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Characterization and sorption behavior of some toxic metal ions on *Fusarium oxysporum* as biomass adsorbent

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ABSTRACT

In this study the possibility of the pretreated biomass of *Fusarium oxysporum* in biosorption of heavy metal ions such as Pb^{2+} and Co^{2+} from single metal solutions is investigated. The structural morphology and composition of the studied biosorbent were evaluated by scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The dead *F. oxysporum* biomass was pretreated and tested in batch system. The effects of the operating parameters, such as pH, contact time, initial metal concentrations, biomass dosage, and temperature on the removal efficiency of metal ions have been studied. The optimum pH for biosorption was 6.0. *F. oxysporum* exhibited selectivity for Pb^{2+} and Co^{2+} in the order of $Co^{2+} > Pb^{2+}$. The interaction between metal ions and biomass function groups was characterized by FTIR spectroscopy. The equilibrium biosorption data were analyzed using different isotherm models. The biosorption data were best described by Langmuir and Flory–Huggins isotherms. The breakthrough capacity obtained from column study was found to be equal to 10.10 and 12.15 mg/g for Pb^{2+} and Co^{2+}, respectively. Thermodynamic parameters ($\Delta H°$, $\Delta G°$, and $\Delta S°$) were calculated and indicated that an endothermic spontaneous process. The main novelty of this work was the preparation of *F. oxysporum* biomass in rigid beads suitable for column operation with reasonably good breakthrough capacity.

Keywords: Biosorption; *Fusarium oxysporum*; Heavy metal ions; Distribution studies; Isotherm models; Thermodynamics

1. Introduction

Pollution by heavy metal ions has become one of the most dangerous environmental problems today. The heavy metal ions move at a very high speed in the aquatic circles, thus increasing their toxicity [1]. Heavy metals are presented in the following elements: cadmium, zinc, copper, mercury, lead, iron, cobalt, arsenic, aluminum, nickel, chromium, gold, tin, selenium, molybdenum, manganese, and silver [2]. Most of these heavy metals are known for their toxicity, carcinogenicity, and a significant risk to all living organisms [3–5]. Many techniques have been applied to remove heavy metal ions from their liquid wastes such as chemical precipitation, ion exchange, electrochemical treatment, membrane technologies, and adsorption [6]. Each of this technique has its own advantages and disadvantages. Chemical precipitation and electrochemical techniques are useless, especially when the concentration of the metal ion in aqueous solution is lower than 50 mg/L. Add to that, such techniques fabricate large quantities of sludge to be treated with great difficulties. Many techniques such as adsorption using active carbon, ion exchange, and membrane technologies are extremely expensive. Therefore, the biosorption

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technology has been applied to remove heavy metal ions as an inexpensive technique, which is known for the last few decades. Algae, fungi, bacteria, and yeast have been used as a highly efficient biosorbents because of their ability to remove heavy metal ions from their waste solutions [7].

The biosorption process involves a solid phase (sorbent or biosorbent; biological materials) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, metal ions). Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and removed by different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases [8]. Heavy metal ions can be removed from wastewater as well as extracted from their solutions by biotechnological methods that use microorganisms as sorbents [9]. Biomass derived from molds and yeasts [8] especially *Candida utilis* [10] has the ability to uptake the heavy metal ions from the environment. Fungi and yeast accumulate micronutrients such as Cu, Zn, Mn, and nonnutrient metals, such as U, Ni, Cd, Sn, and Hg in quantity higher than nutritional demands [9]. The potential of fungal biomass as biosorbent has been applied for sorption of the heavy metal ions from polluted waters [8,11].

In this paper, the dead *Fusarium oxysporum* biomass was pretreated and characterized by means of scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA) and then their sorption behavior for Pb^{2+} and Co^{2+} were investigated by batch system. The equilibrium biosorption data were analyzed using Langmuir, Freundlich, Dubinin–Radushkevich (D-R), and Flory–Huggins isotherms. The biosorption capacities (q_m) were determined and compared with other sorbents.

2. Experimental

2.1. Chemicals and reagents

Stock solutions (1 g/L) of Pb(II) and Co(II) were prepared by dissolving $Pb(NO_3)_2$ and $CoCl_2$ in demineralized water. The reagents were supplied by Merck (Germany) as analytical-grade reagents, and deionized water was used. All other reagents and chemicals were of analytical reagent grade purity and used without further purification. The pH of solutions was measured using pH meter of the bench, model 601A, USA.

2.2. Preparation of the biosorbent

F. oxysporum fungi was kindly provided by Abdel Aziz, 2005 [12] and allowed to grow on flasks containing broth dox medium (g/L), sucrose 30.0, $NaNO_3$ 3.0, KH_2PO_4 1.0, $MgSO_4{\cdot}7H_2O$ 0.5, KCl 0.5, $FeSO_4{\cdot}5H_2O$ 0.001, $CaCl_2$ 0.001 and rose bengal (Merck) as a bacteriostatic agent (0.065) [13,14]. Mycelium of *F. oxysporum* was cultured in 2 L flasks containing 1,000 mL broth dox medium at 25°C, 125 rpm in an incubator shaker for 21 d. Harvested mycelium was autoclaved to obtain dead biomass, and filtered off and washed with double distilled water [15]. Finally, dead biomass was oven dried at 70°C, grinded in a mortar and then stored at desiccators.

2.3. Physical and chemical characteristics of the biosorbent

Moisture percentage of *F. oxysporum* biomass was evaluated by heating a known weight of sample at 105°C ± 2°C in hot air oven for 4 h. Heating, cooling, and weighing were repeated at 20 min interval until the weight became constant. The difference in weights gave the percentage of moisture content. After determining the moisture content the same sample was ignited in muffle furnace at 1,000°C for about 3 h. The process of heating and cooling was repeated until constant weight was obtained. Ash content was calculated from the weight of the remaining solid (g) divided by the initial weight of the sample. The bulk density was estimated as follows: a 20 mL graduated cylinder was weighed accurately and filled to 20 mL mark with *F. oxysporum* fungi biomass and weighed again accurately. The difference in weight gives weight of biomass sorbent. The density was then calculated by dividing the weight of biomass by 20. The chemical stability of *F. oxysporum* biosorbent was studied in water, 3 M HCl, and 3 M NaOH, by mixing 100 mg of each of the prepared sorbent with 100 mL of the desired solution with intermittent shaking for about 3 d at 25°C ± 1°C. The specific surface area of the biosorbents was made by the Brunauer, Emmett and Teller (BET) method using the instrument MICROMERITICS GEMINE 2375. It was carried out in the micro-analytical center, Cairo University, Egypt. The FTIR spectrum of the powdered samples was recorded using a Shimadzu infrared spectrometer (BOMEM-FTIR) obtained from Shimadzu Kyoto "Japan." The KBr disk method was used to recognize the functional groups. In this concern, the sample was comprehensively mixed with KBr as a matrix; the mixture was ground to a very fine powder and then pressed to give a transparent disc with standard diameter and free from moisture. The disk formed was examined in FTIR spectrophotometer from 4,000 to 400 cm^{-1}. The surface morphology was studied using Jeol SEM of JSM-6510A Model, Japan. The morphology of the particles was identified, operating with beams of primary electrons ranging from 5 to 30 keV. TGA was investigated using a Shimadzu DTG-60 thermal analyzer obtained from Shimadzu Kyoto "Japan" with a platinum sample holder. The phase changes and weight losses of the sample were measured for ambient temperature up to 1,000°C in N_2 atmosphere, with the heating rate of 10 deg/min and using alumina powder as a reference material.

2.4. Biosorption studies

Biosorption experiments were achieved by contacting 0.05 g of the dead biomass with 5 mL of 50 mg/L of Pb(II) and Co(II) ions solution at a V/m ratio of 100 mL/g at a shaking speed of 150 rpm for 200 min. Studding the impact of initial pH on metal ion removal was carried out over pH range of 1.0–6.0. The influence of temperature on the biosorption experiments was investigated in the temperature range of 20°C–60°C ± 1°C. The biosorption of heavy metal ions was studied as a function of initial concentrations in the range of 50–500 mg/L. After equilibrium, the solutions were separated by centrifugation at 4,000 rpm for 20 min. The concentration of the metal ions was measured using atomic absorption spectrophotometer (AAS). All tests were repeated for three times and the total experimental error was found to be about ±3%. The percentage biosorption (% R), K_d (mL/g), and q_e (mg/g) were calculated using the following equations, respectively:

$$\%R = \frac{C_o - C_f}{C_o} \times 100 \tag{1}$$

$$K_d\left(\text{mL/g}\right) = \frac{[C_o - C_f]}{C_f} \times \frac{V}{m} \tag{2}$$

$$q_e = \frac{\%R}{100} \times \frac{V}{m} \times C_o \tag{3}$$

where K_d is the distribution coefficients, q_e is the amount of metal ions extracted by biosorbent at equilibrium, C_o and C_f are the concentrations of the ions in solution before and after equilibration (mg/L), respectively, V is the solution volume (mL), and m is the biosorbent mass (g).

2.5. Separation factor

The separation factor was used to examine the separation ability of an adsorbent toward two adsorbed ions of equal concentration and was also expressed as the relation of the distribution coefficients of the ions to be separated as follows:

$$\text{Separation factor } \alpha_B^A = \frac{K_d\left(A\right)}{K_d\left(B\right)}$$

where $K_d(A)$ and $K_d(B)$ are the distribution coefficients for the two competing species A and B in the removal system.

2.6. Continuous flow column

A column of diameter (1.4 cm diameter and 5 cm height) was packed with 1 g *F. oxysporum* biomass. Influent 200 mL of 100 mg/L (pH = 5.50) of metal chloride [M $(\text{Cl})_x$ where M = Pb^{2+} and Co^{2+}] were pumped through the column beds at a constant flow rate of 0.75 mL/min. At this volume the studied biosorbent is completely saturated with Pb(II) and Co(II) ions. The effluent fractions were collected and the concentrations were continuously measured using AAS. The values of breakthrough capacity were calculated using the following equation:

$$Q_{0.5} = V_{(50\%)} \times \frac{C_i}{m} \tag{4}$$

where $Q_{0.5}$ is the breakthrough capacity (mg/g); $V_{(50\%)}$ is the effluent volume at 50% breakthrough (mL); C_i is the concentration of feed solution (mg/L); m is the amount of the column bed (g).

2.7. Thermodynamic parameters

To explore the nature of the biosorption process, the impact of temperatures in removal of Pb(II) and Co(II) ions was studied and the thermodynamic parameters were calculated. The Gibb's free energy change ($\Delta G°$) (kJ/mol) was determined by using the following equation:

$$\Delta G° = -RT \ln K_d \tag{5}$$

where T is the absolute temperature, R is the universal gas constant (8.3143 J/mol K). The values of standard enthalpy change ($\Delta H°$) (kJ/mol) and standard entropy change ($\Delta S°$) (J/mol K) can be estimated by using Van't Hoff equation:

$$\ln K_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \tag{6}$$

Plotting of ln K_d versus $1/T$ gives a linear relationship and the values of $\Delta H°$ and $\Delta S°$ were calculated from the slope ($-\Delta H°/R$) and intercept ($\Delta S°/R$), respectively.

3. Results and discussion

3.1. Characterization of the dried biosorbent

The physical and chemical characterization of *F. oxysporum* fungi biomass is presented in Table 1.

3.1.1. Fourier transform infrared spectroscopy

F. oxysporum biomass was analyzed by FTIR spectroscopy in order to determine its functional groups as shown in Fig. 1. The results gave sufficient information about the functional groups on the surface of the cell wall of the biomass and the possible interaction between metals and these functional groups. Usually, the cell wall of fungal compromise of carboxyl (–COOH), phosphate (–PO), amide (–NH), thiol (–SH), and hydroxide (–OH) which are important functional groups during heavy metal ions binding [16]. From these data, it is obvious that the strong and broad band at 3,393 cm^{-1} might be associated to the overlapping between N–H and O–H stretching vibration. However, the band at 2,924 cm^{-1} could be attributed to the C–H stretch [17,18] and the band at 1,646 cm^{-1} could be assigned to asymmetric stretching vibration of C=O [17]. Moreover, the intense and strong band at 1,053 cm^{-1} might be attributed to the stretching of C–O group on the biomass surface [17,18]. Meanwhile, some bands in the finger print region may be associated to the phosphate groups.

Table 1
Physicochemical characteristic of *Fusarium oxysporum* fungi

Characteristics	Values
Moisture content (%)	10.23
Ash content (%)	7.76
Bulk density (g/mL)	0.75
Surface area (m^2/g)	20
Average particle size (μm)	>100
Matter soluble in water (%)	Nil
Matter soluble in 3 M HCl (%)	Nil
Matter soluble in 3 M NaOH (%)	Nil

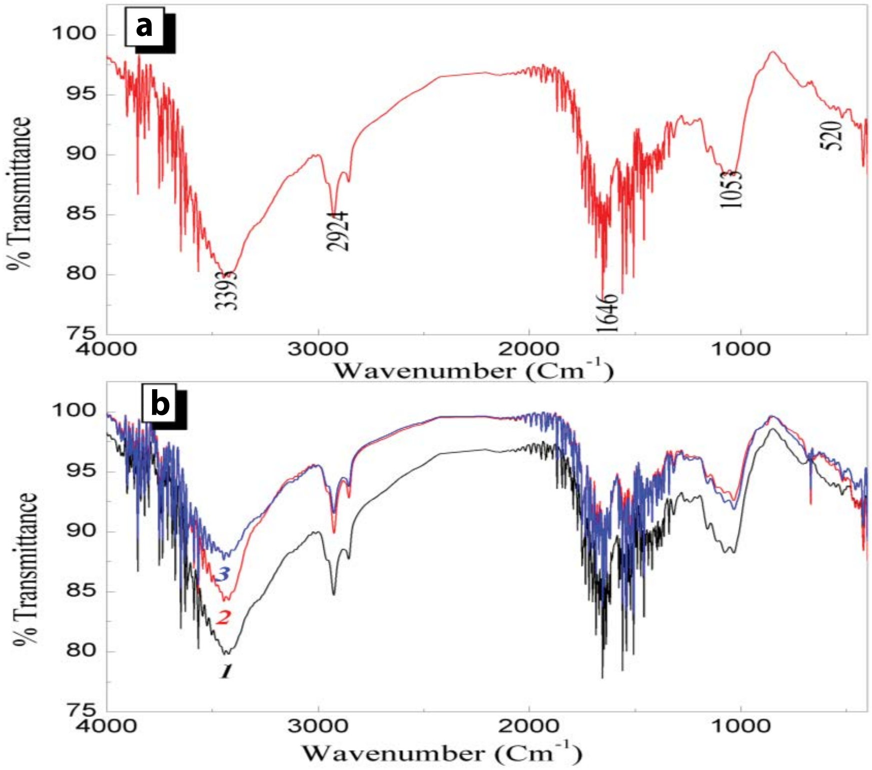

Fig. 1. The IR spectrum of (a) *Fusarium oxysporum* fungi and (b) ((1) unloaded *Fusarium oxysporum* fungi biomaterial, (2) Pb(II)-loaded biomaterial, and (3) Co(II)-loaded biomaterial).

The results also indicated that the bands at 3,393, 2,924, 1,646, 1,053, and 520 cm^{-1} were shifted to 3,411, 2,922, 1,653, 1,043, and 546 cm^{-1} after loading of Pb(II) and Co(II) ions. This significant changes in the wave number of these peaks after loading process illustrate that the functional groups (amido, hydroxyl, C=O and C–O) were consumed in the biosorption of Pb(II) and Co(II) ions on the surface of *F. oxysporum* fungi. Similar results for the biosorption of heavy metals on different species of algae have been previously reported by others [6,19–21].

3.1.2. Scanning electron microscope

SEM of *F. oxysporum* fungi is shown in Fig. 2. The morphology of this material can facilitate the sorption of metal ions, due to the irregular surface of the *F. oxysporum* fungi and presence of some cracks and gaps, thus make the sorption of the studied ions in different parts of this material is possible. From the morphology study, it is possible to conclude that the biomass under study provides an adequate morphological profile to retain metal ions.

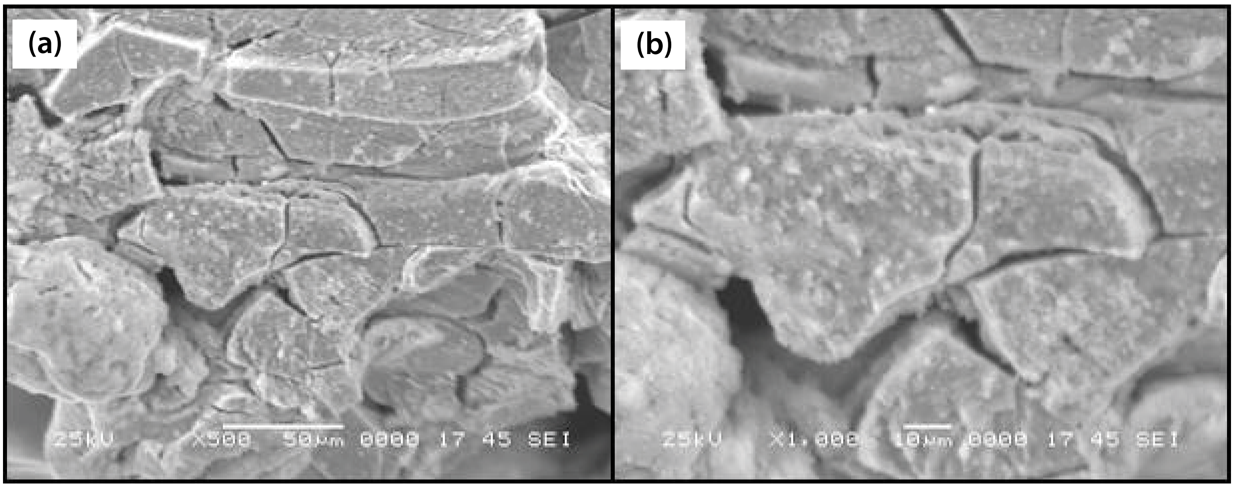

Fig. 2. SEM analyses of *Fusarium oxysporum* fungi biomaterial. (a) Magnitude of 500× and (b) magnitude of 1,000×.

3.1.3. Thermogravimetric analysis

To study the thermal characteristic of the *F. oxysporum* fungi, the sample was analyzed by TGA as illustrated in Fig. 3. From Fig. 3, it was noticed that the *F. oxysporum* fungi exhibits three distinct stages. The first stage ranges between 31°C and 266°C is associated with the loss of adsorbed and bound water [17]. This stage shows 10.23% weight loss. The weight loss (38.29%) occurred in the range 266°C–378°C (Fig. 3), which was due to major degradation of the total lipids [22]. The end stage of the weight loss starts at 378°C and continues up to 800°C. This stage shows that 37.36% weight loss corresponding to the bulk decomposition of the polysaccharide structure [23].

3.2. Factors affecting the biosorption of Pb(II) and Co(II) ions

3.2.1. Effect of biomass dosage

The impact of biomass amount on the removal of Pb(II) and Co(II) ions is illustrated in Fig. 4. With an increase in biosorbent dosage from 0.016 to 0.05 g, the biosorption efficiencies of Pb(II) and Co(II) increased from 26.46% and 27.323% to 89% and 97% for Pb(II) and Co(II), respectively. The percentage removal of Pb(II) and Co(II) reached equilibrium at 0.05 g biosorbent with 89% and 97%, respectively. The increase in Pb(II) and Co(II) removal efficiencies with the biosorbent dosage could be attributing to increase in surface area and the availability of more binding sites [17].

3.2.2. Effect of contact time

The influence of contact time in biosorption of Pb(II) and Co(II) ions was investigated in the range of 5–200 min as shown in Fig. 5. The percentage removal reached 46.3 and 47.23 for Pb(II) and Co(II) ions, respectively, by using 0.05 g biomass in 5 min. Rapid uptake of Co(II) ions occurred in 30 min than Pb(II) ions. The equilibrium was achieved at 150 min and after this time the percentage removal of the studied ions did not change significantly. Thus the results illustrate that 150 min is the best contact time to achieve the maximum percentage removal of Pb^{2+} (89%) and Co^{2+} (97%). Increase the rate of biosorption by increasing contact time due to the interaction occurred between the active sites of biomass and heavy metal ions. After equilibrium, the active sites become completely saturated with the sorbed ions and the percentage removal did not significantly change [24]. This result is important, because contact time is one of the most essential parameters for an economical waste water treatment system.

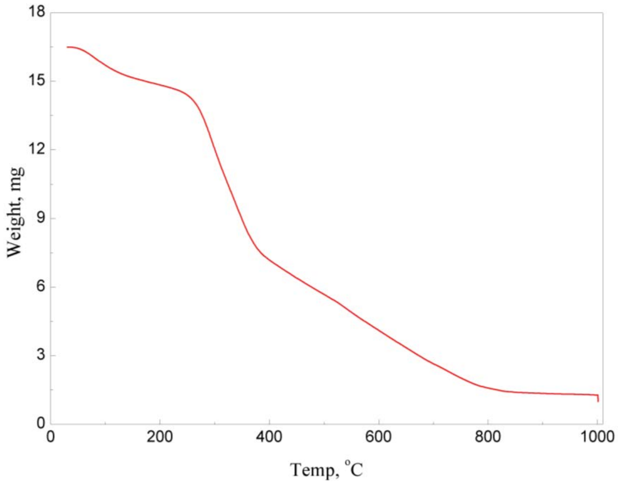

Fig. 3. Thermogravimetric analysis (TGA) curve of *Fusarium oxysporum* fungi biomaterial.

3.2.3. Effect of initial concentrations

Different initial metal ion concentrations in the range of 50–500 mg/L were investigated as impact factor in the removal. Fig. 6 shows that the removal decreases with an

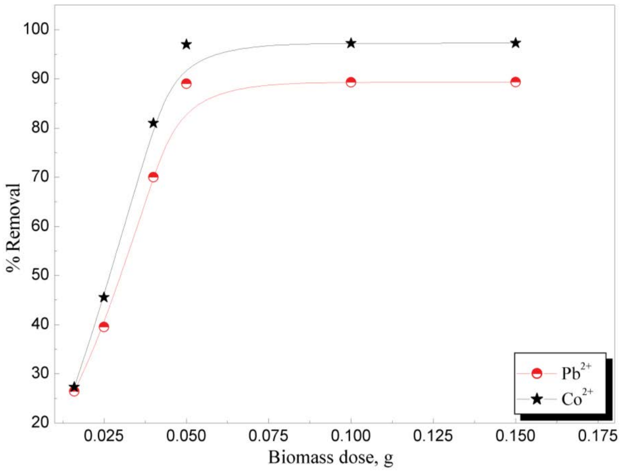

Fig. 4. Effect of biomass dosage on removal of Pb(II) and Co(II) ions by *Fusarium oxysporum* fungi at agitating rate, 150 rpm; pH, 6; temperature, 25°C ± 1°C; initial metal concentration, 50 mg/L; contact time = 150 min.

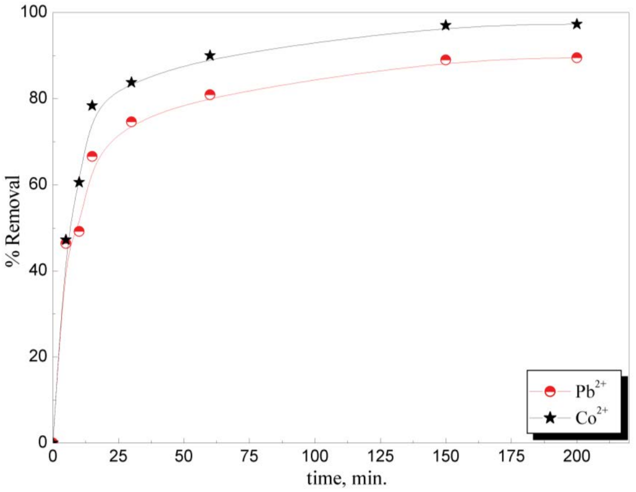

Fig. 5. Effect of contact time on removal of Pb(II) and Co(II) ions by *Fusarium oxysporum* fungi at agitating rate, 150 rpm; pH, 6; temperature, 25°C ± 1°C; initial metal concentration, 50 mg/L; biomass dosage = 0.05 g.

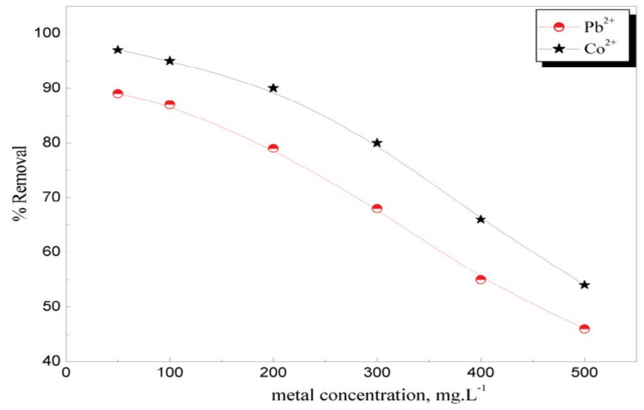

Fig. 6. Effect of the initial metal concentrations on removal of Pb(II) and Co(II) ions by *Fusarium oxysporum* fungi at agitating rate, 150 rpm; pH, 6; temperature, 25°C ± 1°C; contact time = 150 min; biomass dosage = 0.05 g.

increase in initial concentration by using 0.05 g of biomass. The metal ions removal decreased from 89% to 46% and 97% to 54% for Pb(II) and Co(II), respectively, as the initial metal ion concentrations increase from 50 to 500 mg/L. At low concentrations, possible heavy metal ions binding sites of biomass were available for quick binding. At higher concentrations, the binding sites were decreased and hence slow diffusion of the studied metal ions to the biomass surface was occurred due to interparticle interactions caused to decreasing removal percentage of heavy metal ions [25].

3.2.4. Effect of pH

pH is the most essential parameter affecting biosorption of heavy metal ions onto *F. oxysporum* fungi. The net charge on biomass changes with ambient pH. At low pH values, active sites of biomass protonated and possible negatively charged binding sites decreased. In the high pH values, these sites are deprotonated and made available for binding [18]. To determine the influence of pH, the biosorption study took place in the range of 1.0–6.0. From Fig. 7, it can be noticed that the percentage removal of the studied metal ions is increased by raising pH values. At higher $[H]^+$, the surface of the biomass becomes rich in H^+, causing electrostatic repulsion between protonated surface and sorbed metal ions. The competition between H^+ ion and heavy metal cations decreased by increased pH values and results in higher removal percentage at higher pH ranges [21,26]. The maximum removal percentage was achieved at around pH = 6 for the studied heavy metal ions (Fig. 7). Depending on the pH of the heavy metal ion solutions, complexation and ion exchange mechanisms occurred during the biosorption experiments.

3.2.5. Effect of temperature

Temperature is a significant factor for biosorption process. Fig. 8 shows the influence of temperature on removal efficiencies of heavy metal ions. The removal efficiencies increased to 94.96% and 99.76% for Pb(II) and Co(II), respectively, as temperature increased from 20°C to 60°C ± 1°C. At high temperature, the interaction rate between biomass and heavy metal ion increased.

3.3. Biosorption thermodynamics

The thermodynamic parameters were calculated using Eqs. (5) and (6) as illustrated in Fig. 9. Values of this parameter are summarized in Table 2. The positive value of $\Delta H°$ showed the endothermic nature of the biosorption process, while the positive value of $\Delta S°$ indicates that there is an increase in the randomness at solid/solution interface during the biosorption of Pb(II) and Co(II) ions on *F. oxysporum* fungi [17,18]. Values of $\Delta G°$ are negative, confirming that the biosorption of Pb(II) and Co(II) ions onto *F. oxysporum* fungi is spontaneous and thermodynamically favorable [17,18].

3.4. Biosorption isotherm models

The four most common sorption isotherm models were applied to explain the distribution of metal ions between the sorbent and adsorbate solution when equilibrium was

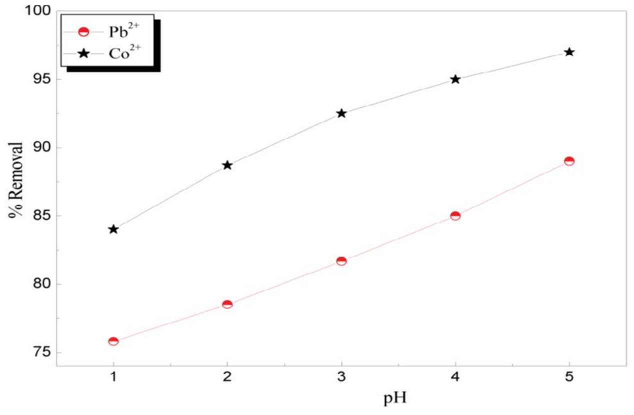

Fig. 7. Effect of initial pH on removal of Pb(II) and Co(II) ions by *Fusarium oxysporum* fungi at agitating rate, 150 rpm; temperature, 25°C ± 1°C; initial metal concentration, 50 mg/L; contact time = 150 min; biomass dosage = 0.05 g.

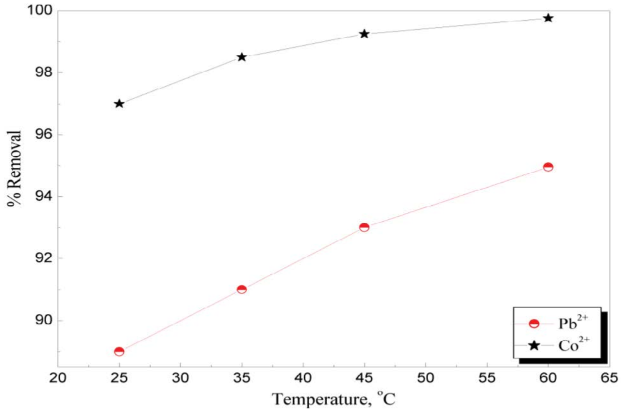

Fig. 8. Effect of temperatures on removal of Pb(II) and Co(II) ions by *Fusarium oxysporum* fungi at agitating rate, 150 rpm; pH, 6; initial metal concentration, 50 mg/L; contact time = 150 min; biomass dosage = 0.05 g.

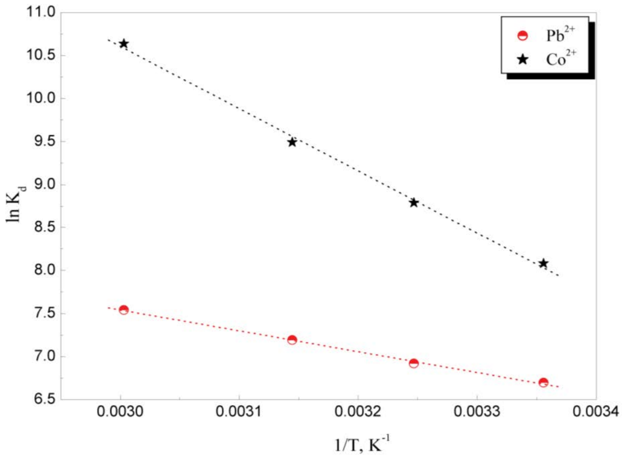

Fig. 9. Van't Hoff plot for adsorption of Pb(II) and Co(II) ions by *Fusarium oxysporum* fungi.

reached. They are Langmuir, Freundlich, D-R, and Flory–Huggins models.

3.4.1. Langmuir isotherm

The Langmuir model assumes that the sorption occurs at specific homogeneous sites on the adsorbent by monolayer adsorption without any interaction between adsorbed ions [27]. The linear form of the Langmuir equation is illustrated in Table 3. The Langmuir isotherm is applicable to the adsorption process if the plot of C_e/q_e versus C_e is linear and passes through the origin. The Langmuir constants q_m and K_L with correlation coefficients (R^2) were calculated from the plots in Fig. 10(a) and the data are given in Table 4. It was deduced that the linear regression coefficient (R^2) were found to be 0.9999 for Pb(II) and Co(II) biosorption. The R^2 values indicate that the biosorption of Pb(II) and Co(II) ions onto *F. oxysporum* biomass fitted well the Langmuir model. The maximum biosorption capacities (q_m) for Pb(II) and Co(II) ions are 25.64 and 28.09 mg/g, respectively. It is observed that Co(II) is sorbed more than Pb(II) at the optimum experimental conditions. Differences of biosorption capacity are due to the smaller ionic radii of Co(II) (0.72 Å) compared with Pb(II) (1.20 Å) [36].

The dimensionless constant separation term (R_L) was calculated to investigate the shape of the Langmuir isotherm and to determine high affinity of adsorption. R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$) [37]. In this study, the R_L values were found to be 0.047 and 0.018 for Pb(II) and Co(II) ions, respectively, which shows the biosorption process was favorable.

3.4.2. Freundlich isotherm

The Freundlich model can be applied for nonideal sorption on heterogeneous surfaces and multilayer sorption. The linear plot of log q_e versus log C_e is shown in Fig. 10(b). The values of 1/n and k_f can be calculated from the slope and intercept, respectively, and the results are given in Table 4. The values of K_F and 1/n were found to be 2.72 and 0.41 for Pb(II) biosorption and 5.13 and 0.34 for Co(II) biosorption, respectively. The 1/n values were between 0 and 1 indicating that the biosorption of Pb(II) and Co(II) onto *F. oxysporum* biomass was favorable at studied conditions [37]. In addition, from Fig. 10(b), the R^2 values were found to be 0.963 and 0.966 for the biosorption of Pb(II) and Co(II) ions, respectively. This result showed that the Freundlich model was not suitable for describing the relationship between the amount of Pb(II) and Co(II) sorbed by the biomass and its equilibrium concentration in the solution. However, the Langmuir isotherm model best fitted the equilibrium data since it presents higher R^2 values than that determined from the Freundlich isotherms.

3.4.3. D-R isotherm

The equilibrium data were also applied to the D-R isotherm model to determine the apparent free energy of biosorption which was used to indicate the nature of biosorption processes as physical or ion-exchange or chemical.

The slope resulted from the linear plot of ln q_e versus ε^2 gives β (mol²/kJ²) and the intercept produces the adsorption capacity, q_m (mg/g). Fig. 10(c) shows D-R plot and the data are summarized in Table 4. The R^2 indicated that this model did not provide a good fit to the biosorption process as the values were 0.9218 and 0.8859 for the biosorption of Pb(II) and Co(II) ions, respectively. This model is not suitable for describing the biosorption process because it is presented the least fit for the biosorption.

Table 2
Thermodynamic parameters for adsorption of Pb(II) and Co(II) ions by *Fusarium oxysporum* fungi

Metal ions	Temperature (K)	Δ*H*° (kJ/mol)	Δ*G*° (kJ/mol)	Δ*S*° (J/mol/K)
Pb^{2+}	298	26.30	–18.26	149.53
	308		–19.46	148.57
	318		–21.23	149.46
	333		–23.42	149.31
Co^{2+}	298	67.38	–21.43	298.02
	308		–24.09	296.98
	318		–26.73	295.94
	333		–31.98	298.38

Table 3
Isotherm equations used in this study

Isotherm models	Equation	Parameters	Reference
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m}$ $C_e = C_o\left(1 - \frac{\%R}{100}\right)$	q_e (mg/g): equilibrium adsorption capacity q_m (mg/g): maximum adsorption capacity C_e (mg/L): equilibrium adsorbate concentration in solution K_L (L/mg): Langmuir constant	[27]
	$R_L = \frac{1}{1 + K_L C_o}$	R_L: The dimensionless constant (separation factor) C_o (mg/L): initial adsorbate concentration in solution	[28]
Freundlich	$\log q_e = \log K_F + \frac{1}{n}\log C_e$	K_F (mg/g): Freundlich constant n: Heterogeneity factor	[29,30]
Dubinin–Radushkevich (D-R)	$\ln q_e = \ln q_m - \beta\varepsilon^2$ $\varepsilon = RT\ln\left(1 + \frac{1}{C_e}\right)$	β (mol^2/kJ^2): D-R constant ε (Jm/mol): Polanyi potential R: universal gas constant (8.314 J/mol/K) T (K): temperature	[31,32]
	$E = \frac{1}{\sqrt{2\beta}}$	E (kJ/mol): means free energy of adsorption	[33,34]
Flory–Huggins	$\ln\left(\frac{\theta}{C_o}\right) = \ln K_{FH} + \alpha_{FH}\ln(1-\theta)$ $\theta = (1 - C_e / C_o)$	θ: the degree of surface coverage K_{FH} (L/mol): the equilibrium constant α_{FH}: the number of metal ions occupying sorption sites	[35]
	$\Delta G = -RT\ln K_{FH}$	ΔG (kJ/mol): the Gibbs free energy	[35]

The mean free energy of adsorption (E) (kJ/mol) is calculated and its values are summarized in Table 4. The values of free energy give information about the mechanism of the biosorption process. If the value of E is less than 8 kJ/mol, the biosorption process is physical in nature. If E value is between 8 and 16 kJ/mol, the biosorption process follows by ion-exchange. If the value of E is between 16 and 40 kJ/mol, the biosorption process is controlled by chemisorption process [38]. The mean biosorption energy was calculated as 17.50 and 22.87 kJ/mol for the biosorption of Pb(II) and Co(II) ions, respectively. These results indicate that the biosorption processes of Pb(II) and Co(II) ions on to *F. oxysporum* biomass may be governed by chemisorption process and this result confirms the previous results.

3.4.4. Flory–Huggins Isotherm

The Flory–Huggins model was used to account the degree of surface coverage characteristics of the adsorbate on the adsorbent [39]. K_{FH} and α_{FH} can be estimated by plotting ln (θ/Co) versus ln (1 − θ) as shown in Fig. 10(d), the Flory–Huggins parameters are summarized in Table 4.

Furthermore, the equilibrium constant (K_{FH}) was used to calculate the Gibbs free energy of spontaneity (ΔG). The negative values of ΔG confirm the feasibility of the process and the spontaneous nature of Pb(II) and Co(II) biosorption onto *F. oxysporum* biomass (Table 4) [39].

Evaluating the correlation coefficients from the four isotherm equations (for fitting the analytical data) showed that the Langmuir and Flory–Huggins isotherm models are more appropriate in describing the data than Freundlich and D-R isotherm, where the values of (R^2) are smaller than the ones obtained in the case of Langmuir and Flory–Huggins isotherm models.

3.5. Comparison of q_m for various adsorbents

Table 5 presents the comparison of biosorption capacity (mg/g) of *F. oxysporum* biomass from the Langmuir isotherm for Pb(II) and Co(II) ions with that of various adsorbent. The biosorption capacity of the studied sorbent for Pb(II) and Co(II) is higher than that of the majority of other adsorbent mentioned. Therefore, it can be concluded that the *F. oxysporum* biomass has important potential for biosorption of Pb(II) and Co(II) ions from waste solutions.

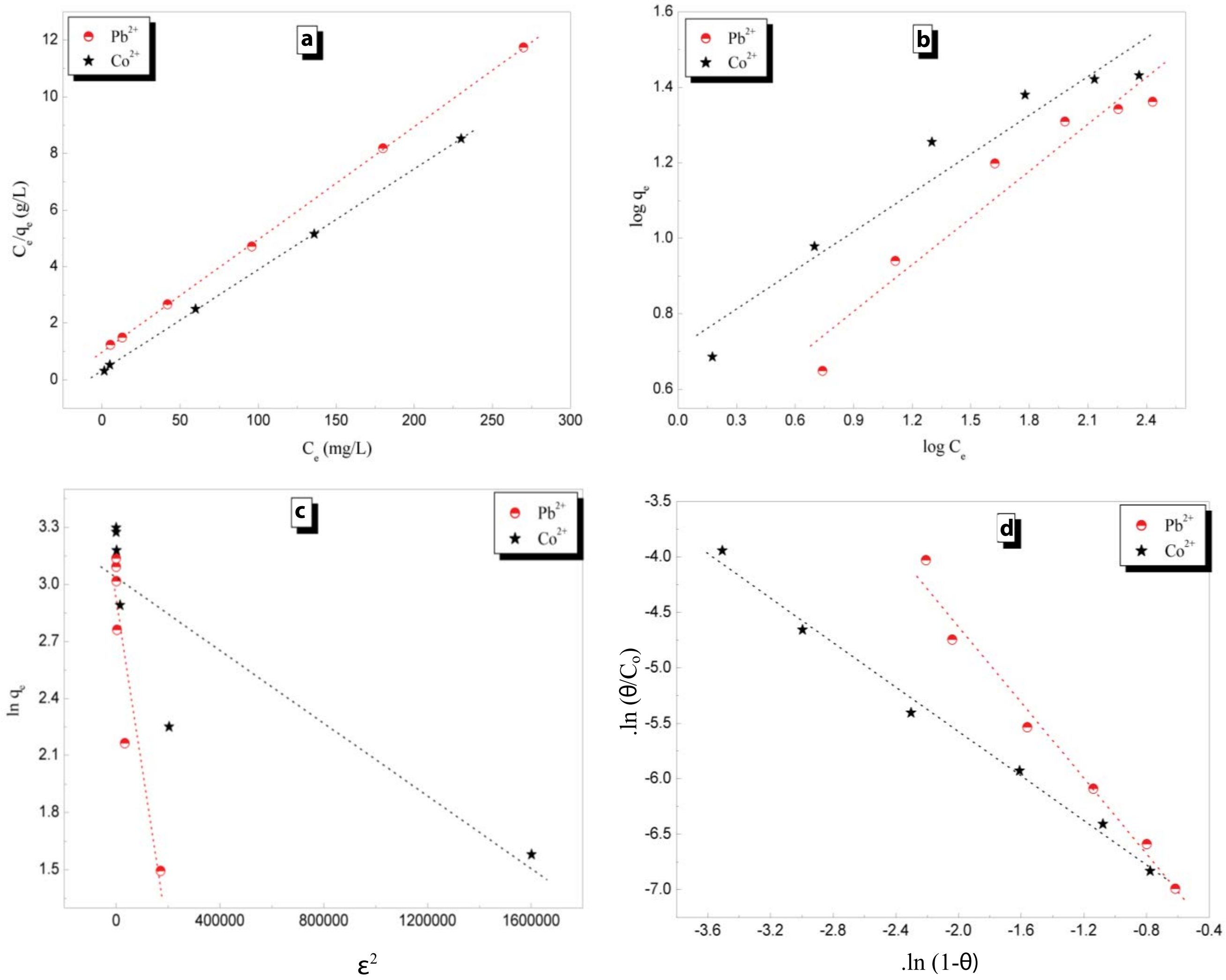

Fig. 10. Langmuir (a), Freundlich (b), Dubinin–Radushkevich (c), and Flory–Huggins (d) isotherm models for sorption of Pb(II) and Co(II) ions.

Table 4
Langmuir, Freundlich, Dubinin–Radushkevich, and Flory–Huggins parameters for sorption of Pb(II) and Co(II) ions

Metal ions	Isotherm model														
	Langmuir				Freundlich			Dubinin–Radushkevich				Flory–Huggins			
	q_m (mg/g)	K_L (L/mg)	R_L	R^2	K_F (mg/g)	$1/n$	R^2	β (mol^2/kJ^2)	q_m (mg/g)	R^2	E (kJ/mol)	K_{FH} (L/mol)	α_{FH}	R^2	ΔG (kJ/mol)
Pb^{2+}	25.64	0.04	0.047	0.9999	2.72	0.414	0.9635	8.86×10^{-6}	18.54	0.9218	17.50	3.22×10^{-4}	–1.71	0.9899	–19.92
Co^{2+}	28.09	0.11	0.018	0.9999	5.13	0.342	0.9666	9.56×10^{-7}	20.70	0.8859	22.87	5.00×10^{-4}	–1.00	0.9958	–18.78

3.6. Column biosorption

The breakthrough capacity of *F. oxysporum* biomass column packed with 1 g *F. oxysporum* biomass for Pb(II) and Co(II) was determined. A 200 mL of 100 mg/L (pH = 5.50) of metal ions was allowed to pass through the column at flow rate of 0.75 mL/min. The effluent fractions were collected and the amount of each fraction of the effluent (for both ions) was measured using AAS. The column was completely saturated after passing 200 mL (100 mg/L) of the studied ions (Fig. 11). The average values of breakthrough capacities of *F. oxysporum* biomass column are estimated to be 10.10 and 12.15 mg/g for Pb(II) and Co(II) ions, respectively. The capacity sequence was in order Co(II) > Pb(II), this difference in breakthrough

Table 5
Comparison of capacity values of Pb(II) and Co(II) ions for various adsorbent

Adsorbent	Capacity, (mg/g)		References
	Pb^{2+}	Co^{2+}	
Fruit shell (Mangostana)	3.56	–	[40]
Peels of banana	2.18	–	[41]
Water hyacinth weed	26.32	–	[42]
Apricot stone activated carbon	21.38	–	[43]
Sawdust	3.19	–	[44]
Hazelnut husk activated carbon	13.50	–	[45]
Coconut shell activated carbon	26.50	–	[46]
Cellulose/chitin	<19.0	–	[47,48]
Sawdust	3.8	–	[49]
CA/TiO_2	25.0	–	[3]
Cocoa shells	6.2	–	[50]
Aspergillus flavus	10.82	–	[51]
Waste Chinese herb Pang	27.1	–	[52]
Barley straw	15.2	–	[53]
Rice husk	4.0	–	[53]
Zoogloea ramigera	10.4	–	[54]
Rhizopus arrhizus	15.5	–	[54]
Pinus sylvesteris	11.4	–	[54]
Saccharomyces cerevisiae	2.7	–	[54]
Mucor rouxii	4.2	–	[55]
Lichen (*C. furcata*)	12.3	–	[56]
CTS	25.00	–	[57]
SB	21.28	–	[57]
Clinoptilolite	1.60	–	[58]
Chitosan	16.36	–	[59]
Activated sludge fed	–	18.76	[60]
Sargassum wightii	–	20.63	[61]
Oscillatoria angustissima	–	7.02	[62]
Attapulgite	–	0.635	[63]
Hydroxyapatite	–	20.92	[64]
Marble	–	2.247	[65]
Rose waste biomass	156	27.15	[66]
Yeast *Saccharomyces cerevisiae*	69.19	11.69	[67]
Fusarium oxysporum	25.64	28.09	[Current work]

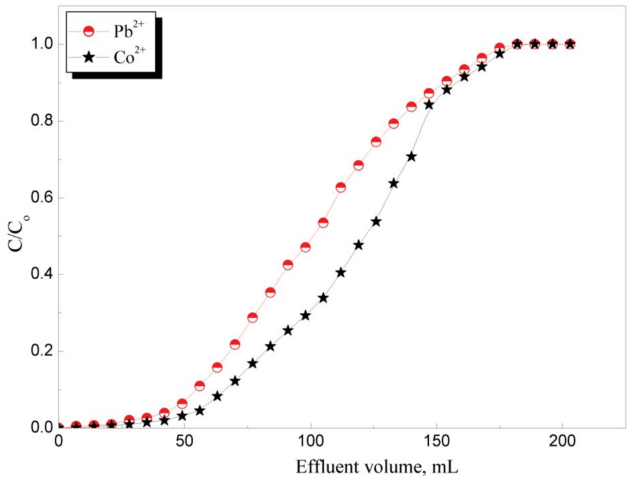

Fig. 11. Breakthrough curves for extraction of Pb(II) and Co(II) ions from aqueous solution.

capacities of these metal ions may be attributed to their different ionic sizes [36].

4. Conclusion

F. oxysporum biomass has a high ability to remove Pb(II) and Co(II) ions from their solutions. The percentage removal of both Pb(II) and Co(II) ions was dependent on pH, contact time, initial metal concentrations, biomass dosage, and temperature. The interaction between both ions and the active functional groups in the *F. oxysporum* biomass was confirmed by FTIR analysis. Thermodynamic data indicated that biosorption of Pb(II) and Co(II) by *F. oxysporum* biomass is feasible, spontaneous, and endothermic in nature. The equilibrium biosorption results agreed well with Langmuir and Flory–Huggins isotherm models. The breakthrough capacity for Pb(II) and Co(II) ions was investigated and found to be 10.10 and 12.15 mg/g, respectively.

References

[1] A. Blazquez, M.A. Martin, M.C. Lara, R. Marti, Y. Campos, A. Cabello, A. Cabello, R. Garesse, J. Bautista, A.L. Andreu, J. Arenas, Removal of cadmium ions with *olive stones*: the effect of some parameters, Process Biochem., 40 (2005) 2649–2654.

[2] R.D. Sonali, P.K. Jayant, Biological methods for heavy metal removal – a review, Int. J. Eng. Sci. Innov. Technol., 2 (2013) 304–309.

[3] K.A. Gebru, C. Das, Removal of Pb (II) and Cu (II) ions from wastewater using composite electrospun *cellulose acetate/ titanium oxide (TiO$_2$)* adsorbent, J. Water Process Eng., 16 (2017) 1–13.

[4] Y. Tian, M. Wu, R. Liu, Y. Li, D. Wang, J. Tan, R. Wu, Y. Huang, Electrospun membrane of *cellulose acetate* for heavy metal ion adsorption in water treatment, Carbohydr. Polym., 83 (2011) 743–748.

[5] N.A. Abdelwahab, N.S. Ammar, H.S. Ibrahim, Graft copolymerization of *cellulose acetate* for removal and recovery of lead ions from wastewater, Int. J. Biol. Macromol., 79 (2015) 913–922.

[6] J.T. Matheickal, Q. Yu, Biosorption of lead(II) and copper(II) from aqueous solutions by pre-treated biomass of *Australian marine* algae, Bioresour. Technol., 69 (1999) 223–229.

[7] B. Volesky, Biosorbent materials, Biotechnol. Bioeng. Symp., 16 (1986) 121–126.

[8] N. Das, R. Vimala, P. Karthika, Biosorption of heavy metals – an overview, Indian J. Biotechnol., 7 (2008) 159–169.

[9] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater., 97 (2003) 219–243.

[10] P. Baldrian, Interactions of heavy metals with *white-rot* fungi, Enzyme Microb. Technol., 32 (2003) 78–91.

[11] J.S. Merrin, R. Sheela, N. Saswathi, R.S. Prakasham, S.V. Ramakrishna, Biosorption of chromium (VI) using *Rhizopus arrhizus*, Ind. J. Exp. Biol., 36 (1998) 1052–1055.

[12] O.A. Abdel-Aziz, Bioremediation of Soil Contaminated with Some Heavy Metals Using Nuclear Techniques, M.Sc. thesis, Al-Azhar Univ., Fac of Sci. Bot and Microb Dep., Cairo, Egypt, 2005.

[13] F. Czapek, Untersuchungen über die Stickstoffgewinnung und Eiweiß-bildung der Pflanzen. - Beitr. Chem. Physiol. Pathol., 1, 540–560; 3, 47–66 (1902–1903).

[14] A.W. Dox, The Extracellular Enzymes of *Penicillium and Aspergillus* with special references to these of *P. amenberte*, U.S. Dept. Agri. Bur. Anim. Ind. Bull., 170. Environ. Int., 26 (1910) 417–423.

[15] K. Yildirim, S. Yilmazer-Keskin, Biotransformation of (–)-verbenone by *Aspergillus tamarii and Aspergillus terreus*, Collect. Czech. Chem. Commun., 75 (2010) 649–652.

[16] G. Bayramoglu, M.Y. Arica, Removal of heavy mercury(II), cadmium(II) and zinc(II) metal ions by live and heat inactivated, *Lentinus edodes* pellets, Chem. Eng., 143 (2008)133–140.

[17] H. Moloukhia, W.S. Hegazy, E.A. Abdel-Galil, S.S. Mahrous, Removal of Eu^{3+}, Ce^{3+}, Sr^{2+}, and Cs^{+} ions from radioactive waste solutions by modified activated carbon prepared from *coconut* shells, Chem. Ecol., 32 (2016) 324–345.

[18] E.A. Abdel-Galil, H.E. Rizk, A.Z. Mostafa, Production and characterization of activated carbon from *Leucaena* plant wastes for removal of some toxic metal ions from waste solutions, Desal. Wat. Treat., 57 (2016) 17880–17891.

[19] V. Murphy, H. Hughes, P. McLoughlin, Cu(II) binding by dried biomass of red, green and brown *macroalgae*, Water Res., 41 (2007) 731–740.

[20] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, The *marine macroalga Cystoseira baccata* as biosorbent for cadmium(II) and lead(II) removal: kinetic and equilibrium studies, Environ. Pollut., 142 (2006) 264–273.

[21] R. Ramya, P. Sankar, S. Anbalagan, P.N. Sudha, Adsorption of Cu(II) and Ni(II) ions from metal solution using cross linked *chitosan-g-acrylonitrile* copolymer, Int. J. Environ. Sci., 1 (2011) 1323–1338.

[22] B. Kanga, K. Honda, K. Okano, T. Aki, T. Omasa, H. Ohtake, Thermal analysis for differentiating between oleaginous and non-oleaginous microorganisms, Biochem. Eng. J., 57 (2011) 23–29.

[23] M.S. Iqbal, S. Massey, J. Akbar, C.M. Ashraf, R. Masih, Thermal analysis of some natural polysaccharide materials by isoconversional method, Food Chem., 140 (2013) 178–182.

[24] I. Dahlan, S.R. Hassan, M.L. Hakim, Removal of iron (Fe) from aqueous solutions using *siliceous* waste sorbent, Sustainable Environ. Res., 23 (2013) 41–48.

[25] M.J. Horsefall, A.I. Spiff, Effect of Metal ion concentration on Biosorption of Pb^{2+} and Cd^{2+} by *Caladium Bicolor (Wild Cocoyam)*, African J. Biotechnol., 4 (2005) 191–196.

[26] Y.B. Onundi, A.A. Mamun, M.F. Al Khatib, Y.M. Ahmed, Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by *palm shell* activated carbon, Int. J. Environ. Sci. Technol., 7 (2010) 751–758.

[27] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc., 40 (1918) 1361–1403.

[28] T.W. Webber, R.K. Chakkravorti, Pore and solid diffusion models for fixed-bed adsorbers, AIChE J., 20 (1974) 228–238.

[29] S.T. Akar, A.S. Ozcan, T. Akar, A. Özcan, Z. Kaynak, Biosorption of a reactive textile dye from aqueous solutions utilizing an agro-waste, Desalination, 249 (2009) 757–761.

[30] H.M.F. Freundlich, Uber die adsorption in lasungen, J. Phys. Chem., 57 (1906) 385–470.

[31] M.M. Dubinin, L.V. Radushkevich, Equation of the characteristic curve of *activated charcoal*, Proc. Acad. Sci. Phys. Chem. Sect. USSR, 55 (1947) 331–333.

[32] M.M. Dubinin, The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface, Chem. Rev., 60 (1960) 235–266.

[33] C.S. Zhu, L.P. Wang, W.B. Chen, Removal of Cu(II) from aqueous solution by agricultural by-product: *peanut hull*, J. Hazard. Mater., 168 (2009) 739–746.

[34] Q. Li, L. Chai, Z. Yang, Q. Wang, Kinetics and thermodynamics of Pb(II) adsorption onto modified *spent grain* from aqueous solutions, Appl. Surf. Sci., 255 (2009) 4298–4303.

[35] M. Horsfall, A.I. Spiff, Equilibrium sorption study of Al^{3+}, Co^{2+} and Ag^{2+} in aqueous solutions by *fluted pumpkin (Telfairia occidentalis HOOK)* waste biomass, Acta Chim. Slov., 52 (2005) 174–181.

[36] I.M. El-Naggar, E.A. Mowafy, E.A. Abdel-Galil, M.F. El-Shahat, Synthesis, characterization and ion-exchange properties of a novel 'organic-inorganic' hybrid cation-exchanger: *polyacrylamide Sn(IV) molybdophosphate*, Global J. Phys. Chem., 1 (2010) 91–106.

[37] E.A. Abdel-Galil, H.E. Rizk, A.Z. Mostafa, Isotherm, kinetic, and thermodynamic studies for sorption of Cu(II) and Pb(II) by activated carbon prepared from *Leucaena* plant wastes, Part. Sci. Technol., 34 (2016) 540–551.

[38] M.S. Mansy, R.S. Hassan, Y.T. Selim, S.H. Kenawy, Evaluation of synthetic *aluminum silicate modified by magnesia* for the removal of ^{137}Cs, ^{60}Co and $^{152+154}$Eu from low-level radioactive waste, Appl. Radiat. Isot., 130 (2017) 198–205.

[39] M.M. Hamed, M. Holiel, I.M. Ahmed, Sorption behavior of cesium, cobalt and europium radionuclides onto *hydroxyl magnesium silicate*, Radiochim. Acta, 104 (2016) 873–890.

[40] R. Zein, R. Suhaili, F. Earnestly, I. Indrawati, E. Munaf, Removal of Pb(II), Cd(II) and Co(II) from aqueous solution using *Garcinia mangostana L.* fruit shell, J. Hazard. Mater., 181 (2010) 52–56.

[41] J. Anwar, U. Shaique, Waheed-uz-Zaman, M. Salman, A. Dar, S. Anwar, Removal of Pb(II) and Cd(II) from water by adsorption on *peels of banana*, Bioresour. Technol., 101 (2010) 1752–1755.

[42] C. Mahamadi, T. Nharingo, Utilization of *water hyacinth weed (Eichhornia crassipes)* for the removal of Pb(II), Cd(II) and Zn(II) from aquatic environments: an adsorption isotherm study, Environ. Technol., 31 (2010) 1221–1228.

[43] L. Mouni, D. Merabet, A. Bouzaza, L. Belkhiri, Adsorption of Pb(II) from aqueous solutions using activated carbon developed from *apricot stone*, Desalination, 276 (2011) 148–153.

[44] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by *sawdust* adsorption removal of lead and comparison of its adsorption with copper, J. Hazard. Mater, 84 (2001) 83–94.

[45] M. Imamoglu, O. Tekir, Removal of copper(II) and lead(II) ions from aqueous solutions by adsorption on activated carbon from a new precursor *hazelnut husk*, Desalination, 228 (2008) 108–113.

[46] M. Sekar, V. Sakthi, S. Rengaraj, Kinetics and equilibrium adsorption study of lead(II) onto activated carbon prepared from *coconut shell*, J. Colloid Interface Sci., 279 (2004) 307–313.

[47] F. Ji, C. Li, B. Tang, J. Xu, G. Lu, P. Liu, Preparation of *cellulose acetate/zeolite* composite fiber and its adsorption behavior for heavy metal ions in aqueous solution, Chem. Eng. J., 209 (2012) 325–333.

[48] D. Zhou, L. Zhang, J. Zhou, S. Guo, *Cellulose/chitin* beads for adsorption of heavy metals in aqueous solution, Water. Res., 38 (2004) 2643–2650.

[49] Metcalf & Eddy, George Tchobanoglous, Franklin L. Burton, H.D. Stensel, Wastewater Engineering – Treatment and Reuse, McGraw Hill Education Inc., New York, 2004.

[50] A.R. Iftikhar, H.N. Bhatti, M.A. Hanif, R. Nadeem, Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using *rose waste* biomass, J. Hazard. Mater., 161 (2009) 941–947.

[51] O. Keskinkan, M.Z.L. Goksu, A. Yuceer, M. Basibuyuk, C.F. Forster, Heavy metal adsorption characteristics of a submerged aquatic plant (*Myriophyllum spicatum*), Process Biochem., 39 (2003) 179–183.

[52] T. Akar, S. Tunali, Biosorption characteristics of *Aspergillus flavus* biomass for removal of Pb(II) and Cu(II) ions from an aqueous solution, Bioresour. Technol., 97 (2006) 1780–1787.

[53] P. King, N. Rakesh, S. Beenalahari, Y. Prasanna Kumar, V.S.R.K. Prasad, Removal of lead from aqueous solution using *Syzygium cumini* L.: equilibrium and kinetic studies, J. Hazard. Mater., 142 (2007) 340–347.

[54] T. Akar, S. Tunali, I. Kiran, *Botrytis cinerea* as a new fungal biosorbent for removal of Pb(II) from aqueous solutions, Biochem. Eng. J., 25 (2005) 227–235.

[55] G. Yan, T. Viraraghavan, Heavy metal removal in a biosorption column by *immobilized M. rouxii* biomass, Bioresour. Technol., 78 (2001) 243–249.

[56] A. Sarı, M. Tuzen, O.D. Uluozlu, M. Soylak, Biosorption of Pb(II) and Ni(II) from aqueous solution by *lichen (Cladonia furcata)* biomass, Biochem. Eng. J., 37 (2007) 151–158.

[57] W.P. Putra, A. Kamari, S.N.M. Yusoff, C.F. Ishak, A. Mohamed, N. Hashim, I.M. Isa, Biosorption of Cu(II), Pb(II) and Zn(II) ions from aqueous solutions using selected waste materials: adsorption and characterisation studies, J. Encaps. Adsorp. Sci., 4 (2014) 25–35.

[58] M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren, D.E. Shanks, Removal of heavy metals and other cations from wastewater using *zeolites*, Sep. Sci. Technol., 25 (1990) 1555–1569.

[59] C.P. Huang, Y.C. Chung, M.R. Liou, Adsorption of Cu(II) and Ni(II) by *pelletized biopolymer*, J. Hazard. Mater., 45 (1996) 265–277.

[60] Y. Liu, X. Chang, Y. Guo, S. Meng, Biosorption and preconcentration of lead and cadmium on waste Chinese *herb Pang* Da Hai, J. Hazard. Mater., 135 (2006) 389–394.

[61] S. Tunali, A. Cabuk, A. Akar, Removal of lead and copper ions from aqueous solutions by *bacterial strain* isolated from soil, Chem. Eng. J., 115 (2006) 203–211.

[62] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of cobalt (II) and nickel(II) by *seaweeds*: batch and column studies, Sep. Purif. Technol., 44 (2005) 53–59.

[63] M. Abbas, S. Kaddour, M. Trari, Kinetic and equilibrium studies of cobalt adsorption on *apricot stone* activated carbon, J. Ind. Eng. Chem., 20 (2014) 745–751.

[64] I. Smičiklas, S. Dimović, I. Plećaš, M. Mitrić, Removal of Co^{2+} from aqueous solutions by *hydroxyapatite*, Water Res., 40 (2006) 2267–2274.

[65] M.M. Hamed, M.I. Aly, A.A. Nayl, Kinetics and thermodynamics studies of cobalt, strontium and cesium sorption on marble from aqueous solution, Chem. Ecol., 32 (2016) 68–87.

[66] M.A. Javed, H.N. Bhatti, M.A. Hanif, R. Nadeem, Kinetic and equilibrium modeling of Pb(II) and Co(II) sorption onto *rose waste* biomass, Sep. Sci. Technol., 42 (2007) 3641–3656.

[67] A.A. Al-Fakih, M.M. Gharieb, M.I. Ali, Bioadsorption of Pb(II) and Co(II) ions by the yeast *Saccharomyces cerevisiae*, Al-Jazeera Univ. J., 1 (2018) 5–29.