Equilibrium isotherm studies of copper and zinc removal from model solutions using natural and alkaline treated hornbeam sawdust

Zdenka Kováčová¹, Štefan Demčák², Magdaléna Bálintová¹

¹Technical University of Košice, Faculty of Civil Engineering, Institute of Environmental Engineering, Slovakia
e-mail: zdenka.kovacova.2@tuke.sk, magdalena.balintova@tuke.sk

²University of Prešov, Faculty of Management, Department of Environmental Management, Slovakia
e-mail: stefan.demcak@unipo.sk

Abstract

In the present study, sawdust an industrial by-product available in large quantities as sorbent material was studied. The removal adsorption capacity of Cu(II) and Zn(II) from aquatic solutions was obtained. The batch experiments were carried out to determine the effect of initial concentration of copper/zinc solution at pH=4.0 onto natural hornbeam and hornbeam modified with NaOH and KOH. The Fourier transform infrared spectroscopy (FTIR) determined the changes in functional groups after the modification of sawdust. The equilibrium data were fitted with four isotherm models - Langmuir, Freundlich, Tempkin and Dubinin-Radushkevich. The Langmuir model was found to be most suitable and the maximum adsorption capacity obtained for modified hornbeam sawdust was 2 to 4-times higher as in natural one for both heavy metals.

Key words: copper, zinc, sorption, wooden sawdust, adsorption isotherm, FTIR spectroscopy

1 Introduction

In the last decades, the chemical and biological pollution of water sources has become a serious environmental problem affecting people's health. The pollution of water can be released naturally by geological and biological activity, but the human activity associated with urban development, energy use, pesticides and fertilizers, industrial waste, sewage water, mining and others has a significant impact on environmental contamination [1-3].

Wastewaters from industry production can be harmful and caused severe and long-time issues for surface and underground water sources due to significant low value of pH and increased concentration of heavy metals that transcends many times the maximum acceptable concentration defined by legal regulations (SR Government Regulation 269/2010 Coll. which stipulates criteria for achieving good water balance – limit values for zinc and copper discharged waste water are 2.0 and 0.5 mg/L, respectively) [4, 5].

The conventional methods using for heavy metals removal from wastewaters are reverse

osmosis, precipitation, ion exchange, chemical oxidation or reduction, ultrafiltration, extractions, electrodialysis. These techniques can be sensitive to operation conditions, produce of a large amount of sludge, and have high cost and energy consumption [6-8]. The adsorption onto low-cost sorbents can be a promising technique for removal of pollutants from aquatic solutions because it's effective, cheap and environmental friendly. The natural materials, industrial and agricultural waste products have potential to be used as sorbents due to their low price, availability in large quantities and easy disposed without long regeneration [9]. Lots of low cost materials such as cocoa shells [10], cashew nut shells [11], cactus leaves and pine needles [12], green tea waste [13], olive stone [14], rice husk [15], zeolite [16], juniper bark [17], sawdust [18] are investigated as a sorbents for the removal of heavy metals. The wooden sawdust is one of the most attractive agricultural by-products available in large quantities in lumber mills as solid waste. It consists mainly of lignin, cellulose and hemicelluloses, which easily traps impurities present in wastewater [19-21].

The aim of this paper has been to determine the sorption capacity of hornbeam sawdust in its natural and chemically activated state using potassium and sodium hydroxide to adsorb Cu(II) and Zn(II) from aquatic solutions. Both kinds of sawdust were characterized by FTIR spectroscopy to determine functional groups involved in the process of adsorption. The experimental data are fitted to the Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich isotherm with the purpose to find best model describing process.

2 Materials and methods

2.1 Sawdust preparation

The raw hornbeam sawdust (particle size less than 2.0 mm) was obtained from locally available wood and used in the experiments.

Chemical modifications of sorbent were realized using 200 mL of 1.0 M solution of hydroxide sodium/potassium with 20 g of hornbeam sawdust for 24 h. Subsequently the sawdust was filtered, washed with demineralised water and dried.

2.2 Metal solution preparation

The stock solution of copper and zinc were prepared by dissolving predefined amounts of copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), respectively in distilled water to achieve concentration of 10,000 mg/L in each flask. The initial concentrations (10, 30, 50, 70, 110, 130 and 150 mg/L) of Cu(II) and Zn(II) were obtained by diluting the stock solution. The initial concentration was chosen based on previous research of Bulut and Tez [22] and kinetic study realized in previous research [23]. The pH was adjusted using 0.1 M sulfuric acid to the value 4.0.

2.3 Experimental procedures

Sorption assays were carried out at constant temperature by adding 0.5 g of hornbeam wood sawdust with or without modification to the breakers containing 50 mL of copper/zinc

synthetic solution. The suspensions in all sorption experiments were left for 24 h and then filtered through filtrate paper. Initial and final concentrations of Cu(II) and Zn(II) were determined by Colorimeter DR 890 (HACH LANGE, Germany). The final pH value was measured by FiveGo pH meter FG2 (Mettler Toledo, Switzerland).

The amount of heavy metals removal by the hornbeam sawdust and the percentage removal of were calculated by the following Equations (1) and (2), respectively.

$$q = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

$$\% \text{ Efficiency} = \frac{(C_0 - C_e) \cdot 100}{C_0} \quad (2)$$

where, q is the sorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentration (mg/L), V is the volume of solution in mL and m is the total amount of sawdust (g).

2.4 FTIR spectroscopy

Fourier transform infrared spectroscopy is using for:

- studying wood decay chemistry,
- characterizing the chemistry of wood,
- determination of lignin content in pulp and wood and
- analysis of chemical and structural changes in wood components due to NaOH and KOH treatments [24].

The FTIR spectroscopy of the natural and modified wood sawdust was recorded in Bruker Alpha Platinum-ATR spectrometer (BRUKER OPTICS, Germany) with the wavenumber ranging of 4000 to 400 cm^{-1} to observe functional groups involved in decontamination process. FTIR analysis was performed to investigate the reaction the change of the functional groups of sawdust due to base modification.

2.5 Adsorption models

Adsorption isotherms express the relationship between the concentration of a contaminant in a liquid and the amount of that contaminant bound to a unit weight of sorbent at a constant temperature. They are important to describe the mechanism of elimination process and to obtain the adsorption capacity of sorbent for contaminates removal. In general, all sorption models are characterized by specific constants that represent the surface properties and the affinity of the tested sorbents materials towards pollutant removal.

Four isotherm models Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich (D-R) are described in the following sections, where the differences between them and the significance of the characteristic parameters of each sorption model are indicated.

2.5.1 Langmuir isotherm

The Langmuir isotherm [25] is used in case of homogenous monomolecular layer adsorption. This model assumes the same affinity at all adsorption sites and that sorption at one site does not affect adsorption at an adjacent site. The maximum adsorption capacity is obtained from complete coverage of the adsorbent surface in monolayer and is given by the Eq. (3):

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

where q_e is amount of metal ions adsorbed per specific amount of adsorbent (mg/g), C_e is equilibrium concentration (mg/L), q_m is quantity of heavy metal ions necessary to form a single monolayer on unit mass of sorbent (mg/g) and K_L is Langmuir equilibrium constant which is related to the apparent energy of sorption process (dm³/mg).

The separation factor R_L indicates the isotherm shape and is given by Eq. (4):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (4)$$

where C_0 is initial concentration of contaminant in solution. The values of separation factor are in Table. 1.

Table 1 Values of sorption factor

Separation factor	Sorption process
$R_L = 0$	irreversible
$0 < R_L < 1$	favourable
$R_L = 1$	linear
$R_L > 1$	unfavorable

2.5.2 Freundlich isotherm

Freundlich isotherm [26] considered empirical isotherm assumes that the ratio of the amount of solute bound onto a given quantity of sorbent at different solute concentrations is not constant. In many processes, the heat of adsorption decreases with increasing the extent of adsorption. For sorption from solution, the isotherm is expressed by Eq. (5).

$$q_s = K_F \cdot C_s^{1/n} \quad (5)$$

where K_F is Freundlich equilibrium constant which describe the relative sorption capacity related to the bonding energy ((mg/g)·(L/mg)^{1/n}) and n is Freundlich coefficient the or heterogeneity factor which indicates the deviation from linearity of process.

2.5.3 Tempkin isotherm

Tempkin isotherm [27] equation assumes that the heat of sorption of all the molecules in the layer decreases linearly with the coverage of molecules and the process of adsorbate is evenly distributed. Unlike the Freundlich isotherm, the decrease in heat of adsorption is more linear than logarithmic and is given by Eq. (6):

$$q_s = \frac{R \cdot T}{b_T} \cdot \ln(A_T \cdot C_s) \quad (6)$$

where T is the absolute temperature (K), R is the universal gas constant (8.314 J/ mol·K), b_T is the constant which is related to the heat of sorption (J/mol), K_T is the equilibrium constant which describes the maximum binding energy (dm³/mg).

2.5.4 Dubinin–Radushkevich (D-R) isotherm

Dubinin and Radushkevich [28] (D-R) isotherm is applied to estimate the free energy of sorption (E), if $0 < E < 16$ kJ/mol is the physical adsorption and if $E > 16$ kJ/mol chemisorption prevails. The form of D–R equation is given by Eq. (7):

$$q_e = q_m \cdot \exp(-K_{D-R} \cdot \varepsilon^2) \quad (7)$$

where K_{D-R} (mol²/kJ²) is a constant which describe the adsorption energy and ε can be calculated from Eq. (8):

$$\varepsilon = R \cdot T \cdot \ln\left(1 + \frac{1}{C_e}\right) \quad (8)$$

3 Results and discussion

3.1 Infrared spectra

The heavy metal removal from contaminated aquatic solutions by natural sorbents as sawdust is closely linked to the surface structure where functional groups such as –OH, –COOH, –NH, –NH₂, and –NH₃ are presented [18].

The FTIR spectrum of natural and modified sawdust with NaOH and KOH are shown in Figure 1. The alkaline treatment with NaOH significantly intensified the wide peak of the hydroxyl functional group results in stretching at wavenumber 3331 cm⁻¹.

The band at 2892 cm⁻¹ corresponded to the C–H stretch. Presence of C=O from the acetyl groups at 1731 cm⁻¹ band was attributed to the characteristic of the hemicelluloses. Some new strong peak at 1593 cm⁻¹ was attributed to the C–C stretch and that at 1320 cm⁻¹ to the C–O stretch. The band at 1690 cm⁻¹ represents aldehydes and ketones.

Aromatic skeletal vibrations in the lignin components were assigned to 1503, 1454, 1321 cm⁻¹. The absorbance near 1422, 1369, 1321, 1156 and 1031 and 897 cm⁻¹ was attributed to the cellulose. Wavenumbers at 830 cm⁻¹ were determined as functional groups of aromatics, carboxylic acids and alkyl halides [29-31].

Figure 1 FTIR spectrum of raw and modified sawdust

3.2 Sorption isotherm study

Sorption isotherms are important to describe the mechanism of elimination process and to obtain the adsorption capacity of sorbent for contaminates removal. In general, all sorption models are characterized by specific constants that represent the surface properties and the affinity of the tested sorbents materials towards pollutant removal. The isotherm data using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich equation for copper and zinc removal are shown in Figure 2. Table 2 shows the values of corresponding isotherm parameters together with their correlation coefficients (R^2).

Figure 2 Isotherm data of natural and modified hornbeam sawdust

Correlation coefficient (R^2) (Figure 2 and Tables 2 & 3) are derived by fitting experimental data into the Langmuir, Freundlich, Temkin and the Dubinin-Radushkevich isotherm model. The highest value of R^2 for copper was reached by hornbeam (0.956), hornbeam NaOH (0.954) and hornbeam KOH (0.964) fitting to Langmuir model. In case of zinc adsorption the highest values of R^2 was achieved by hornbeam (0.889), hornbeam NaOH (0.978) and hornbeam KOH (0.082) following Langmuir isotherm.

Table 2 Isotherm constants for isotherm models sawdust for adsorption of Cu(II) on sawdust

Model	Parameter	Sawdust		
		Hornbeam	Hornbeam NaOH	Hornbeam KOH
Langmuir	q_m (mg/g)	4.318	11.064	18.181
	K_L (dm ³ /mg)	0.082	0.062	0.027
	R^2	0.956	0.954	0.964
Freundlich	K_F ((mg/g)(L/mg) ^{1/n})	0.944	2.282	0.905
	n	3.167	1.568	1.583
	R^2	0.903	0.867	0.931
Tempkin	K_T (dm ³ /mg)	1.101	0.682	0.400
	b_T (J/mol)	1.934	5.378	7.383
	R^2	0.950	0.875	0.920
Dubinin–Radushkevich	q_m (mg/g)	4.170	12.537	10.429
	K_{D-R} (mol ² /KJ ²)	0.114	0.073	28.643
	R^2	0.922	0.675	0.957

Table 3 Isotherm constants for isotherm models sawdust for adsorption of Zn(II) on sawdust

Model	Parameter	Sawdust		
		Hornbeam	Hornbeam NaOH	Hornbeam KOH
Langmuir	q_m (mg/g)	4.539	10.015	10.309
	K_L (dm ³ /mg)	0.086	0.120	0.110
	R^2	0.889	0.978	0.982
Freundlich	$K_F ((\text{mg/g})(\text{L/mg})^{1/n})$	1.075	2.015	2.125
	n	3.329	2.612	2.713
	R^2	0.869	0.945	0.936
Tempkin	K_T (dm ³ /mg)	1.998	1.471	1.873
	b_T (J/mol)	1.790	4.648	4.361
	R^2	0.884	0.971	0.957
Dubinin–Radushkevich	q_m (mg/g)	4.196	11.608	11.550
	K_{D-R} (mol ² /KJ ²)	0.077	0.044	0.042
	R^2	0.826	0.864	0.919

As shown, the values of maximum adsorption capacity for Cu(II) removal determined using Langmuir model was 4.318, 11.064 and 18.181 mg/g for hornbeam, hornbeam NaOH and hornbeam KOH, respectively. For zinc removal was maximum adsorption capacity, and for hornbeam (4.539 mg/g), hornbeam NaOH (10.015 mg/g) and hornbeam KOH (10.309 mg/g). The values correspond closely to the Langmuir model, which indicates the copper and zinc removal process might be realized as the monolayer adsorption and dominate ion exchange mechanism [22]. From the results (Tables 2&3) it can be assumed that the adsorption ability for copper is better as zinc one in case of alkaline treated sawdust, the similar results was publicized by Bozic et al [3].

4 Conclusion

Utilization of wooden sawdust for the removal of Cu(II) and Zn(II) from the synthetic solutions was investigated. Sawdust was found to be a promising adsorbent because consist of lignin, cellulose and hemicelluloses which are capable of catch pollutants from waters.

FTIR spectra demonstrated the existence of groups responsible for heavy metal ions binding, where NaOH modification intensified the wide peak of the strong broad -OH stretching at wavenumber 3331 cm⁻¹. The equilibrium adsorption data was fitted with four isotherm models - Langmuir, Freundlich and Tempkin, Dubinin–Radushkevich. The equilibrium data are best fitted with Langmuir isotherm model (due to highest value of R^2) which confirms the monolayer adsorption of heavy metals ions onto the natural and modified hornbeam sawdust. The treatment with NaOH and KOH increased the sorption capacity for both metals from 2.5 to 4.2 times for copper and about 2.2-times for zinc in comparison to untreated sawdust.

The maximum adsorption capacity for Cu(II) is obtained with the Langmuir isotherm model as 4.318 mg/g, 11.064 mg/g and 18.181 mg/g for hornbeam, hornbeam NaOH and hornbeam KOH, respectively. The adsorption capacity is better with modified sawdust as in natural one. In case of zinc removal, the maximum adsorption capacity was reached by Langmuir isotherm for hornbeam (4.539 mg/g), hornbeam NaOH (10.015 mg/g) and hornbeam KOH (10.309 mg/g). Hornbeam sawdust with modification of NaOH and KOH can be used as sorbent to

copper and zinc removal from aquatic environments.

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