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REMOVAL OF Mn(II) AND Fe(II) BY *Aspergillus Sp. TU-GM14* IMMOBILIZED ON *Detarium Microcarpum* MATRIX

KAREEM S.O.[1]
OMEIKE S.O.[2]*
BALOGUN S.A.[1]
ADEWUYI S.[1]

[1]*Department of Microbiology, Federal University of Agriculture*
PMB 2240, Abeokuta, Ogun State, Nigeria
[2]*Institute for Human Resources Development*
Federal University of Agriculture
PMB 2240, Abeokuta, Ogun State, Nigeria

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**to whom all correspondence should be addressed:*
e-mail: tutnefert@yahoo.com

ABSTRACT

Removal of Fe(II) and Mn(II) ions from aqueous solution by fungal biosorbent *Aspergillus sp. TU-GM14*immobilized on *Detarium microcarpum* matrix was investigated in this study. Effects of biosorption parameters pH, biosorbent concentration, bead size and equilibrium time on Fe(II) and Mn(II) ions sorption were also determined. Equilibrium was attained within in 3 hours while optimum Fe(II) and Mn(II) ions removal was observed at pH 6, 8 mm bead size, 2 g l^{-1} spore load respectively. Adsorption capacity was described using Langmuir, Freundlich and BET isotherm models. The experimental data fitted best to the Freundlich model (R^2 0.992 and 0.996 for Mn(II) and Fe(II) respectively). Favourable surface sorption process was described by Langmuir isotherm for both metals (Q_{max} 34 and 14 mg g^{-1} for Mn(II) and Fe(II) ions) while the BET isotherm constant, B, described high metals sorption beyond the biosorbent surface in a multi-layer sorption process (4.8 and 9.0 for Mn(II) and Fe(II) respectively). Results of the study showed that *Aspergillus sp. TU-GM14* biosorbent can remove large quantities of Fe(II) and Mn(II) ions from solution in both surface and multi-layer sorption process with *Detarium microcarpum* acting as a cheap immobilization matrix.

Keywords: Biosorption, Manganese (II), Iron (II), immobilization, *Detarium microcarpum*, *Aspergillus sp. TU-GM14*, isotherm model.

1. Introduction

Continuous industrialization and improvement of industrial processes has resulted in concomitant increase of effluent volume released into the environment, especially into water bodies. These effluents discharged contain mostly toxic waste substances, with heavy metals a major constituent.

Industries including steel, electroplating and metal finishing, metallurgical, chemical manufacturing, mine drainage, battery manufacturing, pigment manufacturing industries *etc.* are culpable in the release of heavy

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metals such as Mn(II), Fe(II), Pb(II), Cr(III) *etc.* into water bodies. Presence and accumulation of heavy metals in water bodies could have harmful effects on the environment and organisms found in it.

Manganese and Iron are naturally-occurring metals that constitute 0.1% and 0.5% respectively of earth's crust (EPA, 2004). They are present in raw materials for metal manufacturing companies where they are further deposited in the environment as effluent.

Manganese and Iron act as essential nutrients for humans but their presence in high quantity could result in harmful effects. They are reported to be present in the environment at high concentration (0.5-20 mg l^{-1}), while the regulating agency has set a sanitary limit of 0.5-20 mg l^{-1} (EPA, 1996; EPA, 2004; Davison *et al*., 2005), therefore necessitating their removal from the environment. Also, exposure to these metals sources result in epidemiological conditions, most debilitating being the different neurodegenerative disorders (Sullivan, 1981; Kondakis *et al.,* 1989; ATSDR, 2000; Perez *et al.,* 2010), thereby necessitating the need for total removal or reduction to safe-level concentrations in the environment.

Biosorption is the use of biological materials to sequester metals from solution through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). Biosorption technology has replaced previously used chemical procedures for removing metal ions from solution such as chemical precipitation, coagulation, ion exchange, reverse osmosis and solvent extraction due to their cost, high environmental toxicity and generation of sludge which reduces efficiency and effectiveness (Kratochvil and Volesky, 1998). Biosorption which involves the passive uptake of toxicants by dead/inactive biological materials or by materials derived from biological sources offers advantages such as low cost, high efficiency, sorbent regeneration and re-use, sludge minimization sludge, no nutrient requirement and the possibility of metal recovery (Volesky, 1990; Veglio and Beolchini, 1997).

Different metals have been sequestered from solution and in effluents using products of biological origin with comparative result (Kannan and Veemaraj, 2010; Oliveira *et al*., 2010). Similarly, recent biosorption studies of potential Fe(II) and Mn(II) ions removal have been investigated using various agricultural wastes and their products (Adeogun *et al.*, 2011; Rose and Rajam, 2012; Adeogun *et al*., 2013; Moghadam *et al.*, 2013), however there is little to no work on the use of microscopic molds for Mn(II) and Fe(II) removal, therefore the need to search for microscopic fungal biosorbents with Manganese and iron removal potential. These organisms are ubiquitous in the environment and are used widely in different food/pharmaceutical industries such as breweries, antibiotics, fermented foods production and enzyme-producing industries *etc*. where they are generated as waste which can be obtained free in the environment. Fungi biosorbents are easy to grow, produce high yields of biomass and can be manipulated genetically and morphologically, which may result in better raw biosorbent materials (Volesky, 1990). Also, their immobilization on suitable matrices could result in continuous use and therefore, cost reduction.

Detarium microcarpum is a high yielding tree native to the rain forest and savannah of tropical Africa (Hopkins and Stanfield, 1966). Its seeds, used as a traditional soup thickener in Nigeria and some other West African countries, have gelling and thickening properties (Onweluzo *et al*., 1999). This is due to the presence of mucilage, a thick gluey substance containing polar glycoproteins and exopolysaccharide sugars in the seeds which aid its thickening and stabilizing property. The seed's properties are well known and are applied in food processes; however their ability to form immobilization matrix has not been reported,

This study was carried out to investigate the potential of *Aspergillus sp. TU-GM14* immobilized on *D. microcarpum* in the removal of Mn(II) and Fe(II) ions from aqueous solutions.

2. Materials and methods

2.1 Chemicals and Substrate

Stock solutions of Mn(II) and Fe(II) ions (500 mg l^{-1}) were prepared using $MnSO_4.7H_20$ and $FeSO_4.H_2O$ (Sigma, UK) and appropriate dilutions were made. The pH of solutions were determined using an Omega PHB-212 microprocessor pH meter standardized with buffer solutions at pH 4.00 and 7.00 while appropriate adjustment of solution pH was done using 0.1M HCl or NaOH solutions. Seeds of *D. microcarpum* were bought from a local market, properly identified and sterilized in the hot-air oven (Gallenkamp, UK) at 70 °C for 6 hours before use. All chemicals and substrates used were prepared using doubly de-ionized water and experiments were done in duplicates.

2.2 Preparation of biosorbent

Fungal biosorbent *Aspergillus sp. TU-GM14* screened from metal industry was obtained from Microbiology Department of the Federal University of Agriculture Abeokuta (FUNAAB), South-West, Nigeria. It was maintained on metal-supplemented Sabouraud dextrose agar (SDA, Biorex) slants at 4 °C and sub-cultured bi-monthly. Spores were obtained as described Hemambika *et al.* (2011). Cell mass was suspended in de-ionized water and centrifuged at 6000 r min^{-1} for 20 minutes. Supernatant was decanted and precipitated spores were autoclaved at 121 °C and 1 atm. for 15 minutes and thereafter dried to constant weight in the hot-air oven before use.

2.3 Immobilization of biosorbent

Seeds of *D. microcarpum* were blended into powder and defatted using a Soxhlet extractor (Electrothermal, UK) with ethanol as extracting solution. Defatted seeds were sterilized and dried to constant mass in the hot-air oven (Gallenkamp, UK).

Immobilization of *Aspergillus sp. TU-GM14* was carried out according to the report of Kareem *et al.* (2013). Seed powder (10% v/v) was cross-linked with 2.5% glutaraldehyde solution at 30 °C for 10 minutes. Known mass (g) of dry biosorbent was added to seed slurry and stirred continuously for 5 minutes. Gel mixture was injected drop-wise into ethanolic-formaldehyde solution (60:40% v/v) for 24 hours to produce beads of produce immobilized beads. Spore load was varied between 0.4 and 2.2 g by mixing specific spore mass with cross-linked seeds while bead sizes were varied from 4 - 9 mm by dispensing different gel volume (ml) into stabilizing solution.

2.4 Biosorption studies

Batch biosorption experiments were carried out using 100 mg l^{-1} Mn(II) and Fe(II) ion concentration in 100 mL solutions and all experiments were carried out in duplicates while control experiment for each sorption study involved the use of blank *D. microcarpum* beads to attempt metal ions removal from aqueous solution.

Equilibrium time for Mn(II) and Fe(II) removal from aqueous solution by immobilized biosorbent was determined by placing immobilized biosorbent in Erlenmeyer flasks containing 100 mg l^{-1} Mn(II) and Fe(II) salts solutions, incubating in an incubator shaker at 30 °C and 1000 r min^{-1}. Mixture was monitored at 3 hour interval for 15 hours. At every interval, residual Mn(II) and Fe(II) ions in solution was determined using the Atomic adsorption Spectrophotometer, AAS (Electrothermal, UK) sorption was determined.

Effect of pH on Mn(II) and Fe(II) sorption was investigated by adding immobilized biosorbents (3 g) into metal solutions adjusted to different pH values (3-9) and incubated appropriately at 30 °C and 1000 r min^{-1} for 6 hours after which residual Mn(II) and Fe(II) ions concentration were determined.

Effect of initial sorbent load was determined by appropriately adding immobilized beads with different spore loads (0.4-2.4 g l^{-1}) into metal solutions in separate Erlenmeyer flasks and reaction proceeded appropriately.

Effect of bead size was investigated by adding immobilized beads of different sizes (4-9 mm) containing optimum spore load in appropriate metal solutions and sorption process proceeded.

Sorption process at optimized conditions was investigated by varying the concentration of metal solutions (50-200 mg l^{-1}) and adjusting the pH to pre-determined optimum. Beads with optimum spore load and size were added to the solutions appropriately and sorption proceeded at 100 r min^{-1} and 30 °C till equilibrium time was attained.

At equilibrium, rate of metal removal (%) and specific metal uptake, *q* (mg g^{-1}) was determined from the residual metal ions concentration at equilibrium using Equations 1 and 2 respectively.

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

$$q = \frac{V.(C - C_f)}{S} \tag{2}$$

C and C_f represent the initial and residual Mn(II) and Fe(II) concentrations in solution, *S* (g) is the mass of dry biosorbent added while *V* (L) is the volume of metal solutions.

3. Results

Effect of equilibrium time on interaction between metal ions and immobilized biosorbent on sorption is illustrated in Figure 1. Equilibrium was attained at 6 hours with 73 and 79% removal of Mn(II)and Fe(II) respectively. Initial high removal of both metals was observed between 0-6 hours and there was reduction in sorption rate to less than 60% when sorption preoceeded beyond equilibrium time.Also, an anomaly was observed in which removal efficiency briefly increased beyond equilibrium time (at 12 hours for Mn(II) ions sorption).

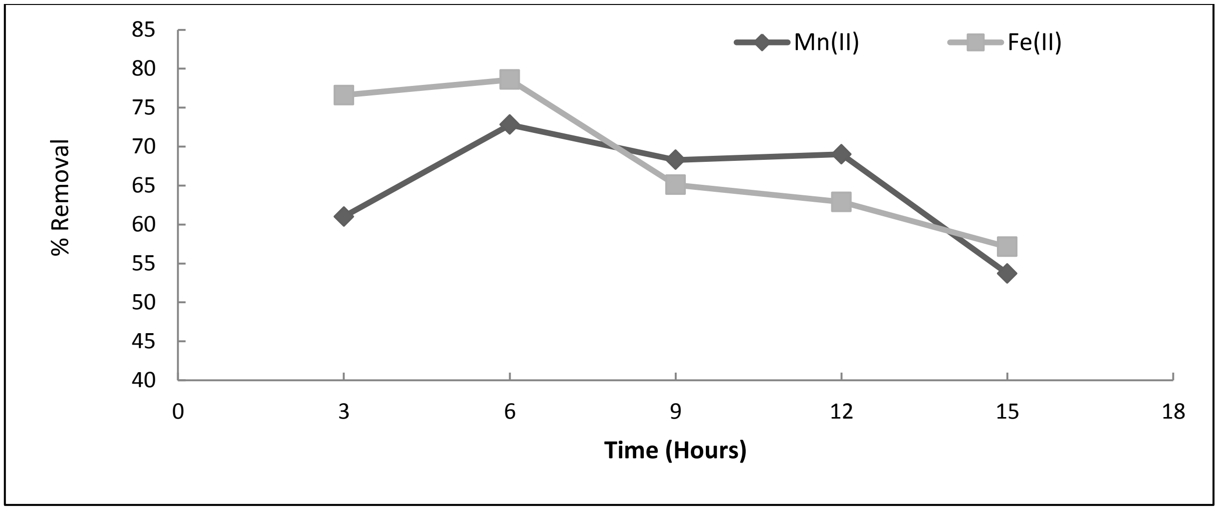

Figure 1. Effect of equilibrium time on biosorption of Fe(II) and Mn(II) ions by immobilized *Aspergillus sp. TU-GM14* at 100 mg l^{-1}, 2.5 g l^{-1} biosorbent dose, mean bead size 7 mm, 30 °C and pH 5.

Sorption rate of metals at different pH of solutions by immobilized *Aspergillus sp. TU-GM14* was determined and the effect is represented in Figure 2. Optimum Mn(II) and Fe(II) ions sorption of 69 and 78% was achieved at pH 6. Reduction in sorption rate when pH of solution was lower and higher than the optimum was observed. Also, more than 50% Mn(II) and Fe(II) ions removal was removed across the pH range (3-9) investigated.

Effect of immobilizing biosorbent in different bed sizes was described in Figure 3. At low bead size there was higher removal of Fe^{2+} (58%) compared to Mn^{2+} (40%) sorption. Increasing the bead size from 4 – 8 mm resulted in increased Fe(II) and Mn(II) sorption (58 and 40% to 71 and 68% respectively). Further increase in bead size beyond 8 mm resulted in reduced metals removal from aqueous solution.

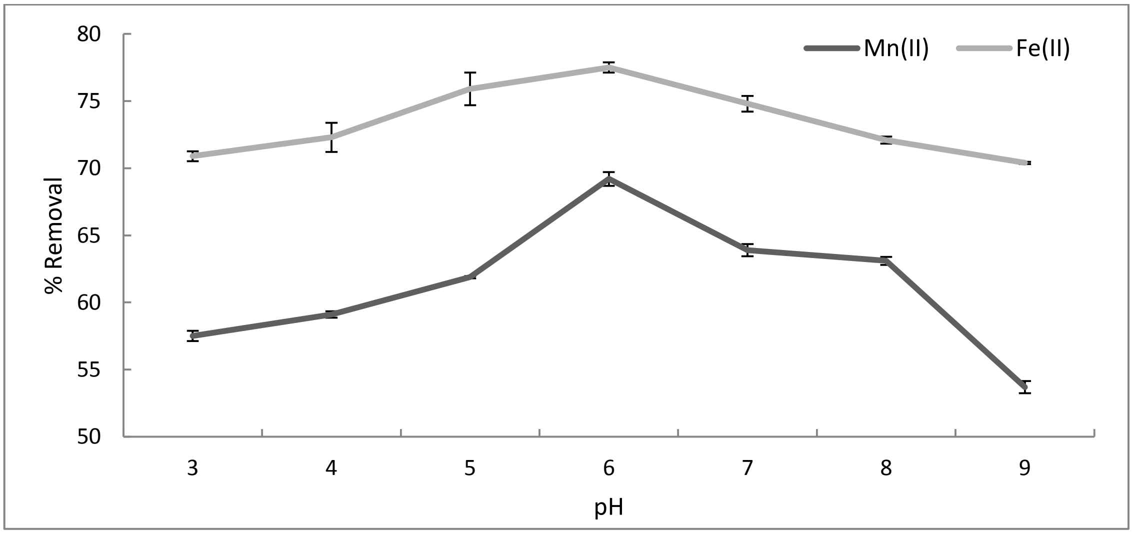

Figure 2. pH effect on biosorption of Fe(II) and Mn(II) ions by immobilized *Aspergillus sp. TU-GM14* at 100 mg l^{-1}, biosorbent dose 2.5 g l^{-1}, mean bead size 7 mm and 30 °C

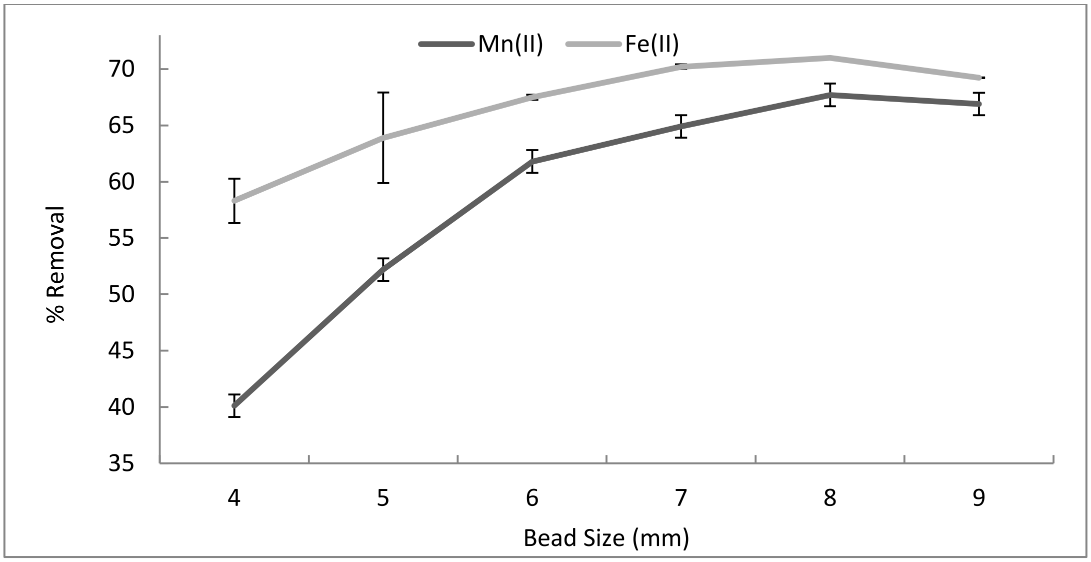

Figure 3. Bead size effect on biosorption of Fe(II) and Mn(II) ions by immobilized *Aspergillus sp. TU-GM14* at 100 mg l^{-1}, pH 6, biosorbent dose 2.5 g l^{-1} and 30 °C

Effect of *Aspergillus sp. TU-GM14* biomass immobilized in the support matrix on removal of Mn(II) and Fe(II) from aqueous solution is described in Figure 4. Increase in sorption with increased spore loading was observed and optimum sorption was achieved at 2 g l^{-1} with 73 and 76% removal of Mn(II) and Fe(II) ions from solution. High metal removal rates were achieved at the different biosorbent loads investigated (more than 60%). However, reduction in sorption rate beyond equilibrium spore loading of 2 g l^{-1} was observed and this can be attributed to the screening of binding sites by excess biosorbent present in the matrix.

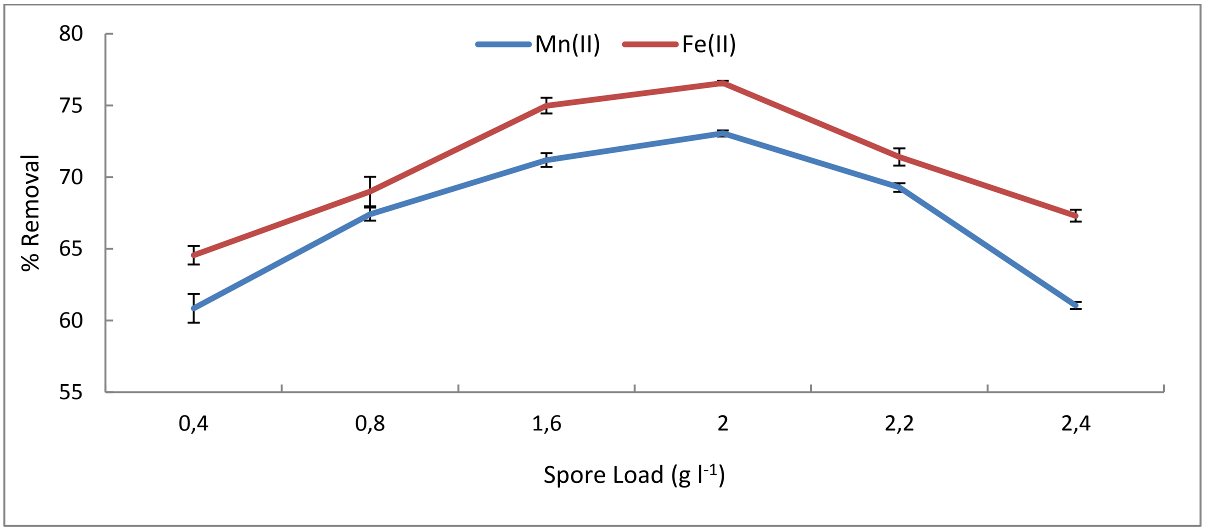

Figure 4. Effect of biosorbent dose on biosorption of Mn(II) and Fe(II) ions by immobilized *Aspergillus sp. TU-GM14* at 100 mg l^{-1}, pH 6 and 30 °C

The Students *t*-test was also carried out to determine significance of the various sorption factors. As described in Table 1 below, the p-value greater than 0.1 for effects of bead size, fungal sorbent load and contact time shows the values observed are significant and these factors are greatly affect the sorption rate of *D. Microcarpum*-immobilized *Aspergillus sp. TU-GM14*. However, p-value less than 0.01 for pH studies shows that the pH does not greatly affect metal ions sorption by immobilized biosorbent with over 50% sorption rate observed over a wide pH range.

Table 1. Analysis of significance of data from the different biosorption experiments using the Students t-test

	Sorption factors			
	pH	Bead size	Spore load	Contact time
p-value	9.93E-05*	0.139655	0.242834	0.576814

*p<5% significance level

Equilibrium isotherm data of Mn(II)and Fe(II) ions sorption by immobilized *Aspergillus sp. TU-GM14* was interpreted using Langmuir, Freundlich and Brunnauer-Emmet-Teller (BET) isotherm models respectively. Isotherm plots are presented in Figures 5-7 while isotherm constants and other derived values are summarized in Table 2.

Langmuir model describes sorption of metal ions on a biosorbent with homogenous surface and equal binding energy (Langmuir, 1918). The linear form of the model expressed in Equation 3 was used:

$$\frac{C_e}{q_e} = \frac{1}{q_o.b} + \frac{1}{q_o}C_e \tag{3}$$

q_e and q_o are the actual and maximum metal uptake (mg g^{-1}) while b (l mg^{-1}) is Langmuir constant related to the affinity between the sorbent and sorbate.

Linear Langmuir isotherm plot showed good fittings and high R^2 values close to 1 (Figure 5). Iron(II) sorption plot showed better fittings than Mn(II) sorption with R^2 0.97 and 0.76 respectively. Maximum sorption capacity of immobilized *Aspergillus sp. TU-GM14* for Mn^{2+} (34 mg g^{-1}) was higher than for Fe^{2+} (15 mg g^{-1}) but relatively similar Langmuir constants (0.013 and 0.014 respectively).

The characteristics of the Langmuir isotherm was expressed using the dimensionless parameter, R_L represented by the expression in Equation 4 (Weber and Chakkravorti, 1974). The dimensionless parameter values were less than 1 for both Mn(II) and Fe(II) sorption by immobilized *Aspergillus sp. TU-GM14*.

$$R_L = \frac{1}{(1+bC_o)} \tag{4}$$

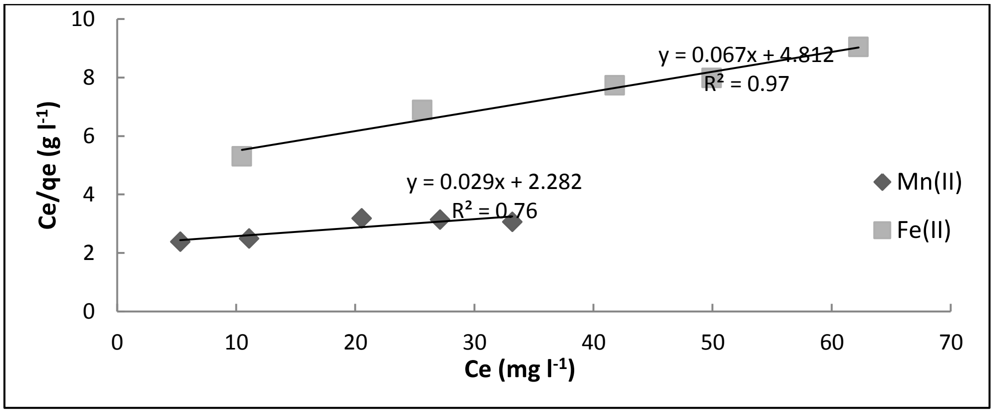

Figure 5. Langmuir isotherms for the biosorption of Fe(II) and Mn(II) ions by immobilized *Aspergillus sp. TU-GM14*

Freundlich isotherm model assumes a non-ideal adsorption on heterogeneous surface of biosorbent (Freundlich, 1926). The linearized equation was also used in describing Mn(II) and Fe(II) sorption process and it is represented by the Equation 5. C_e is the equilibrium concentration of the adsorbate (Mn(II)), K_F is the Freundlich constant which describes sorption capacity of biosorbent and slope, $1/n$ is related to intensity of metal ion sorption by immobilized biosorbent.

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

Freundlich isotherm plot described a good fit for both Fe(II) than Mn(II) sorption (Figure 6). Low Freundlich constant was derived and lower K_F was determined for Fe(II) sorption by immobilized fungal sorbent. Slope of the Freundlich isotherm was less than 1 for Fe(II) sorption but higher than 1 for Mn(II) sorption.

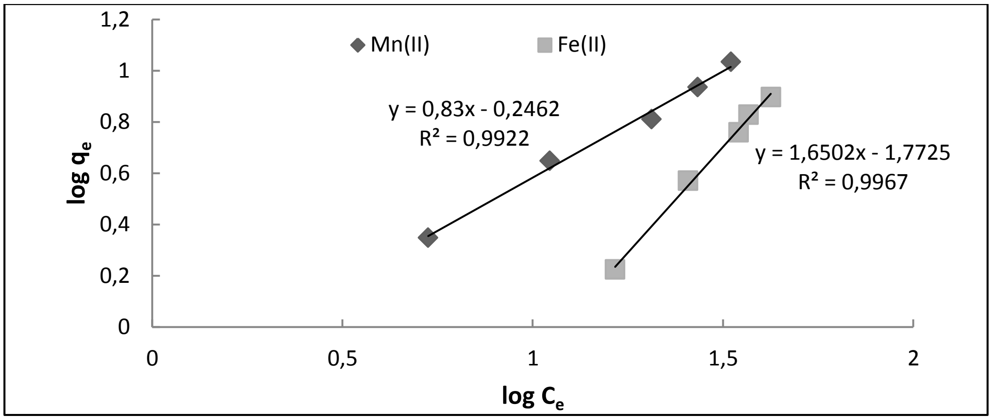

Figure 6. Freundlich isotherms for the biosorption of Fe(II) and Mn(II) ions by immobilized *Aspergillus sp. TU-GM14*

BET isotherm model which describes multi-layer sorption system was expressed using its linear form represented in Equation 6 (Brunauer *et al*., 1938).

$$\frac{C_e}{\left[q_e\left(C_s - C_e\right)\right]} = \left[\frac{1}{Q_s.B}\right] + \left[\frac{\left(B-1\right)}{Q_s.B}\right].\left(\frac{C_e}{C_s}\right) \qquad (6)$$

where B is the BET constant; Q_s is the concentration of solute adsorbed in forming a complete monolayer on the surface; q_e is amount of metal uptake in the next layer; C_e and C_s are the equilibrium and saturation concentration of metal solutions. Plotting $\frac{C_e}{\left[q_e\left(C_s - C_e\right)\right]}$ against $\left(\frac{C_e}{C_s}\right)$ will give a linear isotherm plot with slope $\left[\frac{\left(B-1\right)}{Q_s.B}\right]$ and intercept $\left[\frac{1}{Q_s.B}\right]$ respectively.

Linear BET isotherm plot obtained also expressed good fit for both Mn(II) and Fe(II) sorption (Figure 7). High BET constant was determined for both metals sorption with BET constant for Fe(II) sorption two-fold higher than for Mn(II) sorption. Higher maximum sorption capacity was also determined in multi-layer process than in monolayer sorption. Also, increased sorption below the surface of immobilized biosorbent was higher in Fe(II) sorption than Mn(II) sorption.

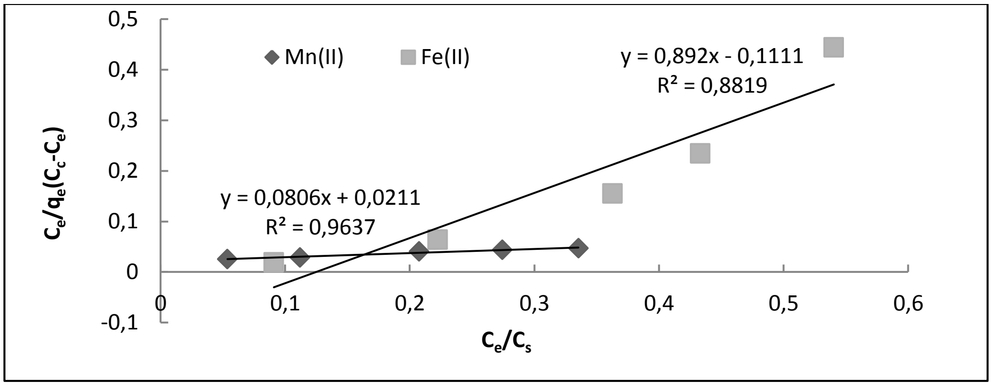

Figure 7. BET isotherms of Fe(II) and Mn(II) ions sorption by immobilized *Aspergillus sp. TU-GM14*

Table 2. Isotherm parameters for biosorption of Fe(II) and Mn(II) ions by *D. microcarpum*-immobilized *Aspergillus sp. TU-GM14*

	Langmuir				Freundlich			BET		
	R^2	Q_{max} (mg g^{-1})	b	R_L	R^2	K_F	1/n	R^2	B	Q_{max} (mg g^{-1})
Mn(II)	0.756	34.32	0.013	0.28	0.992	0.57	0.83	0.963	4.83	44.12
Fe(II)	0.972	14.77	0.014	0.26	0.996	0.02	0.91	0.881	9.03	51.77

4. Discussion

Equilirium time during sorption is an important factor to be monitored in batch sorption experiments because it determines when highest metal sorption can be achieved. Increased sorption rate with increasing interaction time up to 6h can be attributed to increased interaction between metals and the abundant binding sites present on immobilized biosorbent. Consequently, reduction in metal ions removal when sorption proceeded beyond equilibrium time indicates exhaustion of binding sites. Similar interaction pattern and equilibrium time has been reported with rapid initial adsorption stage on the biosorbent surface followed by a slower internal diffusion process as interaction time increases suggested (Adeogun *et al.,* 2013). Unusual increase in sorption rate beyond equilibrium time observed at 12 hours could be linked to prolonged exposure which resulted in slight surface disintegration observed on beads and increased beads' swelling (data not provided). Bead surface disintegration could result in desorption and release of fungal sorbent immobilized on matrix surface into solution to react with desorbed ions, while swelling of bead could result in movement of more ions into the matrix to either react with hitherto unavailable binding sites and/or take up pore spaces in the matrix without sorbent interaction as observed in control sorption experiments involving blank *D. microcarpum* beads and metal ions in solution. Solution pH affects metals' sorption due to its effect on solution chemistry and site dissociation of the biomass' surface. Optimum Mn(II) and Fe(II) sorption at pH 6 by immobilized biosorbent indicates that negatively charged ions are present on immobilized sorbent's binding sites in abundance. These negatively charged sites will therefore attract and bind the positively charged Fe(II) and Mn(II) ions unto it. Similar optimum pH 6 has also been previously been reported in which fungal species acted as biosorbent (Hemambika *et al.,* 2011; Rodríguez *et al.*, 2013). Also, removal of more than 70% and 50% of Fe(II) and Mn(II)ions from solution across pH range 3-9 shows that the biosorbent can effectively interact and bind metal ions over a wide pH range.

Immobilization of biosorbents in appropriate bead sizes is also important for continuous sorbent usage as it dictates the availability of pore spaces and biosorbent orientation within the pore spaces. Increased removal rate of metals in larger bead sizes indicates the presence of more pore spaces available for biosorbent localization which promotes higher interaction with the metals. Reduced sorption below optimum bead size can be attributed to higher competition for the small number of available pore spaces while at bead size above optimum, there is less competition for available space and sorbent mass may take up spaces where metal interaction is reduced.

The biosorbent load also influences the amount of metals removed from solution. Initial increase in metals' removal rate of could be attributed to presence of sorbent cells with high surface area which increases the number of adsorption sites available for adsorption (Adeogun *et al.,* 2013). Increase in spore load above optimum resulted in significant reduction of ions sorption and this can be attributed to competition between excess biosorbent mass for limited pore spaces in the matrix thereby causing the screening of binding sites.

Adsorption isotherm models are used in determining and describing the existence of a relationship between sorbed metal ions on the biosorbent surface and the biosorbent at equilibrium.

The Langmuir constant derived indicates affinity of immobilized biosorbent to sorbate ions in solution while High maximum sorption capacity determined described high interaction between immobilized biosorbent and the metal ions with higher interaction with Mn(II) than Fe(II) ions. This confirms sorption of both Fe(II) and Mn(II) ions unto immobilized *Aspergillus sp. TU-GM14* surface as a favorable and feasible process.

The dimensionless parameter, R_L indicates the isotherm to be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$), or irreversible ($R_L = 0$) (Weber and Chakkravorti, 1974). $R_L$values less than 1 determined for both metals sorption indicating a favourable sorption process. Lower R_L value for Fe(II) sorption indicates a more favorable Fe(II) sorption process than Mn(II) sorption.

Low Freundlich constant, K_F, determined indicates heterogeneous sorbent surface (Fytianos *et al*., 2003) and this is due to non-uniformity in size of immobilized *Aspergillus sp. TU-GM14*. Higher K_F for Mn(II) sorption indicates higher surface manganese interaction and sorption than Fe(II) sorption. Also, slope, $1/n$ less than 1 for both Mn(II) and Fe(II) sorption (0.83and 0.91) indicates favourable sorption process.

High BET constant, *B* higher than 1 was determined for both Fe(II) and Mn(II) sorption by immobilized biosorbent, indicating actual multi-layer sorption at levels below the immobilized sorbent's surface. Also, higher *B* observed for Fe(II) sorption than Mn(II) sorption indicates higher multi-layer sorption activity. Similarly, three-fold increase in maximum Iron(II) uptake in multi-layer sorption also correlates with the low Freundlich constant which described high non-uniformity of biosorbent surface (Table 2).

Table 3. Comparison of Mn(II) and Fe(II) ions sorption capacity of *D. microcarpum*-immobilized *Aspergillus sp. TU-GM14* with different biosorbents

	Biosorbents	Maximum Adsorption Capacity ($mg\ g^{-1}$)	Reference
Mn(II)	Untreated Corn cob biomass	6.54	Adeogun *et al*., 2011
	Treated Corn cob biomass	7.87	Adeogun *et al*., 2011
	Raw maize husk	8.518	Adeogun *et al*., 2013
	Modified maize husk	9.004	Adeogun *et al*., 2013
	Maize stalks	16.61	El-Sayed *et al*., 2011
	Immobilized *Aspergillus sp. TU-GM14*	34.32	Present study
Fe(II)	Activated carbon from barks of wild jack tree	0.257	Rose and Rajam, 2012
	Activated carbon from barks of jambul tree	0.1978	Rose and Rajam, 2012
	Activated carbon from Pomegranate peel	18.52	Moghadam *et al*., 2013
	Raw Calabrian pine bark	2.03	Acemioglu, 2004
	Immobilized *Aspergillus sp. TU-GM14*	14.77	Present study

Sorption of Mn^{2+} and Fe^{2+} by immobilized *Aspergillus sp. TU-GM14* is best explained by the Freundlich isotherm, while high intra-matrix interaction between immobilized sorbent and metal ions was deduced based on value of *B* higher than one. Also, three-fold increase in maximum Fe^{2+} uptake capacity within the matrix compared with surface uptake indicates that higher interaction between sorbent and ions occurs within the matrix than at the surface. These observations could result from the presence of higher amount of sorbent immobilized within the matrix and which are readily available for interaction with metal ions.

Comparison of maximum Mn(II) and Fe(II) ions uptake by *D. microcarpum*-immobilized *Aspergillus sp. TU-GM14*with previous studies which used sorbents from various agricultural wastes is described in Table 3. The uptake capacity compares favorably with other biosorbents.

5. Conclusions

Result of the study showed that immobilized mass of *Aspergillus sp. TU-GM14* exhibited high removal of Fe(II) and Mn(II) ions from aqueous solution (> 14 mg g^{-1}). Freundlich isotherm described the sorption processes best, while the BET model indicated a high intra-matrix interaction between the immobilized *Aspergillus sp. TU-GM14* and Fe^{2+} and Mn^{2+} ions. It can be further stated that *D. microcarpum* is an inexpensive matrix which can be used as an alternative to conventional cell matrices because it effectively entrapped biosorbent and promoted interaction with metal ions in solution.

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