Biosorption studies for the removal of ferrous ion from aqueous solution by *Aspergillus terreus* and *Trichoderma viride*: kinetic, thermodynamic and isothermal parameters

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ABSTRACT

Environmental implications and the tendency of heavy metals to accumulate in selected tissues of plants and animals, as well as their overall potential to be toxic even at relatively minor levels of exposure, are a source of concern. The use of cheap and effective biological means for heavy metal remediation has been advocated. This study examines the biosorption and bioaccumulation of ferrous ion by *Aspergillus terreus (A. terreus)* and *Trichoderma viride (T. viride)* in a batch system. The effects of some important parameters, such as initial metal concentration, temperature and inoculum concentration on biosorption capacity were examined. Langmuir, Freudlinch, Temkin and Dubinin–Radushkevich models were applied to explain the biosorption isotherms of Fe(II) onto the biosorbents. The process fitted well into pseudo first order kinetic model and was best explained by the Langmuir isotherm with maximum absorption capacity of 6.33 and 7.50 mg/g for *A. terreus* and *T. viride*, respectively. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the biosorption of the ferrous ion to the organisms is feasible, spontaneous and exothermic in nature at low temperature.

Key words | *Aspergillus terreus*, biosorption, kinetics and isotherms, *Trichoderma viride*

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INTRODUCTION

The presence of heavy metal ions in the environment is a major concern due to their toxicity to many life forms. Industrial processes, such as mining operations, sludge disposal, metal as plating and the manufacture of electrical equipment lead to the release of metal ions into the environment and, invariably, they become pollutants in the environment. The toxic nature of these pollutants has caused increased concern regarding their removal from industrial effluents (Senthilkumar *et al.* 2000). Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders (Manaham 2000; Yu 2005).

Although iron is an essential element for life, its excess in plant and animal tissues may be responsible for a wide range of metabolic disorders, due mainly to its involvement in Fenton reactions leading to the production of high levels of toxic hydroxyl radicals ($^{\cdot}OH$) and other reactive oxygen species (H_2O_2, O^{2-}) (Bode *et al.* 1995; Thongbai & Goodman 2000). These compounds react with polyunsaturated fatty acids, protein and nucleic acids, thus giving rise to the destruction of numerous endocellular structures (Alscher *et al.* 1997). Serious toxicity is likely with ingestion of more than 60 mg/kg. Toxic effects of iron may occur at doses of 10–20 mg/kg of elemental iron (Rao & Georgieff 2009). When high concentrations (over 200 ppm) of iron are absorbed, for example by haemochromatosis patients, iron is stored in the pancreas, the liver, the spleen and the heart and may damage these vital organs. Thus, the need for the removal of ferrous ion from wastewater is justified.

Iron removal from water is mostly carried out in drinking water preparation, because mineral water contains high amounts of iron ions. These influence water color, odor and turbidity. In wastewater treatment, iron removal may be achieved by cumbersome and high-cost processes which justify alternative technology. Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for recovery of heavy metals from industrial waste streams. Most studies of biosorption for metal removal have involved the use of either laboratory-grown microorganisms or biomass generated by the pharmacology and food processing industries or wastewater treatment units (Tsezos & Velosky 1981; Townsley *et al.* 1986; de Rome & Gadd 1987; Macaskie 1990; Costa & Leite 1991; Rao *et al.* 1993; Dias *et al.* 2002). Many aquatic microorganisms, such as fungi, bacteria, yeast and algae can take up dissolved metals from their surroundings onto their bodies and can be used for removing heavy metal ions successfully (Aksu *et al.* 1992). In this study, *Aspergillus terreus* (*A. terreus*) and *Trichoderma viride* (*T. viride*) were used as effective and low-cost sorbents for the removal of ferrous ion from aqueous solution. The effects of initial metal concentration, pH, temperature and biosorbent dose were also studied. The equilibrium data were analyzed with Langmuir, Freundlich, Redlich–Peterson and Dubinin–Radushkevich (D–R) isotherms. The thermodynamic parameters were also elucidated from the temperature dependent of the biosorption process.

MATERIALS AND METHODS

Biosorbent preparation

Metal-degrading fungal strains of *A. terreus* and *T. viride* isolated from contaminated soil were collected from the Microbiology Department of the Federal University of Agriculture Abeokuta, southwestern Nigeria. The biomass was suspended in 10 mL deionized water and centrifuged at 4,000 rpm for 10 min to separate vegetative materials from spores. The supernatant was decanted and the precipitated spores were dried in a hot air-oven and weighed to constant mass (Hemambika *et al.* 2010). One mL of deionized water was added to the dried spores as necessary.

Preparation of aqueous solution of metal ions

The aqueous solutions of ferrous ion were prepared freshly as necessary from analytical grades of $Fe_2SO_4.H_2O$ (Sigma, USA). One thousand mg/L aqueous solution (stock solution) of this salt was prepared with deionized water in 1% HNO_3 solution and the stock solution was diluted with deionized water to obtain the working standard solutions. The pH adjustments of the solutions were made with aliquots of 1.0 mol/L of HCl and NaOH. The pH of the solution was checked on an electronic pH meter (Thermo Russell, USA), which had earlier been standardized with standard buffer solution.

Equilibrium studies

Equilibrium adsorption isotherms were performed in a batch process as previously described (Bello *et al.* 2008; Adeogun *et al.* 2010, 2011). The amount of metal ion adsorbed by the biosorbent at equilibrium, Q_e (mg/g), was calculated using Equation (1):

$$Q_e = \frac{(C_o - C_e)V}{W},$$

(1)

where C_o and C_e (mg/L) are the liquid-phase concentrations of the metal ion at initial and equilibrium, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

Bioaccumulation studies

The procedure was similar to that of equilibrium studies, except that samples were prepared and withdrawn at an interval of 24 hours for the determination of residual iron in the solution. The amount of iron absorbed at intervals was expressed as a percentage:

$$Q\% = \frac{(C_o - C_e)V \times 100}{W}$$

Batch kinetic studies

The procedures for kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at pre-set time intervals, and the concentrations of the metal ions were similarly determined. The amount of metal ion adsorbed at time t, Q_t (mg/g), was calculated using Equation (2):

$$Q_t = \frac{(C_o - C_e)V}{W} \qquad (2)$$

where C_o and C_t (mg/L) are the liquid-phase concentrations of the metal ion at initial and at time t, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

RESULTS AND DISCUSSION

Effect of hydrogen ion concentration

pH is described as the most important factor for ion uptake (Geddie & Sutherland 1993). It strongly influences the speciation and biosorption availability of the metal ions (Esposito *et al.* 2002), alters activity of binding sites and also affects the types of ion in the solution (Adeogun *et al.*
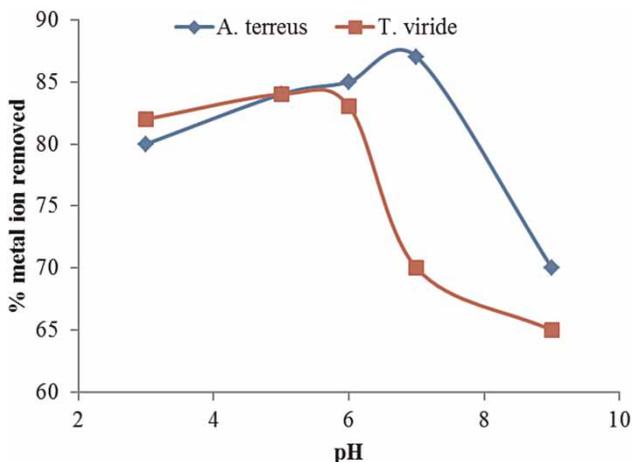
2012). Optimum iron sorption at pH 6 and 7 was observed for *A. terreus* and *T. viride*, respectively (Figure 1). This indicates the presence of weakly positive to negative ions on the surface of the biomass to interact with ferrous ion present in the solution and form bonds, binding the metals to the biomass surface (Faria *et al.* 2004). At high pH, there is an abundance of negatively charged ions on the surface of the biomass and this will attract more positively charged metal ion to the surface for binding.

Effect of biosorbent dosage

The effect of biosorbent dosages on the removal of Fe(II) ion from aqueous solution is presented in Figure 2. The highest metal concentration was obtained at the dosage of 1.6 mg of the biosorbents. Although at lower dosage *T. viride* remove more of the metal ion than *A. terreus*, as the dosage increases the capacity for the removal of the metal ion increases to the maximum of about 89% at 1.6 mg dosage for the two biosorbents. As the biosorbent dosage increases above optimum dosage values, a decrease in the percentage of metallic ions removal was observed. This may be attributed to the concentration gradient between adsorbate and biosorbent with increasing biomass concentration causing a decrease in the amount of metallic ion adsorbed per gram of biomass (Vaghetti *et al.* 2009).
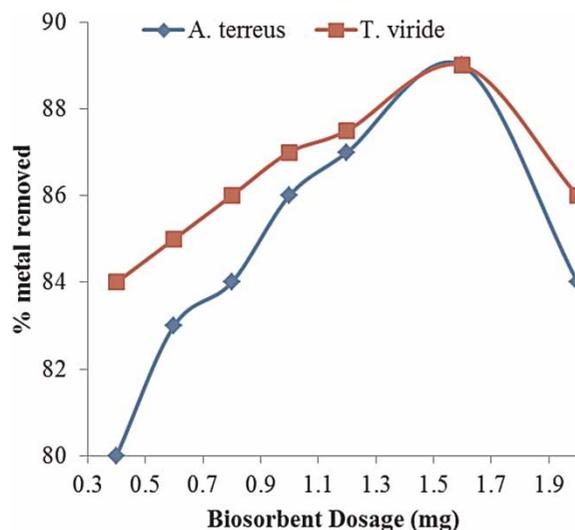

Figure 1 │ Effect of pH on sorption capacities of *A. terreus* and *T. viride*.

Figure 2 │ Effect of biosorbent dosage on sorption capacities of *A. terreus* and *T. viride*.

Effect of temperature

Optimization parameters for iron removal showed an optimum uptake at a temperature of 30 °C (Figure 3), with reduced uptake above and below this temperature indicating that sorption occurs best at the growth temperature of sorbents. This conforms with several studies which state that temperature has less influence on sorption performances in the range of 20–35 °C, and its overall effect is minimal because sorption takes place over a narrow temperature range of 10–70 2035 °C (Aksu *et al.* 1992; Vegliò & Beolchini 1997).

Effect of contact time and initial metal concentration

Figures 4 and 5 illustrate the effect of contact time on Fe(II) ion biosorption by *T. viride* and *A. terreus*, respectively. From the figures, it can be seen that the equilibrium time for metal ion biosorption *T. viride* is concentration dependent while that of *A. terreus* does not depend on initial metal ion concentration. This is as a result of the high affinity of *A. terreus* for metal ion (Dias *et al.* 2002).

Biosorption kinetics

Pseudo first order kinetics

The study of adsorption kinetics is important in the treatment of aqueous effluents as it provides valuable information on
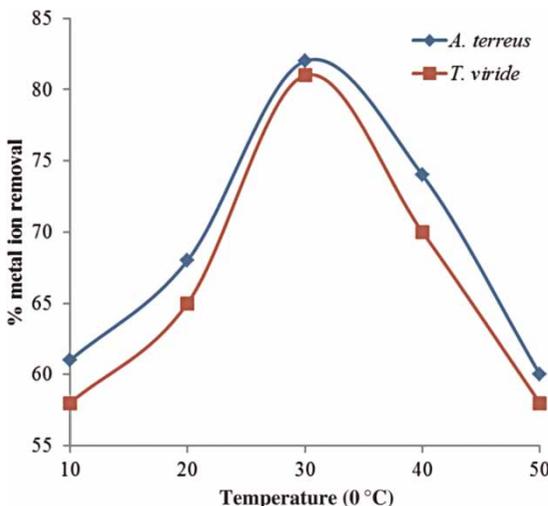

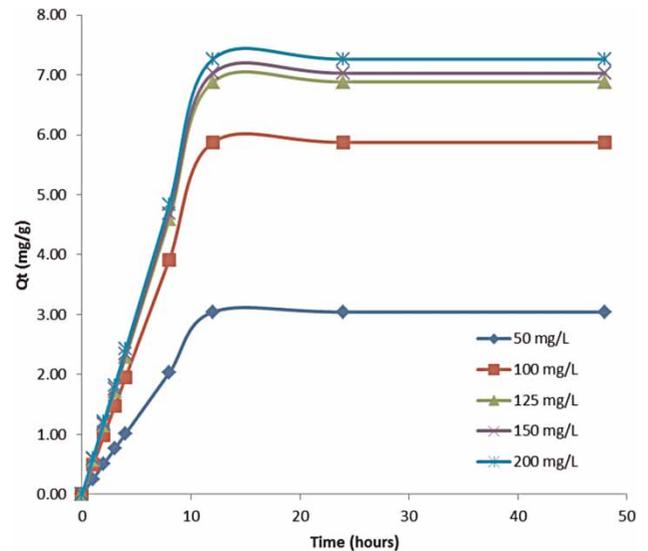**Figure 3** │ Effect of temperature on sorption capacities of *A. terreus* and *T. viride*.

Figure 4 │ The effect of contact time on Fe(II) ion biosorption by *T. viride*.
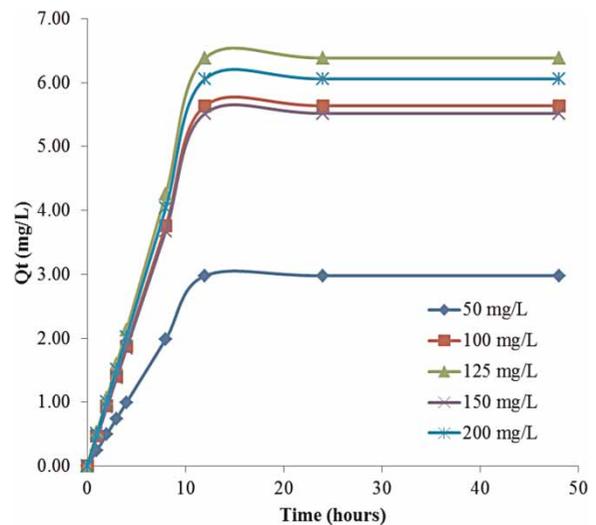

Figure 5 │ The effect of contact time on Fe(II) ion biosorption by *A. terreus*.

the reaction pathways and the mechanism of the adsorption process. Many kinetic models have been developed in order to find intrinsic kinetic adsorption constants; traditionally, the kinetics of metal ions adsorption is described following the expressions originally given by Largegren (1898). A simple kinetic analysis of adsorption under the pseudo first order assumption is given by Equation (3) below:

$$\frac{dQ_t}{dt} = k_1(Q_e - Q_t) \qquad (3)$$

where Q_e and Q_t are the amounts of the metal ion biosorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, k_1 is the rate constant of biosorption (min^{-1}) and t is the contact time (min). The integration of Equation (3) with initial conditions, $Q_t = 0$ at $t = 0$ and $Q_t = Q_t$ at $t = t$, yields Equation (4):

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{4}$$

The kinetic data were analyzed with non-linear regression analysis method using a program written on MicroMath Scientist software (Salt Lake City, USA). The parameters used for fitting the pseudo first order kinetics are shown in Table 1. The correlation coefficient values of 0.996 and the experimental Q_e values are not far from the calculated ones.

Pseudo second order kinetics

A second order kinetic model which is based on equilibrium adsorption (Malik 2004) was used to compare the Q_e values with that of pseudo first order rate model. It is expressed as shown by Equation (5):

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \tag{5}$$

Upon integration and rearrangement, the second order rate equation becomes Equation (6):

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{6}$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of second order adsorption. The parameters for pseudo second order theoretical fitting of time-dependent biosorption of the metal ion onto the biosorbent (Q_t) are presented in Table 1. The correlation coefficients for the second order kinetic model ranged between 0.986 and 0.989 indicating the suitability of the pseudo first order kinetics over that of the second order kinetic equation model.

Statistical test for the kinetic data

Although the R^2, i.e., the correlation coefficients used to compare the data, the pseudo first and second order kinetic models were also evaluated further by the percentage error function which measures the differences (% SSE) in the amount of the metallic metal ion uptaken by the adsorbent predicted by the models, (Q_{cal}), and the actual, i.e., Q_{exp} measured experimentally (Vaghetti *et al.* 2009; Adeogun *et al.* 2011). The validity of each model was determined by the sum of error squares (SSE, %) given by Equation (7):

$$\%\text{SSE} = \sqrt{\frac{(q_{(\exp)} - q_{(cal)})^2}{N}} \tag{7}$$

where N is the number of data points. The higher the value of R^2 and the lower the value of SSE, the better will be the goodness of fit. From Table 1, the lower values of % SSE for the first order model confirm the acceptability of the model over the second order model.

Table 1 | Kinetic parameters for the biosorption of Fe(II) by *A. terreus* and *T. viride*

| | C_o (mg L^{-1}) | C_e (mg L^{-1}) | Pseudo first order | | | | | Pseudo second order | | | |
			$Q_{e\ (\exp)}$ (mg g^{-1})	$Q_{e(cal)}$ (mg g^{-1})	k_1 (h^{-1})	R^2	% SSE	$Q_{e\ (calc)}$	k_2 (g mg h^{-1})	R^2	% SSE
A. terreus	50	2.37	2.977	3.112	0.113	0.996	0.015	3.867	0.028	0.989	0.099
	100	9.84	5.635	5.891	0.113	0.996	0.028	7.319	0.015	0.989	0.187
	125	22.89	6.382	6.672	0.113	0.996	0.032	8.289	0.013	0.989	0.212
	150	61.74	5.516	5.767	0.113	0.996	0.028	7.165	0.015	0.989	0.183
	200	103.11	6.056	6.331	0.113	0.996	0.031	7.865	0.014	0.989	0.201
T. viride	50	1.33	3.042	3.180	0.113	0.996	0.015	3.951	0.027	0.986	0.101
	100	6.03	5.873	6.140	0.113	0.996	0.030	7.628	0.014	0.986	0.195
	125	14.88	6.883	7.195	0.113	0.996	0.035	8.940	0.012	0.989	0.229
	150	37.55	7.028	7.347	0.113	0.996	0.035	9.129	0.012	0.986	0.233
	200	83.79	7.263	7.593	0.113	0.996	0.037	9.434	0.011	0.989	0.241

Adsorption isotherms

An adsorption isotherm represents the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbent's surface at a given condition. Several isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir, Freundlich, D–R and Redlich–Peterson models were used to describe the equilibrium data. Data were analyzed with the non-linear regression analysis method using a program written on MicroMath Scientist software (Salt Lake City, USA). The parameters obtained for the isotherm models in Figures 6 and 7 are shown in Table 2.
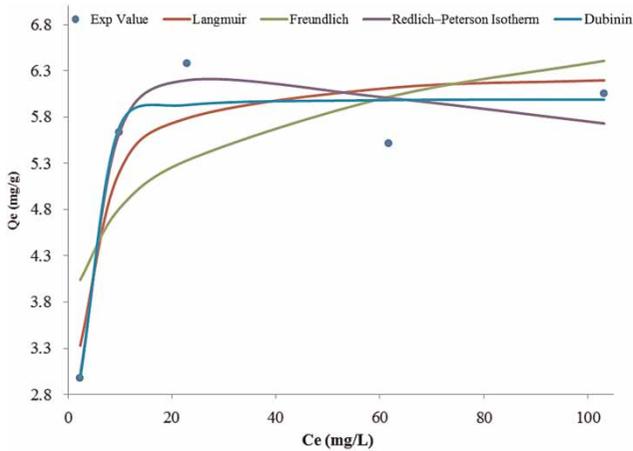

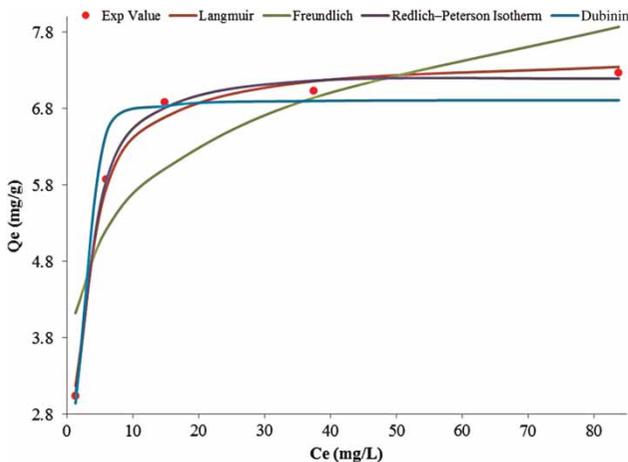**Figure 6** | Biosorption isotherms for Fe(II) biosorption on *A. terreus*.

Figure 7 | Biosorption isotherms for Fe(II) biosorption on *T. viride*.

Table 2 | Isotherm parameters for the biosorption of Fe(II) by *A. terreus* and *T. viride*

	Langmuir				Freundlich			Redlich–Peterson				Dubinin			
	Q_o (mg g^{-1})	b (L mg^{-1})	R^2	R_L	K_F ((mg g^{-1}) (L g^{-1}))$^{1/m}$	n	R^2	K_{RP}	a_{RP}	β	R^2	Q_m (mg g^{-1})	$\beta \times 10^7$ mol^2 J^{-2}	R^2	E_a (kJ mol^{-1})
A. terreus	6.325	0.469	0.927	0.011	3.636	8.183	0.978	1.830	0.163	1.138	0.997	5.99	9.18	0.970	7.38
T. viride	7.505	0.549	0.996	0.009	3.945	6.413	0.986	3.607	0.423	1.033	0.999	6.91	4.42	0.978	10.63

Langmuir isotherm model

Langmuir, in 1918, observed sorption phenomena and suggested that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules. He proposed the sorption isotherm based on the assumptions that: (i) adsorbates are chemically adsorbed at a fixed number of well-defined sites; (ii) each site can only hold one adsorbate species; (iii) all sites are energetically equivalent; and (iv) that there are no interactions between the adsorbate species.

The Langmuir isotherm equation is written as Equation (8):

$$q_e = \frac{Q_{max} b C_e}{1 + b C_e} \qquad (8)$$

where C_e is the supernatant concentration after the equilibrium of the system (mg L^{-1}), b the Langmuir affinity constant (L mg^{-1}) and Q_{max} is the maximum adsorption capacity of the material (mg g^{-1}) assuming a monolayer of adsorbate uptaken by the adsorbent.

The values of R^2 in Table 2 for the Langmuir isotherm showed better fittings (Figures 6 and 7) for the metal ions by the two biosorbents. Separation factor (R_L) is defined by the relationship in Equation (9) (Anirudhan & Radhakrishnan 2008):

$$R_L = 1/(1 + b C_i) \qquad (9)$$

where C_i is the initial concentration (mg L^{-1}). The value of the separation parameter provides important information about the nature of adsorption. If R_L value of zero implies irreversible adsorption, it is a favorable process when $0 < R_L < 1$, linear when R_L is 1 or unfavorable when R_L is greater than 1 (Chen *et al.* 2008). The values of R_L in this study and presented in Table 2 implied that the process is favorable.

Freundlich isotherm model

The Freundlich isotherm is based on the assumption of non-ideal adsorption on heterogeneous surfaces and the linear form of the isotherm can be represented as in Equation (10) (Freundlich 1906):

$$Q_t = K_F C_e^{1/n} \qquad (10)$$

where K_F is the Freundlich constant related to sorption capacity ((mg g^{-1}) (L g^{-1}))$^{1/n}$ and n is related to the adsorption intensity of the adsorbent. The value of K_F from this study showed that biosorbents have similar affinity for the metal ion. The value of $1/n$ showed that the surfaces are heterogeneous (Krobba *et al.* 2012).

Redlich–Peterson isotherm

A three parameter Redlich–Peterson equation has been proposed to improve the fit by the Langmuir or Freundlich equation and is given by Equation (11):

$$Q_{eq} = \frac{K_{RP} C_e}{1 + a_{RP} C_e^{\beta}} \qquad (11)$$

where K_R, b_R and β are the Redlich–Peterson parameters, β lies between 0 and 1 (Vaghetti *et al.* 2009). For $\beta = 1$, Equation (11) converts to the Langmuir form. The adsorption model constants are presented in Table 2 and the isotherms are shown in Figures 5 and 6. The value of β obtained in this study shows that the model operates closely to the Langmuir isotherm.

D–R isotherm

The D–R model (Dubinin *et al.* 1947) was chosen to estimate the heterogeneity of the surface energies and also to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than the Langmuir isotherm as its derivation is not based on
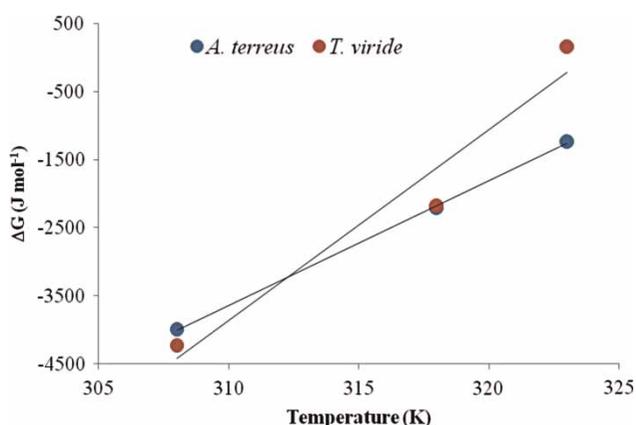

Figure 8 | Thermodynamic plot for Fe(II) biosorption on *A. terreus* and *T. viride*.

Table 3 │ Thermodynamic parameters for the biosorption of Fe(II) by A. terreus and T. viride

Temperature (K)	A. terreus				T. viride			
	ΔG (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	R^2	ΔG (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	R^2
308	− 4.00	− 0.138	− 60.43	0.99	− 4.23	− 0.279	− 90.52	0.95
318	− 2.21				− 2.18			
323	− 1.24				0.15			

ideal assumptions such as, equipotent of the sorption sites, absence of hindrance between sorbed and incoming particles and surface homogeneity on microscopic level (Weber & Morris 1963; Malik 2004). The D–R isotherm is represented by Equation (12):

$$Q_t = Q_m e^{-\beta \varepsilon^2} \tag{12}$$

where Q_m is the theoretical saturation capacity (mol g^{-1}), β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2 J^{-2}) and ε is the polanyi potential given by the relation $\varepsilon = RT \ln(1 + 1/C_e)$. C_e is the equilibrium concentration of adsorbate in solution (mol L^{-1}), R (J mol^{-1} K^{-1}) is the gas constant and T (K) is the absolute temperature. The constant β gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship (Kundu & Gupta 2006):

$$E = 1/\sqrt{-2\beta} \tag{13}$$

If the magnitude of E is between 8 and 16 kJ mol^{-1}, the sorption process is supposed to proceed via chemisorption, while for values of $E < 8$ kJ mol^{-1}, the sorption process is physical in nature. Since the values obtained in this study are within the ranges specified by the model, the process therefore, is purely chemisorption.

Biosorption thermodynamics

Distribution of the metal ion between the solution and the biosorbent is an equilibrium process associated with the equilibrium constant, K_D. The equilibrium constant was used to estimate the thermodynamic parameters owing to its temperature dependence as previously explained (Nkiko *et al.* 2013). A plot of $\Delta G°$ against the temperature (Figure 8) gives a straight line graph with intercept as $\Delta H°$ and slope as $\Delta S°$. The thermodynamic parameters are presented in Table 3. The negative values of $\Delta G°$ free energy change of the process implies a thermodynamically feasible and spontaneous biosorption process.

CONCLUSION

Results of this study showed that iron could be effectively removed from solution by low amounts of *A. terreus* and *T. viride* biomass in solution. The biosorption capacity values of 6.33 and 7.51 mg/g for *A. terreus* and *T. viride*, respectively, in this study compared favorably with those reported in the literature. Sag *et al.* (1996) reported a value of 5.1 mg/g using *Rhizopus arrhizus* while Shokoohi *et al.* (2009) reported a value of 6.04 mg/g using dried sludge for iron removal. High uptake of iron even at a concentration of 250 mg/L shows that suspension or trapping of the spore mass on suitable matrices will further enhance their sorption capabilities and its scaling-up for use in effluent clean-up, while the Langmuir and Freundlich models further confirm the high sorption property of these biomasses. *A. terreus* and *T. viride* biomass can be effectively used as material for biological removal of iron from aqueous solution over a wide range of concentration and pH.

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