Biosorbent from Industrial Hemp Hurds for Copper Ions Removal

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Abstract: Screening a new biosorbent with low-cost and high efficiency from a biological waste material is a key to the adsorption of heavy metal ions from wastewater. The biosorbent from industrial hemp hurds was prepared from waste materials. In this study, the potential of this biosorbent has been investigated in removing of Cu(II) ions from the aqueous solution under optimized conditions. Waste material biosorbent was activated by hydrochloric acid in room temperature. The synthesized biosorbent was characterized by SEM, EDX, specific surface area and pore size distribution. The impact of pH, contact time and initial concentration on the pollutant removal efficiency was observed. The sorption kinetics were evaluated with pseudo-first and pseudo-second order kinetic models. Adsorption process has been modeled by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms using linear regression. The results of this study indicated that the application of hemp hurds of *Cannabis sativa* waste material as a biosorbent is highly effective for the removal copper ions from wastewater.

Keywords: Cu(II), biosorbent, wastewater.

1. Introduction

The wastewater contaminated with heavy metal ions has become a serious environmental issue in recent years. Many industrial activities such as mining, electroplating and smelting resulted in the release of heavy metal ions into water. Therefore, there is an imperative need for the removal of Cu(II) from wastewater. Some conventional methods such as chemical precipitation, ion exchange and membrane separation have been widely used for removing metal ions from wastewater. These practices have several disadvantages such as high cost, high energy input and secondary pollution. Hence, it is essential to develop cost-effective and eco-friendly approach to remove Cu(II) from wastewater. Compared with the conventional methods, biosorption, as an emerging and attractive method, has gained an increasing attention on the removal of heavy metal ions from wastewater owing to its high efficiency, low cost and non-secondary pollution.

Adsorption is considered to be one of the most applied processes of recent years for the cleaning of waters and wastewaters. Price, availability, adsorption capacity and strong affinity to pollutants are limiting factors for sorbent application in waste water treatment hence new used materials as sorbents are evaluated constantly [1]. The use of the common materials (activated carbon, chitosan, zeolite, and clay) is very popular due to their high adsorption capacities, but huge disadvantage of these materials is high price [2]. Intensive growth of world population imposes the need for comfortable, biodegradable, biocompatible and ecological biosorbents [3].

In recent years, there is a growing interest in utilization of low-cost and abundantly available waste biological materials like ground coffee, nut and walnut shells [4], papaya wood [5], peanut hull pellets [6], teak leaf powder [7], lalang (Imperata cylindrica) leaf powder [8], Coriandrum sativum [9], grape stalks wastes generated in the wine production process [10], hazelnut shells [11], peanut husks [12] and etc. A large number of biological waste materials has been successfully converted into activated biosorbent by chemical activation on a laboratory scale [13]-[15].

Hemp hurds (Cannabis sativa), an annual herbaceous plant, has been planned agriculturally for many centuries to get its bast fiber and hempseed oil [16]. Currently in the world cultivates hemp over an area of around 20 thousand hectares in 1997 [17], and the planting area will increase to about 670 thousand hectares in 2020. In the processing of hemp fibers, the hemp seed, hemp bast, hemp hurds and hemp stem become interesting byproducts. The hemp waste often forms about 70 % of the hemp plant [18], so it would be a huge waste and give enormous pressure on the environment.

In this study, an alternative use of hemp-based materials in the form of hurds was investigated for the removal of Cu(II) from aqueous systems. The aim of the present study is to use the activated hemp hurds as appropriate biosorbents for Cu(II) removal from aqueous systems in order to find alternative applications for these low-cost biomaterials and thus increase their added value. The evaluation as biosorbents was done after running adsorption experiments for the effect of pH, contact time and initial ion concentration.

2. Materials and Methods

2.1. Preparation of Stock Solution

All the chemicals and reagents used in the present study were of analytical grade. The tests were carried out with aqueous solutions of Cu(II). The stock solution of Cu(II) (1000 mg.l⁻¹) was prepared by dissolving the weighed amount of Cu(NO₃)₂ in double distilled water. Concentrated HNO₃ (2–3 drops) was added in the stock solution to avoid precipitation. The working solutions of different concentration were prepared by progressive dilution of the stock solution using deionized water.

2.2. Preparation of the Biosorbent

Raw industrial hemp hurds (IHH*) sample was collected from locally available cannabis growing facility. The IHH* sample was obtained from the harvest located in the Czech Republic in October 2011. The raw IHH* sample used in this study was certified as hemp Bialobrzeskie. This variety was raised for cultivation in our latitude and for these climatic conditions.

The IHH* sample has not been necessary to mechanically modify and grain-modified, because it was in the form of hurds, which is the input biosorbent (Fig. 1).



Fig. 1 Raw industrial hemp hurds sample

For the activation of the functional groups for bonding with metal ions, it was used chemical treatment of the IHH* sample. As activation reagent was used hydrochloric acid at the concentration of 0.1mol.l⁻¹. The input weight of IHH* was 8 g.l⁻¹ of activating reagent. The concentration of the activating HCl solution was 10 g.l⁻¹. The activation was carried out under constant stirring on the stirring machine IKA EUROSTAR at 300-400 RPM for 90 min. After stirring time the IHH* sample was filtered by used vacuum filtration. The activation was carried out twice in the same manner. The residue on the filter cake on the filter paper was dried at 105 °C for 24 hours. This activated biosorbent was marked as IHH and used for the sorption experiment.

2.3. Characterization of the Biosorbent

Scanning electron microscopy (SEM) LYRA 3 (TESCAN, Brno, Czech Republic) was utilized to investigate the structure of raw IHH* sample and activated IHH sample, and to perform a detailed analysis of particles morphology. SEM micrographs were taken at different magnifications. Secondary electron (SE) (TESCAN, Brno, Czech Republic) detector (TESCAN, Brno, Czech Republic) was used for the surface analysis.

Surface area and pore size distribution were measured using a QUADRASORB EVO/SI analyzer (Quantachrome, Prague, Czech Republic). The surface area was measured by the BET (Brunauer-Emmett-Teller) nitrogen adsorption technique at -195.8 °C and argon adsorption technique at -185.8 °C. The raw IHH* sample and activated IHH sample were outgassed in a vacuum for 72 h at 40 °C before analysis. The pore size distribution was measured by analyzing the desorption branches of the isotherm using the Barrett-Joyner-Halenda (BJH) method. The measured data were evaluated by QuadraWin software (Quantachrome, Prague, Czech Republic).

Determination of the metal ions concentration in the water solutions was performed by atomic absorption spectrometry with a flame atomization FA-AAS SOLAAR M6 (Analyte Jena AG). To adjust the pH of the solutions was made by pH meter ION 340i.

2.4. Methodology of the Experiments

The activated IHH sample was employed for the sorption experiments carried out with the 0.75 g of sorbent suspended in 75 ml solution with 10 mg.l⁻¹ Cu(II) ions concentration at the laboratory temperature. The suspensions were stirred for 5, 10, 30, 60, 120 and 180 minutes. The prepared suspension was shaken using a stirring machine at laboratory temperature. The pH of the metal ions solution was followed by pH value 3, 4, 5, 6. Then the biosorbents were separated by filtration through a 0.45 μ m membrane filter. The concentration of Cu(II) ions in filtrate was determined by atomic absorption spectroscopy with flame atomization after stabilization of solution by HNO₃, analytical grade, in all experiments.

Adsorption studies were carried out using the batch technique to obtain the equilibrium data. 0.75 g of biosorbent was suspended in 75 ml of metal ions solution with defined initial ions concentration. For modeling of the sorption isotherms were prepared model solutions of Cu(II) ions with defined initial concentration 5, 10, 25, 35, 50, 100 mg.l⁻¹ and pH of model solution was adjusted on value 5. All experiments were conducted at the room temperature. Samples were stirred for 120 min according to the preliminary study, the ions adsorption has reached equilibrium at that time. The biosorbent was then separated using 0.45 μ m pore size membrane filter and, after conservation, ions concentrations were determined.

2.5. Data Processing

Evaluation of the sorption process is governed by several important processes which should be considered and can be described by adsorption efficiency, distribution coefficients, and kinetic models.

The amount of adsorbed metal per gram of adsorbent (q expressed in mg.g⁻¹) was calculated from the

experimental data of Cu(II) ions concentration at equilibrium as follows Equation (1):

$$q = \frac{c_0 - c_e}{m_{ads}} \tag{1}$$

where c_0 and c_e are the metal concentrations in liquid phase before and after adsorption experiments (expressed in mg.l⁻¹), respectively, and m_{ads} is mass of adsorbent in the solution (expressed in g).

The adsorption efficiency (E) is the quantity that expresses the amount of adsorbate removed from the aqueous solution calculated from the initial concentration. The adsorption efficiency is expressed as a percentage in (2):

$$E = \frac{c_0 - c_e}{c_0} \times 100$$
 (2)

where c_0 is the initial concentration of adsorbate (mg.l⁻¹) and c_e is the equilibrium of adsorbate concentration (mg.l⁻¹).

Kinetic studies are important for detecting adsorption mechanisms and controlling rate possibilities, such as mass transfer or chemical reaction processes. Adsorption kinetics are most commonly described by kinetic models of the pseudo-first and pseudo-second order.

The kinetic model of the pseudo-first order, also called the Lagergen model, was firstly used to describe the adsorption at the solid-liquid interface. The basis of this model is the capacity of the solid. Derivation from the Lagergren equation requires that the concentration of the two ions is time-independent and, therefore, the constant should correspond to the linear combination of both concentration values. The Lagergren equation represents the adsorption in the case of diffusion across the liquid phase boundary to a solid sorbent. The constant of the equation varies depending on the particle size and surface film thickness, where the constant is dependent on the concentration of ions in the solution and the process temperature in the case of chemisorption. The particle size does not affect adsorption [19]. The pseudo-first order equation can be expressed by (3):

$$q_t = q_e (1 - e^{-k_1 t}) \tag{3}$$

where q_e is the amount of the adsorbed metal ions in equilibrium and q_t is the amount of the adsorbed metal at a specific time t (min) per unit mass of sorbent in mg.g⁻¹. k_1 is the Lagergren pseudo-first order rate constant (min⁻¹), and t corresponds to the adsorption time (min). The speed constant k1 determines the time factor necessary to achieve the system equilibrium [20].

The kinetic model of the pseudo-second order is based on the assumption of chemisorption as the main mechanism of the process, and is capable of sufficiently predicting the adsorption behavior throughout the process. It is based on the assumption that chemical adsorption may limit the rate of adsorption/desorption. This model is compared to the pseudo-first order model and is considered to be more suitable to represent kinetic data because of the assumption that the chemisorption can be a step limiting the rate of adsorption. Metal ions in the chemisorption are trapped on the surface of the adsorbent and form a chemical bond [21].

The pseudo-second order kinetic model is based on Langmuir's adsorption model on a solid surface, where it is assumed that the adsorption rate is proportional to the concentration of the dissolved substance in the solution and the number of free adsorption sites. Desorption is the release of one substance from another, either from the surface or through the surface. Desorption can occur when an equilibrium situation is altered [22]. The kinetic equation of the pseudo-second order is described by (4):

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$
(4)

where q_e is the amount of the adsorbate in equilibrium and q_t is the amount of the adsorbate at time t (min) per unit weight of the sorbent (mg.g⁻¹). k_2 is the pseudo-second order adsorption velocity constant (g.mg⁻¹.min⁻¹).

The experimental data were processed by two-parameter theoretical models. The most commonly used isotherm are the Langmuir [23], Freundlich [24], Temkin [25] and Dubinin-Radushkevich [26] models. The isotherms parameters can be calculated from adsorption data by converting the equations into linear form. The mathematical expression of used isotherms and theirs linear forms are summarized in Table 1.

Adsorption	Mathematical formula	Linear plot	
isotherms	Mathematical formula	<i>X</i> -axis	Y-axis
Langmuir	$q_e = \frac{q_{max}K_Lc_e}{q_{max}K_Lc_e}$	Ce	$c_{ m e}/q_{ m e}$
Freundlich	$q = K_F \cdot c^{1/n}$	ln c _e	In q _e
Temkin	$q_e = \frac{RT}{h} \ln(A_T c_e)$	[RT ln(1+/1/c _e)] ²	ln q _e
Dubinin-Radushkevich	$E = \left[\frac{1}{\sqrt{2B_{DR}}}\right] \rightarrow \varepsilon = RT \ln\left[1 + \frac{1}{c_e}\right]$	ln c _e	q_e

Table 1. Mathematical Expression of the Langmuir, Freundlich, Temkin and Dubinin-RadushkevichIsotherms and Theirs Linear Forms

The amount of the adsorbed metal ions per sorbent unit q_e (expressed in mg.g⁻¹) was calculated from the metal concentration in liquid phase before adsorption and the unadsorbed metal concentration in solution at equilibrium c_e (mg.l⁻¹). The coefficients of adsorption isotherm mean: q_{max} (mg.g⁻¹) is the maximum amount of the metal ions to form a complete monolayer on the surface, K_L (l.mg⁻¹) is a constant related to the affinity of the binding sites, K_F (l.mg⁻¹) and n are the Freundlich constants related to the adsorption capacity and adsorption intensity respectively, b (J.mol⁻¹) is the Temkin isotherm constant, A_T (l.mg⁻¹) is the Temkin isotherm equilibrium binding constant, R (J.K⁻¹.kmol⁻¹) is the ideal gas constant and T (K) is the temperature of adsorption, B_{DR} (mol².J⁻²) is a constant related to the mean free energy of adsorption per mol of the adsorbate.

Determination coefficient of linear regression analysis (R^2) -representing the proportion of the dependent variable expressed by the regression line – was used to determine the best corresponding adsorption isotherm.

3. Results and Discussion

3.1. Characterization of the Biosorbent

Scanning electron microscope is an extremely useful tool to observe the surface texture and morphology of the biosorbent.

The SEM images of the raw biosorbent are given in Fig. 2. The raw IHH sample shows a relatively uneven and irregular surface with pores. The biosorbent is formed from the high amounts of fibrous structure with pores, which may be more helpful for adsorption process. The SEM images of the activated biosorbent are given in Fig. 3. As could be seen in Fig. 2 that a biosorbent before HCl activation has a dense and rigid morphology. The SEM images of biosorbent after HCl activation obviously indicate surface modifications during the activation process. The HCl-activated biosorbent appearance an irregular surface with cavities of several sizes, demonstrating more porous with a well-built porous structure. It is clear that biosorbent possesses different and a rough surface morphology, where is a good possibility for adsorption. The cavities on biosorbent surface proper canals for diffusion of metal ions into the biosorbent, make available access to

its micro and mesopores, wherein they can interact with the surface of functional groups.



Fig. 2. SEM micrographs of the raw IHH* sample at 500x magnification (left) and at 2000x magnification (right).



Fig. 3. SEM micrographs of the activated IHH sample at 833x magnification (left) and at 2000x magnification (right).

3.2. Surface Area Analysis

The specific surface area and pore volume of biosorbent were determined by the Brunauer-Emmett-Teller (BET) methods were presented in Table 2. The BET surface areas of biosorbent before and after activation were found to be 94.95 m².g⁻¹ and 189.99 m².g⁻¹, respectively. Activation of biosorbent using HCl cause increasing in total pore volume and specific surface area. The activation method by HCl providing the growth of various pores with different sizes and high surface area. The pore size data obtained by BJH method was typical of mesoporous materials. The IHH biosorbent has a good surface area compared with other sorbent, for instance, brown algae (1.79 m².g⁻¹) [27], lignocellulosic waste biomass (1.84 m².g⁻¹) [28], pine cone shell (0.65 m².g⁻¹) [29], used for Cu(II) removal.

Biosorbents	Specific Surface Area (m².g [.] 1)	Pore Volume (cc.g ^{.1})	Pore Size (nm)
IHH* without activation	94.95	8.08 × 10 ⁻²	1.90
IHH with activation	189.99	1.50×10^{-1}	1.90

Table 2. BET Surface Area, Pore Volume and Pore size of Biosorbent

3.3. Effect of pH

One of the most important factors of the adsorption process is the pH of the solution. It is a fact that many adsorbents change their behavior with the change of pH conditions. For this reason, preliminary experiments were carried out to determine the optimum adsorption pH value for the removal of Cu(II) after adsorption onto the prepared biosorbent. It is useful to firstly observe the pH-behavior before next experiments, for definition of ideal conditions for adsorption process. The dependence of pH value on removal efficiency is shown in Fig. 4. Based on the pH-effect results, it is obvious that the removal efficiency reached the high for pH in the range 5 - 6. The Cu(II) removal at pH 3 was low (76%), but by increasing the solution pH to 5 and 6 an increase of the metal ions uptake was noticed on 97%. For the next experiment was selected the pH value around 5.



Fig. 4. Effect of pH on removal efficiency of Cu(II) on activated IHH.

3.4. Effect of Contact Time

The uptake of Cu(II) ions on activated IHH was studied as a function of contact time to determine the equilibrium time (Fig. 5). Initial concentration of metals was selected on 10 mg.l⁻¹. It was found that within the first 5 min of contact time about 85% of Cu(II) was adsorbed, and thereafter the adsorption rate was speeded up. The equilibrium adsorption time was recorded to be 60 min and after that, more or less constant removal of metal ions was observed. Therefore, equilibrium time was set at 60 min for further experiments.



Fig. 5. Effect of contact time on removal efficiency of Cu(II) on activated IHH.

3.5. Effect of Initial Concentration

The uptake of metal ions was evaluated as a function of initial concentration ranging from 5 to 100 mg.l⁻¹, at pH 5 and at 60 min. As illustrated in Fig. 6, when initial concentration of metal ions increased from 5 to 10 mg.l⁻¹, the removal efficiency encountered a rise and in the range of initial concentration from 10 to 25 mg.l⁻¹ reached the top, where efficiency of removal reached over 91%. The adsorption efficiency decreased with increasing initial metal concentration. This can be explained by the fact that in lower initial concentrations of metal ions could simply attach to the abundant adsorption sites on the surface of biosorbent. However, at higher initial metal concentrations, the number of adsorption sites remains the same, so the access of metal ions to adsorption sites is limited and as a result the adsorption efficiency decreases.



Fig. 6. Effect of initial concentration on removal efficiency of Cu(II) on activated IHH.

3.6. Isotherms Study

For biosorbent studied the equilibrium Cu(II) uptake was affected by the initial metal concentration using constant dosage of adsorbent. At low initial concentrations, the adsorption of Cu(II) was very intense and reached equilibrium rapidly (Fig. 6). This phenomenon indicated the possibility of the formation of monolayer coverage of ions at the outer interface of materials. An equilibrium condition is achieved, when solute concentration remains unchanged as a result of zero net amount of solute adsorbed and desorbed. At the constant temperature, these associations between the equilibrium concentration of the adsorbate in the solid and liquid phase are defined by the equilibrium adsorption isotherms [30]. In the present work, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich biosorption isotherm equations were used to find the correlation between the amount of biosorbent and the liquid phase concentrations of the adsorbate.

Table 3 shows the equilibrium parameters of adsorption on Cu(II). As it can be also seen from Table 3, the best fitting was achieved with the Langmuir model (Fig. 7) rather than the Freundlich, Temkin and Dubinin-Radushkevich models. The calculated maximum adsorption capacity of biomaterial was 5.5 mg.g⁻¹. Langmuir model assumes that adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface. At room temperature the concentration of metal in solution will be in equilibrium with metal ions biosorbed onto the surface of biosorbent. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter [31]. R_L value indicates the adsorption nature to be either unfavorable if $R_L>1$, linear if $R_L = 1$, favorable if $0 < R_L$. From the data calculated in the Table 3, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favorable. The Langmuir constant (or affinity constant $-K_L$) expresses how strongly are the adsorbed ions attracted to a surface.

Isotherm models	Isotherm constants	Cu(II) ions
	q_{max} (mg.g ⁻¹)	5.485
Langmuir	K_{L} (l.mg ⁻¹)	0.221
	RL	0.238 - 0.041
	R ²	0.9763
Freundlich	n	2.117
	K _F (l.g ⁻¹)	1.020
	R ²	0.8648
Temkin	b	2667
	AT	4.407
	R ²	0.9754
Dubinin-Radushkevich	B _{DR}	3,67E-07
	R ²	0.7135

Table 3. Equilibrium Parameters for the Adsorption of Activated IHH of Cu(II)



Fig. 7. Langmuir isotherm of activated IHH.

3.7. Adsorption Kinetics

Adsorption kinetics data are presented in Table 4, which presents the kinetic parameters resulting from the fitting. The fitting was performed using pseudo-first and pseudo-second order model. As can be seen from the results, the correlation coefficients were lower for pseudo-first order than pseudo-second order model. The experimental data of pseudo-first order deviated considerably from the theoretical data. The obtained correlation coefficients (R²) were not as high as those for the pseudo-second equation. Furthermore, the experimental data fitted to the pseudo-second order equation (Fig. 8), calculating the respective parameters (Table 4). The slope $(1/q_e)$ and intercept $(1/k_2q_e)$ of plot (t/q_t) versus t were used to calculate the parameters of k_2 and $q_{e,cal}$. The straight lines in the plots of Fig. 8-right showed an excellent agreement of the experimental data with this model. The correlation coefficients were equal to 0.999. Also, the calculated $q_{e,cal}$ values are completely the same with those exported from the experimental data. These findings indicate that the adsorption system studied belongs to the second-order kinetic model.



Fig. 8. Kinetic curves after fitting to pseudo-first order (left) and pseudo-second order equation (right).

Kinetic models	Kinetic constants	Cu(II) ions
	k1 (min-1)	0.0223
Pseudo-first order	$q_{e, cal} (mg.g^{-1})$	0.1612
	R ²	0.7499
	k2 (g.mg ⁻¹ .min ⁻¹)	1.1889
Pseudo-second order	$q_{e, cal} (mg.g^{-1})$	0.9264
	R ²	0.9998

Table 4. Kinetic Constants for the Adsorption of Cu(II) ($c_0 = 10 \text{ mg.}I^{-1}$)

4. Conclusion

This study investigates an alternative use of hemp-based materials (hurds form) as biosorbents for the removal of Cu(II) from aqueous solutions. The hemp materials were used after activation with hydrochloric acid in order to remove any impurities and add extra carboxyl groups (which improve adsorption). The optimum pH found after adsorption experiments was 5. The equilibrium adsorption time was recorded to be 60 min. The adsorption efficiency decreased with increasing initial metal ions concentration. Adsorption kinetics data showed, that the correlation coefficients were lower for pseudo-first order than pseudo-second order model. The process of adsorption was relatively fast. Evaluation of the equilibrium adsorption isotherms showed that the best fitted reached with Langmuir isotherm model, which gives the assumption that the adsorption occurs at specific homogeneous adsorption sites within the adsorbent and intermolecular forces decrease rapidly with the distance from the adsorption surface.

The results of this study indicated that activated industrial hemp hurds can be used as low cost, eco-friendly adsorbent for Cu(II) ions removal with high efficiency.

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