Utilization of *Pleurotus eryngii* biosorbent as an environmental bioremediation for the decontamination of trace cadmium(II) ions from water system

Farah Amin, Farah Naz Talpur, Aamna Balouch, Muhammad Kashif Samoon, Hassan Imran Afridi and Muhammad Ali Surhio

**ABSTRACT**

In many parts of the world, cadmium metal concentration in drinking water is higher than some international guideline values. To reduce its level below the safety limit, a sustainable and environmental friendly approach is crucial. Thereby, present article introduce an efficient, non-pathogenic and a novel fungal biosorbent *Pleurotus eryngii* for the removal of Cd(II) ions from aqueous system. The efficiency of *P. eryngii* were improved and optimized by investigating many significant factors such as; pH, biosorbent dose, initial Cd(II) ion concentration, temperature and contact time. Maximum Cd(II) ions removal (99.9%) was achieved at pH 5.0, biosorbent dosage 0.2 g/10 mL, concentration 20 mg L^{-1}, time 10 min and temperature 50°C. The isotherm and kinetic models revealed bioremediation of Cd(II) ions as monolayer coverage with biosorption capacity of 1.51 mg g^{-1} following pseudo second order reaction. Moreover, thermodynamic parameters such as $\Delta G^\circ$, $\Delta H^\circ$, and $\Delta S^\circ$ showed that the removal of Cd(II) ions is spontaneous and endothermic in nature. Batch elution process revealed that the complete elution of Cd(II) ions from the biomass were achieved using 0.1 N HNO₃ solution. The sorption efficiency decreased from 99.99 to 56.89% as the biomass were recycled up to five times. The efficiency of Cd(II) ions removal from real water samples lies between 85 and 90%. Fourier transform infrared (FTIR) spectrometry, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopic (EDS) and atomic force microscopic (AFM) analysis of fungal biomass confirmed that the Cd(II) ions were the most abundant species on the biomass surface after the sorption process.

**Key words** | bioremediation, cadmium, isotherms, kinetics, *Pleurotus eryngii*, thermodynamics

**INTRODUCTION**

Cadmium is a toxic, non-essential heavy metal of considerable environmental and occupational concern (Jaishankar *et al.* 2014). It is released into the environment through combustion of fossil fuels, manufacturing of batteries, metal production, fertilizers, refining processes, electroplating, smelting, alloy industries, mining, pigments and screens (Ojedokun & Bello 2016). Its non-biodegradable property causes severe accumulation in living organisms with significant threats to the environment and public health (Gaur *et al.* 2014). Typically, the traces of cadmium ions in human body classified as carcinogen and teratogen impacting lungs, kidneys, liver and reproductive organs (Abdel-Shafy and Mansour 2016).

According to the World Health Organization (WHO) standards, the maximum permissible limit of Cd(II) ions in drinking water is 3 ppb (0.003 mg L^{-1}) (WHO 2015). So far, the measured Cd(II) ion concentration in many regions is higher than that prescribed by the WHO. Hence, there is an urgent need to use low cost but sustainable technologies to remove this toxic metal from the aqueous environment.

Consequently, several physico-chemical strategies for instance; filtration, chemical precipitation, electro-chemical treatment, oxidation/reduction, ion exchange, membrane technology, reverse osmosis and evaporation recovery have been developed for the removal of heavy metals, including Cd(II) ions from polluted water (Gao *et al.* 2015;
Biosorption is an alternative technique that utilizes various natural resources of microbial origin (live/dead) or their derivatives that overcome many of the harmful effects of chemical and physical methods (Fomina & Gadd 2014). This microbial mediated green approach offers many advantages, including economic viability, easy processing and biomass handling, regeneration of the biosorbent and possibility of metal recovery (Rezaei 2016).

For two decades, a large number of research papers have been published focusing on development and exploitation of inexpensive biosorbents (Gautam et al. 2014; Sadaf & Bhatti 2014). Among all reported biosorbents, the fungus has proved to be the most efficient biomass due to its high compatibility toward heavy metals, rigidity, high amount of biomass and easy availability. Collectively, these advantages mark fungus as an ideal candidate for the removal of toxic metals from the water system (Gok & Aytas 2014; Mohsenzadeh & Shahrokhi 2014).

Although there are numerous reports available on bioremediation efficacy of fungi toward Cd(II) ions, most of the fungal species used are pathogens and produced toxins in the media. The aim of this research is to introduce a novel fungal species, P. eryngii with its high remediation potential towards Cd(II) ions in aqueous solution. It is non-parasitic, safe-to-use and less expensive mycelium species. Its greater amount of biomass, macro size, tough texture, nontoxic nature and other physical characteristics makes it conducive biosorbent without the need of immobilization, as essential in case of several micro-organism species.

In the current study, various experimental parameters were optimized and the equilibrium isotherm, thermodynamics along with kinetic models were applied to elaborate sorption chemistry between biosorbent (P. eryngii) and sorbate (Cd). Additionally, the reusability, interference, and application to real water samples were also investigated.

**Experimental**

**Chemicals and reagents**

For the preparation of nutrient medium potato dextrose agar (PDA), Glucose, and Peptone were procured from Scharlau, Spain and Daejung, Korea. All the chemicals and reagents (analytical grade) used in this study (CdSO$_4$·8H$_2$O, NaCl, KH$_2$PO$_4$, EDTA, NaOH, HCl, HNO$_3$, H$_2$SO$_4$) were purchased from Sigma-Aldrich Co., USA.

**Stock solution preparation**

The stock solution of Cd(II) ions (1,000 mg L$^{-1}$) were prepared by dissolving 2.28 g of cadmium sulfate octa-hydrate salt in 1,000 mL ultra-pure water (conductivity 0.05 μS cm$^{-1}$). The working concentration of Cd(II) ions were prepared by successive dilution of the stock. The pH of the test solutions were adjusted to the desired values according to subsequent experimental design with 0.1 M NaOH or 0.1 M HCl solutions.

**Fungal biosorbent preparation**

For the biosorption study, the fungal strain of *P. eryngii* (ATCC® 90888 were procured from Edible Fungi Institute, Shanghai Academy of Agricultural Sciences, China. Fungal culture were routinely maintained on PDA slants and petri dishes.

For biosorption experiments, the bulk quantity of fungal mycelium were prepared by loop inoculation of seed culture in glucose peptone broth (GPB). The formulation of liquid nutrient medium (broth) prepared in a laboratory was composed of g L$^{-1}$; glucose (50), peptone (5), KH$_2$PO$_4$ (5) and NaCl (5), adjusted to pH 6.0 ± 0.2 and incubated for 27 days at 27 ± 2 °C (Amin et al. 2015).

After 27 days of cultivation period, the mycelium were harvested from the growth medium and washed with a copious amount of ultra-pure water. The resultant fungal biomass was dried at 60 °C for 24 h. After suitable drying, the biomass were finely divided (particle size of 0.18 mm) into powder form and stored in a screw capped plastic bottle for subsequent usage in biosorption experiment. Before using fungal biosorbent, no immobilization/impregnation or activation was performed on biomass surface.

**Biosorption process for Cd(II) ions**

The sorption studies were initiated by the batch experimental procedure. In a typical procedure, 0.1 g biomass were taken in conical flask and 5 mg L$^{-1}$ Cd(II) solution were added to the continue sorption procedure for 15 min at known pH and temperature. After completion of the sorption process, the mixture was filtered using Whatman’s filter paper No. 42 and later Cd(II) ions were quantified in the filtrate solution. Control experiments (without Cd(II) ions) were also conducted
with same experimental conditions for measuring the exact initial metal ion concentration after removal of biomass.

To enhance the sorption efficiency different experimental conditions were optimized such as pH (3.0–8.0), biosorbent dose (0.1–0.5 g), initial Cd(II) ion concentration (4–20 mg L\(^{-1}\)), temperature (20–70 °C) and time (1–15 min) into 100 mL flasks with 10 mL solution of single Cd(II) ions.

**Analytical instrumentation**

Innova 4230 Incubator (New Brunswick Scientific Co.; Huntingdon, UK) were used for the batch experiments. The pH meter (InoLab-WTW GmbH, Weilheim, Germany) with glass electrode and an internal reference electrode were used for pH measurements.

Before and after the sorption equilibrium, quantification of Cd(II) ions were carried out by Varian AA 20 spectra atomic absorption spectrometer (Mulgrave, Victoria, Australia) equipped with cadmium cathode lamp. The optimum conditions used for flame atomic absorption spectrometry (F-AAS) are given in Table 1.

The chemical and morphological characterization of *P. eryngii* was studied by Fourier transform infrared (FTIR) spectrometry (Nicolet 5700 FTIR spectrometer-Thermo Electron, USA) as KBr pellets, scanning electron microscope (SEM) equipped with cadmium cathode lamp. The optimum conditions used for flame atomic absorption spectrometry (F-AAS) are given in Table 1.

<table>
<thead>
<tr>
<th>Conditions of F-AAS for Cd(II) determination</th>
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<tr>
<td><strong>Parameters</strong></td>
</tr>
<tr>
<td>Wavelength (nm)</td>
</tr>
<tr>
<td>Hollow cathode lamp current (mA)</td>
</tr>
<tr>
<td>Type of flame</td>
</tr>
<tr>
<td>Background correction</td>
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<tr>
<td>Slit width (nm)</td>
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<tr>
<td>Acetylene flow rate (L min(^{-1}))</td>
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<td>Air flow rate (L min(^{-1}))</td>
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**RESULTS AND DISCUSSION**

**Characterization of the biosorbent (FTIR, SEM-EDS and AFM studies)**

To investigate the changes in functional group regions of fungal biomass (before and after Cd(II) ions sorption) FTIR studies were carried out. As shown in Figure 1(a) and (b) broad, strong and superimposed bands around 3,500–3,200 cm\(^{-1}\) specifi es overlap of O–H and N–H stretching vibrations. Prominent shifts in the band from 3,380 to 3,397 cm\(^{-1}\) indicate changes in the O–H and N–H stretching vibrations during Cd biosorption. This type of band shifts were also observed by Sheng *et al.* (2004) during sorption of lead, copper, cadmium, zinc, and nickel by marine alga biomass. The strong absorption peak at 2,923 and 2,852 cm\(^{-1}\) assigned to \(\text{–CH}\) stretching vibration, which shows the presence of \(\text{–CH}_3\) and \(\text{–CH}_2\) functional groups, respectively. In addition, the strong adsorption band at 1,654 cm\(^{-1}\) represents a C=O stretching vibration and NH deformation (amide I) was also observed. The peak at 1,558 cm\(^{-1}\) was assigned to a motion combining both-NH bending (amide II) and –CN stretching vibration of the protein. A typical amide III band appeared at 1,380 cm\(^{-1}\), and C–N stretching band at 1,229 cm\(^{-1}\). Some absorption

Equation (1):

\[
Q = \frac{(C_i - C_f)}{M}V
\]

where

- \(Q\) = Cd(II) metal ions uptake (mg g\(^{-1}\)),
- \(V\) = solution volume (L),
- \(C_i\) and \(C_f\) = initial and final ionic concentrations in the solution (mg L\(^{-1}\)), and
- \(M\) = mass of biosorbent (g).

**Biosorption efficiency (%)** calculated by following the Equation (2):

\[
\text{Biosorption efficiency (%) = } \frac{C_i - C_f}{C_i} \times 100
\]

Desorption efficiency were calculated from the following formula (3):

\[
\text{Desorption efficiency (%) = } \frac{\text{Amount of sorbate desorbed per effluent}}{\text{Amount of sorbate loaded on biosorbent}} \times 100
\]
bands, i.e. P–O stretching at 1,153 cm\(^{-1}\) and P–O–C stretching at 1,043 cm\(^{-1}\) were indicative of a phosphonate group (Lin-Vien et al. 1991). After adsorption, a significant peak at 1,724 cm\(^{-1}\), corresponds to C = O was disappeared. The significant changes in the wave number of above mentioned specific peaks suggested that amide, hydroxy, C = O and C–O groups could be involved in the biosorption of Cd(II) ions on P. eryngii biomass.

It is observed in SEM analysis (Figure 2(a)) that the surface of biomass is irregular, porous, rough and heterogeneous in nature. Figure 2(b) represents the micrographs of Cd(II) loaded fungal biomass. The flecked structure was
observed on the surface of sorbent which may due to the sorption of Cd(II) ions. However, the rest of surface morphology seems similar as before sorption.

EDS elemental composition of the unloaded (Figure 2(c)) biosorbent proved the presence of C, O, Na, P, Cl, K and S elements as natural species on fungal biomass. The presence of these elements may influence the sorption mechanism through ion exchange interactions (Pino et al. 2006). Furthermore, Figure 2(d) reveals the sorption of Cd(II) ions on biomass by indicating a strong signal of Cd at ∼3.1 KeV. In addition, the disappearance of Cl, K and Na peaks after sorption signifies the involvement of an ion exchange mechanism during biosorption.

To further confirm the surface morphology of fungal biomass, AFM study was carried out. It is an ideal tool for determining the changes in cellular morphology before and after interaction of sorbate (Cd). The micrograph as shown in Figure 3(a) exhibits relatively smooth surface of the fungus. The fungal image is found to be clearly resolved into three-dimensional height image (Figure 3(b)). The surface of the biomass undergoes a significant change due to the sorption of Cd(II) ions (Figure 3(c)). In general, results of AFM study showed that the uppermost layer of fungal biomass become rougher or irregular due to the formation of metal ion bumps impact on the surface (Figure 3(d)).

The root mean square (RMS) surface roughness were also calculated from the topography images (Figure 3). For untreated fungal biosorbent (Figure 3(a) and 3(b)), the cell surface was relatively smooth with an RMS of 98.6 nm and Ra (roughness average) of 26.9 nm (data not shown). After Cd(II) adsorption, the cell appeared to be coated with a soft, compressible material. The RMS and Ra values, respectively, increased to 186.4 nm and 28.8 nm. Apparently, because prominent components were unevenly distributed on the cell surface, and stretched out upon retraction of the tip to hundreds of nanometers in length (Figure 3(c) and 3(d)), possibly resulting from the bonding of Cd(II) with the polysaccharide, protein, and amide (Zhang et al. 2006).

Optimization of biosorption experimental parameters

To increase the Cd(II) ions uptake by fungal biosorbent, the influence of various experimental parameters, i.e. pH, biosorbent dose, initial Cd(II) ion concentration, temperature and time, were optimized.

The biosorption efficiency is considerably influenced by the pH of an experimental solution. Figure 4(a) illustrates the effect of pH on the sorption capacity of *P. eryngii* biomass for Cd(II) ions. It is demonstrated from Figure 4(a) that the sorption efficiency of *P. eryngii*...
were 48% at initial pH 3.0, but a significant increase in efficiency was observed from 55 to 70% as the pH of the solution changed from 4.0 to 5.0, respectively. Owing to the high density of proton (H\(^+\)) on sorption sites of biomass surface, positively charged metal ions were restricted as a result of electrostatic repulsion. As the pH increases, the negatively charged (OH\(^-\)) group becomes available, which promote the sorption of the positively charged metal ion. Later, a drastic decline in the graph was observed as the pH was further increased from 6.0 to 7.0 which indicates the low efficiency of *P. eryngii* at higher pH. This effect attributed to the saturation of negative charge at higher pH, due to the formation of anionic hydroxide complexes [Cd(OH)\(_2\)]. These complexes appeared as precipitates in solution and begin their competition with the active sites. Afterward, the subsequent experiments were continued at pH 5.0 ± 0.2 as optimum pH. The carboxylic groups of the fungal cell wall are major sites for metal ion absorption, as these functionalities significantly deprotonated and are readily bound to Cd(II) ions (Chena et al. 2012).

After pH optimization, the biosorbent dosage were considered as an important parameter. The results illustrated in Figure 4(b) shows that the amount of biosorbent significantly influenced the extent of Cd(II) biosorption. In lower doses, sorption level is lower due to less adsorption sites. It was observed that maximum sorption of about 95% Cd(II) ions were achieved using 0.2 g/10 mL biomass compared to other dosages. This is probably due to an increase in number of available adsorption ionic sites as the sorbent dose increased. Since the concentration of metal ions (Cd) in solution is fixed, initially more ions get exchanged with the metal ions but after the saturation is reached, adsorption decreased. After this dosage, there was a decrease in adsorption levels that could be attributed to the consequence of partial aggregation of biomass at higher concentrations (Al-Homaidan et al. 2014).

The effect of Cd(II) ion concentration on the adsorption efficiency of *P. eryngii* fungal biomass was also checked under optimum conditions as shown in Figure 4(c). The sorption efficiency increased from 37.5 to 98.1% for Cd(II) ions with increasing initial concentration from 4.0 to 20 mg L\(^{-1}\). It is because the initial concentration provides necessary driving force to overcome the mass transfer resistance of Cd(II) ions between the aqueous and the solid phases (Akpa & Nmegbu 2014). Hence an increase in initial Cd(II) concentration will increase the mass transfer of Cd (II) and ultimately enhance the adsorption rate of Cd(II) by the fungal biomass.

Temperature played a vital role in the sorption process that is why the effect of temperature in the range of 25 to 70 °C for removal of Cd(II) ions were also determined. By examining the sorption trend in Figure 4(d), a
significant increase in percent removal (90 to 96%) was achieved when temperature increased from 25 to 50 °C. However, further increase in temperature (>50 °C) shows a decline in the sorption efficiency due to deterioration of biomass boundary layer thickness. This deterioration alters the active functionalities and attractive forces between biomass surface and metal ion. Maximum sorption of Cd(II) ions were achieved at 50 °C, which is similar as reported in the literature of various metal ions (Opeolu et al. 2011).

Contact time for sorbent and sorbate effects the percent removal efficiency of targeted analyte and simultaneously used to elucidate the kinetics of reaction. Figure 5 shows that the sorption process were slow at 1 to 2 min but later the sorption efficiency was increased gradually with respect to time. The maximum removal of Cd(II) ions ~99.9% was obtained within 10 min of reaction time. This apparent change occurs because numerous sites are available for sorption at the initial stage which provides the space for adsorption. After a few minutes, the remaining vacant surface sites were hard to occupy because of the repulsive forces between Cd(II) ions and the aqueous phases (Prasanthi et al. 2016).

From the observed sorption trend, it was concluded that an agitation time of 10 min is suitable for complete removal of Cd(II) ions from aqueous system. Further increase in contact time did not show any change which symbolizes the attainment of equilibrium condition.

**Biosorption isotherm studies**

Isotherms demonstrate the amount of solute sorbed per unit of sorbent and provides information about the qualitative statistics of the sorption progress and the degree of biomass surface coverage by sorbate (Osman et al. 2015).

In this study, Langmuir and Freundlich adsorption isotherm models were used to evaluate the sorption phenomenon between the surface of *P. eryngii* and Cd(II) ions.

**Langmuir isotherm**

Langmuir model assumes a monolayer coverage of sorbate (metal) over a uniform sorbent surface. The linear form of the Langmuir adsorption isotherm is represented as Equation (4):

\[
\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q}
\]

where

- \(C_{ads}\) = amount of Cd(II) ion biosorbed per unit mass of biosorbent (mg g⁻¹),
- \(C_e\) = amount of Cd(II) ion in liquid phase at equilibrium (mg L⁻¹),
- \(Q\) = monolayer biosorption capacity (mg g⁻¹), and
- \(b\) = Langmuir constant related to the free energy of biosorption (L mg⁻¹).

The essential characteristics of Langmuir isotherm model can be expressed in terms of dimensionless constant separation factor (RL), which has four probabilities:

1. \(0 < R_L < 1\), favorable adsorption;
2. \(R_L > 1\), unfavorable adsorption;
3. \(R_L = 1\), linear adsorption; and
4. \(R_L = 0\), irreversible adsorption.

The separation factor \(R_L\) is calculated using Equation (5):

\[
R_L = \frac{1}{1 + bC_i}
\]

For Langmuir isotherm model, the straight line graph \(C_e/C_{ads}\) versus \(C_e\) (g L⁻¹) were extrapolated which showed good regression coefficient (Supplementary material, SM_1(a), available with the online version of this paper). The calculated data presented in Table 2 confirm the favorable uptake of Cd(II) ions at all working Cd(II) concentrations. The separation factor (RL) values between 0 and 1, also indicates the favorable uptake of Cd(II) by fungal biomass.

**Freundlich isotherm**

Freundlich model was elaborated for the non-ideal sorption on heterogeneous surfaces involving multilayer sorption. It assumes that stronger binding sites on the biosorbent surface are occupied first and that the binding strength decreases
with increasing degree of site occupation by sorbate. The linear form of the Freundlich adsorption isotherm is represented as Equation (6):

$$\log C_{ads} = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

where $K_f$ and $n$ are the constants incorporating all the factors (i.e. adsorption capacity and intensity) affecting adsorption process.

The graph Log $C_e$ (mg L$^{-1}$) versus Log $C_{ads}$ (mg g$^{-1}$) was plotted (SM_1(b), available online) that shows a low value of $R^2$ then Langmuir isotherm model. The calculated data obtained are given in Table 2.

It is concluded from the acquired parameters that the biosorption reaction follows Langmuir isotherm which indicates the monolayer sorption phenomenon and chemical type of interaction between sorbent surface and sorbate.

### Thermodynamic studies

The temperature dependence of the biosorption process is associated with several thermodynamic parameters such as a change in Gibbs free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$). These parameters were calculated from van ‘t Hoff plot of ln$K_c$ versus $1/T$ (SM_2, available online) according to Equations (7) and (8), respectively:

$$\Delta G^\circ = -RT \ln K_c \quad (7)$$

$$\ln K_c = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

where

$R$ = universal gas constant (0.0083 kJ mol$^{-1}$ K$^{-1}$),

$T$ = absolute temperature (K), and

$K_c$ = equilibrium constant.

The thermodynamic parameters for the sorption of Cd(II) ions on fungal biomass are given in Table 3. The negative values of $\Delta G^\circ$ and $\Delta H^\circ$ at the studied temperature range confirmed the spontaneous and exothermic nature of biosorption process, respectively and indicates the feasibility of reaction against elevated temperatures (Mehrizad & Gharbani 2014). Moreover, enthalpy change data are useful for distinguishing the physical and chemosorption mechanism. Physiosorption is typically associated with the heat of adsorption in the range of 2.1–20.9 kJ mol$^{-1}$, while chemiosorption with $\Delta H^\circ$ values of 20.9–418.4 kJ mol$^{-1}$. From the enthalpy value represented in tabulated data, it is concluded that the biosorption of Cd(II) ions on $P. eryngii$ is chemisorptive in nature.

The negative value of $\Delta S^\circ$ reflects the decreased randomness at the solid–liquid interface during sorption. The entropy value less than zero demonstrate the occurrence of a certain order for the metal ions on the biosorbent surface. This allowed that the biosorption were governed by enthalpy factors as opposed to entropic factors.

### Biosorption kinetic studies

To analyze the biosorption kinetics and to calculate the adsorbate uptake rate of Cd(II) ions on $P. eryngii$, two kinetic models, i.e. Lagergren’s pseudo-first and Ho-McKay’s pseudo-second-order (Doke et al. 2013) were used.

The first-order-rate equation of Lagergren is widely used for the sorption of solute from a liquid solution and is represented as:

$$\ln (q_e - q_t) = \ln q_e - \frac{k_1 t}{2.303} \quad (9)$$

where

$q_t$ and $q_e$ = the amount of Cd(II) ions in mg g$^{-1}$ biosorbed at time ‘$t$’ and equilibrium, respectively, and

$k_1$ = Lagergren rate constant of the pseudo-first-order biosorption process (min$^{-1}$).

### Table 2 | Isotherms model constants and their respective coefficients for Cd(II) ions sorption onto fungal biomass

<table>
<thead>
<tr>
<th>Langmuir isotherm parameters</th>
<th>$Q$ (mg g$^{-1}$)</th>
<th>$B$ (L mg$^{-1}$)</th>
<th>$R_L$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_f$ (mg g$^{-1}$)</td>
<td>1.515</td>
<td>2.268</td>
<td>0.002-0.099</td>
<td>0.928</td>
</tr>
<tr>
<td>Freundlich isotherm parameters</td>
<td>$K_f$ (mg g$^{-1}$)</td>
<td>15.595</td>
<td>1.22</td>
<td>0.855</td>
</tr>
</tbody>
</table>

### Table 3 | Thermodynamic parameters for Cd(II) ions biosorption on $P. eryngii$ at various temperatures

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta G^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta H^\circ$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^\circ$ (kJ mol$^{-1}$ K$^{-1}$)</th>
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<tr>
<td>288</td>
<td>-12.05</td>
<td>-67.751</td>
<td>-0.192</td>
</tr>
<tr>
<td>293</td>
<td>-11.63</td>
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<tr>
<td>298</td>
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<td></td>
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<tr>
<td>303</td>
<td>-3.174</td>
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<tr>
<td>343</td>
<td>-2.469</td>
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</table>
Straight line plot of t against ln(qe–qt) (SM_3(a), available online) were used to determine the rate constant and biosorption capacity. The values of k₁ and R² along with the calculated uptake capacity qₑ₀ are 0.202 min⁻¹, 0.866 and 0.290 mg g⁻¹, respectively.

The pseudo-second-order kinetics of adsorption was applied to verify the kinetic mechanism between the sorbate and sorbent. The parameters k₂ and qₑ were calculated by the following equation:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

where

\[ k_2 = \text{rate constant of pseudo-second-order biosorption (g mg}^{-1}\text{ min}^{-1}). \]

The straight-line plot (SM_3(b), available online) of t versus t/qt indicate the relevancy of the above equation for the biosorption of Cd(II) ions on fungal biomass. The second order rate constant k₂ 1.867 g mg⁻¹ min⁻¹, correlation constant R² 0.999 along with calculated uptake capacity (qₑ) is 0.838 mg g⁻¹.

Calculated correlations are closer to unity for the pseudo-second-order kinetic model and the predicted value of qₑ is comparable to the experimental one (qₑ exp. 0.889 mg g⁻¹); therefore, the biosorption kinetics could be well approximated by second order kinetics model than pseudo-first-order kinetics.

The results were also analyzed in terms of Weber and Morris intra particle diffusion model (Chang et al. 2016) to investigate whether the intra particle diffusion is the rate controlling step in biosorption of Cd(II) ions on P. eryngii biomass. According to this model intra particle diffusion varies with the square root of time as given in Equation (11):

\[ q_t = k_{id} \sqrt{t} + C \]

where

\[ k_{id} = \text{intra particle diffusion rate constant (mg g}^{-1}\text{ min}^{-1/2}), \]

and

\[ C = \text{constant related to the thickness of boundary layer}. \]

The values of k₁d 0.073, C 0.547 and R² 0.892 were obtained from the slope of t¹/² versus qₑ plot (SM_4, available online). It is observed from the plot that intercept does not pass through the origin, thus pore diffusion is not only the rate determining factor for the biosorption of Cd(II) ions on P. eryngii.

By comparing constants of all kinetic models, it is evaluated that pseudo-second-order kinetic model best fitted for the biosorption experiment.

**Elution of Cd(II) ion and re-usability of biosorbent**

To check the reusability of the spent sorbent for the consecutive cycles, elution and reuse experiments were performed at room temperature. For this study, the Cd(II) metal ion loaded biomass (after washing with ultra-pure water) were shaken in 0.1 N each of HNO₃, H₂SO₄, HCl, and NaOH, EDTA, NaCl eluents for 30 min at 100 rpm to desorb loaded Cd(II) ion from fungal biomass at a predetermined temperature, then the resultant filtrate was analyzed for the residual content. The results presented in Figure 6(a) shows maximum recovery of 99.89% Cd(II) ions with the use of HNO₃ as eluent. As per our observation, the order of elution performance is as follows: HNO₃ > HCl > EDTA > H₂SO₄ > NaOH > NaCl.

For the complete unloading of Cd(II) ions, the biomass were washed with an excess amount of HNO₃ (0.1 N) followed by appropriate washing with ultra-pure water to a maximum removal of H⁺ ions from the surface of sorbent to maintain the removal efficiency of sorbent.

Thereafter, the reusability studies of the biosorbent were conducted by introducing desorbed biomass again in the fresh ionic solution. The data present in Figure 6(b) show that

*Figure 6* | (a) Influence of various eluents on percentage recovery of Cd(II) ions by P. eryngii fungal biomass. (b) Desorption efficiency of P. eryngii with cycle number.
the sorption efficiency was decreased from 99.99 to 56.89% as the biomass was recycled up to five times. The reduction in efficiency could be attributed to the use of HNO₃ solution which enriches the H⁺ ions on the biomass surface and results in the electrostatic repulsion of positively charged Cd(II) ion that eventually causes the decrease in sorption capacity.

Influence of interfering ions

In addition to targeted metal ion, an aqueous solution also contains several other ions. Therefore, to check the selectivity/efficiency of P. eryngii biomass toward specific ion, sorption experiments of Cd(II) were performed in the existence of supplementary ions, keeping different combination of folds. Table 4 shows the effect of different interfering ions during biosorption of Cd(II) from aqueous system. Selected concentration of co-existence ions were added in 10 mL test solution of Cd(II) ion (5 mg L⁻¹) and then subjected to the general procedure of batch sorption.

From the results of an interfering study it was found that the ions naturally existing in real samples (Na⁺, K⁺, Ca²⁺, Mg²⁺, SO₄²⁻, NO₃⁻, PO₄³⁻, Cl⁻) have no significant effect on the removal of Cd(II) ions under optimized experimental conditions. Exceptionally, PO₄³⁻ anion may severely interfere in the determination of Cd(II) probably due to the formation of precipitates in the working pH. These results confirmed that the proposed method could be applied to samples that contain a high number of interfering ions at ppm (mg L⁻¹) level.

Analytical application

To set up the validity of our proposed method, the batch biosorption study were performed in real field application. Three water samples having a higher concentration of Cd(II) ions were collected from river, canal, and lake of Sindh, Pakistan. In general, the removal efficiency for Cd(II) was higher for synthetic wastewater (>98%) than for real water samples (~90%), as presented in Table 5. It is because in real water samples, in contrast to synthetic wastewater, supplementary cations are competing with Cd(II) for active sites on the fungal biomass and at the same time many anions are in complexation reaction with Cd(II). Both effects may cause reduction of the sorption efficiency in real samples. Although the efficiency of Cd(II) removal from real water samples lies between 85 and 90% which accomplished that this proposed technique is feasible, reliable and suitable for the removal of Cd(II) ions from real water samples.

Table 5 | Field trial results of biosorption studies using real water samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cd(II) concentration (mg L⁻¹) in sample water</th>
<th>Cd(II) sorption (%)</th>
<th>Amount of Cd(II) after biosorption (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S - 1</td>
<td>0.037</td>
<td>90</td>
<td>0.003</td>
</tr>
<tr>
<td>S - 2</td>
<td>0.030</td>
<td>92</td>
<td>0.002</td>
</tr>
<tr>
<td>S - 3</td>
<td>0.050</td>
<td>91</td>
<td>0.003</td>
</tr>
</tbody>
</table>

*5-1 – Phuleli canal, Hyderabad; 5-2 – River Indus, Jamshoro; 5-3 – Manchar Lake, Distt. Dadu.

CONCLUSION

The present study provides an efficient, cost-effective and environmentally friendly biosorbent with its high potential in removing Cd(II) ions from aqueous system. The sorption of Cd(II) ions was found to be pH dependent and maximum removal were observed at pH 5.0. P. eryngii biomass were successfully utilized for the removal of Cd(II) ions from aqueous solution with 99.9% sorption efficiency. Rapid sorption and equilibrium were achieved within 10 min. Langmuir isotherm offers the best correlation for the adsorption of Cd(II) ions confirming monolayer coverage. The sorption process obeyed a pseudo-second-order kinetic model. The elution of Cd(II) ions were achieved from the biomass using 0.1 N HNO₃ solution. The used fungal biomass can be easily disposed of since it is biodegradable and can also be used as an alternative raw material for the large scale composting process. Besides, people of affected areas can take advantage of this natural safe method for removal of toxic Cd(II) ions from contaminated water.

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CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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