

BIOSORPTION OF MANGANESE (II) AND ALUMINIUM (III) IONS FROM AQUEOUS SOLUTION BY IMMOBILIZED *TRICHODERMA ASPERELLUM BHU216*

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ABSTRACT

Removal of Al^{3+} and Mn^{2+} from solution by *Trichoderma asperellum BHU216* immobilized on *Irvingia gabonensis* matrix in a batch system was investigated. Effect of biosorption conditions contact time, pH, bead size and spore load were studied. Equilibrium isotherms and re-usability of biosorbent were also determined. The result showed that optimum sorption of Mn^{2+} and Al^{3+} by immobilized sorbent was achieved at 7 mm bead size and 1.6 g l^{-1} spore load. Optimum pH were 5 and 6 while equilibrium was attained at 120 and 180 min for Mn^{2+} and Al^{3+} sorption respectively. Immobilized biosorbent was used in more than 5 batch cycles with over 50% removal achieved in 3 and 5 cycles for Al^{3+} and Mn^{2+} sorption. Brunauer-Emmett-Teller (BET) isotherm had the best-fit than both Langmuir and Freundlich isotherms for both metals (R^2 0.98 and 0.92 for Mn^{2+} and Al^{3+} respectively). Manganese sorption proceeded at both surface and multi-layer levels with high sorption rates 18.88 mg l^{-1} and 19.72 mg l^{-1} , while aluminium sorption was feasible in a multi-layer process with low uptake (0.87 mg g^{-1}). This study showed that immobilized *T. asperellum BHU216* can effectively act as biosorbent for Mn(II) and Al(III) sorption from solution.

KEYWORDS: Manganese (II), Aluminium (III), Immobilization matrix, *Irvingia gabonensis*, *Trichoderma asperellum BHU216*, Equilibrium Isotherm models.

INTRODUCTION

Effluents discharged by different industries contain metal ions which accumulate as toxic substances in the environment and pose major threats to human health as well as other living organisms (Kanu and Achi, 2011). Conventional chemical processes for metal removal include chemical precipitation, lime coagulation, ion exchange, reverse osmosis etc. These chemical methods have several disadvantages such as high processing cost and generation of toxic waste products that require disposal (Atkinson *et al.*, 1998). Alternative methods are required for the reduction of heavy metal concentration to acceptable levels in the environment at affordable cost, therefore the use of biological method of sorption which is effective, efficient and can be industrially applied in environmental protection and metal recovery (Volesky, 1990).

Biosorption which is the process of passive ion binding by dead or living biomass represents a cost-effective way of eliminating toxic heavy metals found in the environment (Kratochvil and Volesky, 1998). It is preferred to chemical methods due to absence of toxicity constraints, effective metal recovery amongst others. Different bacteria, fungi and seaweeds species used as biosorbents in the removal of manganese, aluminium and other metals from wastewater or solution has been reported (Wang and Chen, 2009).

The use of organisms as biosorbents is limited due to small size, operational instability and disintegration. Immobilization of biosorbents on suitable matrices which offers advantages including enhanced operational stability, ease of regeneration, increased effectiveness and re-usability have been used to solve the effects of these limitations (Volesky and Naja, 2005). Hydrogels such as

polyacrylamide, gelatine, calcium alginate and k-carrageenan have also been used as immobilization matrices (Sharanagouda and Karegoudar, 2002; Adhinarayana *et al.*, 2005; Ivanova *et al.*, 2010; Usha *et al.*, 2010; Vijayanand *et al.*, 2012). However, there is the need to search for other low-cost materials that can serve as effective immobilization matrices.

Irvingia gabonensis is a tree native to West Africa that produces very common seeds known by different native names in the region and are traditionally being used as thickening agents (Orwa *et al.*, 2009). The seeds have hydrocolloid property which suggests its possible use as an immobilization matrix for microbial cells.

This work focuses on effective sorption of manganese and aluminium ions from solution in a batch system by fungal biosorbent entrapped in *I. gabonensis* matrix.

METHODOLOGY

Substrate and Chemicals

Seeds of *I. gabonensis* were blended into powder form and defatted according to the method of AOAC (1995) before use in matrix preparation. *Trichoderma asperellum* BHU216 was obtained from the Microbiology department of the Federal University of Agriculture, Abeokuta, Nigeria. It was maintained on metal-supplemented Sabouraud dextrose agar, SDA (Biorex) and sub-cultured bi-monthly.

Chemicals were of analytical grade and used without further purification. Al (III) and Mn (II) solutions were prepared using $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$, respectively. Solution pH was adjusted using 0.1 M HCl and NaOH solutions prepared from a 1M stock. For all equilibrium studies, 100 mg l^{-1} of metal solutions was used with each experiment carried out in triplicate.

Preparation of biosorbent

Spores were prepared for biosorption experiments by exposure to 1M HCl for 30 min. Treated spores were rinsed in excess water, dried and weighed to constant mass.

Immobilization of biosorbent

Immobilization of prepared *T. asperellum* BHU216 was carried out using a modified method of Kareem *et al.*, (2013). *I. gabonensis* powder (6% w/v) was cross-linked by glutaraldehyde solution (2.5% v/v) at room temperature and stirred continuously for 10 minutes. Prepared biosorbent (2 g l^{-1}) was mixed the cross-linked *I. gabonensis* slurry under vigorous stirring at 30 °C. Gel mixture was made into spherical beads by injecting drop-wise into absolute ethanol solution (100% v/v), the stabilizing solution for 24 hours.

Immobilized beads were rinsed thoroughly in excess water and dried at 40 °C for 20 minutes before use.

Biosorption studies

Effect of equilibrium time on sorption of Mn^{2+} and Al^{3+} ions from solution was determined by adding immobilized *T. asperellum* BHU216 to metal solutions in a conical flask and incubated at 30 °C in an orbital incubator (Gallenkamp, UK) operating at 100 rpm speed and monitored at 3-hour interval for 6 hours. At each interval, level of metal sorption was determined through the residual metal ions concentration in solution using the Atomic Adsorption Spectrophotometer, AAS (Electrothermal, UK). The effect of pH was investigated by placing immobilized biosorbent in Mn and Al solutions adjusted to pH range 3 – 9 using 0.1 M HCl and NaOH. Solutions of different pH were incubated appropriately and sorption rate determined.

Effect of initial mass of *T. asperellum* BHU216 loaded in matrix was investigated by varying the biosorbent mass ($2 - 10 \text{ g l}^{-1}$) mixed with the cross-linked matrix slurry. Beads with different sorbent loads were placed in the metal solutions and sorption proceeded appropriately.

Effect of matrix size on sorption was determined by immobilizing sorbent in beads of different diameter (4 – 8 mm) by varying volume of gel mixture injected into stabilizing solution. The different bead sizes containing constant immobilized sorbent were placed in metal solutions and sorption proceeded appropriately.

Percentage removal and amount of Mn and Al ions adsorbed onto the immobilized biosorbent (per gram of immobilized sorbent) was determined using the following expressions:

$$\text{Percentage removal (\%)} = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

$$q = \frac{V \times (C_0 - C_f)}{S} \quad (2)$$

Where q (mg g^{-1}) is the amount of metals adsorbed onto the immobilized biosorbent, C_0 and C_f (mg l^{-1}) are the initial and final concentrations of the metals in the solution respectively; V (l) is the volume of the solution and S (g) is the dry weight of the immobilized sorbent.

Re-usability study

Immobilized biosorbent beads were harvested after each batch cycle, rinsed thoroughly in doubly deionized H_2O and dried at 40°C for 20 minutes. The dry beads were re-used by placing in 100 mg l^{-1} of Mn and Al solutions and sorption proceeded under optimized conditions with rate of sorption determined. The procedure was repeated until loss of activity and/or bead disintegration.

Equilibrium Isotherms

Sorption of Mn and Al by immobilized *T. asperellum* BHU216 was carried out at different initial metal concentrations ranging between $50 - 200 \text{ mg l}^{-1}$ at optimized sorption conditions. Langmuir, Freundlich and BET models were applied to interpret equilibrium values.

Langmuir isotherm model was used in equilibrium interpretation (Langmuir, 1916) and its linear form of was expressed by the following equation:

$$\frac{C_e}{Q_e} = \frac{1}{Q_0} b + \left(\frac{1}{Q_0}\right) C_e \quad (3)$$

Where C_e (mg l^{-1}) is the equilibrium metal concentration, Q_e (mg g^{-1}) the amount of metal ions adsorbed per unit mass of sorbent, Q_0 (mg g^{-1}) is the maximum adsorption capacity and b is the Langmuir constant. A linear plot of C_e/Q_e against C_e is created from which other constants will be determined.

Essential features of a Langmuir isotherm used to predict if an adsorption system is favorable or unfavorable is expressed by a dimensionless equilibrium constant, R_L and is represented by the expression:

$$R_L = \frac{1}{[1 + (b \times C_0)]} \quad (4)$$

C_0 (mg l^{-1}) is the highest metal concentration solution used in biosorption study. Values of R_L indicates the sorption process to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L \leq 0$).

Freundlich model is also used to describe surface sorption (Freundlich, 1906), with the linear form of this model expressed by the equation below:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (5)$$

A plot of $\log q_e$ against $\log C_e$ will give a linear curve from which values of the Freundlich constant, K_f , and slope, $1/n$, of the curve will be determined.

The BET model describes multi-layer adsorption observed by an increase in metal sorption at high metal concentrations (Bruanuer *et al.*, 1938). The equation is expressed as:

$$q = \frac{BQC_e}{(C_s - C_e) \left[1 + (B-1) \left(\frac{C_e}{C_s} \right) \right]} \quad (6)$$

The BET constant, B , describes the extent of multi-layer adsorption; Q is the amount of metal adsorbed in forming a complete monolayer on the surface; q is amount of metal uptake at multi-layer levels; C_s is the saturation constant of the solute; and C_e the final metal concentration.

RESULTS AND DISCUSSION

Effect of Contact time

The effect of equilibrium time on Mn^{2+} and Al^{3+} ions removal was described in Figure 1. Uptake of Mn^{2+} and Al^{3+} ions by immobilized *T. asperellum BHU216* attained equilibrium at 120 and 180 min with high removal rates 81% and 79% respectively. Similar equilibrium time was reported in the sorption of Cu(II) ions from solution by different chitosan-prepared gel adsorbents (Julkapli *et al.*, 2013). More than 50% removal was achieved in 1 hr, indicating the presence and availability of high number of vacant active sites for binding of the metals at the initial stage of the sorption process. Reduced sorption beyond equilibrium time can be attributed to the presence of repulsive forces between metal ions and the immobilized sorbent, and exhaustion of binding sites (Qaiser *et al.*, 2009; Gupta *et al.*, 2011).

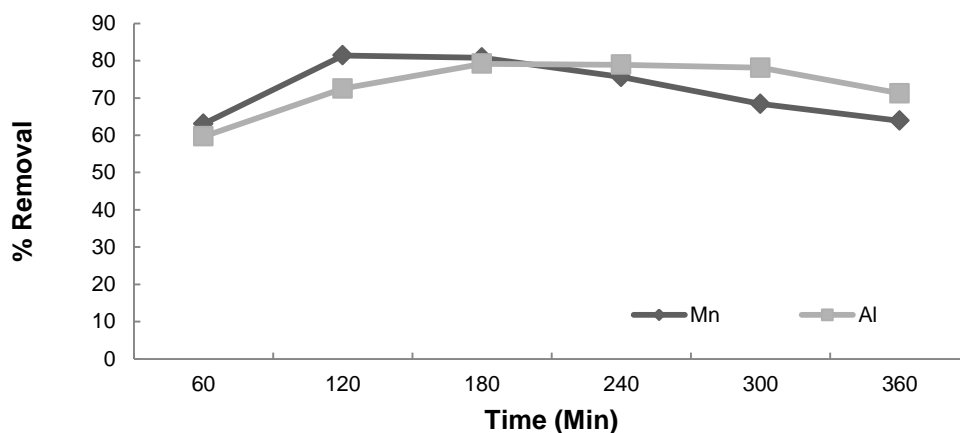


Figure 1. Effect of contact time on sorption performance of immobilized *T. asperellum BHU216*

Effect of pH

Effect of pH on sorption performance of immobilized *T. asperellum BHU216* is described in Figure 2. Optimum sorption of Mn^{2+} and Al^{3+} ions occurred at acidic pH 5 and 6 respectively, indicating the presence of negative ions on biosorbent surface interacting and binding Mn^{2+} and Al^{3+} ions in solution to their surface (Vijaya *et al.*, 2010).

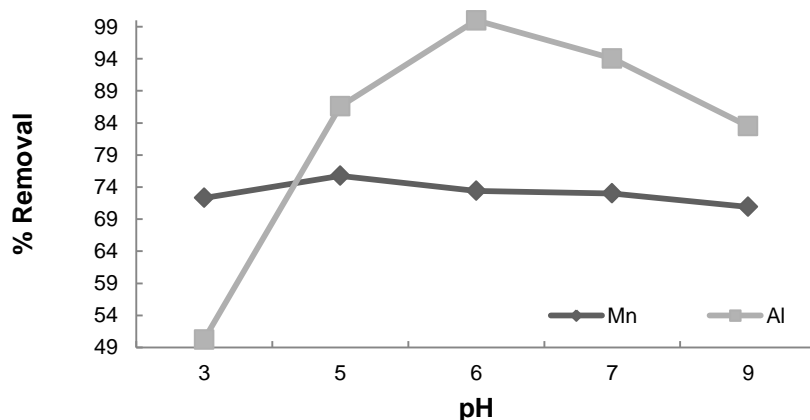


Figure 2. Effect of pH on sorption performance of immobilized *T. asperellum BHU216*

Similar pH optimum was reported in the removal of Cu^{2+} , Cd^{2+} and Pb^{2+} from solution by fungal strains of *Aspergillus sp.*, *Penicillium sp.* and *Cephalosporium sp.* (Hemambika *et al.*, 2011). High sorption of Mn^{2+} and Al^{3+} ions (> 50%) observed at pH 5-9 shows *T. asperellum BHU216* is effective over a wide pH range.

Effect of bead size

Bead size also had a significant effect on Mn^{2+} and Al^{3+} ions sorption from solution by *I. gabonensis*-immobilized *T. asperellum BHU216* as described in Figure 3. The bead size determines the number of available spaces accessible for the interaction of biosorbent with the metal ions. Optimum Mn^{2+} and Al^{3+} removal of more than 83% by immobilized *T. asperellum BHU216* was observed at 7 mm bead size. This indicates the availability of highest amount of pore spaces for sorbent-metal interaction and ions uptake. At lowest bead size 4 mm, 70% removal was attained and removal rate increased with increased bead size till optimum size. Increasing sorption with increased bead size can be attributed to presence of more pore spaces for sorbent-metal interaction. Reduced sorption capacity beyond optimum matrix size observed could be due to excess solute in the matrix which may influence the release of previously adsorbed ions (Badyal *et al.*, 2004). Also, presence of excess solute results in matrix swelling which could affect binding site availability and therefore reduce sorbent-sorbate interaction in the matrix.

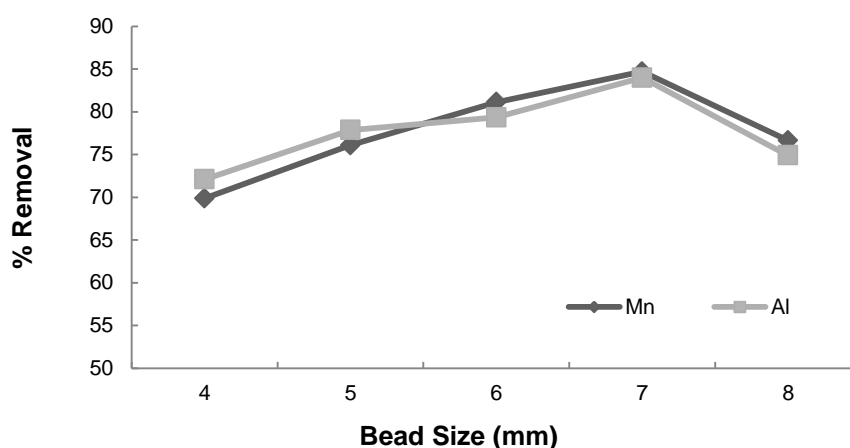


Figure 3. Effect of Bead size on sorption performance of immobilized *T. asperellum BHU216*

Effect of Spore Load

Effect of spore load on interaction and uptake of sorbate from solution is described in Figure 4.

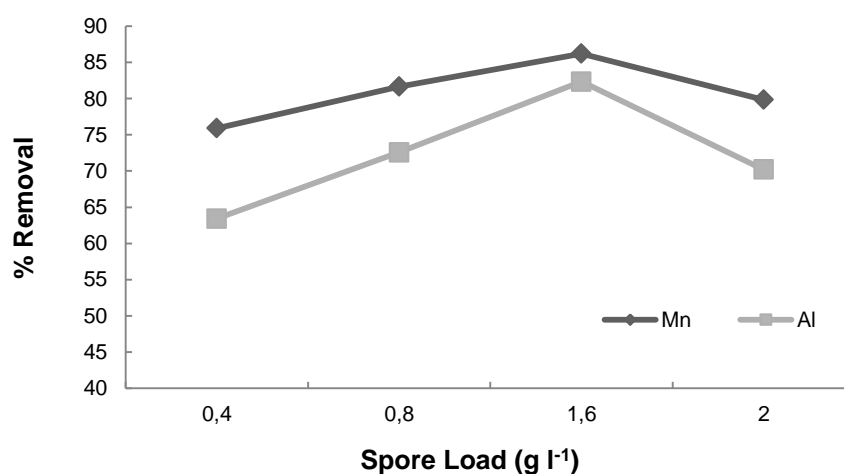


Figure 4. Effect of spore load on sorption performance of immobilized *T. asperellum BHU216*

Optimum sorption of Mn^{2+} and Al^{3+} (86 and 82%) was obtained when immobilized spore load was increased to 1.6 g l^{-1} while further increase in sorbent load within the matrix to 2 g l^{-1} resulted in reduced sorption. Similar conclusion has been proposed that low sorbent dose can promote increase metal removal and efficiency (Aksu and Cagatay, 2006). At higher spore loading above the optimum, accumulation of biosorbent could cause spores clogging within the matrix, resulting in screening of binding sites and limiting the biosorption process (Malkoc and Nuhoglu, 2003).

Re-usability of *I. gabonensis* – immobilized *T. asperellum* BHU216

The potential use *I. gabonensis*-immobilized *T. asperellum* BHU216 in different batch sorption cycles was described in Figure 5. Immobilized biosorbent was used for 6 and 9 batch cycles with over 50% removal of Al^{3+} and Mn^{2+} ions observed in 3 and 6 cycles respectively. This compares with the repeated use of polyacrylamide, gelatine beads and K-Carrageenan (Adhinarayana *et al.*, 2005; Vijayanand *et al.*, 2012). Higher number of cycles achieved for Mn^{2+} sorption can be attributed to the reduced equilibrium time compared to Al^{3+} sorption. Subsequent loss of activity which has also been reported can be attributed to cell leakage (Sharanagouda and Karegoudar, 2002; Usha *et al.*, 2010). Loss of activity attributed to cell leakage can be as a result of gradual shrinkage of matrix size after batch cycle (data not provided). Immobilization matrix did not disintegrate after loss of activity and therefore disagrees with reports of activity loss linked to matrix disintegration reported elsewhere (Trevors *et al.*, 1998; Sharanagouda and Karegoudar, 2002; Usha *et al.*, 2010). Re-usability and stability exhibited by *I. gabonensis* matrix presents it as a favourable matrix for immobilization of fungal cells and subsequent use in biosorption of metals.

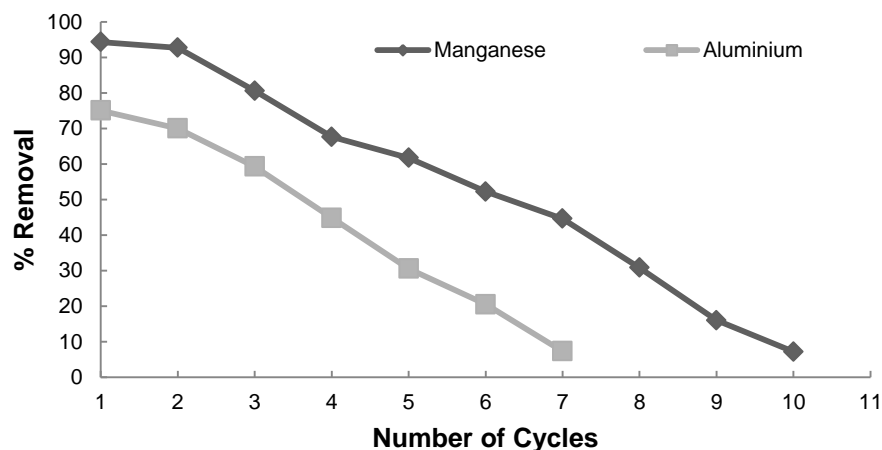


Figure 5. Re-usability of immobilized *T. asperellum* BHU216 on removal of Mn and Al from solution

Adsorption Isotherms

Equilibrium isotherms described by the Langmuir, Freundlich and BET models were described in Figures 6-8 respectively. Langmuir isotherm plot (Figure 6) described better fit for Mn^{2+} sorption ($R^2=0.93$) than Al^{3+} sorption ($R^2=0.598$), indicating that Langmuir model does not suitably explain Al sorption mechanism due to non-expressive Langmuir constants (Table 1). High maximum Mn^{2+} uptake ($Q = 18.88\text{ mg g}^{-1}$) indicates high surface interaction of manganese ions with *T. asperellum* BHU216 spores, while no surface interaction was deduced for aluminium sorption ($Q = -0.76$).

Also, the dimensionless equilibrium parameter, R_L value less than one indicates favorable Mn^{2+} sorption process ($R_L = 0.0007$) while R_L less than zero describes an irreversible co-operative process for Al^{3+} sorption process ($R_L = -0.0001$) (Weber and Chakravorti, 1974).

Linear Freundlich isotherm described good fit for both Mn and Al sorption (Figure 7). High Freundlich constant, K_F , observed for Mn^{2+} but very low K_F for Al^{3+} sorption. This indicates favorable surface sorption of Mn^{2+} ions but otherwise for Al^{3+} ions (Aksu and Cagatay, 2006). Also, slope, $1/n$, was < 1 for Mn sorption and > 1 for Al sorption. This confirms a normal Langmuir curve for Manganese and co-operative Al^{3+} sorption (Fytianos *et al.*, 2003).

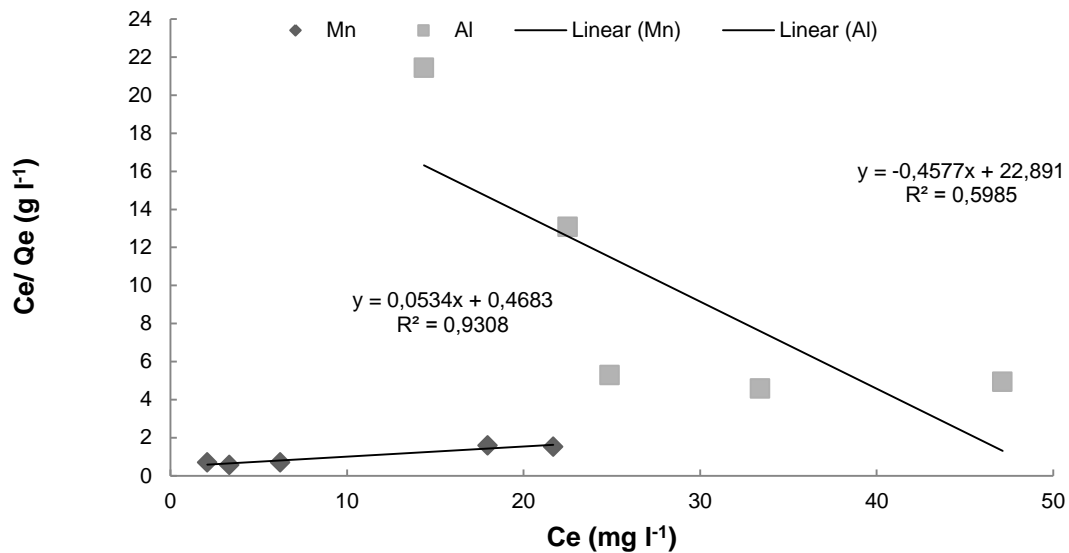


Figure 6. Linear Langmuir adsorption isotherm for the biosorption of Mn^{2+} and Al^{3+} on immobilized *T. asperillum* BHU216.

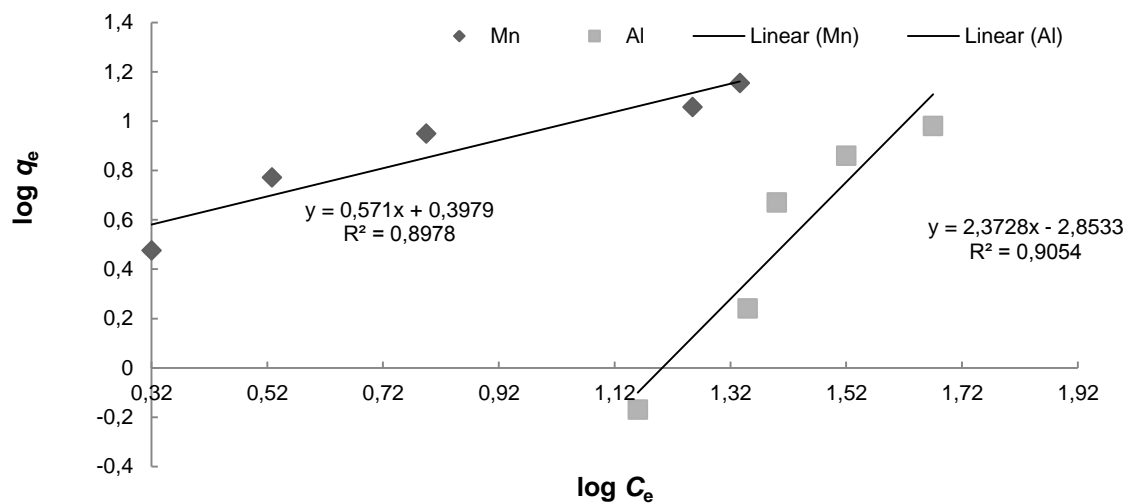


Figure 7. Freundlich adsorption isotherm for the biosorption of Mn^{2+} and Al^{3+} on immobilized *T. asperillum* BHU216.

The BET isotherm described good fit of both Mn and Al sorption isotherm plot with $R^2 > 0.97$ (Figure 8). BET constant, B, relates to the energy of interaction with the surfaces within the matrix and $B > 1$ observed for Mn^{2+} ion removal indicates continuous multi-layer sorption, while $B < 1$ for Al^{3+} sorption describes reduction of multi-layer sorption to monolayer process (Volesky, 2004).

Table 1. Summary of isotherm constants for Mn(II) and Al(III) ions sorption at 30 °C

	Langmuir				Freundlich			BET		
	Q	b	R_L	R^2	K	1/n	R^2	B	Q	R^2
Mn (II)	18.88	6.98	0.0007	0.93	2.5	0.57	0.89	1.04	19.72	0.98
Al (III)	-0.76	-50.9	-0.0001	0.598	0.002	2.35	0.91	0.524	0.87	0.92

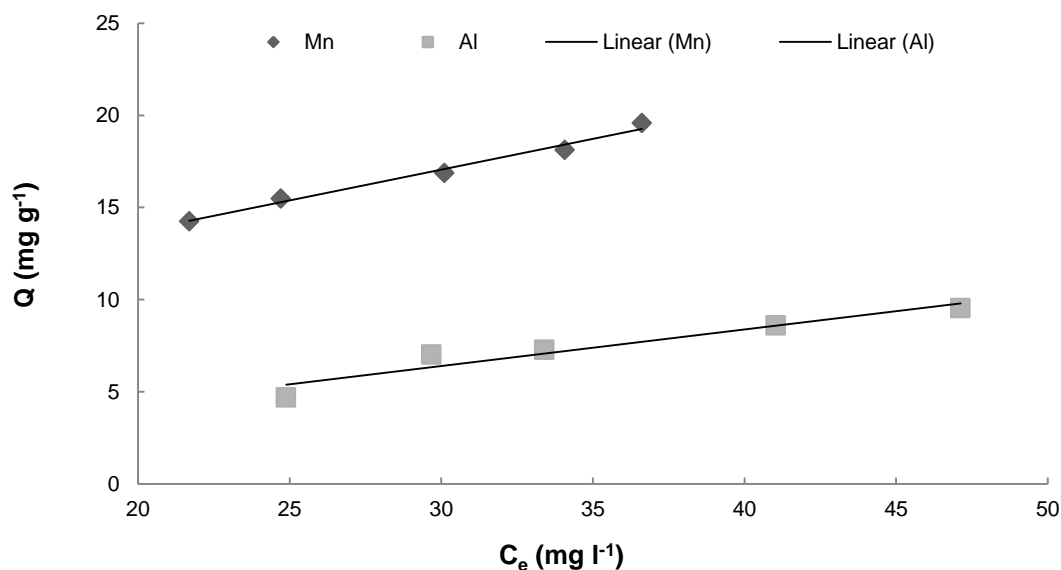


Figure 8. BET isotherm for the biosorption of Mn²⁺ and Al³⁺ on immobilized *T. asperellum* BHU216

CONCLUSIONS

The present study showed that immobilized *T. asperellum* BHU216 was able to remove 19.72 mg g⁻¹ and 0.87 mg g⁻¹ of both Mn and Al ions from solution. It was also shown that Immobilization of *T. asperellum* BHU216 on *I. gabonensis* matrix allows for both surface and multilayer sorption of Mn and Al by the immobilized biosorbent. Furthermore, high sorption activity and matrix stability in re-usability study presents *I. gabonensis* matrix as an alternative to conventional matrices.

REFERENCES

- Adhinarayana K., Jyothi B. and Ellaiah P. (2005), Production of alkaline protease with immobilized cells of *Bacillus subtilis* PE-11 in various matrices by entrapment technique, *AAPS Pharm. Sci. Technol.*, **6**, 91-97.
- Aksu Z. and Çağatay S.S. (2006), Investigation of biosorption of GemazolTurquoise Blue-G reactive dye by dried *Rhizopusarrhizus* in batch and continuous systems, *Sep. Pur. Technol.*, **48**, 24–35.
- Atkinson B.W., Bux F. and Kasan H.C. (1998), Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents, *Water SA.*, **24**, 129–135.
- Badyal J.P., Cameron A.M., Cameron N.R., Oates L.J., Øye G., Steel P.G., Davis B.G., Coe D.M. and Cox R.A. (2004), Comparison of the effect of pore architecture and bead size on the extent of plasmachemical amine functionalisation of poly (styrene-codivinybenzene) permanently porous resins, *Polymer*, **45**, 2185–2192.
- Bruanuer S., Emmett P.H. and Teller E. (1938), Adsorption of gases in multimolecular layers, *J. Am. Inst. Chem. Eng.*, **60**, 309–316.
- Freundlich H.M.F. (1906), Over the adsorption in solution, *J. Phy. Chem.*, **57**, 385–471.
- Fytianos K., Voudrias E. and Kokkalis E. (2003), Sorption – desorption behavior of 2, 4 -dichlorophenol by marine sediments, *Chemosph.*, **40**, 3 – 6.
- Gupta A., Yadav R. and Devi P. (2011), Removal of hexavalent chromium using activated coconut shell and activated coconut coir as low cost adsorbent, *The IIOAB J.*, **2**(3), 8-12.
- Hemambika B., Kannan V.R. and Rani M.J. (2011), Biosorption of heavy metals by immobilized and dead fungal cells: A comparative assessment, *J. Eco. Nat. Environ.*, **3**(5), 168-175.
- Ivánová D., Horvathova H., Kadukova J. and Kavulicova J. (2010), Stability of immobilized biosorbents and its influence on biosorption of copper, *Nova Biotechnologica*, **10**(1), 45-51.

- Julkapli N.M., Ahmad Z. and Md Akil H. (2013), Preparation, characterization, equilibrium, isotherm and kinetic studies of crosslink chitosan for adsorption of Cu(II) ions, *Malay. Polymer J.*, **8**(1), 14-26.
- Kanu I. and Achi O.K. (2011), Industrial Effluents and Their Impact on Water Quality of Receiving Rivers in Nigeria, *J. Appl. Technol. Environ. San.*, **1**(1), 75-86.
- Kareem S.O., Oladipupo I.O., Omemu A.M. and Babajide J.M. (2013), Production of citric acid by *Aspergillusniger* immobilized in *Detarium microcarpum* matrix, *Malay. J. Microbiol.*, **9**(2), 161-165.
- Kratochvil D. and Volesky B. (1998), Advances in the biosorption of heavy metals, *Trend. Biotech.*, **16**, 291–300.
- Langmuir I. (1916), The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.*, **38**(1), 2221–2295.
- Malkoc E. and Nuhoglu Y. (2003), The Removal of chromium (VI) from synthetic wastewater by *Ulothrixzonata*, *Fres. Environ. Bull.*, **12**(4), 376–381.
- Orwa C., Mutua A., Kindt R., Jamnadass R. and Simons A. (2009) Agroforestry Database: A tree reference and selection guide version 4.0. <http://www.worldagroforestry.org/af/treedb/>
- Qaiser S., Saleemi A.R. and Umar M. (2009), Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: Batch and column study, *J. Haz. Mat.*, **166**(2-3), 998–1005.
- Sharanagouda U. and Karegoudar T.B. (2002), Degradation of 2- methyl-naphthalene by free and immobilized cells of *Pseudomonas* sp. strain NGK1, *World J. Microbiol. Biotech.*, **18**, 225-230.
- Trevors J.T., Elsas V.J.D. and Lee H. (1992), Use of alginate and other carriers for encapsulation of microbial cells for use in soil, *Microbiol. Release*, **1**, 61-69.
- Usha M.S., Sanjay M.K., Gaddad S.M. and Shivannavar C.T. (2010), Degradation of H-Acid by Free and Immobilized cells of *Alcaligeneslatus.*, *Braz. J. of Microbiol.*, **41**, 931-945.
- Vijaya B., Saradhi S., Rao R.K., Kumar P., Vijetha P., Rao V. and Kalyani G. (2010), Applicability of Freundlich and Langmuir theory for biosorption of Chromium from aqueous solution using test of Sea urchin, *Int. J. of Chem. Eng. Res.*, **2**(2), 139-148.
- Vijayanand S., Hemapriya J., Selvin J. and Kiran S. (2012), Operational Stability and Reusability of *Halobacterium* sp. JS Cells 1 Immobilized in Various Matrices for Haloalkaliphilic Protease Production, *Int. J. Microbiol. Res.*, **3**(1), 1-6.
- Volesky B. (1990) Removal and recovery of heavy metals by biosorption. In: Volesky B. (ed.), Biosorption of heavy metals. CRC Press, Boca Raton, FL, 7-43.
- Volesky B. 2004, Sorption and biosorption. BV Sorbex, Quebec, pp. 320.
- Volesky B. and Naja G. (2005), Biosorption: Application Strategies. International Biohydrometallurgy Symposium, Cape Town, South Africa.
- Wang J. and Chen C. (2009), Biosorbents for heavy metals removal and their future, *Biotech. Adv.*, **27**, 195–226.
- Weber T.W. and Chakkravorti R.K. (1974), Pore and solid diffusion models for fixed-bed adsorbers, *J. Am. Inst. Chem. Eng.*, **20**, 218–228.