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Cadmium biosorption potential and kinetic behavior of endophytic *Fusarium verticillioides* and its green synthesized silver nanoparticles (GSNPs)

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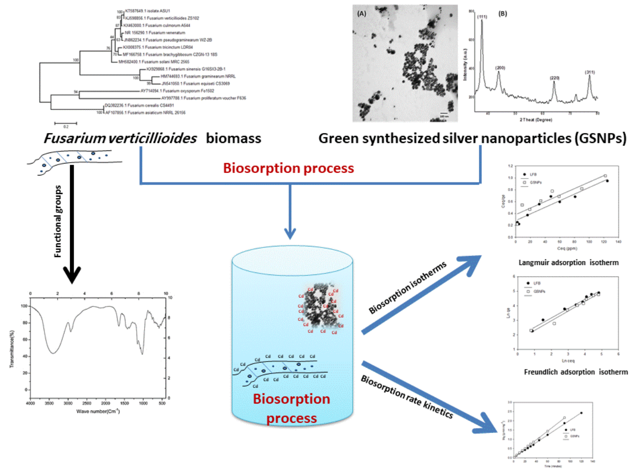
Graphical abstract



Abstract

Silver nanoparticles (GSNPs) were synthesized from extracellular metabolites of endophytic isolates of *Fusarium verticillioides* (KT587649) to evaluate their efficiency as new biosorbent agents for the exclusion of cadmium Cd (II) from aquatic systems. The GSNPs were characterized through X-ray diffraction (XRD) and transmission electron microscopy (TEM). Results show that the most efficient Cd (II) removal rate by both biosorbents was at pH 7.0. The optimal contact times were 30 and 40 min by *F. verticillioides* and GSNPs, respectively. Langmuir adsorption isotherms revealed that the highest calculated adsorption capacities of *F. verticillioides* and GSNPs for Cd (II) were 185±0.25 mg/g and 176±0.18 mg/g, respectively. The harmonized adsorption isotherms (between the Freundlich isotherm and Langmuir models) indicated a high correlation coefficient ($r^2 > 0.97$). The kinetics of the biosorption process fitted well with the pseudo-second-order kinetic model. This study has thus confirmed the biosorbent capacity of *F. verticillioides* and its GSNPs for the exclusion of Cd (II) from any contaminated aquatic system and shows it is an eco-friendly method with great feasibility and potential to convey economic and other benefits in wastewater treatment technologies.

Keywords: Biosorption kinetic, Cadmium, *Fusarium verticillioides*, GSNPs, Aquatic system

1. Introduction

Water contamination by heavy metals such as cadmium Cd (II) is a side-effect of many industrial and anthropogenic activities (Jadhav and Hocheng, 2012). The contamination of water by effluents, chemical wastes, and heavy metals is extremely toxic to living organisms: the European Union has thus set environmental Cd (II) concentration standards for estuaries and marine waters at 40 µg/L and freshwater at 45–500 µg/L, depending on water hardness (Annibaldi *et al*., 2015).

Generally, Cd is removed from industrial wastes by chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis, membrane technologies, and/or evaporation. However, these methods are expensive, limited in their effectiveness, and liable to cause environmental harm (Green-Ruiz *et al*., 2008; Thaçi and Gashi, 2019). In contrast, biosorption is considered an efficient, eco-friendly, and inexpensive Cd (II) bioremediation strategy when compared to the alternatives.

In the biosorption technique, biomaterials biosorb heavy metals from wastewater through unique operations – either metabolically-mediated pathways or physico-chemical mechanisms. Toxic material can be absorbed by inactive and non-living microbial dry biomass; these accumulate heavy metals from water bodies and thus retain them in concentrated form (Shamim, 2016; Shamim, 2018). The removal of heavy metals from polluted wastewaters by microbial biomass has been

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extensively studied and is now gaining more attention due to the technique's superior performance and capacity to work over a broad range of abiotic conditions (temperature, pH, ionic strength), and for its widespread availability in large quantities (Abdolali *et al.*, 2017; Bakircioglu and Akman, 2010; Hassan *et al.*, 2018).

Microbial biomasses in either living or non-living forms are considered strong prospective candidates for the removal of toxic metals (Deng and Cao, 2017; Gabr *et al.*, 2009; Hassan *et al.*, 2009; Siddiquee *et al.*, 2015), is characterized by reusability (generally, such biomass can be used several times) and resistance to the effects of toxic metals (Aksu, 2002). Fungal biomasses are considered a suitable adsorbent agent for heavy metal ions. The mechanism of heavy metal removal by non-living fungal biomass is a metabolism-independent process, in which metal accumulation to the fungal cell walls is the major mechanism and occurs via an adsorption process (ionic and physicochemical adsorption) (Ahemad and Kibret, 2013; Javanbakht *et al.*, 2014). Fungal cell walls contain a range of functional groups such as COO^-, NH_2, OH^-, PO_4, and SH groups, which react with heavy metals leading to a passive uptake from contaminated wastewater to the biomass (Hassan *et al.*, 2018; Shamim, 2018; Simonescu and Ferdeş, 2012). The mechanism of metal biosorption by microbes occurs through complexation, coordination, physical adsorption, chelation, ion exchange, inorganic precipitation, and/or a combination of these processes (Hassan *et al.*, 2018; Javanbakht *et al.*, 2014; Salvadori *et al.*, 2013).

Several reports show the potentiality of fungi for heavy metal bio-adsorption at sites polluted by heavy metals. The species investigated include *Clonostachys rosea, Trichoderma harzianum*, and *Aspergillus alliaceus* (Cecchi *et al.*, 2017; Zotti *et al.*, 2014), *Trichoderma harzianum* (Mohammadian *et al.*, 2017), *Neopestalotiopsis clavispora* (Hassan *et al.*, 2018), *Absidia cylindrospora* (Albert *et al.*, 2018), *Aspergillus flavus* and *Sterigmatomyces halophilus* (Bano *et al.*, 2018) and *Aspergillus niger* (Amini *et al.*, 2009).

Several support materials have been recommended for the immobilization of biomaterials. Nanomaterials can adsorb metal ions selectively and show a substantial adsorption capability (Bakircioglu and Akman, 2010; Zargoosh *et al.*, 2013). Nanoparticles are considered suitable adsorbent agents for the removal of heavy metals from agro-industrial wastes because they have high adsorption capacity and show the ease of separation, reusability, and environmentally-friendly composition (Zargoosh *et al.*, 2013). The capability of any biosorbent agent in heavy metal isolation depends on the characteristics of the biosorbent biomass, the physico-chemical properties of the heavy metals involved, and prevailing environmental conditions such as the pH value of any solution, reaction temperature, interaction with other ions, ionic strength, contact time, and metal concentration (Frišták *et al.*, 2015; Pan *et al.*, 2011; Wang and Chen, 2009).

This study considers the biosorption ability of fungi. Its objective is to evaluate the efficiency of the green synthesized silver nanoparticles (GSNPs) from extracellular metabolites of a new isolate of the endophytic *Fusarium verticillioides* compared with the lyophilized biomass of the fungus in the adsorption of Cd (II) from wastewater. The study also investigates factors affecting that biosorption, as well as isotherms and kinetics of the biosorption process.

2. Materials and methods

2.1. Fungal strain isolation and identification

Endophytic *Fusarium* species were isolated from maize grains. The grains were washed with tap water, then surface sterilized with ethyl alcohol (75%) for 1 min and subsequently immersed in 5% sodium hypochlorite (1 min) and then re-immersed in ethyl alcohol for 30 seconds (Abdel-Hafez *et al.*, 2015). Finally, the grains were washed with sterilized distilled water and air-dried in sterilized conditions. The sterilized grains were then transferred onto the surface of potato dextrose agar medium (PDA) at 28 ºC until the development of fungal mycelium. *Fusarium* isolates were grown in pure culture (PDA) and identified based on the morphological features of single-spore isolate as described by Booth (1971), Gerlach and Nirenberg (1982), and Leslie and Summerell (2006). Microscopic features of conidiogenous cells, microconidia, macroconidia, conidiophores and chlamydospores were determined. The macroscopic examination of *Fusarium* culture (colony colour and pigmentations) was observed on potato dextrose agar (PDA) (Ismail *et al.*, 2015). One isolate out of four endophytic *Fusarium* isolates, that showed the highest adaptation towards silver nanoparticles biosynthesis and Cd (II) biosorption, was identified using the molecular technique. The genomic DNA of *Fusarium* isolate was extracted using the cetyltrimethyl ammonium bromide method. Universal internal transcribed spacer (ITS) primers ITS1 and ITS4 were used for the amplification of ~520 bp rDNA fragments using a polymerase chain reaction (PCR) as described by Abdel-Sater *et al.* (2016). The Basic Local Alignment Search Tool of Nucleotides program was used to compare the sequences and to retrieve the homologous nucleotide sequences from the National Center for Biotechnology Information (NCBI) database (www.ncbi.nlm.nih.gov/BLAST/).

2.2. Green synthesis and characterization of silver nanoparticles

For the preparation of green silver nanoparticles (GSNPs), the fungus was grown in a potato dextrose broth medium at 28±2 °C and agitated at 150 rpm for 3 days. Silver nanoparticles were synthesized using a biological method described by Mekkawy *et al.* (2017). The sizes and shapes of biogenic GSNPs were characterized using transmission electron microscopy (TEM) (JEOL TEM 100CXII). The crystalline nature of the GSNPs was determined by X-ray diffraction (XRD) analysis using an X-ray diffraction meter (Shimadzu XD-3A).

2.3. Preparation of biosorbent fungal biomass

The purified *F. verticillioides* was grown in 50 mL Czapek's broth medium (1% glucose, 1% peptone, 0.05% $MgSO_4.7H_2O$, 0.05% KCl, and 0.001% $FeSO_4.7H_2O$; pH 7.3±0.2) for 7 days at 28 °C under vibration at 120 rpm. Then, biomass was harvested by centrifugation at 5000 rpm for 30 min. The biomass pellets were rinsed three times with sterilized distilled water, and then freeze-dried using a lyophilizer. The lyophilized fungal biomass (LFB) was used as a biosorbent material for Cd (II).

2.4. Heavy metal solution

A 1000 mg/L stock Cd (II) solution was prepared from pure analytical grade $CdCl_2$ purchased from Sigma Aldrich (Sigma Aldrich, St. Louis, MO), by dissolving 1.63 of the metal g in 1000 mL of de-ionized water.

2.5. Effect of contact time on the biosorption efficiency of Cd (II) by LFB and GSNPs

50 mg of LFB or GSNPs was suspended in 50 mL of Cd (II) solution (50 mg/L). The biosorbent/metal suspensions were shaken at 150 rpm at 30 °C. The initial solution pH was adjusted to 6.0, to prevent the precipitation of Cd (II) as cadmium hydroxides. At the desired time intervals (0-60 min), samples from the solutions were taken and centrifuged for 5 min at 10000 rpm. The concentration of Cd (II) in the resulting supernatant was assayed using atomic absorption spectrometry (AAS).

2.6. Effect of pH on biosorption efficiency of Cd (II) by LFB and GSNPs

The effect of solution pH's on Cd (II) biosorption was investigated using LFB and GSNPs at different pH values (ranging from 1.0 -7.0) containing 20 mL of metal solution at 30 ± 2°C. The pH adjustment was achieved by adding either 0.1M NaOH or 0.1M HCl.

2.7. Biosorption isotherms of Cd (II) by LFB and GSNPs

The Cd (II) biosorption isotherm experiments were assessed using 20 mg of each biosorbent agent (LFB and GSNPs) and different concentrations of Cd (II) in 20 mL deionized water at pH 7.0. The tubes containing the solutions were shaken at 200 rpm for 30 min at room temperature 30 ± 2°C. Subsequently, the tubes were centrifuged for 5 min at 10000 rpm and the supernatant was analyzed by AAS for the determination of Cd (II) concentration.

2.8. Cadmium biosorption evolution

Cadmium biosorption was calculated using the following equation:

$$q_e(mg/g) = \left[\frac{C_i - C_e}{M}\right] * V \tag{1}$$

Where q_e is the specific metal biosorption (mg metal /g dry biomass), *Ci* and *Ce* are the metal initial and equilibrium concentration (mg metal /L), respectively, V is the metal solution volume (L), and M is the biomass dry weight (g).

2.9. Analysis of fungal biomass by FTIR spectroscopy

The functional groups of dried fungal biomass were investigated by the KBr pressed disk technique (Thermo Scientific Nicolet iS10 FT-IR Spectrometer, USA) in the Chemistry Department of the Faculty of Science at Assiut University.

3. Results and discussion

3.1. Selection of heavy-metal-tolerant fungus

In this study, four endophytic *Fusarium* species were isolated from maize grains. The isolate *Fusarium* ASU1 exhibited a high degree of adaptation towards nanoparticle biosynthesis and Cd (II) biosorption. This isolate showed an ability to tolerate high concentrations of Cd (II) when it was grown in media containing the metal. The isolate was identified by the molecular method as it was subjected to partial sequences of 18S rRNA. The sequence of 18S rRNA of strain ASU1 (517 bp) was compared with the available sequences in the GenBank databases. The result showed that the strain has 100% nucleotide base homology to *Fusarium verticillioides* ZS102 (KJ598856). Therefore, the strain was identified as *Fusarium verticillioides* ASU1 (Figure 1) and the nucleotide sequences of the fungus have been deposited in the GenBank nucleotide sequence database under accession number KT587649. The 18S rRNA gene was considered effective for the species-level identification of *Fusarium*. Many authors have reported that the ITS sequence is a powerful tool in the differentiation of *Fusarium* spp. (Kumar *et al*., 2013; O'Donnell *et al*., 2010; Thomas *et al*., 2019).

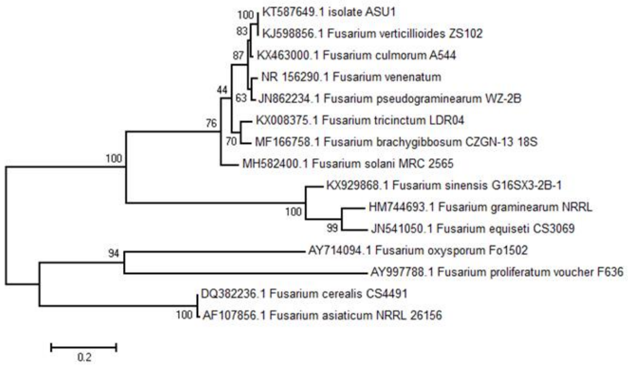

Figure 1. The phylogenetic tree of the identified strain KT587649 isolate ASU1. The evolutionary relationships of 15 different taxa showing the identity of the isolate as *Fusarium verticillioides.* The evolutionary history was inferred using the Neighbor-Joining method. The evolutionary distances were computed using the Maximum Composite Likelihood method. Phylogenetic analyses were conducted in MEGA7.

3.2. Biogenic synthesis and characterization of GSNPs

The biogenic synthesis of green silver nanoparticles (GSNPs) was carried out using an aqueous extract of endophytic *F. verticillioides* ASU1 (KT587649). The sizes and shapes of the biogenic GSNPs produced by this strain were determined by TEM (Figure 2A). The results show that the average diameter of the GSNPs was 24.8 ± 10.3 nm. There was diversity in GSNPs shapes, with polyhedral and spherical nanoparticles being found. The obtained XRD pattern showed various Bragg reflections, which may be indexed based on the face-centered cubic (FCC) structure of silver (JCPDS files no. 03-0921) (Figure 2B). Metal nanoparticles produced by green methods often show a consistent size distribution pattern, compared to other methods (Abdel-Hafez *et al*., 2016). The peaks at 2Ɵ values of 37.65°, 44.01°, 63.99°, and 76.92° were correspondent to (111), (200), (220), and (311) Bragg reflections, respectively. X-ray diffraction results clearly showed that the silver nanoparticles formed by the reduction of Ag^+ by *F. verticillioides* ASU1 extract were crystalline in nature. The unassigned peaks were thought to be related to crystalline and amorphous organic phases (Abdel-Hafez *et al*., 2016; Mekkawy *et al*., 2017; Ukkund *et al*., 2019).

Nanoparticles were produced using a clean, fast, and eco-friendly method, in which the crude fungal extract operates as a reducing and capping agent (Abdel-Hafez *et al*., 2016; Alghuthaymi *et al*., 2015). Endophytic fungi have been reported as candidates for important bioactive natural compounds (Fouda *et al*., 2015). Numerous studies have investigated the biosynthesis of silver nanoparticles using endophytic fungi (Abdel-Hafez *et al*., 2016; Liu *et al*., 2013; Tanvir *et al*., 2012). Some reports have declared the ability of *Fusarium* spp. to reduce aqueous Ag ions extracellularly to generate nanoparticles (Ahmad *et al*., 2003; Alghuthaymi *et al*., 2015), and among these *F. acuminatum*, *F. semitectum*, *F. solani* and *F. oxysporum* were noted for their extracellular reduction of Ag ions to nanoparticles of variable size (4-60 nm) (Nowack *et al*., 2012). It has been suggested that the mechanism of mycogenic synthesis of nanoparticles can occur through the action of reductase enzymes, electron shuttle quinones, or both (Khandel and Shahi, 2018). Nitrate reductase and α-NADPH-dependent reductases were proven to be responsible for nanoparticle synthesis in fungi (Alghuthaymi *et al*., 2015).

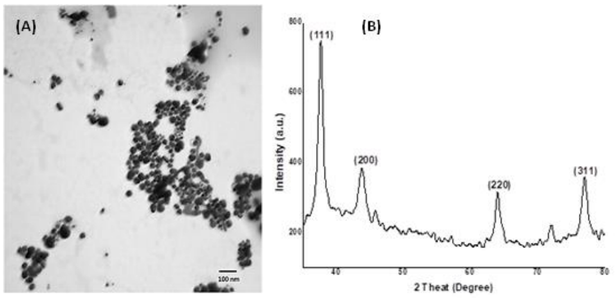

Figure 2. Transmission electron micrographs of biogenic silver nanoparticles (GSNPs) synthesized extracellularly using endophytic *Fusarium verticillioides* (A), X-ray diffraction pattern of crystalline biogenic silver nanoparticles (B).

Table 1: The Langmuir and Freundlich adsorption isotherm constants for Cd (II) biosorption by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs

Biosorbent	**Langmuir**			**Freundlich**		
	q_{max} **(mg/g)**	***b*** **(l/mg)**	r^2	q_{max} **(mg/g)**	***b*** **(l/mg)**	r^2
LFB	185 ± 0.25	0.002	0.92	6.48 ± 0.31	1.56 ± 0.06	0.97
GSNPs	176 ± 0.18	0.003	0.94	5.15 ± 0.47	1.43 ± 0.023	0.97

3.3. Effect of contact time on biosorption of Cd (II) by LFB and GSNPs

Contact time is an important factor in the effectiveness of biosorption and kinetic processes (Nadeem *et al*., 2016). The contact time affecting biosorption of Cd (II) by the LFB and GSNPs is shown in Figure 3. In our study, the rate of biosorption was very fast and occurred within a few minutes due to a high cadmium concentration in the solution and the high affinity of free cadmium ion binding sites on the biosorbent (fungal biomass or GSNPs). After a few minutes, the rate of biosorption decreased until the equilibrium time for Cd (II) adsorption was achieved after 30 min. The slower cadmium adsorption on the biosorbents is likely due to the saturation of Cd (II) binding sites and the time (30 min) that was considered to be the equilibrium time. These contact time results were further used to determine the kinetics of cadmium adsorption for both biosorbents. Interestingly, the time required for biosorption was in a harmony with the results obtained by other authors (Hassan *et al*., 2009; 2018; Sar *et al*., 1999). For example, the rate of biosorption and Cd (II) metal uptake by *Neopestalotiopsis clavispora* KY624416 occurred within 30 min (Hassan *et al*., 2018).

3.4. Effect of pH on biosorption of Cd (II) by LFB and GSNPs

The results plotted in Figure 4 show the impact of pH values on the biosorption of Cd (II) by LFB and GSNPs. The results indicated that biosorpitive capacity of Cd (II) by either fungal biomass (LFB) or GSNPs increased with increasing pH until it reached the maximum at pH 7.0. However, Cd (II) begins to precipitate at pH values more than 7.0. The decrease in adsorption efficiency at low pH could be attributed to the competitive biosorption processes between H^+ and Cd (II) (Zhao *et al*., 2011). However, once the pH increases, more functional and acidic groups (e.g. carboxyl, imidazole, phosphate, and amino groups) would carry negative charges and thus attract the Cd (II) ions with a positive charge, followed by biosorption onto the biosorbent surface (LFB or GSNPs) (El-Gendy *et al*., 2017; Gola *et al*., 2016). In line with our findings, El-Gendy *et al*. (2017) reported that *Drechslera hawaiiensis* achieved 100% removal of Cd (II) at pH 6.0, 7.0 (El-Gendy *et al*., 2017). In similar studies, the maximum biosorption of the metal by *Aspergillus versicolor*, *Rhizopus oligosporus*, *Penicillium purpurogenum*, was obtained at pH 6.0 and decreased above pH 6.0 (Martínez-Juárez *et al*., 2012). However, the maximum values of metal ions removal by *Alternaria* *alternata*, *Aspergillus wentii*, *Eupenicillium katangense,* and *Penicillium resedanum* were achieved at pH between 5–8.6 (Shakya *et al*., 2015; Verma *et al*., 2016).

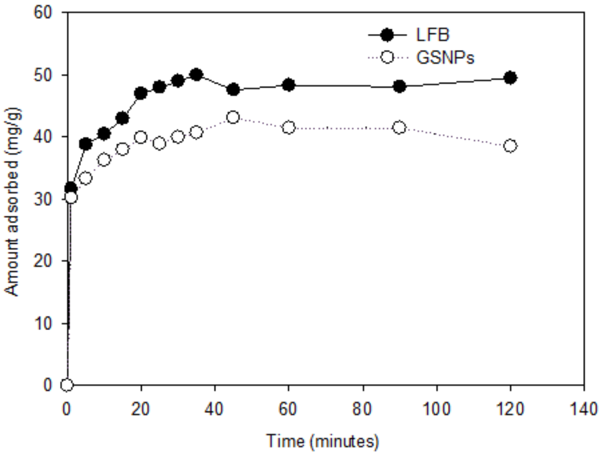

Figure 3. Effect of contact time on the biosorption of Cd (II) by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs.

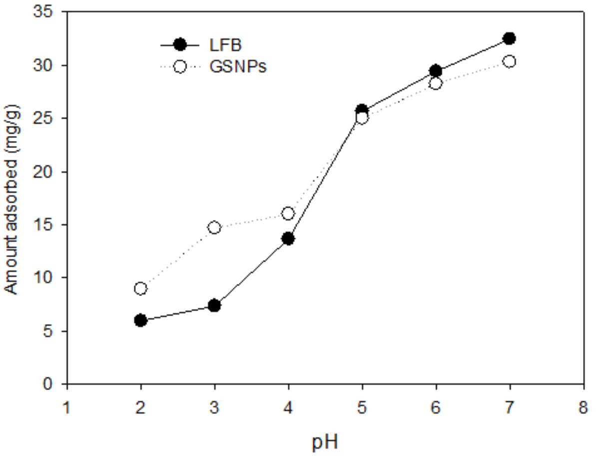

Figure 4. Effect of pH on the biosorption of Cd (II) by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs.

3.5. Biosorption isotherm of Cd by LFB and GSNPs

The plateau of biosorption of isotherms of Cd (II) by LFB and GSNPs indicated that, by increasing the Cd (II) equilibrium concentration, the adsorption rate increased. Data given in Figure 5 shows that the Cd (II) adsorption isotherm removal by LFB and GSNPs was a chemically equilibrated and saturable mechanism. Therefore, the Cd (II) uptake increased as long as binding sites of LFB and GSNPs were free. For the description of biosorption, the Langmuir and Freundlich models were applied (Hassan *et al*., 2009; Hassan *et al*., 2018), as shown in Figures 6 and 7. The equilibrium data matched better with the Freundlich adsorption isotherm than Langmuir for Cd (II) biosorption at different initial metal concentrations for both biosorents (Table 1). The maximum biosorption capacity (q_{max}) of Cd (II) by LFB and GSNPs were 185±0.25 mg/g and 176±0.18 mg/g, respectively. However, the *b* value obtained for Cd (II) was 0.003, which indicated that GSNPs possess a higher adsorption affinity for Cd (II) than LFB (0.002) (Table 1). The Freundlich analysis determined the sorptive capacity (K_f) and the sorptive intensity (*n*) of both biosorbents for Cd (II). The biosorptive capacity and intensity for Cd (II) by LFB was 6.48±0.31; 1.56±0.06, while it was 5.15±0.47; 1.43±0.023 for GSNPs. The data in Table 1 show that LFB has a better adsorption capacity and intensity compared to GSNPs. Our results are supported by those of other researchers, who applied Langmuir and Freundlich to model their experimental results to highlight the important characteristics of the biosorption mechanism (Desta, 2013; El-Gendy *et al*., 2017).

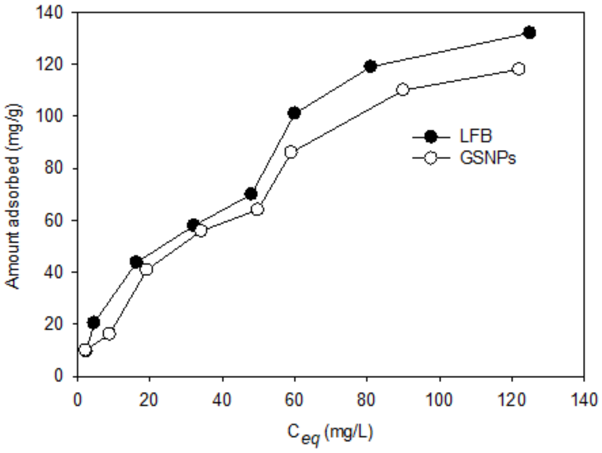

Figure 5. Biosorption of Cd (II) by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs at different concentration of Cd (II) (0-200 mg/L).

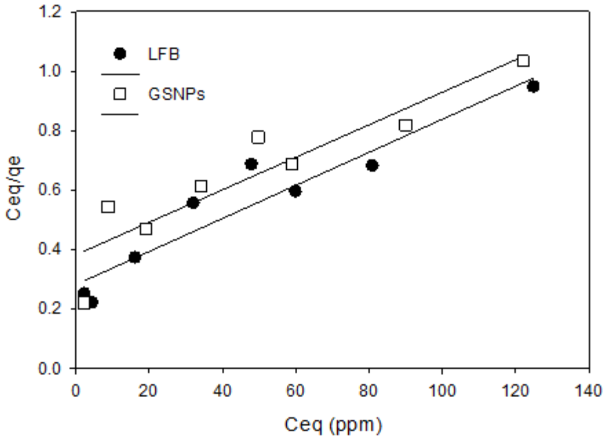

Figure 6. The linear form of Langmuir adsorption isotherm of Cd (II) by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs (biomass dosage 1 g/L, Cd (II) (0-200 mg/L), contact time (30 minutes) pH (6.0) and temperature (30 °C).

3.6. Biosorption rate kinetics of Cd by LFB and GSNPs

The biosorption kinetic data were calculated using pseudo-first and pseudo-second order kinetics (Bulgariu and Bulgariu, 2012). The pseudo-first order model is expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1.ads}{2.303}t \qquad (2)$$

Where q_e and q_t (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}). However, if the calculated q_{eq} does not match the equilibrium metal uptake, then the reaction is not followed by the first order. The linear plots of log (q_e-q_t) versus t for the pseudo-first order model for Cd (II) by LFB and GSNPs are shown in Figure 8A. The correlation coefficient calculated for the pseudo-first order equations for LFB and GSNPs is 0.97, and the calculated q_e is not the same as the experimental q_{eq} as indicated in Table 2, suggesting the pseudo-first-order is not matched for this biosorption experiment.

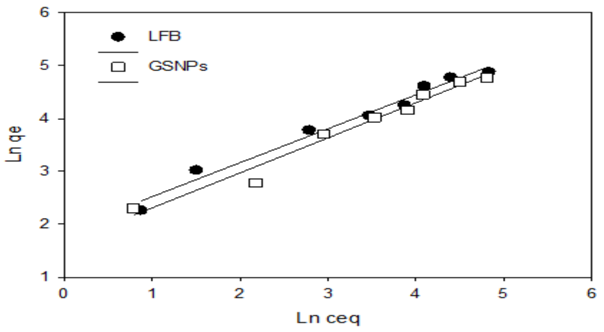

Figure 7. The linear form of the Freundlich adsorption isotherm equation for Cd (II) by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs (biomass dosage 1 g/L, Cd (II) (0-200 mg/L), contact time (30 minutes), pH (6.0), and temperature (30 °C).

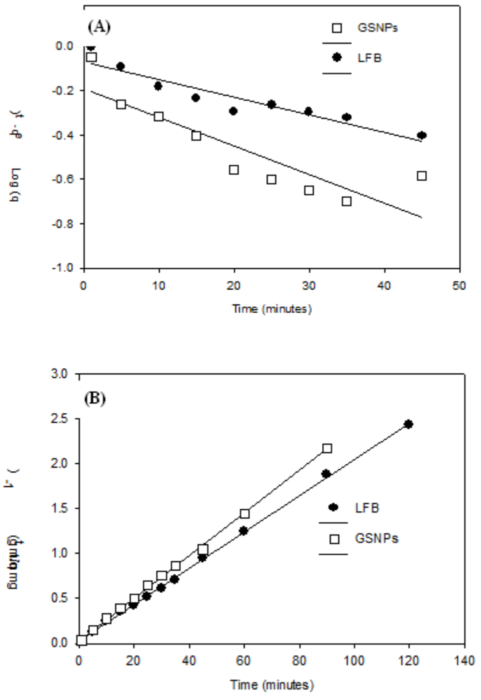

Figure 8. Pseudo-first-order kinetics of Cd (II) adsorption by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs (A), Pseudo-second-order kinetics of Cd (II) adsorption by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs (B).

Table 2: Kinetic parameters obtained from pseudo-first-order and pseudo-second-order for Cd (II) bisorption by lyophilized biomass of *F. verticillioides* (LFB) and GSNPs

Biosorbents	Initial conc. (mg/L)	$q_{e\ exp}$ (mg/g)	Pseudo first order			Pseudo second order		
			K_1 (min^{-1})	$q_{e\ calc}$ (mg/g)	R^2	K_2 (g mg^{-1} min^{-1})	$q_{e\ calc}$ (mg/g)	R^2
LFB	60.0	46.8±0.01	0.64±0.005	1.87±0.024	0.97	0.025	43.4±0.014	0.99
GSNPs	60.0	46.2±0.01	0.66±0.002	1.64±0.017	0.97	0.029	38.5±0.011	0.99

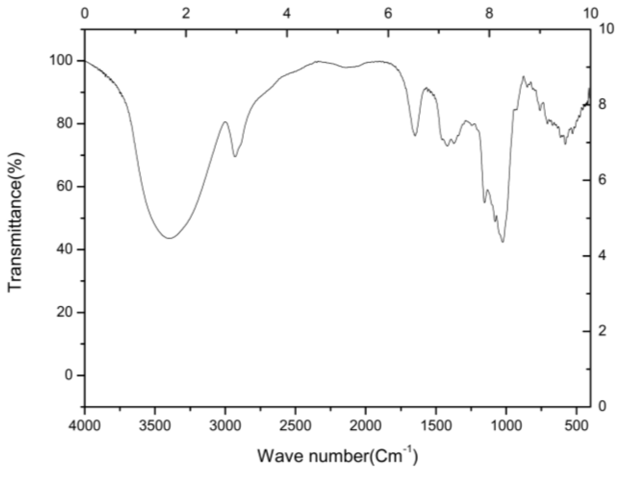

Figure 9. FTIR analysis of *F. verticillioides* biomass.

A pseudo-second-order model proposed by Ho and McKay (1999) was used to explain the sorption kinetics. It was expressed as:

$$\frac{dq}{dt} = k_2(q_{eq} - q)^2 \qquad (3)$$

Integrating the equation yields:

$$\frac{t}{q} = \frac{1}{k_2\,ads\,q_e^2} + \frac{1}{q_e}t \qquad (4)$$

The parameters q_e and $k_{2\ ads}$ were obtained from the linear form (Eq. 2&3), (Figure 8B). Such a model and its linear form were described in previous works (Hassan *et al.*, 2018; Hussein *et al.*, 2011).

The Cd (II) rate constants and the correlation coefficients results are shown in Table 2. The correlation coefficient for the pseudo-second-order adsorption was found to be

0.99. The biosorption capacities calculated by the pseudo-second-order of LFB and GSNPs for Cd (II) were recorded 43.46±0.014 and 38.5±0.011mg/g, respectively, which are quite similar to those determined by experiments. Thus, it was concluded that pseudo-second-order is more favorable to describe the biosorption kinetics of Cd (II) by the fungal biomass and GSNPs.

3.7. FTIR analysis of functional groups of fungal biomass

The characteristic infrared peaks of tested fungus were acquired within the range of 500–4000 cm−1. Data in Figure 9 showed the assignment of a functional group for the metal-loaded biomass. The absorption bands represent the presence of hydroxyl (OH) at 3390 cm^{-1}, amino (NH) at 1652 cm^{-1}, carbonyl (C=O) at 1554 cm^{-1}, phosphate (P=O) groups at 1154 cm^{-1} in the fungal biomass, could be possibly involved in the adsorption process. The mechanisms of the heavy metal biosorption process mainly depended on the physicochemical interactions between the heavy metal ions and the fungal cell wall functional groups (Dhankhar and Hooda, 2011; Arivalagan *et al*., 2014 and Pugazhendhi *et al*., 2018). The participation of the fungal cell wall negatively charged groups (hydroxyl (OH), amino (NH), and carbonyl (C=O) groups) proposed the interactions with positively charged metal ions during heavy metal removal (Zhang *et al*., 2020, Grossart *et al*., 2021) as well as the kind of cell wall functional groups depended on the fungal species (Li *et al*., 2018).

4. Conclusions

The study applied, for the first time, lyophilized biomass of endophytic *F. verticillioides* ASU1 (LFB) and its green synthesized silver nanoparticles (GSNPs) as efficient cadmium-absorptive biomaterials for water systems. In light of this study, the authors commend the fungal biomass and its green synthesized silver nanoparticles (GSNPs) as prospective biosorbents to overcome water pollution and improve wastewater treatment technologies and note that they show great potential advantages as cost-effective, renewable, and ecofriendly biosorbents of biological origin. Recently, nanoparticles (NPs) have a great potential application in many industries and are more and more used. So, many free NPs are released into the environment and consequently, the cumulative effects of these nanoparticles over time may have many environmental issues on different ecosystems. Thus, many studies are urgently required to measure the potentially harmful impacts of these useful NPS to allow an effective application as well as for efficient environmental protection. Nowadays, NPs are considered as emergent potentially toxic substances for air, soil, or water ecosystems (Exbrayat et al., 2015; Martínez et al., 2021), and consequently a great effort to investigate the effects of NPs on the environment remains to be done to understand the new biological mechanisms, which may provide new scientific knowledge about ecosystems cell life.

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Authors' contributions

Elhagag Hassan, Nivien Nafady & Sedky Hassan, performed the experiments, proofed data, and text, formatting and submission of the paper, conceptualization, formal analysis, investigation, writing - original draft, writing - review & editing. Saad Alamri, Yasser Moustafa & Mohamed Hashem: proofed data and text, and formatting and submission of the paper. All authors read and approved the final manuscript.

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