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CHARACTERIZATION OF LEAD (II) UPTAKE FROM SOLUTION BY ALGINATE – IMMOBILIZED *ASPERGILLUS FUMIGATUS* AND *PENICILLIUM* SP.

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ABSTRACT

This study was carried out to evaluate and compare the biosorption efficiencies of immobilized *Aspergillus fumigatus* and *Penicillium* sp. biomasses for Pb(II) ions in solution. The effect of adsorbent dosage, initial solution pH, contact time and initial metal ion concentration were investigated. The results showed that the biosorption efficiency increased with an increase in adsorbent dosage and pH. The maximum Pb(II) biosorption by *Aspergillus fumigatus* was 99.62% which was achieved at 100 mg adsorbent weight, pH of 7.0, contact time of 120 minutes and initial Pb(II) concentration of 20 mg/L. For *Penicillium* sp., maximum efficiency of 98.10% was attained at adsorbent weight of 50 mg, pH value of 5.0, contact time of 120 minutes and Pb(II) concentration of 20 mg/L. The isotherm data showed that the biosorption process could be described by both the Langmuir and Freundlich isotherms. The maximum biosorption capacity Q^o for *Aspergillus fumigatus* was 29.19 mgg^{-1} while for *Penicillium* sp. it was 15.58 mgg^{-1}. The kinetic plots also showed that the pseudo – second order kinetics was the rate – controlling step for the two adsorbents. These results show that the investigated biosorbents are good low cost adsorbents for the removal of Pb(II) from wastewaters.

Key words: Alginate, *Aspergillus fumigatus,* Biosorption, Freundlich, Langmuir, Isotherm, *Penicillium*

INTRODUCTION

The gravity of water pollution is of great concern to human life as water is the prime necessity of life. The presence of considerable amounts of heavy metal in industrial wastewater poses serious threat to the environment because the recoveries of heavy metals using conventional chemical methods are not economical [1]. Lead is one of the metals of concern because of its toxicity even at low concentrations. The removal of lead and other heavy metals from industrial wastewaters is a problem of increasing concern that has been mostly solved by chemical and physical methods of treatment [2]. However, these methods are not only costly and require trained personnel, but also use chemicals that generate wastes which may be hazardous or toxic [3, 4]. The search for new cost-effective technologies for the removal of heavy metal from wastewaters has therefore been directed towards biosorption which involves the use of either live or dead microorganisms or their derivatives.

Biosorption of heavy metal ions using biological materials such as algae, bacteria, fungi and yeast has received greater attention recently due to its advantages over conventional methods [5]. Some of the advantages include low cost, high efficiency, minimization of sludge production, possibility of regeneration of biosorbent and metal recovery [2, 6]. Biosorption is therefore seen as an alternative method that can be categorized as a green technology for heavy metal removal from industrial effluents [7]. The mechanism of biosorption is influenced by many experimental factors like pH, ionic strength, biomass concentration and temperature. The variability of these factors in rear water systems makes it necessary to know how they influence the sorption capabilities of biomass. The extra information regarding the mechanisms and the influencing factors are highly useful in optimization of experimental conditions.

This study is therefore aimed at examining the sorption capabilities of two fungal species, *Aspergillus fumigatus* and *Penicillium* sp in the removal of Pb(II) ions from aqueous solution and to verify the environmental factors influencing the biosorption.

MATERIALS AND METHODS

Generation of biomass

The fungal mycelia of *Aspergillus fumigatus* and *Penicillium* sp. were cultured over Potato Dextrose Agar (PDA) plates. The PDA plates of the stock culture were maintained by subculturing at 4 ^{o}C. The fungal biomass was cultivated in composition (g/L): K_2HPO_4, 0.5; NaCl, 0.5; $MgSO_4$, 0.5; NH_4NO_3, 0,5; yeast extract, 0.5, peptone, 10.0, glucose, 20. The pH of the media was adjusted to 5.0. The flasks were autoclaved at 121 ^{o}C for 15 minutes and then incubated in a rotary orbital shaker at 180 rpm and 30 ^{o}C. They cells were then dried at 80 ^{o}C overnight and were subsequently used for all the experiments [8].

Immobilization of biomass

About 100 ml of 4 % (w/v) sodium alginate was mixed until homogenous with 2% (w/v) solution of the fungal biomass. The mixture was stirred for 1 hour at 30 ^{o}C and then the slurry was dropped through a 10 ml syringe into 2% (w/v) $CaCl_2$ solution [9]. Durable spherical beads containing the biomass were formed immediately. The beads were washed with distilled water and stored at 4 ^{o}C in distilled water until further use.

Adsorption experiments

The adsorption experiments were carried out by varying one parameter at a time while keeping the others constant. The parameters investigated were effects of adsorbent dosage, solution initial pH, initial metal ion concentration and contact time. The experiments were carried out in 100 ml conical flasks containing 50 ml of solution at a constant temperature of 29 ^{o}C. The samples were agitated on a conical flask shaker at 150 rpm at the stated conditions. After equilibrium was attained, the samples were filtered into polypropylene bottles using Whatman No1 filter paper. The residual concentrations of the Pb(II) ions were determined using an Atomic Absorption Spectrophotometer (AA 280FS, Agilent Technologies, Santa Barbara, California, USA).

Data Analysis

The percentage metal removal was calculated using the following equation:

$$\text{Removal \%} = \frac{(C_o - C_e)}{C_o} x\, 100 \quad \text{.........} \quad (1)$$

where C_o and C_e are the initial and the residual (equilibrium) concentrations in mg/L, respectively. The amount of Pb(II) ion adsorbed was calculated from the difference between the added and equilibrium concentration by using the equation below [10]:

$$q_e = \frac{V(C_o - C_e)}{M} \quad \text{.........} \quad (2)$$

where q_e is the amount adsorbed in mg/g of the absorbent at equilibrium, C_o and C_e are the initial and the equilibrium concentrations in mg/L, respectively, V is the volume in litres of the solution used during the experiment and M is the mass of the adsorbent in grams.

Adsorption Isotherms

The data obtained from the adsorption experiments above were fitted into the Langmuir and Freundlich isotherm models

The Langmuir adsorption isotherm

This is often used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. It is expressed by the equation below.

$$\frac{C_e}{q_e} = \frac{1}{K_L Q^o} + \frac{C_e}{Q^o} \quad (3)$$

where K_L (L/g) is a constant related to the adsorption / desorption energy and Q^o (mg/g) is the maximum sorption upon complete saturation of the adsorption of the adsorbent (biosorbent) surface [11]. A graph of C_e/q_e against C_e will have K_L (L/g) as the slope and Q^o (mg/g) as the intercept.

Freundlich Adsorption Isotherm

This was also used to correlate the adsorption equilibrium data in this work. The linearized form of the Freundlich equation is

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (4)$$

where q_e (mg/g) is the adsorption density, C_e is the concentration of metal ion in solution at equilibrium (mg/L), K_f and n are the Freundlich constants which determine the curvature and steepness of the isotherm[12]. Also the value of 1/n indicates the affinity of the adsorbate towards the biomass. A plot of 1og Ce against 1og qe gave the value of 1/n and 1og K_f from the slope and the intercept respectively.

Adsorption Kinetics

The results obtained from the adsorption processes above were analysed with pseudo-first order (Lagergren) and pseudo-second order kinetic models. The kinetics of adsorption describes the rate of metal ions uptake on biosorbent and this rate controls the equilibrium time. The kinetics of the adsorbate uptake is required for selecting optimum operating conditions for the full-scale batch process.

Pseudo – first order kinetic equation

The integrated form of the pseudo first order kinetic equation is given as follows:

$$Log(q_e - q_t) = Log\, q_e - \frac{k_1}{2.303}t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where q_e (mg/L) and q_t (mg/L) are the adsorption capacities at equilibrium and at time t respectively. k_1 (L/min) is the rate constant for a pseudo –first order adsorption. A plot of log (q_e – q_t) against t gave a straight line from which k_1 (L/min) and qe (mg/L) were determined from the slope and intercept of the plot respectively.

Pseudo – second order kinetic equation

Pseudo – second order kinetic equation is expressed as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

where q_e (mg/L) and q_t (mg/L) are the adsorption capacities at equilibrium and at time t respectively and k_2 (g/mgmin) is the rate constant for a pseudo – second order adsorption. A plot of t/q_t against t gave a linear plot from which q_e and k_2 were determined from the slope and intercept respectively.

RESULTS AND DISCUSSION

Effect of adsorbent dosage

The effect of adsorbent dosage on the removal efficiency of Pb(II) ions by the biomass of *Aspergillus fumigatus* and *Penicillium* sp. is presented in Figure 1. The dependence of lead sorption on adsorbent dosage was studied by varying the amounts of adsorbents from 20 - 200 mg, while keeping other parameters constant (i.e. pH , 5.0; metal ion concentration, 20 mg/L; contact time, 120 minutes and temperature, 29 ^oC). The figure shows an increase in the removal efficiency of lead by *Aspergillus fumigatus* from 76.76% at 10 mg biomass weight to 86.17% at 200 mg biomass weight. The removal efficiency of *Penicillium* sp. for the Pb (II) ions showed the highest percentage removal of 62.51% at 150 mg biomass weight while the lowest (28.21%) occurred at 50 mg biomass weight. The increase in removal percentage with increase in adsorbent concentration is due to increase in active sites and surface area for binding. This trend of Pb(II) removal has been reported by Hussain *et al*. [13] and Iqbal *et al*. [14].

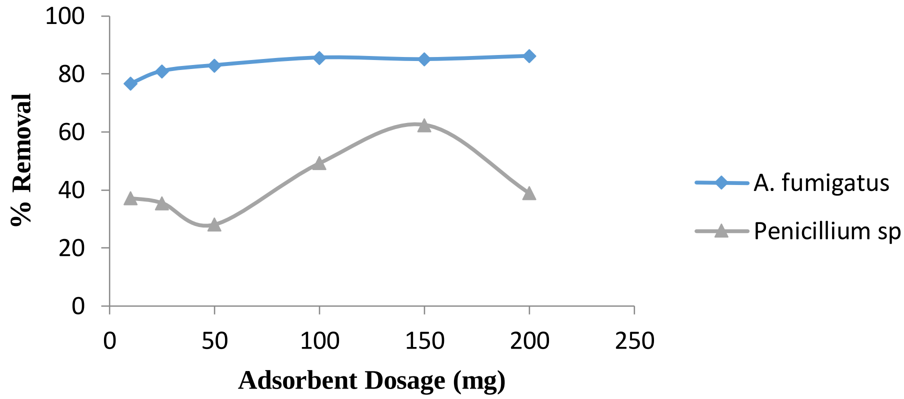

Figure 1: Effect of adsorbent dosage on Pb(II) removal by alginate – immobilized fungal biomass

Effect of solution pH

The effect of the pH on the removal of Pb(II) ions from solution is presented in Figure 2. The effect of the pH on the removal of Pb(II) ions from solution was studied by varying the solution pH from 3.0 – 9.0 while keeping other parameters constant.

As can be seen from the figure, the maximum removal percentage of *Aspergillus fumigatus* was 99.62% at pH 7.0 while the lowest was 67.15% at pH 3.0. For *Penicillium* sp., the removal percentage increased from 23.66% at pH 3.0 to 79.17% at pH 8.0 which was the maximum. At low pH (less than 5), protons compete with Pb(II) ions for active binding sites on the adsorbent. Charge repulsion occurred as the adsorbent became more positively charged due to active sites being protonated under acidic conditions. With increase in pH, the deprotonation of acid functional groups such carboxyl and hydroxyl active sites of the adsorbent were strengthened and the attraction between negative charge of adsorbent and positive charge of Pb(II) cations increased leading to a higher removal of Pb(II) . Vaghetti et al. [15] reported that the optimum removal efficiency of Pb(II) , Cu(II) and Mn(II) by Pecan nutshell was observed in the pH range 5.0 – 6.0.

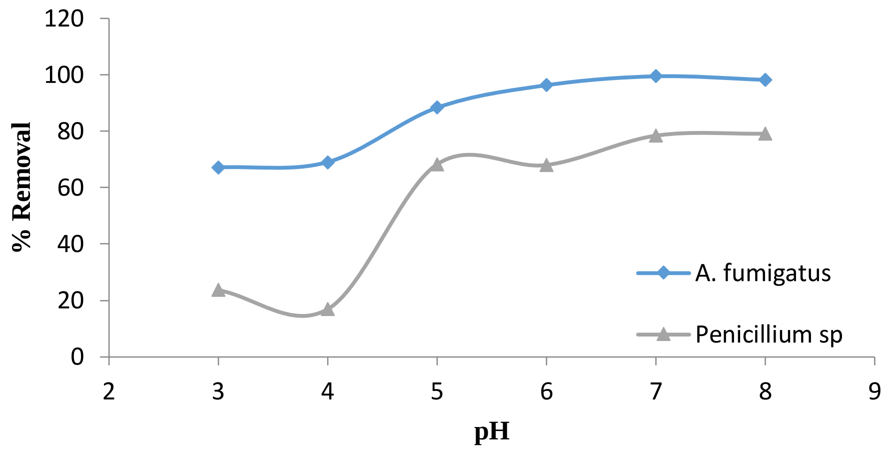

Figure 2: Effect of solution pH on Pb(II) removal by alginate – immobilised fungal biomass

Effect of contact time

The effect of the contact time on the removal of Pb(II) ions from solution is presented in Figure 3. From the figure it can be seen that the removal percentage of the Pb(II) ions by *Aspergillus fumigatus* increased from 82.55% at 10 minutes to the maximum of 98.24% at 100 minutes contact time. For *Penicillium* sp., the removal percentage increased from 3.86% at 10 minutes contact time to 82.00% at 120 minutes which was the highest percentage removal. Two stages of reactions beginning with a rapid increase followed by a saturation stage are depicted in the figure. For *Aspergillus fumigatus* the saturation stage was reached after 20 minutes of contact while the saturation stage was attained after 80 minutes for *Penicillium* sp. This shows that the initial active sites on the adsorbent were occupied in the first stage and the subsequent slow phase occurred due to diffusion of Pb(II) ions into the microporous inner surface of the adsorbent. Pejic et al. [16] reported similar observation whereby reactions started rapidly, followed by a saturation stage with no significant changes with further increase in contact time.

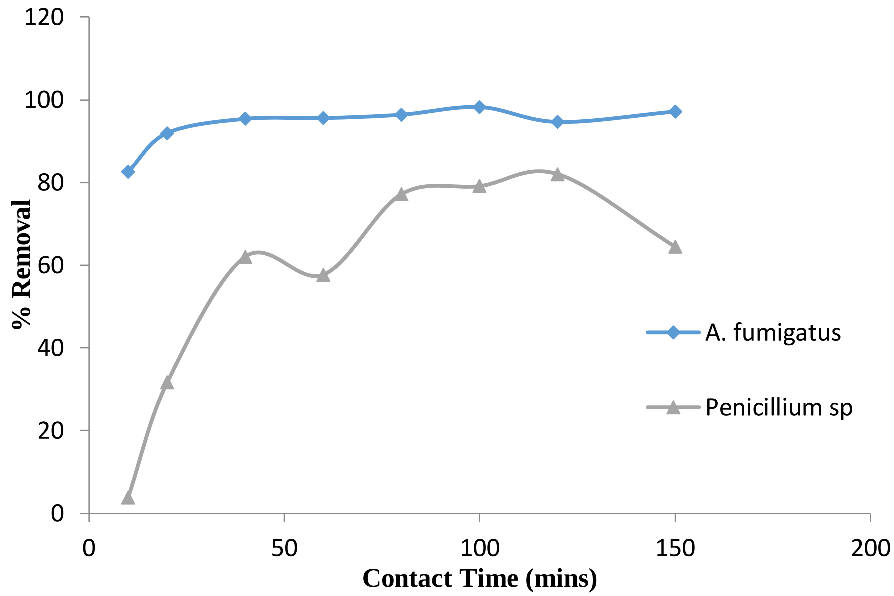

Figure 3: Effect of contact time on Pb(II) removal by alginate – immobilized fungal biomass

Effect of initial Pb(II) ion concentration

The effect of initial metal ion concentration on the removal of Pb(II) ions from solution is presented in Figure 4. From the figure it can be seen that the removal percentage of Pb(II) ions by *Aspergillus fumigatus* decreased from 98.78% at 20 mg/L to 38.26% at 120 mg/L metal ion concentration. For *Penicillium* sp., the removal percentage decreased from 67.17% at 20 mg/L to 11.29% at 120 mg/L. Initial Pb(II) concentrations acted as a driving force that overcame all mass transfer resistances between solution and biosorbent. The increase in initial Pb(II)) concentrations resulted in relative reduction of available binding sites, leading to reduction in Pb(II) removal. Similar results have also been reported by King et al. [17] and Abdel-Ghani et al. [18].

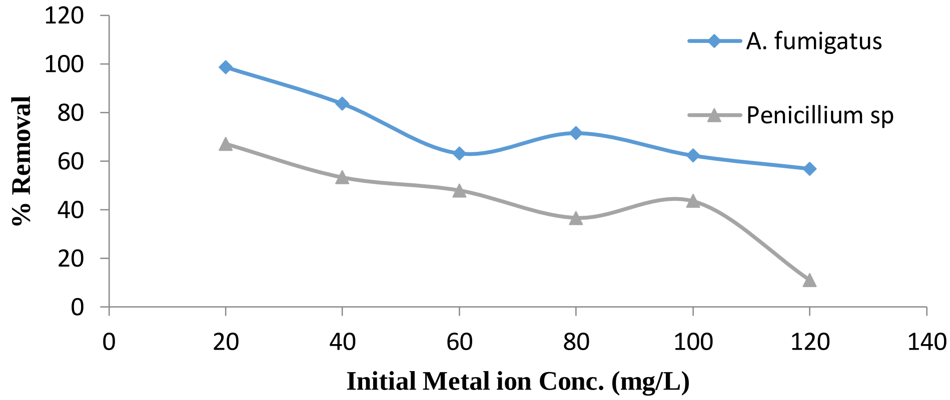

Figure 4: Effect of initial metal ion concentration on Pb (II) removal by alginate – Immobilized fungal biomass

Adsorption Isotherms

Langmuir isotherm

The Langmuir isotherm plots for the biosorption of Pb(II) by the biosorbents are presented in Figure 5. The values of the coefficient of determination, R^2, for Langmuir equations for the two biosorbents are 0.9724 and 0.9980 for *Aspergillus fumigatus* and *Penicillium* sp. respectively. The value of R^2 for the biosorbents are close to unity there by indicating efficacy of fitting Langmuir model to the equilibrium data for the biosorption of Pb(II) onto both biosorbents. Maximum biosorption capacity Q^o (mg g-1) for *Aspergillus fumigatus* and *Penicillium* sp. were calculated to be 29.15 and 15.58 mg g-1 respectively.

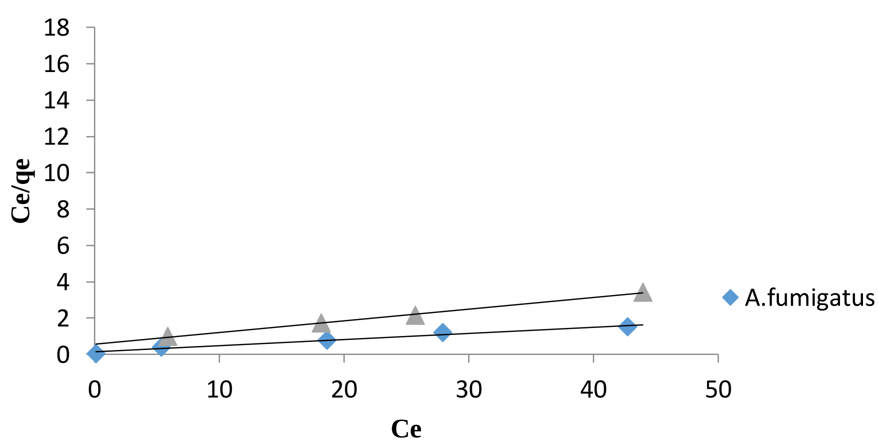

Figure 5: Langmuir isotherm for the biosorption of Pb(II) by alginate – immobilized fungal biomass

Freundlich isotherm

The Freundlich isotherm plots for the biosorbents *Aspergillus fumigatus* and *Penicillium* sp. are presented in Figure 6. The values of the determination coefficient, R^2, for *Aspergillus fumigatus* and *Penicillium* sp. were found to be 0.9139 and 0.9143 respectively which shows that the biosorption of Pb(II) ions onto the biosorbents has followed the Freundlich isotherm model. The values of Kf and n were calculated from slope and intercept of the Freundlich plot between qe and ln Ce as presented in Table 1. The values of n for the biosorbents are 3.64 and 2.11 Lmg-1 for *Aspergillus fumigatus* and *Penicillium* sp. respectively. These values lie between 1 and 10 thus indicating a beneficial adsorption [19]. The values of Q^o and n for the two biosorbents indicate that *Aspergillus fumigatus* will be a more efficient adsorbent for the uptake of lead from solution.

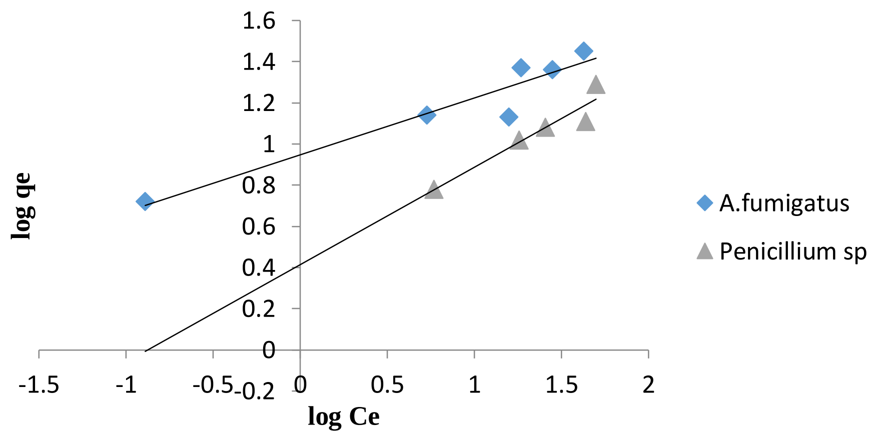

Figure 6: Freundlich isotherm for the biosorption of Pb(II) by alginate – immobilized fungal biomass

Table 1: Langmuir and Freundlich Isotherm Parameters for Lead (II) uptake by fungal biomass

Isotherm	**Biosorbents**		
	Constants	*A. fumigatus*	*Penicillium* sp
Langmuir	Q^o (mgg^{-1})	29.15	15.58
	K_L (Lmg^{-1})	0.25	0.11
	R^2	0.9724	0.9980
Freundlich	K_f (mgg^{-1})	8.86	2.60
	n (Lmg^{-1})	3.64	2.11
	R^2	0.9139	0.9143

Adsorption Kinetics

Pseudo – first order kinetics

The pseudo – first order kinetic plots for the adsorption of Pb(II) onto alginate - immobilized *Aspergillus fumigatus* and *Penicillium* sp. are shown in Figure 7. As the figure shows, the correlation coefficient, R^2, for the pseudo – first order kinetic plot for the biosorbents are 0.7403, and 0.9329 for *Aspergillus fumigatus* and *Penicillium* sp. respectively. Although the values of R^2 are close to unity, the calculated qe values differ wildly from the experimental qe values. These results suggest that this model was unsuitable to fit the experimental data for the biosorption of Pb(II) onto the biosorbents.

Pseudo – second order kinetics

The pseudo – second order kinetic plots for the adsorption of Pb(II) onto alginate – immobilized *Aspergillus fumigatus* and *Penicillium* sp. are shown in Figure 8. The R^2 values for the two biosorbents are 0.9993 and 0.9151 respectively. The adsorption capacity, *qe*, calculated by the model for the two biosorbents are very close to the experimental values (Table 2b). These results indicate that the adsorption process for the metal ion can be described by the pseudo – second order kinetic model. The pseudo – second order model is based on the assumption that the rate – determining step may be a chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and sorbate [20].

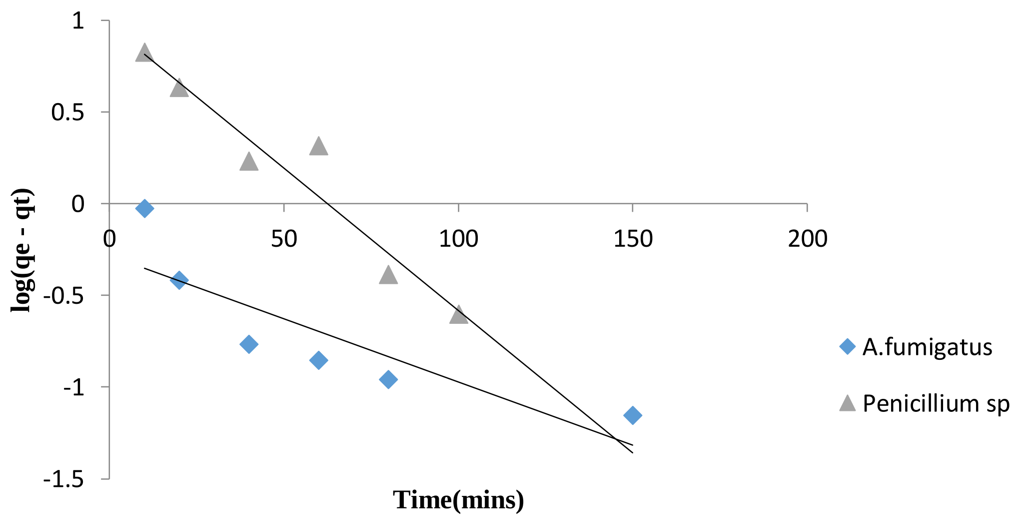

Figure 7: Pseudo – first order kinetic plot for the biosorption of Pb(II) onto alginate – immobilized fungal biomass

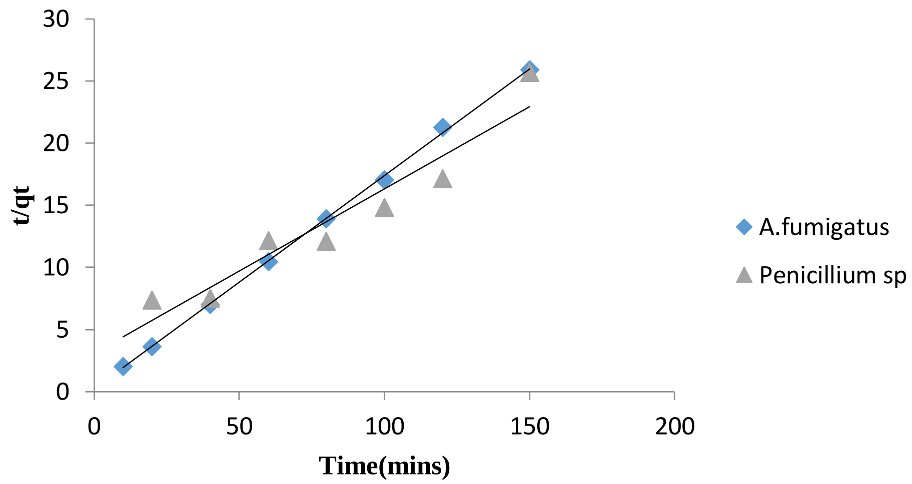

Figure 8: Pseudo – second order kinetic plot for the biosorption of Pb(II) onto alginate – immobilised fungal biomass

Table 2. Kinetic Parameters for Lead (II) uptake by Fungal Biomass

(2a)

	Pseudo – first order kinetic parameters			
	qe (Experimental)	R^2	k_1	qe (Calculated)
A. fumigatus	5.86	0.7403	0.016	0.520
Penicillium sp	6.99	0.9329	0.036	9.358

(2b)

	Pseudo – second order kinetic parameters			
	qe (Experimental)	R^2	k_1	qe (Calculated)
A. fumigatus	5.86	0.9993	0.142	5.817
Penicillium sp	6.99	0.9151	0.251	7.541

CONCLUSION

The results of this investigative study have shown that both *Aspergillus fumigatus* and *Penicillium* sp. are good biosorbents for Pb(II) ions in solution. The removal efficiency of the Pb(II) by both biosorbents increased with an increase in adsorbent dosage and pH. The adsorption isotherms plotted for the results showed that the experimental data fitted the

Langmuir isotherm better than the Freundlich isotherm for both biosorbents. The kinetic modeling showed that the biosorption reaction followed the pseudo – second order model which indicates that chemisorption is the probable mechanism for the process. The isotherm and kinetic parameters also indicated that *Aspergillus fumigatus* has better removal efficiency for lead (II) than *Penicillium* sp.

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