COMPARATIVE ADSORPTION OF COPPER ON OAK, POPLAR AND WILLOW SAWDUST

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Abstract: *Three types of sawdust, oak wood (Querqus robur), white poplar (Populus alba) and willow (Salix alba L.), have been tested for copper removal from 0.01 m solutions. Pre-treatment processes are necessary for optimizing the adsorption substrate, using NaOH 3n, in a contact time of 60 min for oak sawdust, respectively 30 min for white poplar and willow sawdust, t at 22 ^{o}C. The adsorption process depends on duration, quantity of sawdust, initial concentration of copper ions and the number of operation cycles. Efficiency removal of 89% on oak sawdust, 67% on poplar sawdust and 60% on willow sawdust from diluted water solutions were registered. The high efficiencies, even at very low concentrations indicate particular suitability of sawdust for the advanced wastewater treatment.*

Key words: *sawdust, biosorption, wastewater treatment, heavy metals removal.*

1. Introduction

The anthropogenic, especially the industrial activities produce inorganic and organics pollutants. Among them, heavy metals are very dangerous both for people and environment. Many studies present researches developed for removing the heavy metals from wastewaters using different types of adsorbents. A novel frequent tendency is to use biosorbents, low cost adsorbent: sawdust [1], [2], [3], peanut husk [8], sawdust activated carbon [9], kaolin, bentonite, blast furnace slag and fly ash, algae, fungi [7], and others.

In biosorption, studies have tested various type of biomasses [5] and/or different species belonging to a single type of biomass [2], [4].

In this context, this work compares the performance of different biosorbents, based on three types of sawdust: oak, poplar and willow, [6] on the efficiency of copper removal from wastewaters. Studies were done investigating different process parameters such as contact time, adsorbent quantity, Cu(II) ions concentration.

2. Materials and Methods

2.1. Materials

- Sawdust is obtained from oak wood (Querqus robur), white poplar (Populus alba) and willow (Salix alba L.). Before use, the sawdust is dried, in open atmosphere, at the room temperature (22 ^{o}C), for two weeks.

The following substances were used to prepare the solutions:

- HCl conc. (37%, Comchim, Romania);
- NaOH 1n, 2n, 3n, 4n solutions were prepared by using NaOH g.r. (Lach-Ner, Czech Repablic) in distillated water;

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- Copper, standards, for AAS calibration, prepared by diluting the stock solutions 1000 mg/L ions from Merck with distillate water;
- $CuCl_2$ solutions (0.000312 - 0.01 m) were prepared by using $CuCl_2 \cdot 2\ H_2O$ from Merck, in distillate water.

2.2. Methods

Conductivity and TDS measurements were done on sawdust suspensions (1 g sawdust : 100 mL distillate water). The measurements were done up to 125 hours for oak and 96 hours for white poplar.

For analyzing the metallic ions in the raw material, 1 g of sawdust was burnt to ash, at 450 °C, for 12 hours. Afterwards, the ash was dissolved in 50 mL HCl 0.5n and characterized by AAS measurements.

For heavy metal extraction from sawdust:

- in distillated water: 1 g sawdust was treated with 100 mL of distillated water for 10, 30, 60, 120 and 180 minutes, at room temperature (22 °C) and at 80 °C. After filtering, the samples were analyzed by AAS;
- in NaOH: the ratio sawdust:NaOH was 1:100 (g/mL), at 22 °C and 80 °C and the supernatant was analysed by AAS.

The sawdust has been used as biosorbent for copper (II) ions removal.

Batch biosorption experiments were carried out in flasks by transferring 100 mL of metal solutions and 1 g sawdust. The flasks were shaken at 400 rpm for 60 min for oak sawdust, respectively 30 min for 15 min for poplar sawdust treated and 30 min for willow sawdust. The suspension was separated by filtration. The residual metal ion concentration was determined, from atomic absorption spectrometry.

For evaluating the biosorption equilibrium, the residual metal in the supernatant was determined by allowing metal-sawdust contact for different periods between 5 and 90 min.

Similar tests were done for evaluating the optimum ratio adsorbent mass**:** solution volume. The quantity of biomass was varied between 1 and 15 g to determine the sawdust mass required for optimum level of biosorption.

In the adsorption isotherms studies, metal concentrations used for biosorption ranged between 0.000312 m and 0.01 m and while the copper source was $CuCl_2 \cdot 2\ H_2O$.

2.3. Instruments

A Multiparameter Consort C933, Belgium, was used for conductivity and TDS analysis.

A Perkin-Elmer AAS 400 atomic absorption spectrophotometer operated with air-acetylene flame was used to evaluate the concentration of Cu, Zn, Pb ions in aqueous solutions. The wavelength used in analysis was: λ_{Cu} = 324.74 nm; λ_{Zn} = 213.86 nm; λ_{Pb} = 283.31 nm.

3. Results and Discussions

The heavy metals content in the ash for the white poplar wood sawdust comparative to the oak wood [6] and willow wood is present in Table 1.

Sawdust immersed in water releases soluble compounds, mostly electrolytes.

Heavy metal content on the sawdust ash Table 1

Characteristic	Oak	Poplar	Willow
Ash wt%	0.6709	0.5199	1.44
Cu [ppm]	1.0552	1.558	2.157
Zn [ppm]	10.7740	9.611	2.247
Pb [ppm]	0	0	0

Figures 1 and 2 illustrate the modification in conductivity and TDS in time, and the effect of the weigh to these characteristics.

The experiments show an important dissolution process during the first 90 hours followed, after long contact time by a decrease that shows that (re)adsorption of the electrolytes may occur. It is observed the maximal conductivity and TDS values are registered for 1 g sawdust of oak wood [6], and for white poplar wood, but in different time. Almost double electrolyte content is released by the willow sawdust. Still, at 2 g the parameters after 50 hours are less than those registered to 1 g, due to its particular morphology.

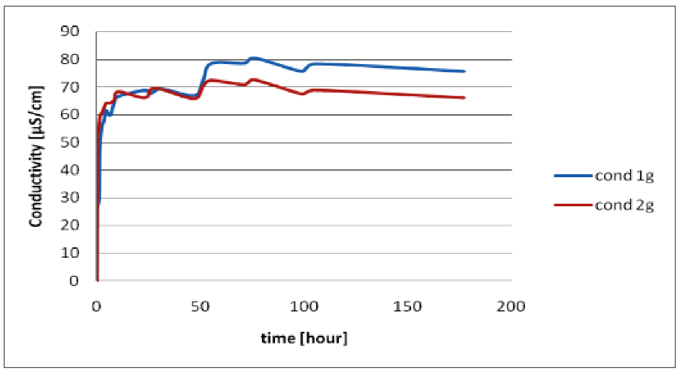

Fig. 1. *Variation of conductivity in time for willow sawdust*

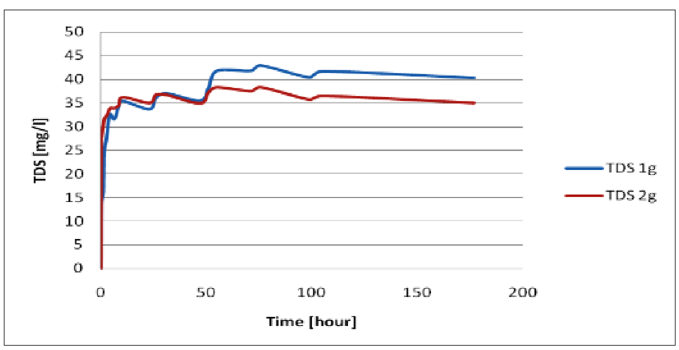

Fig. 2. *Variation of TDS in time for willow sawdust*

In Table 2 and 3 present the conductivity and TDS values, function of weight, for the three types of sawdust. It is observed, in the both situations, the maxims values are obtained after 65-90 hours for white poplar sawdust, after 25-30 hours for oak sawdust [6] and after 55-76 hours for willow sawdust. The curves respect the shape, independent of the weight.

After extraction in distillate water, there are no detected metallic ions at 22 ^{o}C, nor at 80 ^{o}C, independent of the contact time. Usually, sawdust gets in contact with light alkaline or acid environments; therefore the heavy metals must be extracted before a technological application. Since water is not suitable for heavy metal extraction from sawdust, different other solutions must be tested.

In Figure 3 the concentration of copper

extracted in NaOH 3n, at 22 °C and at 80 °C is presented. The maximum is obtained after 30 minutes of contact, in both cases, but the effect is stronger at 22 °C after 30 min.

Table 2

Values of conductivity, function of weight for oak, white poplar [6], *and willow sawdust*

Weight	Conductivity [µS/cm]								
	oak sawdust			white poplar sawdust			willow sawdust		
	Initial value	Max. value at 25-30 hours	Difference	Initial value	Max. value at 65-90 hours	Difference	Initial value	Max. value at 55-76 hours	Difference
1 g	21.9	43.9	22	25.5	44.3	18.8	25.3	80.6	55.3
2 g	37.6	64.2	26.6	51.9	84	32.1	51.6	72.5	20.9

Table 3

Values of TDS, function of weight for oak, white poplar [6], *and willow sawdust*

Weight	TDS [mg/L]								
	oak sawdust			white poplar sawdust			willow sawdust		
	Initial value	Max. value at 25-30 hours	Difference	Initial value	Max. value at 65-90 hours	Difference	Initial value	Max. value at 55-76 hours	Difference
1 g	11.7	23.3	14.6	13.7	23.4	9.7	13.5	42.9	29.4
2 g	19.7	33.9	14.2	28.9	44.4	15.5	28.6	38.3	9.7

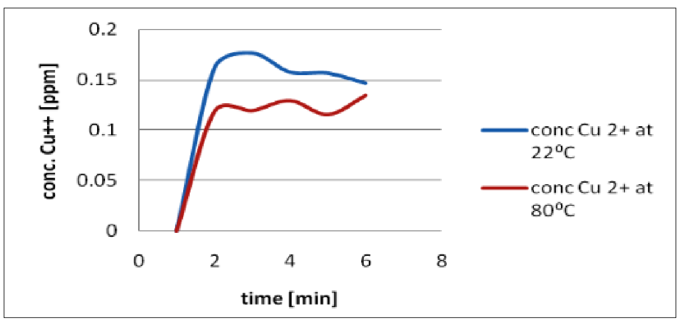

Fig. 3. *Extraction copper ions of sawdust in NaOH 3n*

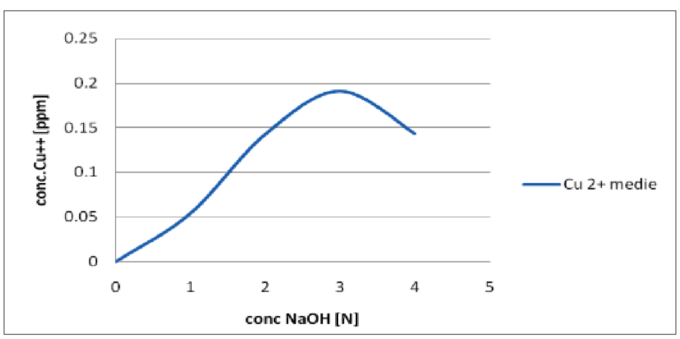

Fig. 4. *Extraction cooper ions in NaOH solution*

The results show that the optimized extraction conditions targeting copper are for oak sawdust: contact time: 30 minutes, solvent: NaOH 3n, $T = 22\ ^oC$; for white poplar and willow the contact time for preparing the substrate is double (60 minutes), while the other conditions remain unchanged (solvent NaOH 3n, $T = 22\ ^oC$).

3.1. Effect of Biosorbent - Biosorbate Contact Time

The time-course studies on the biosorption of copper ions were performed by contacting the 100 mL $CuCl_2$ solutions 0.01 m with 1 g willow sawdust pre-treated with NaOH 3n solution, Figure 5.

The metal removal from copper (II) solutions amounted to max. 23.66% at an equilibrium time of 30 min. After this adsorption time, the copper ions content in the solutions starts again to increase, thus there is a desorption of metal ions from the substrate. In our further experiments we use the optimum contact-time of 30 min for willow sawdust treated with NaOH 3n. We can observe that the best efficiency is registered for willow sawdust (23.66%) comparative with oak (17.62%) and white poplar sawdust (16.45%), [6].

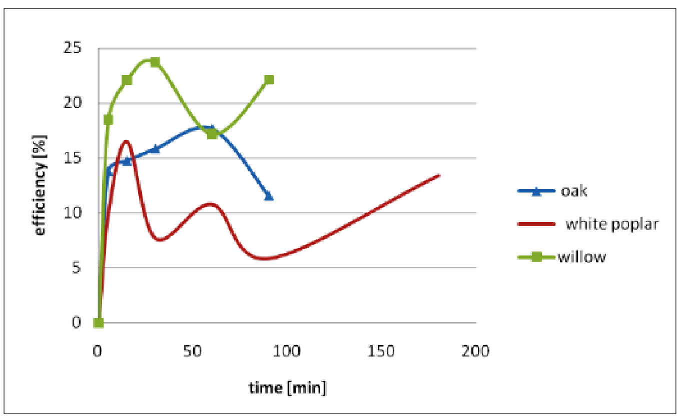

Fig. 5. *Effect of the contact time on Cu(II) ions sorption for the sawdust using an initial metal concentration of 0.01 m*

3.2. Relationship of the Quantity of Sawdust with Metal Sorption

The quantity of willow sawdust was varied between 1 and 10 g to determine the optimum amount of biomass needed for a maximum sorption efficiency in 100 mL of copper solutions.

Different biomass efficiencies were obtained by increasing the sawdust quantity while the copper ions concentration and the solution volume were kept constant. The change in copper adsorption efficiency with the sawdust amount is presented in Figure 6.

Based on the experimental data the optimum quantity of willow sawdust for the adsorption of cooper ions was set at 6 g. The metal removal from solutions of copper (II), during this rapid phase amounted up to 59.29%, at 6 g and 30 min of contact time. Further increase in biosorption was slow, up to 87.56% on 10 g of substrate. Efficiency acquirable in present cases are similar, comparing with the oak wood sawdust and better than the white poplar sawdust.

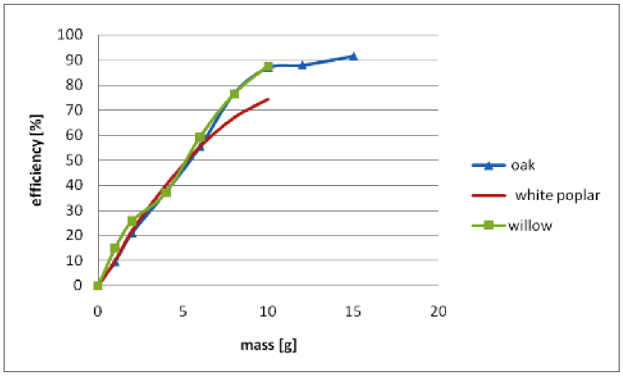

Fig. 6. *Effect of the biomass ration on Cu(II) ions sorption for the sawdust using an initial metal concentration of 0.01 m and contact time: 60 min for oak sawdust; 15 min for white poplar sawdust* [6], *30 min for willow sawdust*

3.3. Effect of Copper (II) Ion Concentration

For determining the sorption capacity of a biosorbent, it is necessary to generate the equilibrium sorption data at various metal solution c_i values. These data are further necessary for modelling adsorption isotherms.

For this purpose 0.01 m, 0.005 m, 0.0025 m, 0.00125 m, 0.000625 m and 0.000312 m of copper (II) solutions, were contacted with 6 g willow sawdust. After the contact period of 30 min the copper adsorption efficiency and the quantity of copper (II) biosorbed per biomass unit were plotted, Figures 7 and 8.

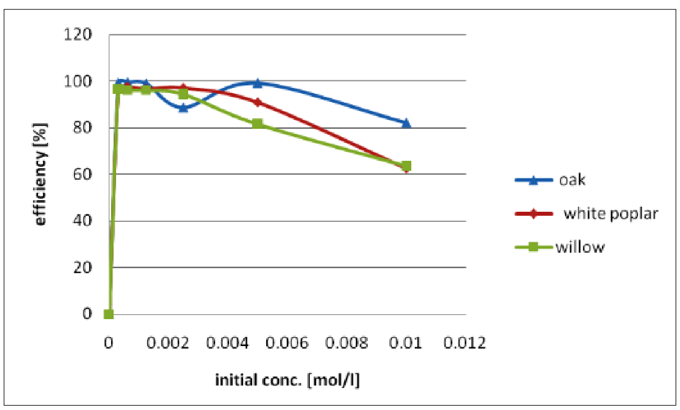

Fig. 7. *Effect of the concentration Cu(II) ions solution on sorption for the sawdust, using an solution volume 100 mL, optimum sawdust mass and optimum contact time*

The high efficiencies, even at very low concentrations indicates particular suitability of sawdust for the wastewater treatment and recommends this waste as a possible solution in advanced removal of heavy metals.

The data in Figure 8 indicate, for willow sawdust, that Langmuir isotherm can be applied, proving strong chemical interactions, similar to the white poplar wood [6].

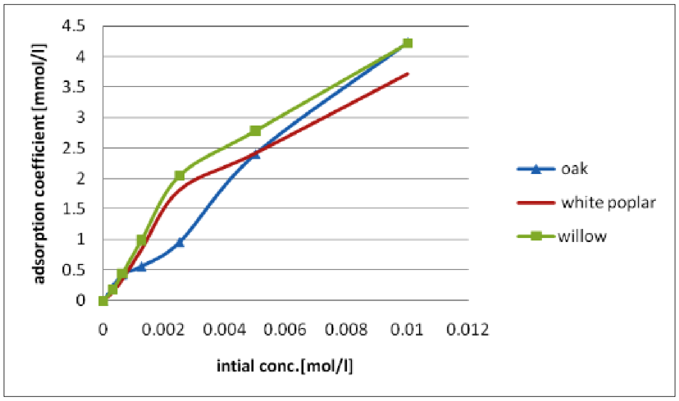

Fig. 8. *Adsorption coefficient vs. copper concentration*

3.4. Effect of Number of Repeated Extractions

In Figure 9 indicate the copper adsorption efficiency on the pre-treated willow sawdust. For this purpose 100 mL 0.01 m copper (II) solutions, were contacted with 6 g willow sawdust at 30 min contact time. The account sawdust: copper (II) solution is 1:16.6 (6 g:100 mL). After four extractions the limit of copper is lower than 1 ppm, (0.93 ppm) and after five extractions the limit of copper in the supernatant solution decreases under 0.5 ppm, (0.349 ppm). Efficiency after two extraction is 93.5% and after four and five extractions more 99% (99.61-99.85%) proving that advanced wastewater treatment, counterbalancing diffusion, can be reached after 4-5 adsorption steps.

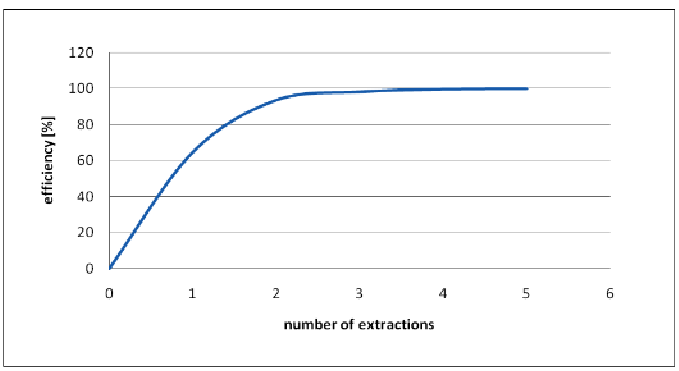

Fig. 9. *Efficiency of copper ions vs. number of extractions*

4. Conclusions

The results proved that in distilled water, the extraction equilibrium depends on the wood type and there is not a significant link between the wood density and the electrolyte extraction equilibrium. This equilibrium involves only highly soluble compounds, but not heavy metal electrolytes. For the willow sawdust, by increasing the sawdust mass and after 50 hours the soluble compounds are readsorbed.

The NaOH 3n solution represents an efficient extraction medium for copper, for all the investigated sawdust types.

The efficiency for willow sawdust is 63.63-96.45%, comparative with oak sawdust, 82.15-99.54% and white poplar sawdust, 62.57-97.53%.

The adsorption coefficient is better for willow sawdust comparative with oak and white poplar sawdust, proving the large amount of heavy metals that can be accommodated on this substrate.

The high efficiencies, even at very low concentrations indicate particular suitability of the willow sawdust for the wastewater treatment.

For obtaining a particularly high efficiency in the copper (II) extraction on willow sawdust it is necessary to use repeated extractions. The number of extractions are function the copper (II) concentration existing in wastewater and can amount 4 if the equilibrium concentration is set below 1 ppm.

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