

BIOSORPTION OF ALUMINIUM FROM SOLUTION BY DEAD *Aspergillus oryzae* BIOMASS ISOLATED FROM ALUMINIUM MILLS WASTE SITE**Omeike, S. O.^{1*}, Kareem, S. O.¹, Adewuyi, S.², Balogun, S. A.¹**¹Department of Microbiology, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria.²Department of Chemistry, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria.Corresponding Author: tutnefert@yahoo.com; Telephone: +2347035799179

(Received: December, 2012; Accepted: May, 2013)

ABSTRACT

Continuous use of aluminium in production process has increased its concentration in industrial effluents and the environment, therefore the need for its removal. This study focused on the possibility of aluminum sorption by metal-accumulating fungi biomass. *Aspergillus oryzae* biomass isolated from an aluminium industry waste site was used for sorption of Al³⁺ ions at low concentrations of 10-50 mg/L. Effect of contact time and pH on biosorption of aluminium ions from solution was also evaluated. The result showed that highest aluminium sorption was obtained at pH 6 after 24 hours. Langmuir and Freundlich isotherm constants described a feasible and favorable sorption process with a low maximum sorption capacity of 0.071 mg/g and high Langmuir constant, *b*, of 21.74; while the Freundlich isotherm was a better model for describing the sorption process. This study therefore showed that *A. oryzae* can be a better sorbent for use in aluminium sorption process with further improvement.

Keywords: Aluminium, *Aspergillus oryzae*, Biosorption, Isotherm, Langmuir, Freundlich.**INTRODUCTION**

Over the last few decades, there has been an increase in industrialization worldwide with Nigeria not left out. Several industries such as leather, paper, rubber, electroplating, iron, aluminium, steel and steel-related production mills have sprung up resulting in the increase in discharge of pollutants to receiving waters, causing undesirable effects on the aquatic environment (AAC, 2001).

The aluminium industry is the largest non-ferrous metal industry in the world economy, with demand for aluminium continuously increasing to around 45 million tonnes in 2004 and its application has extended to variety of economic sectors. Global demand and consumption of aluminum is expected to increase to approximately 57 million tonnes in 2020 (Husband *et al.*, 2009).

Aluminium, Al, may be produced from bauxite, its natural source, or from recycling of scrap metals (Zheng and Antonio, 2005). It is one of the most important metals used in recent times due to its excellent physical properties which make it possible for its use in a variety of products that are important and indispensable to modern life.

Aluminium in industries is used in the production

and design of several important materials and equipment including roofing sheets, household utensils, foil paper and several building materials etc. Other product in which aluminium is utilized in reduced quantity includes abrasives, cement, ceramics, chemicals, metallurgical flux, and refractory products (Bray, 2010b). Aluminium is also used, in combination as a salt, in the coagulation of sediments during water purification process (Ipeaiyeda *et al.*, 2012).

Due to its high economic activities in several industrial sectors and concomitant increase in projected use in the future, effluents emanating from these industries will also follow the same trend, resulting in increased concentration of aluminium in effluent discharged into the environment. Increasing toxicity of Al in the environment may eventually reach human bodies through the food chains; necessitating the need for its removal.

Removal of Aluminium from solution has been carried out mostly by adsorption on chemical materials such as resins, wood charcoal, date-pit and activated carbon (Lee *et al.*, 2004; Hubicki and W'ojcik, 2006; Choski and Jozi, 2007; Al-Muhtaseb *et al.*, 2008). Other adsorbents that have been used include biological materials such as rice husk carbon (Singh *et al.*, 2005).

Biosorption, a biological technique which uses dead bacterial, fungal or algal cells in the removal of metals from the environment has also been used in the active removal of aluminium from the environment. Organisms that have been used as biosorbent for aluminium sorption include *Providencia rettgeri*, *Chryseomonas luteola*, *Rhodococcus opacus* etc. (Abo-Amer *et al.*, 2012; Cayllahua and Torem, 2010; Chia-Chay *et al.*, 2009; Ozdemir and Baysal, 2004).

In Nigeria, for example, there has been very little study on the adsorption of aluminium either by chemical derivatives or biological materials, therefore, it is necessary to search for materials that will be suitable for aluminium degradation in the environment.

This study primarily aimed at investigating the possibility of isolating aluminium-accumulating fungal species and then observes its potential applications in the removal of aluminium from aqueous solution. The effect of pH on sorption capacity was also determined.

METHODOLOGY

Sampling

Soil of a solid waste dumping site of an aluminium industry in Lagos state was collected into sterilized polythene bags. The samples were taken at 10 cm depth into the soil and the sample bags were placed in a sterile container with ice packs before transferring to the laboratory for further analysis.

Fungal Isolation and Identification

Serial dilution of the soil sample (1 g) was prepared in 10 mL of de-ionized water. The diluents (1 mL) was plated out on sabouraud dextrose agar medium (SDA, Biorex, USA) at 30°C for 72 hours. Pure culture of each isolate was obtained by sub-culture and identified according to Barnett and Hunter (1972). Nine mould strains identified as *Penicillium chrysogenum*, *Aspergillus niger*, *Aspergillus clavatus*, *Aspergillus oryzae*, *Aspergillus fumigatus*, *Trichoderma longibrachiatum*, *Trichoderma reesei*, *Rhizopus sp.* were stored on agar slants at 4°C until required for further studies.

Screening for Aluminium-tolerant Fungi

Aluminium chloride salt ($\text{AlCl}_3 \cdot \text{H}_2\text{O}$) of analytical

grade was used in the preparation of a 1 L stock solution from which further dilutions were done. Spores of isolates were aseptically scrapped from the medium and added into cooled agar, swirled gently to mix with agar, dispensed into petri-dishes and allowed to gel. Wells were bored on solidified agar using a sterilized cork borer and 0.1ml solution of different aluminium concentrations (50, 100, 150 and 200 mg/L) was placed in each well. Plates were incubated at 30°C for 96 hours. Metal tolerance was determined by the zone of inhibition around the colonies. Isolate with zone size less than 1 mm was scored as a metal-accumulating isolate (Hemambika *et al.*, 2011).

Preparation of fungal biosorbent

Aspergillus oryzae cell mass was scrapped from the medium after 5 days of growth onto a foil and exposed to heat at 160°C for 2 hours in the hot-air oven (Gallenkamp, UK). The dead dry mass was ground using a dry laboratory blender and kept at room temperature till needed. Before use, the dry mass is exposed to heat in the hot-air oven for 1 hour at 160°C.

Equilibrium Parameters

Effect of equilibrium time was determined by adding 2 g of biosorbent into 100 mg/L of aluminium solution in an Erlenmeyer flask (Pyrex) and sorption proceeding at neutral pH attained by adjusting the solution using 0.1 M HCl and NaOH of analytical grade (Sigma, US), temperature 30°C various contact time of 24 hour intervals for 5 days in an orbital incubator (Gallenkamp, UK) operating at 100 rpm speed. At every interval, the rate of aluminium removal was determined by centrifuging the mixture using a bench-top centrifuge (Electrothermal, UK) and collecting the supernatant for analysis using an Atomic Absorption Spectrophotometer (Electrothermal, UK).

The effect of pH on sorption potential of aluminium ions by *Aspergillus oryzae* biosorbent was determined by adding 2g of biosorbent to 100 mL aluminium solution in an Erlenmeyer flask. The pH of the solution was adjusted within the range of 4-10 using 0.1 M HCl and NaOH solution. The mixture was incubated in an orbital incubator with speed of 150 rpm for 24 hours at

30°C. Residual aluminium concentration was determined as described above.

Biosorption Studies

Sorption potential of the fungal biomass at low metal concentration was determined by preparing aluminium solution with concentration range 10-50 mg/L at constant volume (100 mL). The pH of the solutions were corrected to the optimum and 2g of dead mass added to the solution. The mixtures in the Erlenmeyer flasks were incubated for 24 hours in the orbital incubator operating at 30 °C. Residual aluminium concentrations were determined as described earlier.

Equilibrium Isotherm

Rate of aluminium removal was calculated using the expression below:

$$\text{Percentage removal } \% = \frac{C - C_f}{C} \times 100 \quad (1)$$

$$\text{Metal Uptake, } q_e = \frac{V \cdot (C - C_e)}{S} \quad (2)$$

V (L) is the volume of Manganese salt solution, C and C_e the Initial and final aluminium concentration in solution (mg/L); while S is the mass of added biosorbent (g).

The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_o \cdot b} + \frac{1}{q_o} C_e \quad (3)$$

q_e and q_o are the actual and maximum metal uptake (mg/g); b is Langmuir constant which is related to the affinity of the sorbent to the sorbate.

The characteristics of the Langmuir isotherm expressed using the dimensionless equilibrium parameter, R_L is represented by the following equation (Weber and Chakkravorti 1974):

$$R_L = \frac{1}{1 + b \cdot C_o} \quad (4)$$

R_L value indicates the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

Linear form of the Freundlich model was used in explaining the sorption process as represented below:

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (5)$$

Amount of aluminium adsorbed at equilibrium is q_e (mg/g), C_e is the equilibrium concentration of the adsorbate (Al^{3+}) and K_F is the Freundlich constant.

RESULTS AND DISCUSSION

Metal Degradation Potential of Mold Isolates

The tolerance capacity of the mold isolates in relation to their zones of inhibition is described in Table 1. It was observed that only *Aspergillus oryzae*, with a 3.8 - 6 mm zone of inhibition from 50 mg/L can be classified as an aluminium-tolerant strain according to Hemambika *et al.* (2011). Other *Aspergillus* spp and *Trichoderma* spp. showed very minimal growth with zone sizes less than 1 mm, and observation of no growth at higher aluminium concentrations. This indicates that *Aspergillus oryzae* cell mass will be able thrive in the presence of aluminium (Duxbury, 1981).

Table 1: Tolerance Levels of Isolated Fungal Isolates to Different Concentrations of Aluminium Ions in Growth Medium

Organisms	Zone of Inhibition (mm)			
	50 mg/L	100 mg/L	150 mg/L	200 mg/L
<i>Aspergillus clavatus</i>	-	-	-	-
<i>Aspergillus fumigatus</i>	0.7	0.1	-	-
<i>Aspergillus niger</i>	0.9	0.5	-	-
<i>Aspergillus oryzae</i>	6	6	4	3.8
<i>Penicillium chrysogenum</i>	-	-	-	-
<i>Rhizopus</i> sp.	-	-	-	-
<i>Trichoderma longibrachiatum</i>	0.9	0.8	0.4	-
<i>Trichoderma reesei</i>	0.7	0.2	-	-

Effect of Equilibrium Time

Effect of equilibrium time on sorption is described in figure 1. Equilibrium interaction between the biosorbent and aluminium ions was attained at 24 hours with a removal rate of 43 %. The low removal rate can be as a result of low

interaction and intra-particle diffusion rate (Sangi *et al.*, 2008). Exclusion of binding sites for aluminium ions and other repulsive forces present on sorbent surface will also contribute to the reduced sorption rate observed beyond equilibrium (Qaiser *et al.* 2009).

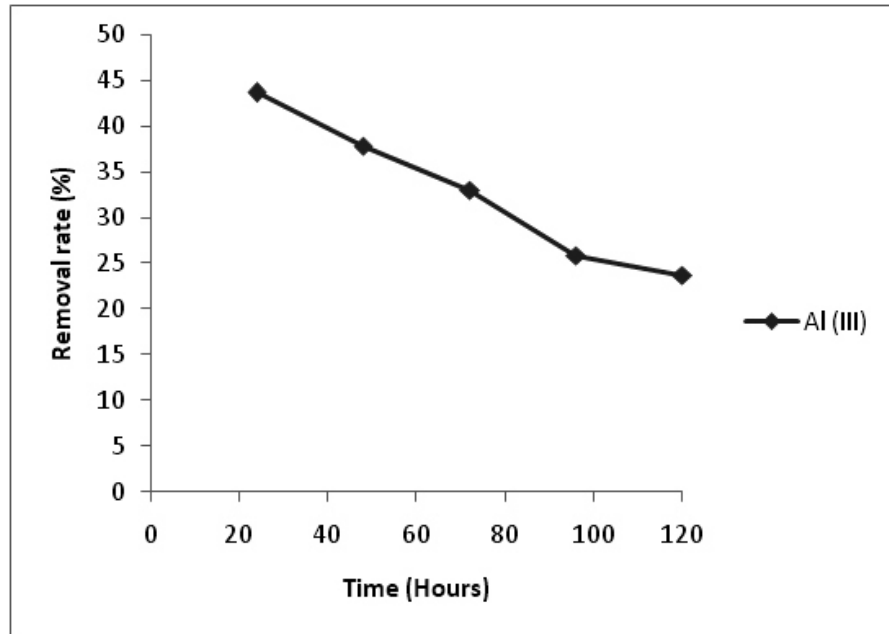


Figure 1: Effect of Equilibrium Time on the Sorption of Aluminium ions by *A. oryzae* Mass.

Effect of pH

As represented in Figure 2, the effect of pH on sorption potential of *Aspergillus oryzae* mass in aluminium solution showed that the highest aluminium sorption of 45 % was observed at pH

6. Similar result was reported by Hemambika *et al.* (2011) and it indicates the presence of weakly positive and neutral ions at the biomass surface which best interact with aluminium ions and bind them from solution (Bello *et al.*, 2008).

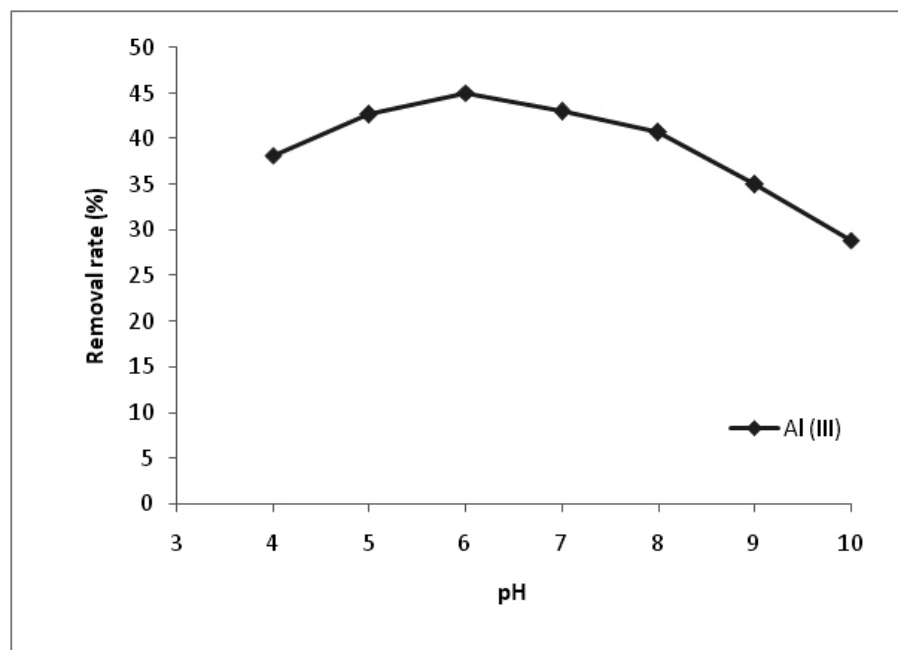


Figure 2: Effect of pH on Sorption Potential of Aluminium by *A. oryzae* Biomass.

Equilibrium Isotherms

Linear Langmuir yielded an isotherm plot with R^2 0.7996 which indicates good fit of aluminium sorption by the biosorbent (Figure 3). Low maximum sorption capacity calculated 0.071 mg/g indicates that although sorption process is favorable, sorption capacity of the biosorbent is low, while the dimensionless equilibrium parameter, R_L of 0.0009 also supports a feasible and favorable sorption process. (Weber and

Chakkravorti, 1974; Volesky, 2004).

A better fit of sorption values was observed with the Freundlich isotherm plot with R^2 of 0.8416 (Figure 4). Low Freundlich constant, K_F , 0.0949 was calculated, while the slope, $1/n$, was 0.684. These data describe a favorable surface sorption process occurring with low ions removal, while it also confirms a normal Langmuir curve (Adamson 2001; Fytianos *et al.*, 2003).

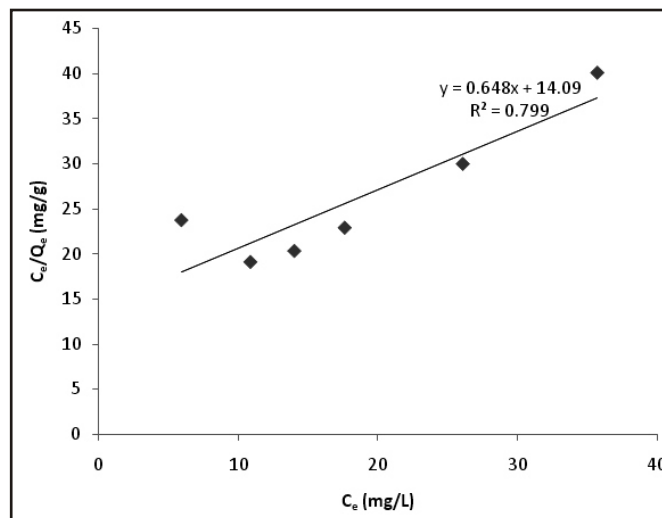


Figure 3: Linear Langmuir Isotherm Plot of the Sorption of Aluminium Ions on *A. oryzae* Biomass.

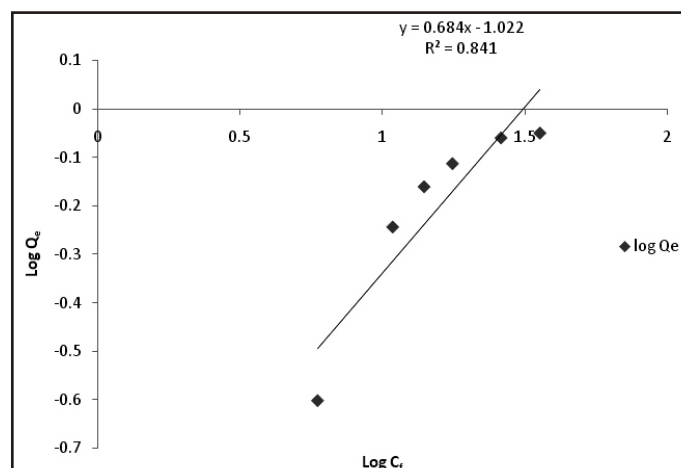


Figure 4: Linear Freundlich Isotherm Plot for the Sorption of Aluminium Ions on *A. oryzae* Biomass.

CONCLUSION

In conclusion, we have shown through this study that sorption of aluminium ions by dead mass of *Aspergillus oryzae* was a feasible and favorable process as explained by the isotherm models which occurred at a weak acid range and was optimum at 24 hours. However, a low sorption capacity of the biosorbent as recorded requires that further improvement which will aid increased

removal of aluminium ions from solution and possibly, from industrial effluents.

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