Study of Cd (II) ions biosorption from aqueous solution by wheat bran

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A B S T R A C T

Wheat bran without any chemical treatment was used as biosorbent for sorption of cadmium ions from aqueous solution. The structure of biosorbent was characterized by ATR-IR spectra and pH of the point zero charge (pHPZC). The effect of initial metal concentration, biosorbent dose, contact time, temperature, initial solution, pH, on biosorption of Cd(II) ion from aqueous solution into wheat bran were determined. The best results were achieved at contact time 30 min at pH 5.5 and temperature 25°C. We used Freundlich and Langmuir isotherms to characterize the adsorption equilibrium. The biosorption of cadmium ions fits well with the Langmuir and Freundlich isotherms, according to experimental data (R² 0.996 and R² 0.995, respectively). The maximum biosorption capacity of cadmium ions with the Langmuir model for wheat bran is q_{max} = 6.25 mg/g, at optimal conditions. Thermodynamic parameters (ΔH°, ΔS° and ΔG°) showed that the exothermic, spontaneous and favourable biosorption process. These results predict that wheat bran can be used for uptake of cadmium ions from aqueous solution.

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Introduction

Today one of the biggest environmental problems is the presence of heavy metals in surface or ground water even at low concentration. Pollution of these waters with heavy metals is done mainly by industrial, urban, and farm waters (Renu et al., 2017). The term heavy metal applies to any metallic chemical substance that has a relatively high density and is toxic (Zulfiqar et al., 2019). This group of metals includes such as aluminum, arsenic, beryllium, cadmium, chromium, copper, iron, lead, mercury, nickel, thallium, and zinc (Karimpour 2018). They are non-biodegradable and harmful to the environment and minimized the biodegradation of organic contaminants in soil (Rashid et al., 2018; Mondal et al., 2020). By directly ingesting contaminated food, coming into physical contact with contaminated soil, passing through the food chain (soil-plant-human or soil-plant-plant-animal-human), drinking contaminated water, lowering food quality, and decreasing the amount of land suitable for farming, metal contamination damages ecosystems and harms human health (Hasan et al., 2019; Hussain et al., 2021).

As one of the most toxic heavy metals, cadmium is also categorized as the “Big Three” heavy metals together with lead and mercury given their serious impacts on the environment (Kahlon et al., 2018; Qian et al., 2022). Cadmium is used for production of dye, pigment, batteries, ceramics, wooden, and plastic products. The metal is also used in electroplating, semiconductors, rectifiers and solder for aluminium (Kalandar and Yadav, 2014). The utilization of synthetic phosphate fertilizers that contain cadmium, as an impurity is a common cause for the elevation of it concentration in groundwater and soil (Kubier et al., 2019).
Toxicity of cadmium affects multiple organs of the human body but accumulates mainly in the kidneys and causes serious damage, including pulmonary emphysema, renal tubular damage, and kidney stones (Arda Karasakal and Nihan Talib, 2022; Mahajan and Kaushal, 2018). Cadmium has detrimental and carcinogenic effects by competitively binding to areas in enzymes, proteins, and DNA (especially with a zinc finger motif), which are necessary for gene control or the preservation of genomic integrity (Huff et al., 2007; Salih et al., 2020). Cadmium in minerals replaces calcium, due to having identical charge and similar ionic radius and chemical behavior (Fasih et al., 2021). Chronic toxicity of cadmium in children includes damages of respiratory, renal, skeletal and cardiovascular. Exposure of people to Cd includes, eating contaminated food, smoking cigarettes, and working in cadmium-contaminated work places and in primary metal industries (Geofrey et al., 2020). Te US EPA’s regulatory limit of Cd in drinking water is 0.005 ppm (Martin and Griswold, 2009). Te WHO recommended safe limits of Cd in both wastewater and soil for agriculture is 0.003 ppm (Aneyo et al., 2016).

Different methods have been applied such as adsorption, complexation, chemical oxidation or reduction, chemical precipitation, reverse osmosis, ion exchange, coagulation etc. for treatment of heavy metal ions (Thaći and Gashi, 2019). In several study, Fe3O4 nanoparticles were used as the magnetic core for fabrication of high capacity heavy metal sorbents (Ramin et al., 2018).

However, some of these techniques have constrains on their application, such as the high operating cost, energy-intensive use hazardous chemicals, and generating disposal of residual metal sludge, which can be a source of secondary contamination (Thaći and Gashi, 2019).

In recent decades, biosorption has been widely investigated, and considered a promising alternative to conventional processes because of its low cost, material regeneration, environmental friendliness, and high performance (Li et al., 2021).

New methods for the removal of toxic heavy metals, has directed attention to biosorption phenomenon which is based on the metal binding capacity of agricultural wastes (Sarada et al., 2017). A number of agricultural and forestry by-products such as Mango seed (Qian et al., 2022), Actinomucor (Ramin et al., 2018), Araucaria heterophylla (Sarada et al., 2017), alga Anabaena sphaerica (Azza et al., 2013), Trifolium resupinatum (Asif et al., 2019), Cola-Nut Leaves (Ibrahim and Faruruwa, 2020), Coconut Copra (Lee et al., 2021), olive waste, coffee waste, maize cobs (Daci-Ajavazi et al., 2018), Agave bagasse (Dianaet al., 2020) etc., have been used for heavy metal removal from waters and wastewaters.

In this work, wheat bran as abundant and low cost biosorbent was used to remove cadmium ions from aqueous solution.

Materials and methods

The biosorbent, wheat bran was obtained commercially from factory “Dardania” Pejë (Kosova). Wheat bran washed thoroughly to remove dust using distilled water then dried at 80 °C for 20 hours. The dried samples were grinded and fractions of >0.2 mm were used for experiments (Thaći and Gashi, 2019).

The sorption of Cd (II) ions on used adsorbents (wheat bran) was studied using a batch technique. The method used for this study was carried out as follows. The stock solution of Cd(II) at different concentrations (52.0, 26.0, 13.0 and 5.5 mg/dm3) was used in experimental runs. A known weight of adsorbent (0.10, 0.25 and 0.50 g) was equilibrated with 50 cm3Cd (II) solutions in a stopper Pyrex glass flask for a known period of time (5, 10, 20, 30, 60, 90, and 120 min), at different pH (3, 4, 5, 6, 7, and 8) and different temperature (25, 35, 45, 55 °C) values in a thermostatic shaker bath (200 rpm). The solutions were adjusted to final desired pH using 0.1 M HCl or 0.1 M NaOH (pH-meter HANA Model, HI 98130). To observe the effect of certain parameters, one selected parameter has been changed progressively keeping the others constant. After equilibration, the suspensions were filtered and analyzed by AAS (Atomic Adsorption Spectrometer, flame Contra AA 300, Analytic Jena).

The amount of biosorbed cadmium ions per gram of wheat bran at equilibrium qe (mg/g), and the removal percentage (% A), were calculated using the following equations:

\[ q_e = \frac{(C_o - C_e)V}{m} \]  

\[ \% (A) = \frac{C_o - C_e}{C_o} \times 100 \]

Where \( C_o \) and \( C_e \) are the initial and equilibrium concentrations of cadmium (mg/dm3); \( V \) is the volume of cadmium solution (dm3); and \( m \) is the weight of used wheat bran (g).

The pH of the point zero charge (pHpzc) of biosorbent was determined by pH drift method (Manoj et al., 2020).
Results and discussion

Characterization of biosorbent

The attenuated total reflectance infrared (ATR–IR) spectra of wheat bran particles were recorded with a germanium ATR accessory (Jasco ATRPRO470-H) over a scan range of 700-4000 cm\(^{-1}\). For spectrum, 1,000 scans were accumulated with a spectral resolution of 4 cm\(^{-1}\). ATR–IR spectrum of wheat bran is presented in figure 1 and table 1.

Table 1. ATR-IR, analysis of wheat bran.

<table>
<thead>
<tr>
<th>Vibration peaks of wheat bran (cm(^{-1}))</th>
<th>Nature of functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 3130.5</td>
<td>O-H, N-H</td>
</tr>
<tr>
<td>2 2289.1</td>
<td>C≡C, C≡N</td>
</tr>
<tr>
<td>3 1651.7</td>
<td>C=O</td>
</tr>
<tr>
<td>4 1583.3</td>
<td>C=C, N-H</td>
</tr>
<tr>
<td>5 1308.5</td>
<td>C-N</td>
</tr>
<tr>
<td>6 1046.5</td>
<td>C-O</td>
</tr>
<tr>
<td>7 1045.3</td>
<td>C-O-C</td>
</tr>
<tr>
<td>8 818.63</td>
<td>C-H</td>
</tr>
</tbody>
</table>

ATR-IR analysis was performed to investigated the functional groups in wheat bran, which might be the possible ways of interactions between biosorption of Cd(II) ions and biomass (Asif et al., 2019).

Effect of pH solution

The pH of the solution is one of the essential parameter in the heavy metal biosorption process, because it controls the speciation of metal ions as well as the charge on the surface of the biosorbent (Asif et al., 2019). This can also affect the degree of ionization of the adsorbate molecules and is accountable for the higher/lower sorption capacity of the biosorbent (Crini et al., 2007). The batch studies were carried out to obtain optimum pH for the removal of cadmium ions, using wheat bran by varying range of pH from 3 to 8, under specific conditions (adsorbent dose 0.25g, contact time 30 min and temperature 25°C). These results are presented in figure 2.
It was showed that, biosorption capacity of cadmium was increased by increasing the pH of the liquid phase and reached the optimum value at pH 8. The removal amount of cadmium ions by the wheat bran at pH 3 was only 3.0 mg/g, but at pH 8 it was increased at 3.72 mg/g. In addition, cadmium is present as free ions below pH 7.5 after which it starts forming the precipitates as Cd(OH)_2. These precipitates are not wanted as these are not available for metal-biosorbent interaction (Asif et al., 2019).

The cadmium ions up taken by wheat bran can be well described based on pH of the point of zero charge (pH_{PZC}), which depends on the chemical structure and electronic properties of the functional groups on the adsorbents surface (Jiao et al., 2017). These results are presented in figure 3.

From figure 3, the pH_{PZC} value is about 6 for wheat bran. There was a negatively charged surface of adsorbent at pH above these values, while there was a positively charged surface of biosorbent at pH below this value. Therefore, below pH_{PZC}, there were competitions between the hydrogen and cadmium ions to reach the surface, because at lower pH, the concentration of H^+ ions increased on the site of biomass surface (Azza et al., 2013). It can be shown that, at pH >pH_{PZC}, the amount of cadmium ions adsorbed increased. The protonation of the functional groups that are present on the surface of the biosorbent can also be used to explain this positive charge. At low value of pH, the functional groups containing O^- and N^- are protonated due to high potential of H^+ ions. This protonation, decrease with increase in pH, which the concentration of H^+ ions decrease (Asif et al., 2019).

**Effect of contact time**

The effect of contact time on the cadmium removal by wheat bran, at pH solution of 5.5, adsorbent dose 0.25g, and 25°C are shown in figure 4.

The cadmium biosorption increases with time until equilibrium is attained between the amounts of cadmium adsorbed on the biosorbent and the remaining cadmium in the solution (Singh et al., 2008). From figure 4, it is seen that the biosorption of cadmium increases with time from 0 to 30 min and then becomes constant, so the equilibrium was reached after 30 min. These results indicated that the biosorption was quite rapid at the beginning. The rate of biosorption of cadmium
ions using wheat bran seems to be in two steps, very rapid in the first step and a slow in the second step (Azza et al., 2013).

**Effect of biosorbent dose**

The effect of biosorbent dose on removal of Cd(II) ions by wheat bran is studied by changing the biosorbent dose: 0.10, 0.25 and 0.50 g for 50 cm³ cadmium solution, while other parameters are kept unchanged. These results are represented in figure 5.

![Fig 5. Effect of biosorbent dose on the biosorption of Cd(II) by wheat bran, at different initial concentration.](image)

As it can be seen, from the figure 5, biosorption capacity, of cadmium increases with increasing biosorbent dose. Based on the results for the condition mentioned above the biosorbent dose has more effect at higher concentrations than at lower concentration. Because, at lower concentrations, the number of cadmium ions is lower and the small biosorbent dose, is sufficient to reach the maximum biosorption capacity. So, in these cases increasing the dose of biosorbent has no more effect on the biosorption of cadmium ions. While, at higher concentrations the number of cadmium ions is higher and the dose of biosorbent has more impact to reach the maximum biosorption capacity. For example, increased the dose of biosorbent from 0.10 to 0.50 g, biosorbent capacity of cadmium ions is increased just 0.04 mg/g at 5.5 mg/dm³, whereas 1.44 mg/g, at initial concentration 52.0 mg/dm³, respectively. This trend is expected because as the adsorbent dose increases the binding sites number of adsorbent particles increases and thus more cadmium is attached to their surfaces (Nuhoglu and Malkoc, 2009).

**Effect of initial concentration**

The effect of initial concentration on the cadmium removal was studied by varying the initial concentration of solution: 5.50, 13.0, 26.0, and 52.0 mg/dm³, adsorbent dose 0.10, 0.25 and 0.50 g, at contact time 30 min, pH 5.5 and temperature 25°C. The graph of different cadmium ion concentrations and biosorption capacity is shown in figure 6.

![Fig 6. Effect of initial concentrations on the biosorption of Cd(II) by wheat bran at different biosorbent doses.](image)

The data presented in figure 6 indicate that, an increase in the cadmium concentration from 5.5 to 52.0 mg/dm³, increased cadmium biosorption for 4.04 mg/g. This increase could be due to an increase in initial concentration of cadmium that led to the higher driving force for the ions from the solution to the biosorbent and facilitated enhanced displacement of protons ions on the surface of the biomass (Ramin et al., 2018; Sarada et al., 2017).

**Biosorption Isotherms models**

The biosorption isotherm is an expression which gives a relationship between the quantity of
solution biosorbed and the amount of solute residual in a given solution (Ibrahim and Faruruwa 2020). Biosorption isotherms were investigated using two equilibrium models, Langmuir and Freundlich.

The monolayer adsorption theory is based on Langmuir’s isotherm model. The Langmuir theory’s fundamental premise is that biosorption occurs at certain homogenous sites within the biosorbent. The Langmuir isotherm is expressed by equation (Sarada et al., 2017):

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} \quad \text{C}_e \]  

\( q_m \) is the maximum biosorption capacity of the biosorbent (mg/g); \( K_L \) (dm³/mg) is the Langmuir constant and it is an affinity parameter related to the energy of biosorption; \( C_e \) is the equilibrium cadmium ion concentration in the solution (mg/dm³) and \( q_e \) is the equilibrium cadmium ion concentration on the biosorbent (mg/g). Plotting \( C_e/q_e \) versus \( C_e \) results in a straight line of slope \( 1/q_m \) and intercepts \( 1/K_Lq_m \). Langmuir isotherm for wheat bran is presented in figure 7.

\[ R_L = \frac{1}{1 + K_L C_o} \]  

\( K_L \) is Langmuir constant (dm³/mg) and \( C_o \) is initial concentration of cadmium (mg/dm³). The value of \( R_L \) can be as a reference to the type of Langmuir isotherm as following: unfavorable \( R_L > 1 \), linear \( R_L = 1 \), favorable \( 0 < R_L < 1 \), and irreversible when \( R_L = 0 \) (Ayawei et al., 2015). These data for wheat bran are presented in table 2.

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the separation factor \( R_L \) (Ayawei et al., 2015):

\[ \log q_e = \log K_F + \frac{1}{n} \log C_o \]  

\( K_F \) (mg/g) is Freundlich isotherm constant, and \( 1/n \) is the biosorption intensity, which varies with the heterogeneity of the material. The constants \( 1/n \) and \( \log K_F \) were calculated from the slope and intercept, respectively. Freundlich isotherm for wheat bran is presented in figure 8.

<table>
<thead>
<tr>
<th>( C_o ) (mg/dm³)</th>
<th>52.0</th>
<th>26.0</th>
<th>13.0</th>
<th>5.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_L )</td>
<td>0.110</td>
<td>0.199</td>
<td>0.331</td>
<td>0.539</td>
</tr>
</tbody>
</table>

Fig 7. Langmuir isotherm for biosorption of Cd (II) ions by wheat bran.
Langmuir and Freundlich isotherms data are presented in Table 3.

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameter</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>6.25</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (dm$^3$/mg)</td>
<td>0.155</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.996</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$K_F$ (mg/g)</td>
<td>0.161</td>
</tr>
<tr>
<td></td>
<td>$1/n$</td>
<td>0.467</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.995</td>
</tr>
</tbody>
</table>

From these results, it is shown that the biosorption of Cd(II) ions on wheat bran fits well with the Langmuir ($R^2$ 0.996) and Freundlich isotherms ($R^2$ 0.995). The correlation coefficient values (Table 3) approaching to one clearly suggests that Langmuir and Freundlich isotherms holds good to explain biosorption of Cd(II) ions on wheat bran. The maximum biosorption capacity of the biosorbent was found to be 6.25 mg/g. The data calculated from Freundlich isotherm showed that the $1/n$ value was 0.467, which is an indication that the biosorption process was favorable (Thaçi et al., 2021). Comparison of the cadmium ions biosorption capacity of some biosorbents is presented in table 4.

<table>
<thead>
<tr>
<th>Adsorption capacity (mg/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agave Bggasse</td>
<td>(Diana et al., 2020)</td>
</tr>
<tr>
<td>28.50</td>
<td></td>
</tr>
<tr>
<td>Actinomucar</td>
<td>(Ramin et al., 2018)</td>
</tr>
<tr>
<td>24.09</td>
<td></td>
</tr>
<tr>
<td>Mucarrouxii</td>
<td>(Yan and Viraraghavan, 2003)</td>
</tr>
<tr>
<td>20.31</td>
<td></td>
</tr>
<tr>
<td>Bamboo-charcoal</td>
<td>(Wang et al., 2010)</td>
</tr>
<tr>
<td>12.08</td>
<td></td>
</tr>
<tr>
<td>Naucleadiderrichii</td>
<td>(Omorogie et al., 2012)</td>
</tr>
<tr>
<td>6.30</td>
<td></td>
</tr>
<tr>
<td>Halzenut-shells</td>
<td>(Cimino et al., 2000)</td>
</tr>
<tr>
<td>5.42</td>
<td></td>
</tr>
<tr>
<td>Coconut copra meal</td>
<td>(Ho and Ofomaja, 2006)</td>
</tr>
<tr>
<td>4.92</td>
<td></td>
</tr>
<tr>
<td>Sugarcane-bagasse</td>
<td>(Gupta et al., 2003)</td>
</tr>
<tr>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Aspergillus Niger</td>
<td>(Kapoor et al., 1999)</td>
</tr>
<tr>
<td>1.31</td>
<td></td>
</tr>
<tr>
<td>Wheat bran</td>
<td>This study</td>
</tr>
<tr>
<td>6.25</td>
<td></td>
</tr>
</tbody>
</table>
Thermodynamic parameters

Temperature is another important factor in the biosorption process. The increasing temperature would favor or oppose the metal biosorption process, depending on energy involved (Asif et al., 2019). The effect of temperature on the biosorption of cadmium ions was studied in the interval 298 – 328 K. The thermodynamic parameters (ΔH°, ΔS° and ΔG°) should provide insight into the mechanism and biosorption process. Thermodynamic parameters were calculated from the following equation:

\[ K_e = \frac{q_e}{C_e} \]  

where \( K_e \) is the equilibrium constant, it’s calculated at different temperatures.

\[ \Delta G^o = -RT \ln K_e \]  
\[ \Delta G^o = \Delta H^o - T \Delta S^o \]  

From Eq. 7 and 8, equation 9 is obtained:

\[ \ln K_e = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \]  

From the plots between \( \ln K_e \) versus \( 1/T \), the slope (\( \Delta H^o \)) and the intercept (\( \Delta S^o \)) can be calculated. These data are shown in figure 9.

![Figure 9](image)

The results in table 4 confirmed that the temperature has a negative effect on the biosorption of Cd(II) ions onto wheat bran, which means that the temperature favors the desorption process. The negative value of \( \Delta G^o \) indicates the spontaneous and feasibility of Cd(II) ions adsorption (Asif et al., 2019). The free energy values increased with increased temperature for biosorption of Cd(II) ion, which indicate that the spontaneous of the biosorption process reduces with increase temperature (Sarada et al., 2017). It was found that Cd(II) biosorption on wheat bran has negative values of the enthalpy change, which means that biosorption is an exothermic process (Azza et al., 2013). In this study the enthalpy change was -7.08 kJ/mol, and entropy change -21.15 J/molK, respectively. This suggests that the biosorption of Cd(II) ions is characterized with physical biosorption and randomness of the biosorption process decrease by wheat bran (Thaçi et al., 2021).

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>( \ln K_e )</th>
<th>( \Delta G ) (J/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (J/molK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.318</td>
<td>-785.4</td>
<td>-7.08</td>
<td>-21.15</td>
</tr>
<tr>
<td>308</td>
<td>0.218</td>
<td>-558.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>0.133</td>
<td>-351.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>0.056</td>
<td>-267.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

The native wheat bran has shown as effective and good material for biosorption of Cd(II) ions from aqueous solution. The results reveal that the sorption of cadmium ions onto the wheat bran was very rapid at the beginning and after 30 minute
the equilibrium was reached. The maximum biosorption capacity of cadmium ions by wheat bran was 6.25 mg/g, at the optimal conditions. The ATR-IR spectra represented functional groups (carboxylic, carbonyl, alcoholic, amine etc.) in the structure of wheat bran were responsible for cadmium ion interaction. The biosorption equilibrium data fit well with Langmuir and Freundlich isotherms. The exothermic, favorable and spontaneous nature of process was determined from thermodynamic parameters. The results confirmed that wheat bran could be used as low cost biosorbent for uptake of cadmium ions from aqueous solution.

Conflict of interest
The authors declare that they have no conflict of interest.

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