06% to 80.25%.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.

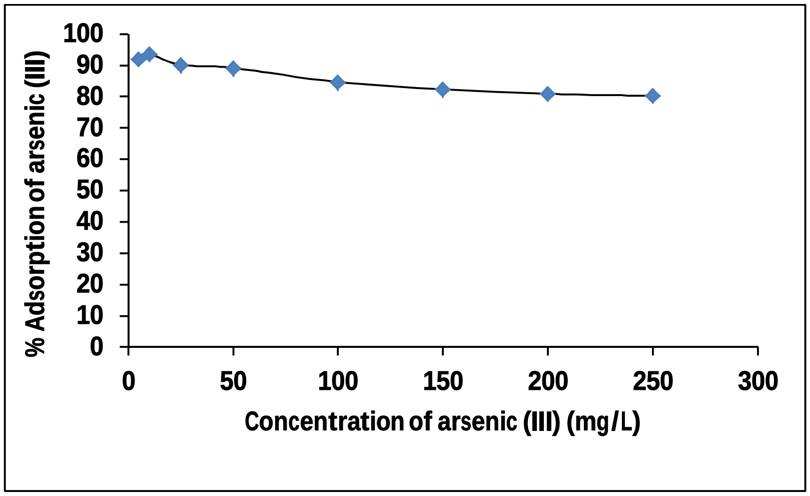


Figure 6: Effect of arsenic (III) concentration on arsenic (III) biosorption by banana peels modified with calcium alginate (pH: 6.0, biosorbent dose concentration: 5 g/L, contact time: 150 minutes, temperature: 30^0C, agitation rate: 120 rpm)

G. Effect of contact time

In order to optimize the contact time for the maximum uptake of metals, 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 adsorption capacity of arsenic (III) onto banana peels modified with calcium alginateshowed that the biosorption increases with increase in contact time until it reached equilibrium. The optimum contact time for biosorption of arsenic (III) ions onto banana peels modified with calcium alginate was 150 minutes with 93.03% 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) ions biosorption. So a contact time of 150 minutes was fixed for further experiments.

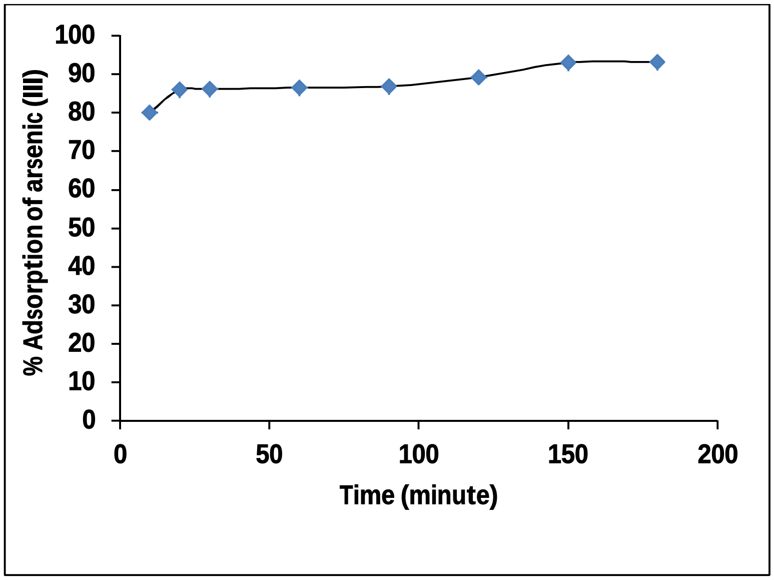


Figure 7: Effect of contact time on arsenic (III) biosorption by banana peels modified with calcium alginate (pH: 6.0, biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, temperature: 30^0C, agitation rate: 120 rpm)

H. Effect of temperature

The effect of temperature on removal of arsenic (III) from aqueous solutions using banana peels modified with calcium alginate 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 93.40%.

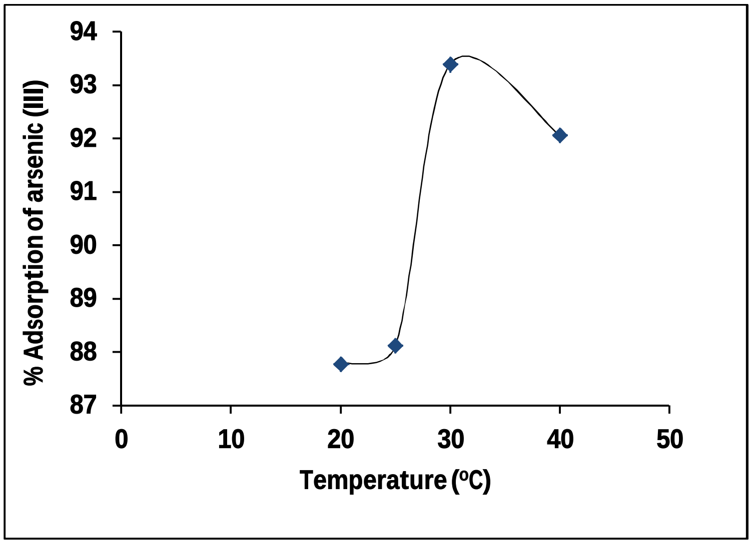


Figure 8: Effect of temperature on arsenic (III) biosorption bybanana peels modified with calcium alginate (pH 6.0, biosorbent dose concentration: 5 g/L, initial arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, agitation rate: 120 rpm)

I. 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 at 30^0C was studied at different agitation rate such as 40 rpm, 80 rpm, 120 rpm, 160 rpm and 200rpm. The efficiency was highest at 120rpm with percentage removal 93.40%. So, 120 rpm was chosen for all further biosorption studies.

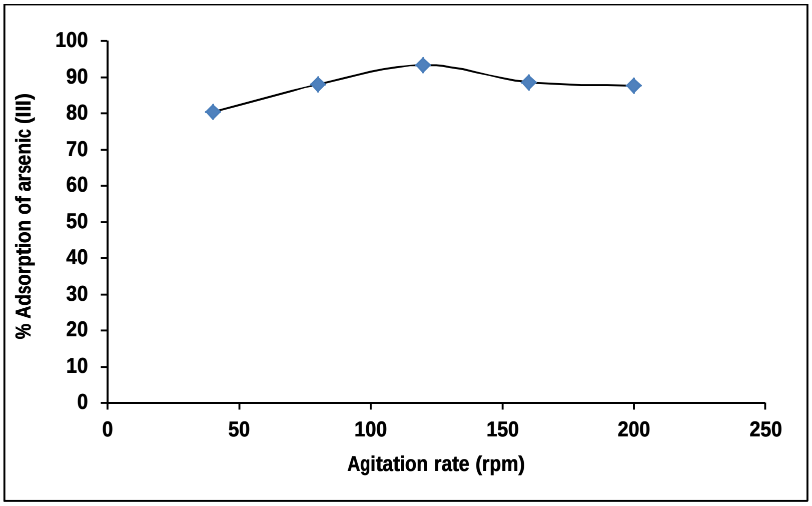


Figure 9: Effect of agitation rate on arsenic (III) bybanana peels modified with calcium alginate(pH 6.0, biosorbent dose concentration: 5 g/L, initial arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, temperature 30°C)

J. Desorption study

In application of real wastewater, desorption of heavy metal ions in the biosorbent is important process. Banana peels modified with calcium alginatewas the most effective waste biosorbent with desorption efficiency 65.69% (0.1 M hydrochloric acid), 65.38% (0.1 M nitric acid)and 76.00% (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 modified with calcium alginate.

K. 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. Adsorption isotherms data for biosorption of arsenic (III) by banana peels modified with calcium alginate is shown in;

L. 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;

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

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 biosorption 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 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 biosorbent (q_m) is found to be 52.083 mg g^{-1} of banana peels modified with calcium alginate.

The essential characteristics of the Langmuir isotherm parameters can be used to predict the affinity between the sorbate and sorbent using

$$R_L = \frac{1}{1+bC_i} \qquad (6)$$

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 0.0769-0.8064 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].

M. Frenudlich adsorption isotherm [19]:

Freundlich equation is represented by:

$$q = KC_e^{1/n} \qquad (7)$$

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:

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

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 biosorption 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 0.3493. Since $n < 1$, this indicates the chemical process biosorption of arsenic (III) ions onto banana peels modified with calcium alginate. The higher value of K (5.5564) indicates the higher adsorption capacity for the banana peels modified with calcium alginate.

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

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

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (9)$$

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:

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \qquad (10)$$

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.

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

The E value was found to be 1.2910KJ 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 [21]. In the present work, E value (1.2910KJ mol^{-1}) which is less than 8 KJ mol^{-1}, the biosorption of arsenic (III) onto banana peels modified with calcium alginateis of physical in nature [22].

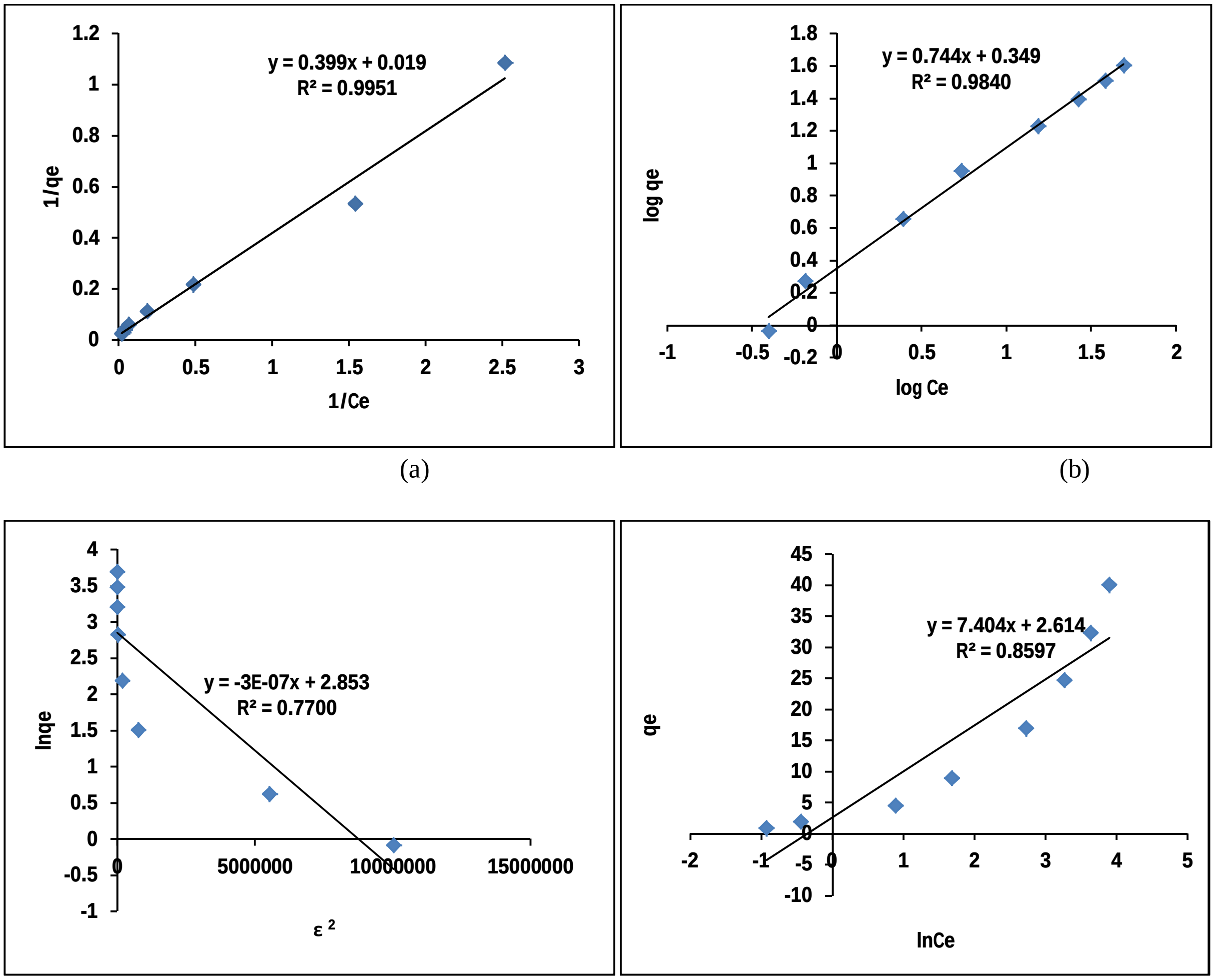
O. Temkin adsorption isotherm [23]:

Linearized Temkin adsorption isotherm is given by the equation:

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

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 lnC_e, as shown in Figure10(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^2 obtained from adsorption isotherms models (Langmuir, Freundlich, Dubinin-Kaganer-Redushkevich (DKR) and Temkin) is 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) bybanana peels modified with calcium alginate (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 banana peels modified with calcium alginate

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
52.083	0.0480	0.9951	5.5564	2.8628	0.9840	-3E-07	4.2772	1.2910	0.7700	16.972	340.240	0.8597

P. 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 [24] (b) the pseudo-second-order equation [25] (c) Elovich equation [26] (d) Weber & Morris intra-particle diffusion model [27] are presented below:

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

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

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

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

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 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 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.

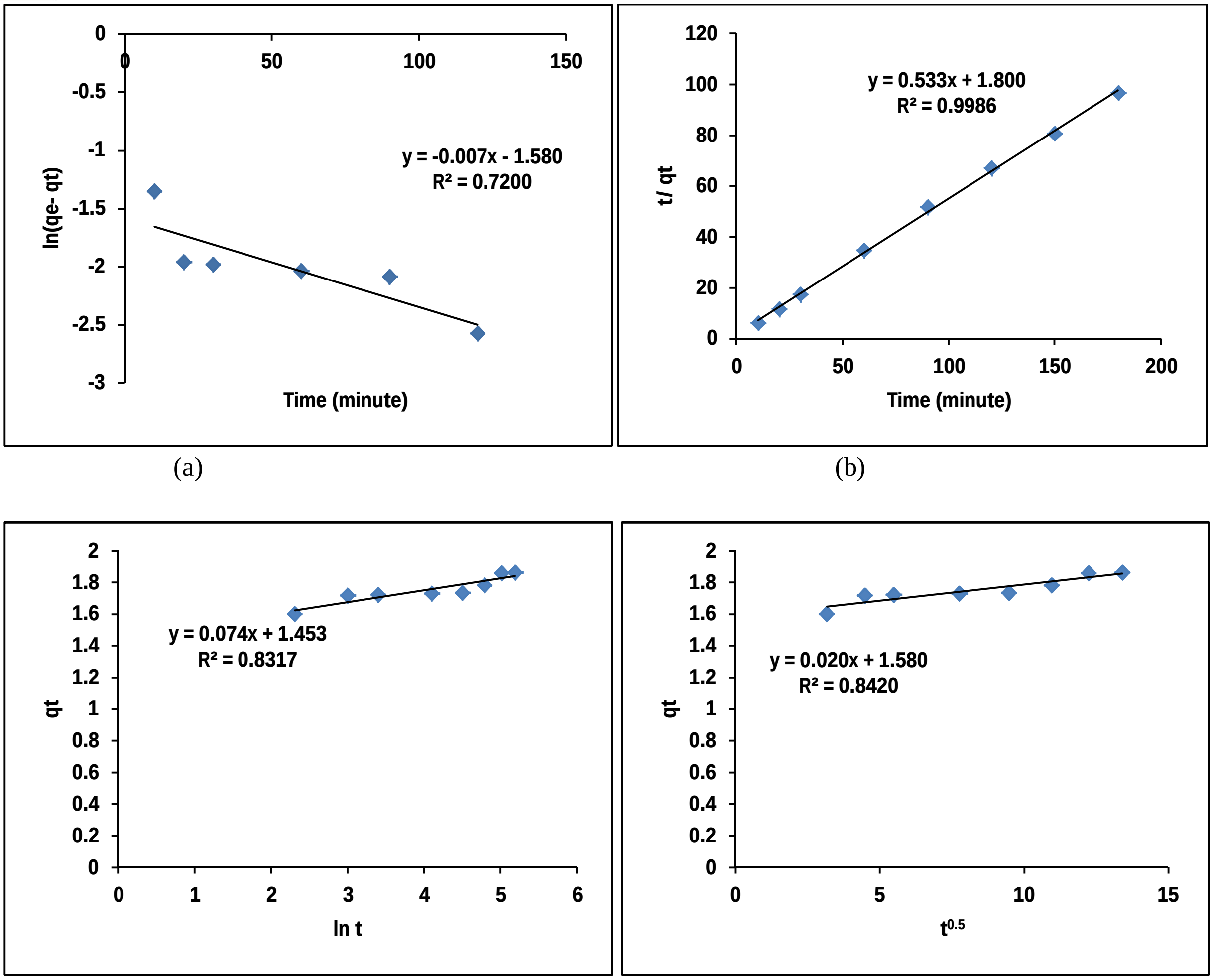
The pseudo-first-order model was plotted for ln $(q_e$-$q_t)$ against t (Figure 11 (a)). The values of k_1 and q_e values were calculated from the slope (k_1) and intercept (lnq_e) of the plot and shown in Table 2. Kinetic adsorption for pseudo-first-order model occurs chemically and involves valency forces through ion sharing or exchange of electron between the biosorbent and the ions adsorbed onto it [28].

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 [29].

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 [27].

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 biosorbate 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 [30].



(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)by banana peels modified with calcium alginate (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 modified with calcium alginate

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	K_i	C	R^2
4.8568	0.0225	0.7200	1.8758	0.1578	0.9986	$2.380\text{x}10^7$	13.477	0.8317	0.0206	1.5804	0.8420

Q. 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 5 mg/ml with optimum pH 6.0 was studied. Experiments were carried out at different temperatures from 20^{0}C-40^{0}C. The samples were allowed to attain equilibrium. Sorption slightly increases from. The equilibrium constant [31] at various temperatures and thermodynamic parameters of adsorption can be evaluated from the following equations:

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

$$\Delta G^0 = -RT\ \mathrm{In}K_c \qquad (18)$$

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

$$\mathrm{In}K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \qquad (20)$$

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 ΔH^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*), 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. 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 Gibbs free energy (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) ions onto banana peels modified with calcium alginate. 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 modified with calcium alginate

Sr. No.	Temperature (^{0}C)	Temperature (K)	Kc	-ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (J/mol)
1	20^{0}C	293	7.1833	4.8030	56.3689	207.193
2	25^{0}C	298	7.4175	4.9645		
3	30^{0}C	303	14.151	6.6749		
4	40^{0}C	313	11.594	6.3766		

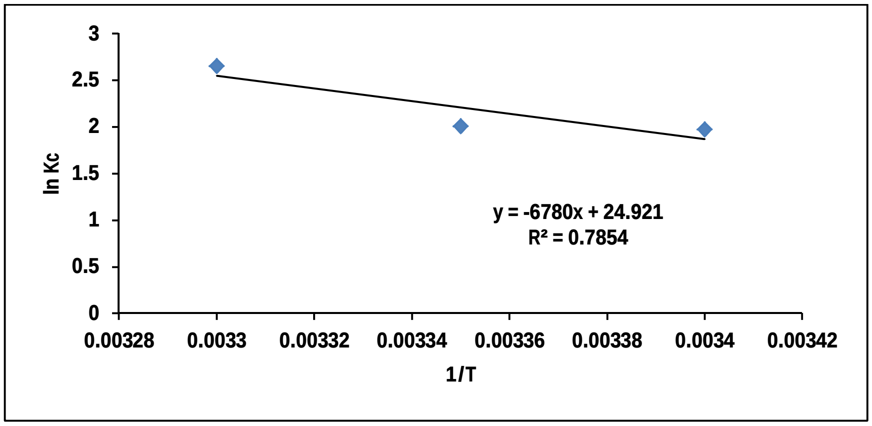


Figure 12:Plot of lnKc against 1/T for determination of thermodynamic parameters for biosorption of arsenic (III) by banana peels modified with calcium alginate (pH: 6.0, biosorbent dose concentration: 5 g/L, arsenic (III) concentration: 10 mg/L, contact time: 150 minutes, agitation rate: 120 rpm)

IV. CONCLUSIONS

The present investigation revealed that banana peels modified with calcium alginate 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 modified with calcium alginate. 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 modified with calcium alginate determined from Langmuir adsorption isotherm was found to be 52.083 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 modified with calcium alginate has considerable biosorption capacity, available in abundant, non-hazardous material can be used as an effective indigenous material for treatment of wastewater stream containing arsenic (III). However, further research should attempt to improve the biosorption capacity of biosorbent and apply this method to the removal of metals in large scale.

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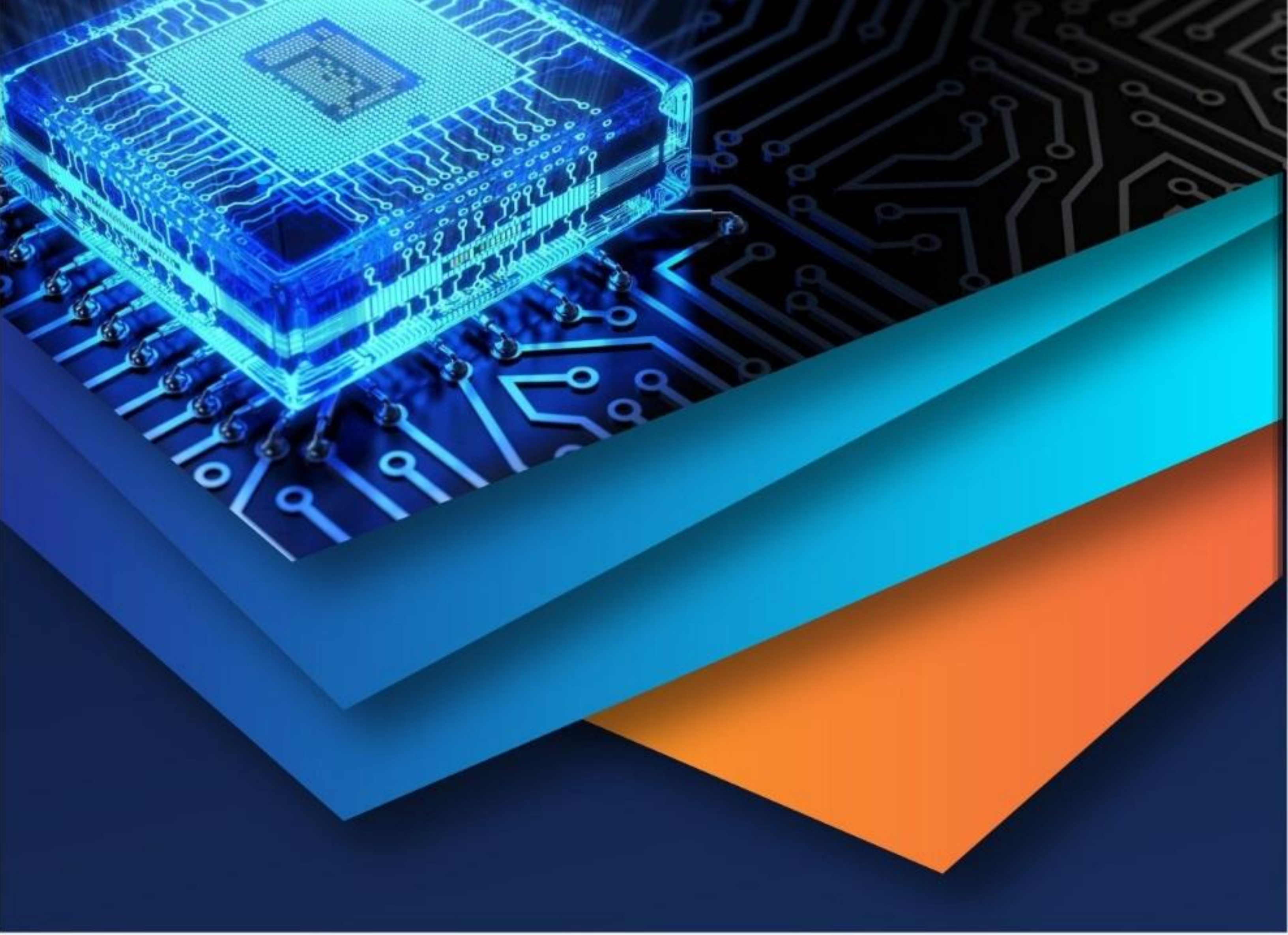

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