Novel Magnetotactic Bacteria Strain for Enhanced Aluminium Ion Biosorption

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Abstract

Over the decades, the removal of heavy metals from aqueous solution using biosorbents such as algae, fungi, yeast, and bacteria has remained a challenging task. This paper explores theAl(III) biosorption efficiencyof magnetotactic bacteria (MTB) via a new strain called SUM 123 of *Alcaligenes* sp. The influence of temperature, pH, initial Al(III) concentration, and adsorbent dosage on the biosorption efficiency of MTB is examined. The achieved optimum conditions for Al(III) ionsbiosorption in the aqueous solution is demonstrated to be80 mg/L, 12 g/Lbiosorbent at 25°C with pH 5.Inthis situation,the isolated bacteria attained the maximal Al(III) loading capacity as much as 15.74mg Al(III)/g (biomass) with 99.53% adsorption. Furthermore, better fitness of the equilibrium data was provided by the Langmuir isotherm model compared to the Freundlichmodel. Again, the feasibility, spontaneous and endothermic nature of the biosorption process at 10-40°C were validated by the evaluated thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$). A pseudo second-order kinetic model that fitted the kinetic data was also achieved with acorrelation coefficient (R^2) value of > 0.993. FTIRspectra manifested the involvement of hydroxyl, amide, and amine groups in Al(III) biosorption process. TGA displayed the existence of Al(III) adsorption on the cell wall. It is established that the SUM 123 biomass assisted biosorption is a prospective cost-effective method for Al(III) recovery fromcontaminated waters.

Keywords: Magnetotactic bacteria, aqueous solution, *Alcaligenes*sp, Aluminium, Biosorption.

1.   Introduction

Metals are integral componentsof all living organisms. However, beyond certain concentrations, these metals appear toxic and cause harmful effects. The ever-increasing heavy metals contamination from industries and agriculturesposed serious health and environmental concern[1]. Generally, these heavy metals accumulation in aqueous waste stream arise from several industrial processes like smelting, mining, metal plating, metallurgical casting, and pigmenting[2]. Interestingly, despite undesirability of Al in the body, humans are frequently exposed to the highly reactive element Aluminium (Al) dueto itsomnipresence in modern civilization including kitchen utensils, vessels, building construction, food packaging, medicine, etc.The bonds of Al in compound form being very strong are difficult to dislodge[3]. Thus, the normal functioning of biological systems could be hampered due to the accumulation of Alin body cellsand the consequent formation of large metal deposits within the cells [4]. Certainly, itsaccretionin bio-system became an alarming issuedue to enhanced use of Al products and Al contaminated water.Consequently, Al is involved in the apparition of bone disease, osteomalacia, Parkinson's disease, &Alzheimer's disease[3, 5].

The normal biological activity of living organisms on land and water environments is threatned by the presence of charged aqua (positively charged and negatively charged), as well as the accumulation of ionic forms of heavy metals. To overcome the risks involving heavy metals infection several methods are developed, wherethe metal contamination is remarkably reduced in waste water via oxidation, reduction, ion exchange, reverse osmosis or evaporative separation, and electrolytic reduction [6].Yet, these methods are expensive because theyinvolve large amount of chemicals and reagentsforproper treatment. Besides,they are often inefficient atvery low ions concentration of 1 to 100 mg l^{-1}[7]. Thus, the biological methods (green chemical route)due to their environmentally amiabilityare considered tobe the good alternative for heavy metals removal from wastewater. On top, they offer economytogether with higher elimination efficacy [8, 9].

In the past, several biosorbents including algae, yeast, bacteria and fungi are exploitedto accumulate various concentration of metals from aqueous solution[1, 10-12]. The ability of bacteria to remove heavy metals is facilitated by the presence of certain functional groups on the cell walls of such microbes; hence, such processes mostly lead to the formation of less chemical sludgeand therefore, they are considered beneficial due to their cost efficiency and wide availability. But despite the effortsdedicated to this process of microorganisms-based metal ions removal from aqueous solutions,achieving a complete biosorption remain a challenging task[13]. In this regard, the biosorption capacity of MTBmay be exploited toresolve metal pollution in water. The presence of magnetosomes (MS) within the bacterial intra-cellular structure is beneficial for the easy eliminationheavy metals from the solution.Most of the previous studies involved the isolation as well as cultivation of MTB and MS[14].Only a few investigations are made on the heavy metals ions biosorption effectiveness of MTB [15].

This paper evaluatestheAl ions biosorption efficiency of a new MTB strain (*Alcaligene*sp SUM 123). The main aim is to inspect the MTB's renewability and cost-effective biomass production potency. Many factors influence the optimum biosorption process, such as pH, temperature, Alcontent, and biomass concentration. Moreover, the equilibrium of isotherm is examined using Langmuir and Freundlich models.The pseudo-first and second order kinetic studiesare made on Al biosorption by MTB in aqueous solution.In this work, the Al biosorption efficiency of strain SUM 123 from aqueous solution is characterized in terms ofthe functional groups of the binding sites and surface structure of the cell.

2. Materials and methods
2.1 Enrichment and identification of MTB
The sediment water sample was collected from Skudai River in Johor Bahru, Malaysia (GPS: 1°28'34.8"N 103°43'21.5"E) and then transferred into the tube containing the enrichment medium to increase the viability of the bacteria cells. Thereafter, the bottle was kept at room temperature in dim light for 3 weeks without disturbance. The enriched medium for the growth of the bacteria was constituted as follows (in g/L): 0.12 g of $NaNO_3$, 0.68 g of KH_2PO_4, 10 ml of Wolfe's vitamin solution, 2.0 ml 0.01 M of ferric quinate solution, 0.05 g of sodium thioglycollate, 5.0 ml of Wolfe's mineral solution, 0.05 g of sodium acetate, 2.0 mg of resazurin, 0.37 g of succinic acid, 1 l of distilled water, and 0.37 g of tartaric acid [16]. The isolation of MTB started after 3 weeks of incubation by placing a magnet bar on the water surface in the container. After two hours, the water sample near to the position

of the magnet bar was collected carefully using a sterile needle. The isolated MTB was purified on growth agar medium and then identified via 16S rRNA analysis (First Base laboratory SdnBhd, Malaysia).

2.2 Biomass preparation

The culturing of the isolated MTB was done $25 \pm 1^{o}C$ in the enriched medium earlier described for its cellular growth to attain stationary phase [16]. The MTB was harvested via centrifugation for 15 min at 4000 rpm, followed by washing (twice) with deionized water. The obtained wet biomass was preserved $4^{o}C$ for the biosorption measurements [17].

2.3 Preparation of Al(III) stock solution for biosorption

The preparation of the stock Al(III) solution was done by dissolving $AlCl_3.6H_2O$ (8.89 g) in dionized water (1 L). The pH of the resulting Al(III) stock solution was adjusted using NaOH (3 M) and/or HCL (3 M) before being filtered through nylon filters (0.22 µm).The working solutions were prepared by diluting the freshly prepared stock solution deionized water.

2.4 Experiments on the removal of Al (III)

The lab scale experiments were carried out in conical flasks (250 ml) containing Al(III) solution (50 ml). An agitation rate of 180 rpm was maintained during the experiments for the desired contact time. The required time to reach equilibrium wasdetermined with 50 ml of 80 $mg.L^{-1}$ Al(III) solution at regular time intervals untilequilibrium is reached at 1 hr[18]. Upon attaining the equilibrium, 5 ml sample is taken from each flask and filtered with Millipore filters of pore size 0.22 µm. Finally, the atomic absorption spectra (AAS) of the filtered sample were measured to determine the Al(III) ion concentration in the MTB. All experiments were performed in triplicates to improvement data accuracy andminimize statistical errors.

2.4.1 Effect of pH

The Al(III) solution was adjusted to an initial pH value range of 2 - 9using HCl and NaOH solutions under the influence of agitation with 12 g/Lofwet MTB biomass. 0.746 g/L of dry MTB weight was thoroughly mixed with Al(III) solution 80 mg/L at $25^{o}C$,and shaken at 180 rpm. Thereafter, a5 ml sample is taken from each flask and filtered with Millipore filters of pore size 0.22 µm. Finally, the biosorption capacity of the isolated MTB is determined by comparing the initial Al(III) concentration with the final concentration in the solution[17].

2.4.2 Effect of Initial Al(III) Concentration

The influence of the initial Al(III)contents was examinedatvarying concentrations(80, 100, 200, 300, 400, and 500 $mg\ L^{-1}$), where the biosorbent (12 $mg\ L^{-1}$) in 250 mL conical flasks is incubated at 25 ºC on a rotary shaker (180 rpm). Samples (5 mL) with different Al(III) concentrations are collected at optimum contact time (60 min) andsterilized using 0.22 µm filters.The residual concentration of Al (III) ions is determined using AAS.

2.4.3 Effect of Biomass Concentration

The effect of MTB biomass concentration plays an important role for Al(III) ion biosorption. Different concentrations of wet biomass were used to optimize Al biosorption at 25°C withpH 5, where2, 4, 6, 8, 10, 12,14 g. L^{-1}wet cellsare incubated at 160 rpm till the equilibrium is reached.The supernatant of Al(III) are collected at optimum contact time (60 min) for further analysis. The remaining concentration of Al(III) in the supernatant is also determined.

2.4.4 Effect of Temperature (biosorption thermodynamics)

The temperature dependent Al(III) biosorption efficiency bythis novel strainwasmonitored by adding 12 g/L of wet MTB biomass into 80 mg L^{-1} Al(III) solution in 250 conical flasks incubated at varying temperatures (10, 20, 25, 30, 35, 40ºC). The solution was shaken at 160 rpm at pH 5. Samples (5 mL) at different temperatures were collected and the remaining Al(III) in the supernatant is analysed with AAS.

2.4.4.1 Evaluation of thermodynamic parameters

The thermodynamic pattern of Al biosorption by the studied microbe was determined by calculating the thermodynamic parameters such as the free energy change (ΔGº), entropy (ΔSº), and enthalpy (ΔHº) using Equation 1:

$$\Delta G° = -RT \ln K_D \tag{1}$$

where R = 8.314 Jmol^{-1} K^{-1}(the universal gas constant), T = temperature (K), K_D (q_e/C_e) = distribution coefficient [2]. The values of ΔHº and ΔSº were calculated using Equation 2.:

$$\ln K_D = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{2}$$

2.5 Metal Ions Determination

Atomic absorption spectrophotometer (AAS; Perkin Elmer) was used to determine the Al ions concentration in the aqueous solution. The test criteria were the metal ion uptake q_e(mg.g^{-1}) and the adsorption yield Y (%); they were determined as follows:

$$q_e = \frac{C_0 - C_e}{m} \times v \tag{3}$$

$$Y = \frac{C_0 - C_e}{C_0} \times 100\% \tag{4}$$

whereC_0= initial free Al ion concentration at equilibrium (mg/L), C_e = final free Al ion concentration (mg/L) at equilibrium;m = wet biomass concentration (g/L), v = solution volume, Y = removal yield (%).

2.5 Biosorption Isotherms

The determination of the biosorption isotherms was done under optimal pH, temperature, and equilibrium time conditions by adjusting the initial concentration in the range of 80, 100, 200, 300, 400, and 500 mg/L. The relationship between the sorbed metal ion on the MTB surfaces and the metal ions present in the solution was determined by carrying out modeling by sorption isotherms. The measurement of the sorption curve or isotherm for a range of initial metal ion concentrations can be done at a constant

temperature. The plot of the sorbed solute (qe, mg/g) of the biomass against the residual or final concentration at equilibrium was prepared using the Freundlich and the Langmuir sorption models.

2.6   Kinetic studies

The kinetic studies were performed at a solution pH value of 5,temperature of 25°C,adsorbent concentration of 12 g/L, and initial ion concentrationsof 80 and 100 mg/L. During the studies, samples were withdrawnat varyingtimes, spinnedand evaluated for residual metal ion concentrations.

3.   Results and Discussion
3.1   Identification of MTB

The identification of the isolated novel MTB strain was done via 16S rRNA analyses; the 16S rRNA gene sequences of the strain was compared with the available sequences in the NCBI database. The comparison result suggested that the isolated SUM 123 strain is a member of the *Alcaligenes* sp. With the aid of the using MEGA 6 Software, the phylogenetic tree of the strain was drawn using the neighbour joining method asshown in Figure 1. *Alcaligenes*sp is taxonomically related to the Betaproteobacteria class. Based on available data on phylogenic characteristics, it was proposed that *Alcaligenes*sp strain SUM 123 be categorized as new MTB species due to their ability to produce magnetite magnetosomes. The gene sequence of this novel bacterium was deposited in the NCBI GeneBank database (www.ncbi.nlm.nih.gov) and assigned with the accession number KR107950.
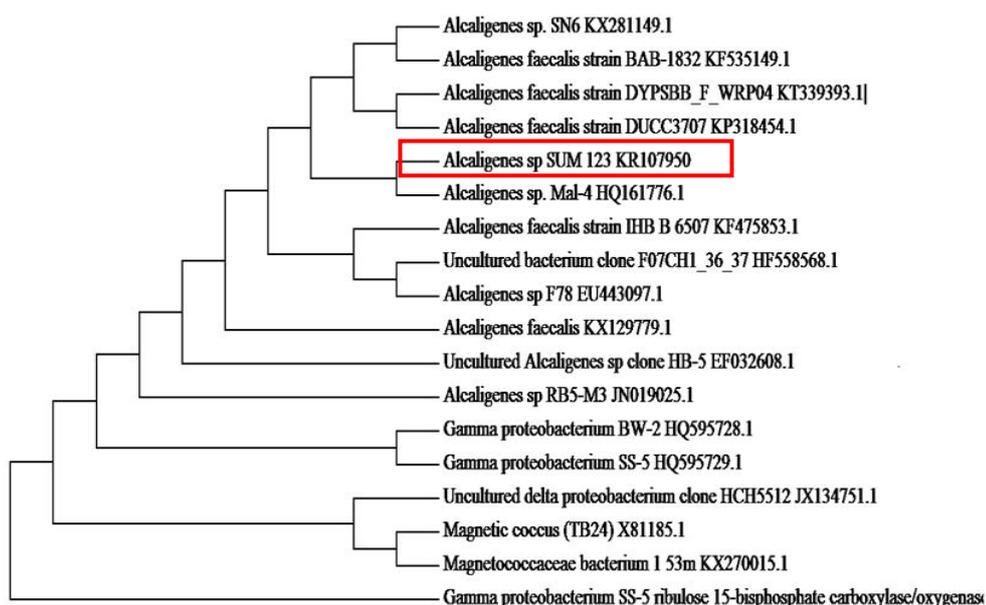
Figure 1:   Evolutionary relationships of *Alcaligenes*sp SUM 123

3.2   Optimum Adsorption Conditions
3.2.1   Effect of pH

The pH is the most important factor as alterations in its value affects the surface charges of the biosorbent and the sorption process [19, 20]. The pH range of Al (III) is considered to be 2 to 9. As

illustrated in Figure 2, the adsorption efficiency of Al (III) ion on *Alcaligenes*sp SUM 123 at pH 5 is97.12%.The corresponding uptake capacity of Al(III) ions is approximately7.96mg.g^{-1}. The component of the MTB cell wall revealedthe presence of specific binding sites forionisablegroups such as amino groups, carboxyl, hydroxyl, and imino moieties. The presence of H_3O^+on cell wall ligands accounts for their acidic pH values; it prevents the penetration of metal ions into ligands via electrostatic repulsion. Increasing the pH inevitably exposesmore ligands to negative charges which subsequently results in higher attraction for positively charged metal ions into the cell. This phenomenon led to higherAl (III) ion adsorption efficiency by *Alcaligenes*sp SUM 123 at pH 5. Similar pH effect on Cu (II) ions adsorption is also reportedforMagnetospirillumgryphiswaldense[18].

Numerous studies have studied the impact of pH on Al (III) sorption of MTBs, where various sorbentsrevealed similar dependence and maximum biosorption at near pH values. The Al biosorption is seldom studied due to its very narrow pH range that permitsmetal binding metal without the formation of precipitates. The study by [21]reported improvements in the biosorption capacity of Al on *C.caldarium* following imcrease in the pH value from 2 to 4. The study reported the optimum biosorption capacity at the pH value of 5 without consideringAl ions precipitation at this pH.Furthermore, improvement in the biosorption efficiency of Al on Padina pavonica biomass has been reported by [2] following increases in the pH value; however, pH 4.5 has been determined as the optimum for achieving maximum recovery. The precipitation of Alusually begins at the pH range of 4.5 to 5.0, with the ionization of the major functional groups (COOH) occurring at pH > 3.
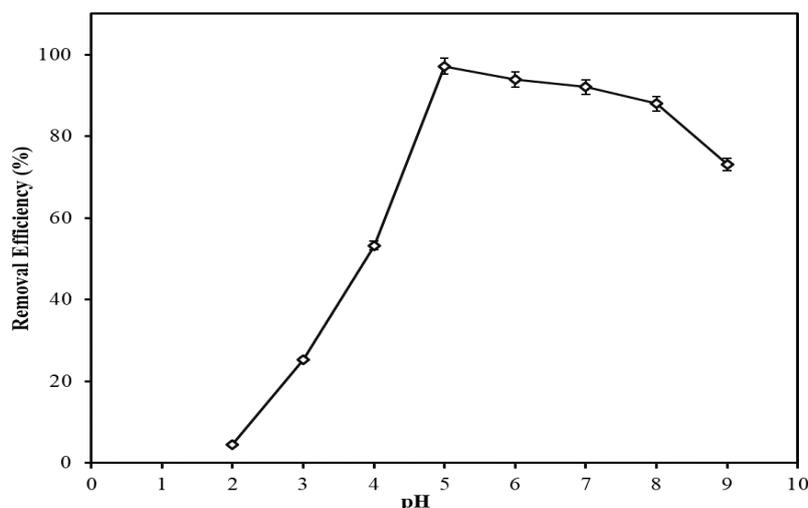
Figure 2. Effect of pH variations on the Al (III) ions removalefficiency of SUM 123

3.2.2 Effect of Temperature

The temperature of aqueous solutionsinfluence the removal efficiency of Al (III) ionby MTB. The temperature in this study was varied between 10 to 40°C at the optimum pH value 5 while the biomass concentration was maintained at 12 g/L. The results showed that increases in the temperature within the range of 10-25ºC significantly improved the adsorption yield, but further increases (above 25°C) had negative impacts on the yield (Figure 3). Hence, 25ºCwas mainained as the optimal temperature with the optimal removal efficiency of 95.85 %. The biosorption yield was swiftly reduced from 94% to 68.63% with corresponding temperature increase from 35 ºC to 40 ºC, respectively. Overall, the temperature effect on the adsorption yield of *Alcaligenes*sp SUM 123 for Al (III) was

similar to [22]results. Song et al., [18] showed 100% biosorption yield of Au (III) at 25 ℃, whichdecreased to 99.89% at 35 ℃.
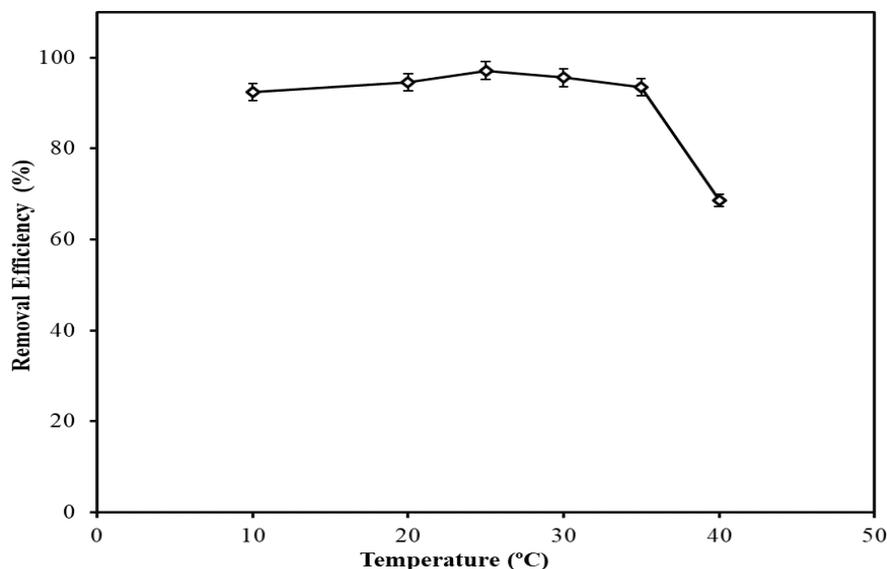
Figure 3. Effect of temperature on the performance of SUM 123 forAl(III) removal

Experiments were conducted to determine the thermodynamic parameters for the biosorption process at different temperatures; the determined parameters include enthalpy (ΔH^o), the Gibbs free energy (ΔG^o), and entropy (ΔS^o) of biosorption. The expressions for ΔG^o and ΔH^o are given by:

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (5)$$

$$\log \frac{q_e}{C_e} = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (6)$$

where q_e= biosorption affinity (the quantity of adsorbed material per unit mass in mg.g^{-1}), C_e= the solute's equilibrium concentration (mg/l). ΔH^o and ΔS^ovalues were estimated from the slope and intercept of the prepared linear plot of log K_D versus 1/T to calculatethe ΔG^ovalues.

The impact of temperature on biosorption was determined. Values of ΔG^o were calculated as -13.11, -13.66, -13.94, -14.21, -14.49, -14.67 kJ/mol for temperatures 10, 20, 25, 30, 35, 40 ℃, respectively. For ΔG^o, negative values are indcative of the spontaneous nature and thermodynamic feasibility of the biosorption process. The negative increase in ΔG^o values with increasing temperatures denotes enhanced biosorption at higher temperatures. This implies that there exists elevated spontaneity of biosorption processes with high affinity for Al (III) by SUM 123. With the ΔH^o parameter calculated as 2453.46 KJ/mol, a positive ΔH^o is suggestive of the endothermic nature of the process within the temperature values of 10-40℃. The positive ΔS^o value (0.0555 KJ/mol. K) also indicates the increased level of randomness at the solid-solution interface during the adhesion of the Al ions on the biosorbent's active sites.

According to reports, increasing temperature has a beneficial impact on the biosorption ability for endothermic biosorption [23]. Since the equilibrium concentration was close, the minor improvement

in the biosorption capacity that was seen in this study between 10 and 25oC was primarily due to an increase in metallic cation mobility inside the biosorbent. The biosorption of Al on SUM 123 was more endothermic since there was no commensurate decline in biosorption capacity following increase in temperature.Figure 4 shows the plot of ln K_2 versus 1/T to determine the activation energy for aluminium biosorption by SUM 123:.

$R^2 = 0.9994$

Plot Equation:
ln K_2 = -295.19(T^{-1}) + 6.6865
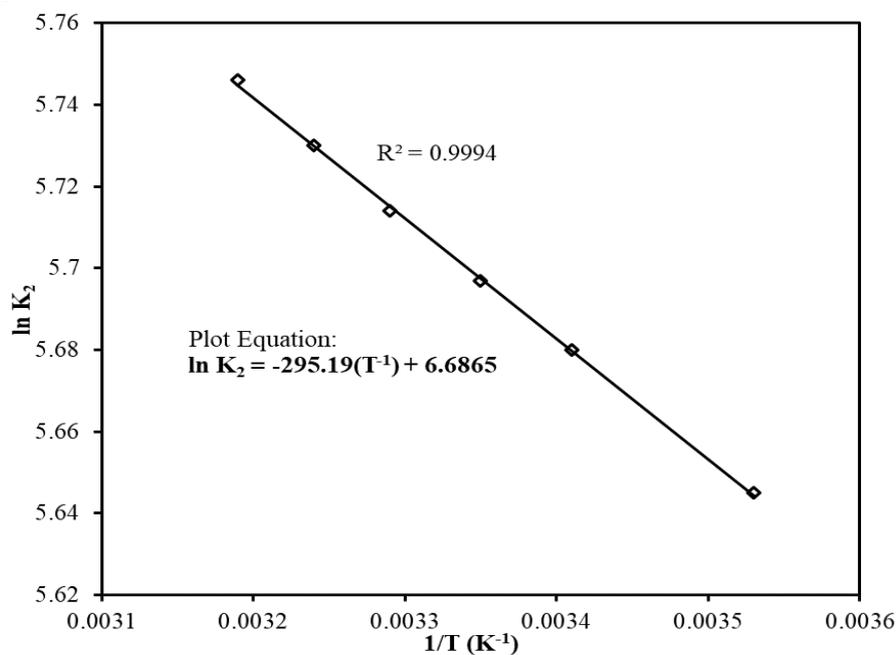
Figure 4. Determining the activation energy for aluminium biosorption by SUM 123: Plot of ln K_2 versus 1/T.

The observed increase in Al biosorption with temperature could be due to a combination of factors, including a decline in the boundary layer thickness around the adsorbent, the desolvation of the adsorbing species, and an increase in the number of active surface sites accessible for biosorption. At higher temperatures, a larger biosorption was seen because diffusion is an endothermic process. Consequently, increases in temperature consequently increased the ion diffusion rate in the external mass transport mechanism[23].

3.2.3 Effect of Biomass Concentration

Figure 5shows the biomass concentration-dependent Al(III) ions adsorption of SUM 123. The adsorption yield was enhanced with increase of biomass concentration from 2 to 12 g/L at initialAl concentration of 80 mg/L, pH 5. A wet biomass concentration > 10.0 g/L gave the maximum adsorption yield;hence, 12.0 g/L was selected asthe optimum biomass concentration for SUM 123 to attain efficient removal (98.9%) of Al(III) ions in aqueous solution.Wang et al.(2011) showed an increase in the Ag(I) and Cu(II) ions adsorption yield by Magnetospirillum gryphiswaldense with increasing biomass concentration. The enhanced removal yield was attributed to the higher number of available ion adsorption sites due to the increased concentration of MTB.
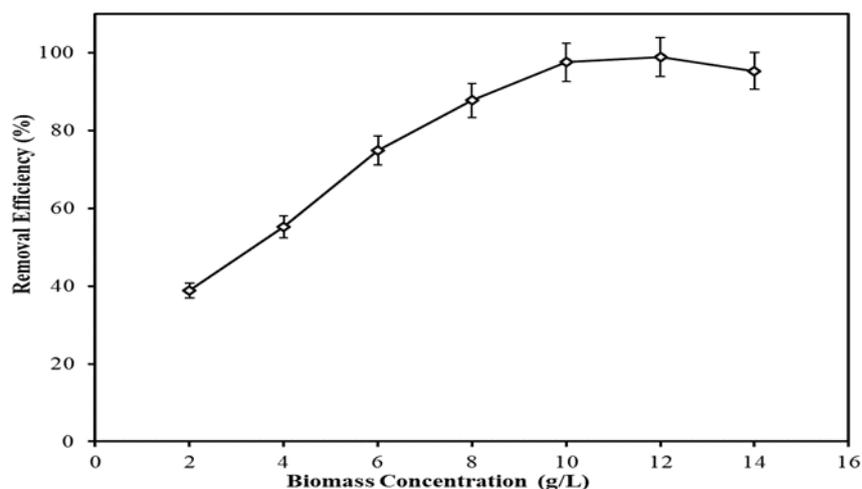
Figure 5. Effect of biomass concentration onAl(III) ions biosorption yield by SUM 123

3.2.4 Effect of Initial Al(III) Concentration

The effect of varying initial Al(III) ions concentration on MTB biosorption efficiency was determined and illustrated in Figure 6.The initial concentration of Alwas varied at80, 100, 200, 300, 400, and 500mg. L^{-1} at the optimum temperature and pH,with12.0 g/L wet biomass concentrated SUM 123 cells of *Alcaligenes*spis shaken at 180 rpm for 60 min.It was observed thathigher Al biosorption efficiency for SUM 123 at 97.13% and 93.84% was apparent with increase in Al(III) concentration from 80-100 mg/L. At higher Al(III) contents 500 mg/L, the biosorption efficiency declined to 56.31%.
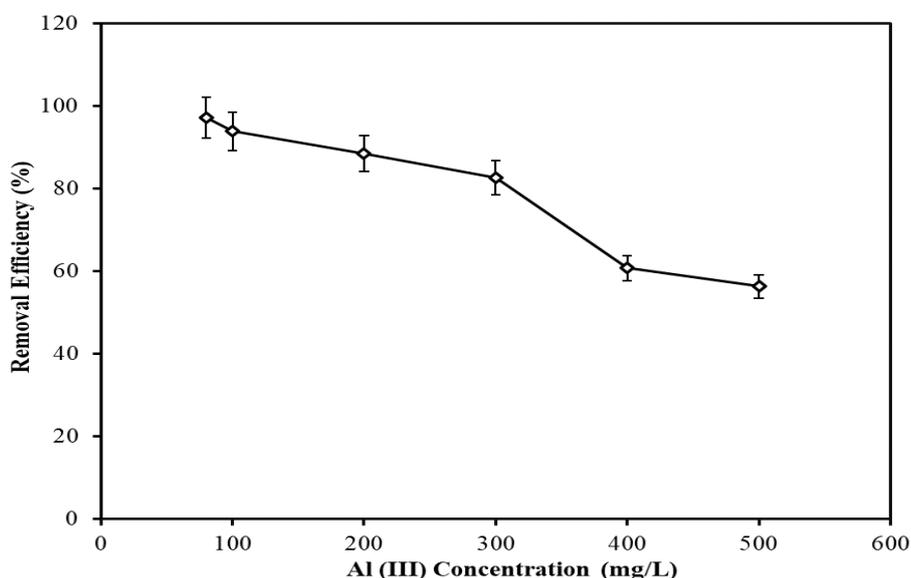
Figure 6. Effect of Al(III) concentration on the biosorption efficiency of SUM 123

Even though the biosorption capacity of *Alcaligenes*sp SUM 123 decreases with increasing concentrations of Al(III), the performance of SUM 123 to higher dosage of Al(III) issuperiorto other biosorbents.SUM 123 has potentials for the adsorption of Al(III) at a capacity of 23.46 mg.g^{-1} when subjected for 500 mg/L dosage. Al biosorption uptake of the novel SUM 123 strain used in this study is also higher than those obtained for activated carbon, or fungi [2, 3].Tassist, Lounici [3]examined the Al biosorption capacity by mycelia biomass (Streptomyces rimosus) in aqueous solution at 30 ppm Al

concentration. The reported optimum biosorption efficiency of *S. rimosus* biomass was 11.76 mg/g at pH 4.25, T = 25ºC. However, studies carried out by [24]reported a maximum sorption capacity was 41 mg.g^{-1}with lower Al concentrations of 50 ppm and pH 5.0 at 25 ºC. Qu et al.,[25] revealed the ability of MTB to adsorb the Cr^{6+} from wastewater at 73% when the initial concentration of Cr^{6+} was 50 mg/L. Therefore, SUM 123 strain can be proficiently employed for remediating high dosage of heavy metal including Al(III) in municipal and industrial wastewaters.

3.3 Biosorption Isotherms

The influence of the concentration of metal ions on the biosorption process was investigated under the established optimal biosorptive conditions (T = 25oC, initial metal ion concentration = 80 mg/L, wet biomass concentration = 12 g/L, pH = 5). The isotherm model and regression parameters in the isotherm equations were adjusted using the experimental results under optimum conditions. The equilibrium between qe and Ce can be described by a number of isotherm models. In this study, the Langmuir and Freundlich equilibrium models were used to study the biosorption isotherms. The Langmuir model yields:

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0}C_e \qquad (7)$$

where Q^0(mg.g/L) signifies theoptimum sorption capacity, b (L/mg) is the sorption constant related to the binding site's affinityas calculated from the C$_e$/q$_e$ vs.C$_e$plot depicted in Figure 7.
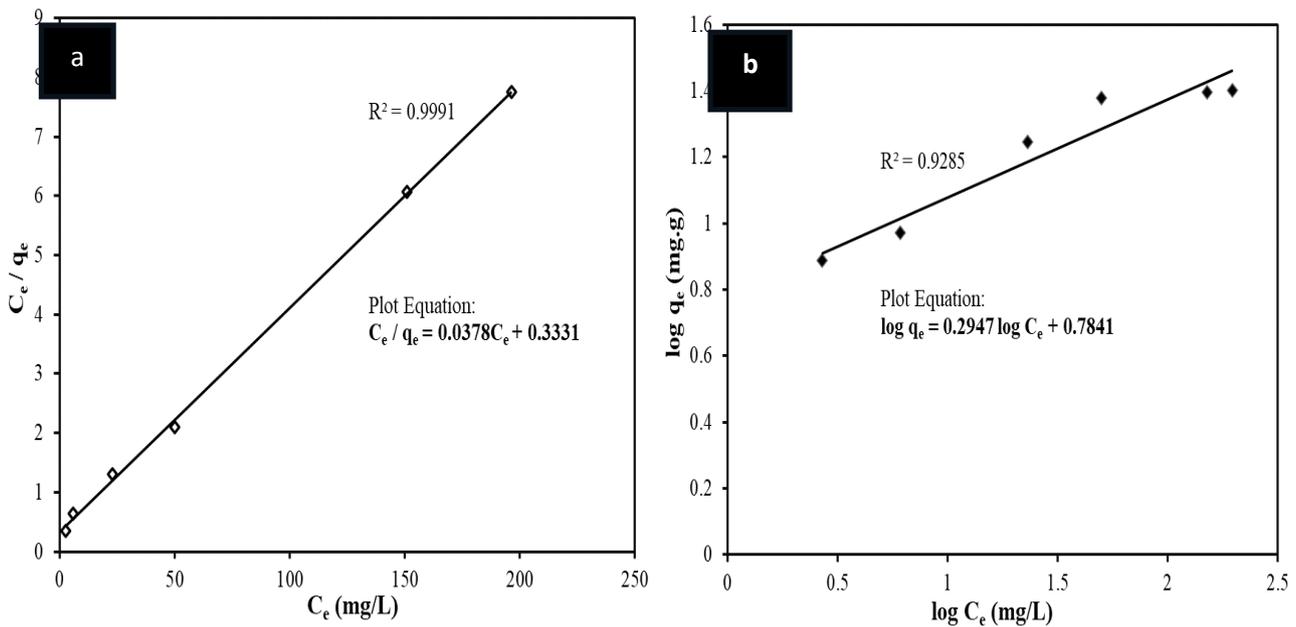
Figure 7. Linearized plot of [a] Langmuir isotherm and [b] Freundlich isotherm for Al (III) biosorption by SUM 123

The biosorption of Al ions onto SUM 123 was adequately fitted by the Langmuir model (R^2 value = 0.999). The study showed that the surface functional groups of the biomass facilitated the sorption of Al ions using *Alcaligenes*sp, which is considered a monolayer biosorption process.

For the Freundlich model, the concept is based on the sorption of metal ions onto a heterogeneous surface; this suggests that functional groups/binding sites are neither independent nor equivalent; this is expressed as:

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

where K_F = an indicator of the adsorbent's adsorption capacity, $1/n$ = the adsorption intensity. K_F and $1/n$ can be determined from the $\log q_e$ vs.$\log C_e$plot.

Table 1 presents the values of the Langmuir and Freundlich constantsdetermined from the thelinear regression analysis. The Langmuir model is found to be more suitable for describing the Al (III) adsorption isotherms with R^2=0.999. Furthermore, value of $Q^0$for Al (III) is found to be 27.02mg/gand b =0.111L/mg.

Table 1. Langmuir and Freundlich parameters and the correlation coefficients of Al(III) ions.

Langmuir		Freundlich	
Q^0 (mg.g^{-1})	27.02	K_F	6.082
b (L.mg^{-1})	0.111	$1/n$	0.294
R^2	0.999	R^2	0.928

3.4 Adsorption Kinetics

Many studies have explained the experimental data of biosorption using different kinetic models [24]. Mostly, the mechanism of biosorption process are explained using different kinetic models but in this work, the employed kinetic models are the pseudo-first and the pseudo-second order kinetic models. The concentration of Al (III) ions concentration used for the kinetics study in this work was 80 mg/Lwhich produced the optimum removal yields. The pseudo-first- order model is premised on the assumption that the rate of changes in the uptake of the solute with time is directly proportional to the vatiation in saturation concentration and the quantity of solid uptake per time. The pseudo-first-order rate equation, as linearized by Lagergren (43), is given as:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad (9)$$

where q_e and q_t (mg/g) = the quantities of biosorbedsolutes (metal ions) at equilibrium (mg/g) and time t, respectively. The biosorption rate constants (K_1) can be experimentally determined by plotting of $\ln(q_e - q_t)$ versus t.

The experimental data was also fitted with the pseudo-second-order kinetic model; it is given thus (44):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} t \qquad (10)$$

where k_2 (g/(mg min)) = rate constant, $q_t$and q_e(mg/g) = quantities of biosorption at time t (min) and equilibrium.

It is more likely that the kinetic behaviour of biosorption can be better predicted by the pseudo-second order model, with chemical sorption being the rate-controlling step [2]. Figure 8 displys the linear plot of $\frac{t}{q_e}$ versust for the pseudo-second-order model for Al (III) biosorption by SUM 123while Table 2 give the values for the rate constant k_2, the R^2 and q_e. The experimental R^2 value of the plot is 0.993 and the experimental $q_{e, cal}$ values were closer to the experimental values. These findings suggest that the pseudo-second-order kinetic model performed better in terms of providing the correlation for the biosorption of Al(III) by the novel *Alcaligenes*sp SUM 123 than the pseudo-first-order model.
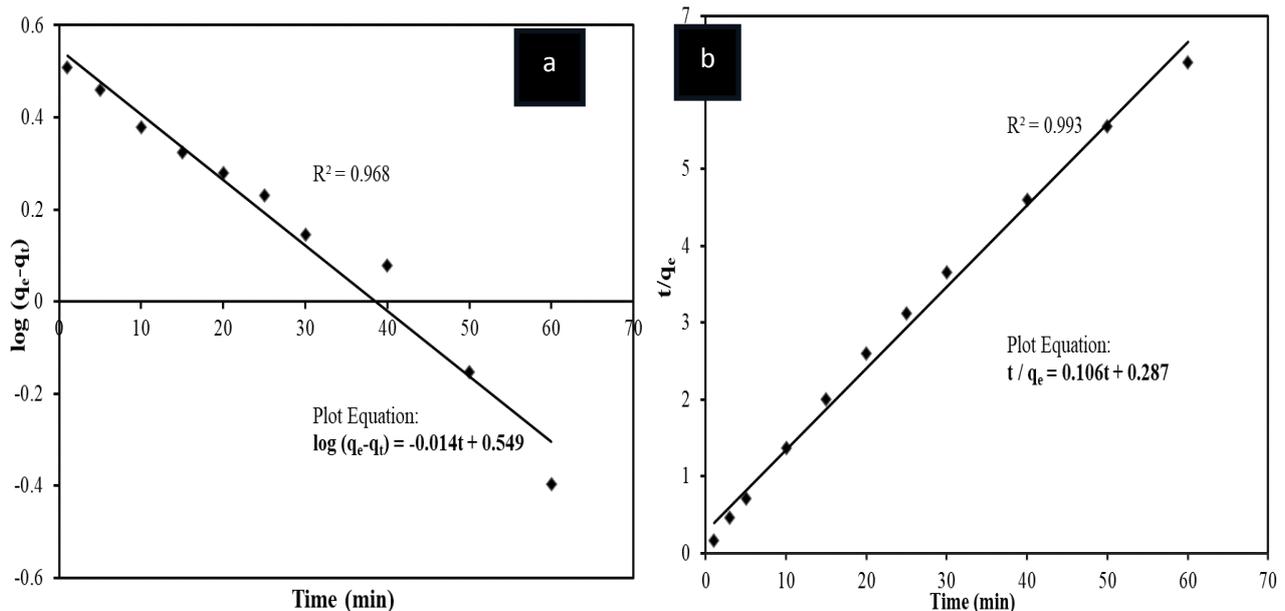
Figure 8. Kinetic model for [a] pseudo-first-order and [b] pseudo-second-order biosorption of Al (III) by SUM 123

Table 2: Obtained kinetic parameters using the pseudo-first and second-order modelsat the Al (III) ion concentration of 80 mg L^{-1} and SUM 123 biomass concentration of 12 g/L.

C_0 (ppm)	Pseudo-first order				Pseudo-second order		
	q_e (mg/g)	K_1 (min^{-1})	R^2		q_e (mg/g)	K_2 (min^{-1})	R^2
80	3.326	0.036	0.974		9.433	0.039	0.993

3.5   Thermogravimetric Analyses (TGA)

The effect of Al(III) ion on the thermal stability of the biosorbent was determined using TGA. Figure 9(a) shows the TGA curves of SUM 123 before and Figure 8(b) after loading with Al(III). This clearly reveals the interaction of Al(III) with the surfaces of the biosorbent. In Figure 9(b) the values of initial decomposition temperature were found to be 88 to 100 ºC for water molecules and a weight loss of 12%. The second decomposition temperature was observed in the range of 270 to 500 ºC, with a weight loss of 55%. These observationsare a result of the drastic removal of carboxylic groups and their combustion from the biomass. Final decomposition occurred in the range of 750 to 950 ºC with weight

loss of 40%, which was ascribed to the degradation of organic fraction of the studied biosorbent. In many cases, the decomposition rate of nanoscale Al/Fe is higher at temperatures above 650 ℃. However, beyond 650 ℃ a gradual weight loss occurred in the temperature range of 760-950 ℃. This gradual loss was attributed to the initial Al metal ions assisted decomposition upon its attachment to the biosorbent and subsequent formation of stable species such as metal oxide. This postulation was further affirmed as no weight loss was observed after 1000 ℃. However, exothermic event were present with the maximum rate of occurrence at about 480 ℃, and remained for Al-magnetite up to 512 ℃.
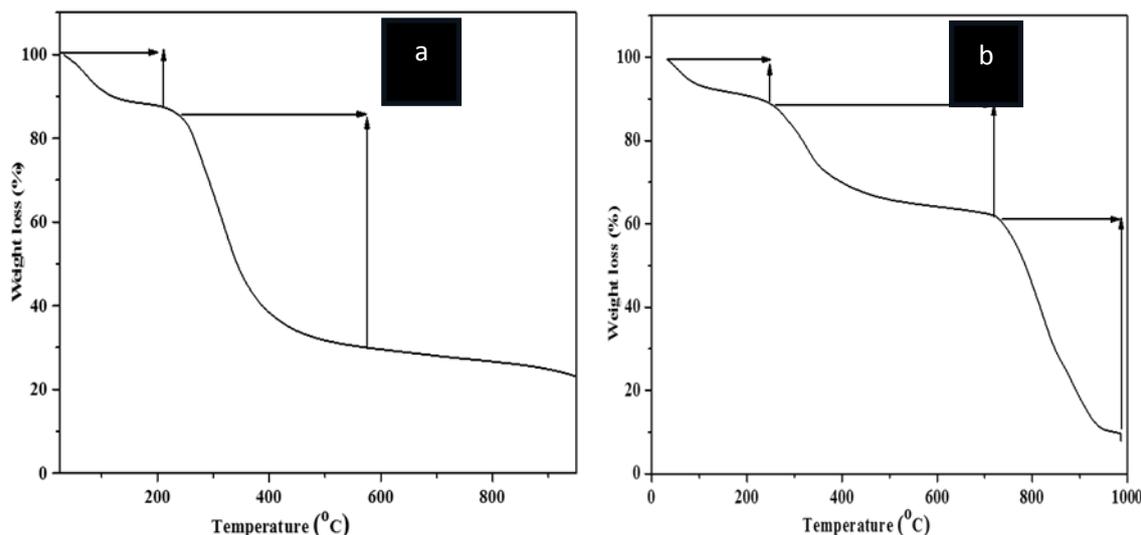
Figure 9. TGA curves of SUM 123 [a] before Al (III) ion loadings, [b] after Al (III) biosorption

3.6 Structural characterization by infrared spectroscopy analysis

The FTIR spectra as displayed in Figure 10 clearly revealed the bonding vibration corresponding to the cell-metal ions interaction. The strong and broad peaks at 3370-3400 cm^{-1} are contributed by the bounded OH- or NH- groups of the SUM 123 biomass while the peaks at 2927-2930 cm^{-1} are assigned to -CH_2 stretching vibration. The symmetric and asymmetric stretching vibration of C=O, C-N, and Amide I groups accounted for the peaks between 1660-1654 cm^{-1} while the presence of phosphate groups is indicated by the peak at 1405 cm^{-1}. The band at 539 cm^{-1} denotes the presence of Fe_3O_4 nanocrystalline. The vibration of Fe-O bonds of the crystalline lattice of Fe_3O_4 contributed the peak at 558 cm^{-1}.
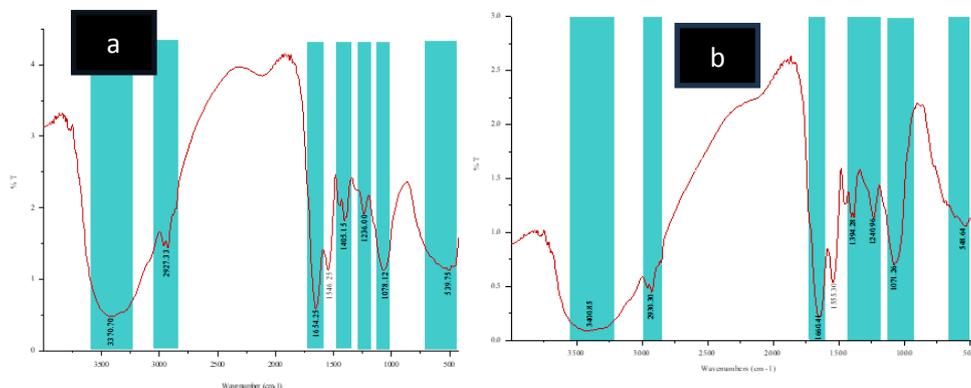
Figure 10. FTIR spectra of the cell-metal ions interaction for SUM 123 [a] unloaded-Al (III) biomass and [b] loaded-Al (III) biomass.

Table 3.FTIR band assignments for the surface functional groups present in strain *Alcaligenes*sp SUM 123

Surface Functional Group	Wave Number (cm^{-1})
Fe-OH	558
CH$_2$	2926
OH and NH stretching	3423, 2345, 2364
C=O	1654
C-O, C-N	1648
NH$_2$ bending	1637
C-N	1560
CN stretching	1534
CH	1458
P=O	1400
N-H	1238
O-H	1074

4.   Conclusion

This study havedemonstrated the successful isolation of a novel MTB strain - *Alcaligenes*sp SUM 123and determined their proficiency for Al (III) ionsadsorption inaqueous solution. The optimum conditions for efficient removal of Al (III) ions by this MTB strain MTB was observed at pH 5, 25 $^{\circ}$C temperature, 12 g.L^{-1}biomass concentration and sorption duration of 30 min. TheAl (III) ions biosorption performances of SUM 123 in aqueous solutions wasstudied viabiosorption kinetics and fitted in isotherm models. The Al (III) ions were rapidly biosorbed by the novel MTB strain, exhibiting a maximum uptake capacity of 23.46 mg.g^{-1} after 30 min contact time. The pseudo-second order equationperfectly fitted the kinetic data withcorresponding high regression coefficient value. Moreover, the Langmuir model provided better fitness of the equilibrium isotherm data than theFreundlich model. The presence of different functional gropus (hydroxyl, methyl, carboxyl, etc,) on the bacteria cell was confirmed by their corresponding FTIR spectra. The outstandingfeatures of thesenovel strain suggests that SUM 123 biomass-assisted biosorption is a prospective cost-effective, economic, and greener method for Al (III) recovery fromcontaminated waters.

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