STUDY ON WOOD WASTE MATERIALS' CAPACITY TO RETAIN HEAVY METAL IONS FROM AQUEOUS SOLUTIONS, UNDER DYNAMIC CONDITIONS

STUDIU ASUPRA CAPACITĂȚII DEŞEURILOR LEMNOASE DE A REȚINE IONII METALELOR GRELE DIN SOLUȚII APOASE, ÎN CONDIȚII DINAMICE

TROFIN Alina[1], UNGUREANU Elena[1],
TRINCĂ LUCIA Carmen[1], SANDU Tatiana[1]
e-mail: alina.trofin@gmail.com

Abstract. *Wood residues are commonly used in the furniture industry and in agriculture, as composts' ingredients or in different techniques as absorbents, having a large specific surface and a chemical composition appropriate for achieving adsorption processes. As a result of previous experiments it is found that the activation by boiling in acidic solutions of sawdust, in addition to increasing the adsorption capacity, it does not add any color to the treated solutions. In the present study we tested the retention capacity of two heavy metal ions (Cu and Co) in solutions of different concentrations, on sawdust processed by grinding, sieving and activation in hydrochloric acid. As main results, copper ions were retained between 63.2 – 91.16% and cobalt ions, between 79.9 – 91.16%, considering the initial concentrations of the solutions.*
Key words: sawdust, heavy metals, pollution, water

Rezumat. *Deşeurile lemnoase sunt de obicei folosite în industria mobilei şi în agricultură, în compoziția composturilor sau în diverse procedee tehnice ca absorbanți, având o suprafață specifică mare şi o compoziție chimică adecvată realizării proceselor de adsorbție. În urma unor experimente anterioare, s-a constat că prin activarea la fierbere în soluții acide a rumeguşului, pe lângă creşterea capacității de adsorbție, acesta nu imprimă nici o culoare soluțiilor tratate. În lucrarea de față s-a testat puterea de reținere a ionilor a două metale grele (Cu şi Co) din soluții de concentrații diferite, pe material prelucrat prin măcinare, sitare şi activare în acid clorhidric. Ca rezultat, ionii de cupru au fost reținuți între 63,2 – 91,16% şi ionii de cobalt, între 79,9 – 91,16%, în funcție de concentrațiile inițiale ale soluțiilor.*
Cuvinte cheie: rumeguş, metale grele, poluare, apă

INTRODUCTION

Capitalization of bark and sawdust as ingredients for composting does not completely solve the problem of the large quantities of woodwaste, even if it is considered as a source of income for different enterprises in forestry domain.

Another way in which these wood waste materials are consumed is their use as absorbent material for different substances.

[1]University of Agricultural Sciences and Veterinary Medicine Iasi, Romania

Ion exchange is probably one of the major adsorption mechanisms for binding divalent metal ions to the maple sawdust. In a study conducted by Bin Y. and co-workers, they used batch techniques for the adsorption of copper on sawdust. The equilibrium adsorption level was determined to be a function of the solution pH, contact time and sorbate concentration (Yu *et al*, 2000).

The same researchers studied the equilibrium adsorption capacity of sawdust for lead, which was measured and extrapolated using linear Freundlich and Langmuir isotherms and compared with that for copper. Metal ions bounded to the sawdust could be stripped by acidic solution so that the sawdust can be recycled. They also conducted non-equilibrium experiments in glass columns. The results indicated the potentially practical value of this method in industries (Yu *et al*, 2001).

Sawdust and wood chips were also used to remove heavy metals from industrial and mining waste waters. Especially bivalent metals were retained on spruce wood chips – Cd up to 94%, Cu - up to 81% and Zn - up to 88% (Argun *et al*, 2008).

Šćiban and Klašnja tested the adsorption of two heavy metals on sawdust and concluded that the main adsorption sites for metal ions in wood are on lignin. Batch and column studies yielded almost equal ratio for the adsorption efficiencies of copper (II) and cadmium (II) (Šćiban and Klašnja, 2003).

Bulut and Tez tested the adsorption of lead, cadmium and nickel from aqueous solution by walnut sawdust, at different temperatures. They concluded that the adsorbent's selectivity order is Pb(II)≈Cd(II)>Ni(II) (Bulut and Tez, 2007).

Another study performed on deciduous sawdust samples found that the kinetics of adsorption is relatively fast, reaching equilibrium in less than 20 min. The maximum adsorption capacity (7-8 mg/g of sawdust) was achieved at a pH between 3.5 and 5 for all the studied types of sawdust (Bozić *et al*, 2009).

In this paper, we used alder sawdust processed by grinding, sieving and activation in hydrochloric acid as adsorbent material for different concentrations of copper and cobalt solutions.

MATERIAL AND METHOD

The adsorbent material was alder sawdust, grinded and sieved in order to keep only the smaller particles. The variants used the sawdust activated by half hour boiling in hydrochloric acid 0.1 n, followed by filtration and pH correction to low acidic to neutral values. We chose the acid activated sawdust due to previous studies conducted on the adsorption of nitrates.

The heavy metal solutions had initial concentrations from 50 to 250 mg Cu^{2+}/L respectively from 50 to 250 mg Co^{2+}/L. For each variant, we used 0.5 g of adsorbent material per 50 ml of each solution, stirred continuously for 15 minutes, then filtered. We used spectrophotometric methods to determine the amount of metal ions in the filtrate of each variant.

RESULTS AND DISCUSSIONS

The considered adsorbent retained both metal ions from the aqueous solutions, the adsorption rate decreasing at higher concentrations of the heavy metal ions' solutions.

We presented the data regarding the calibration curves established for the two considered ions in table 1 and figures 1 and 2.

Table 1

Calibration curves data for copper and cobalt ions

Conc. / Ion/E	2.5 mg/L	5 mg/L	10 mg/L	15 mg/L	20 mg/L	25 mg/L
Copper $E_{(\lambda=585\ nm)}$	0.018	0.02	0.022	0.027	0.029	0.031
Cobalt $E_{(\lambda=395\ nm)}$	0.01	0.015	0.022	0.029	0.032	0.038

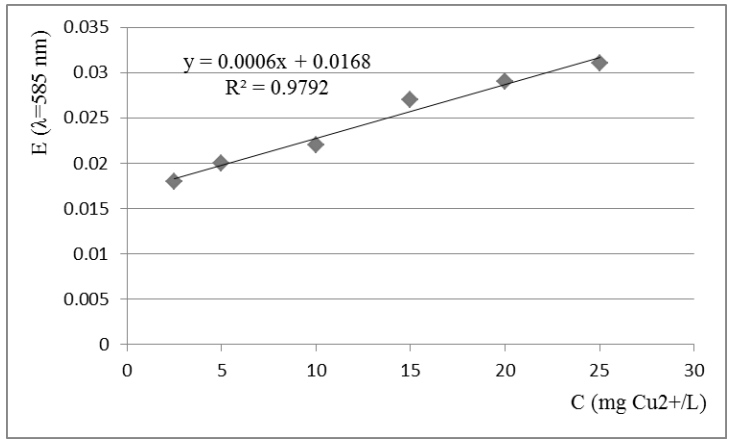

Fig. 1 Calibration curve for copper

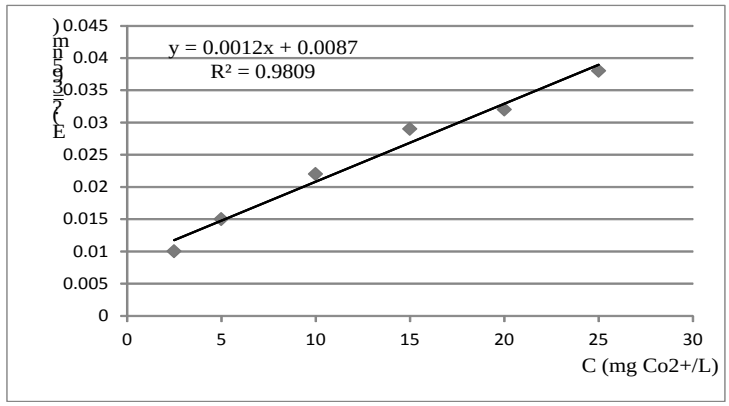

Fig. 2 Calibration curve for cobalt

For each heavy metal ion we calculated the adsorption coefficients related to the initial concentrations, establish the correlation between their values (tab. 2, fig. 3, fig. 4) and also determined the percentage of metal ions retained per one gram of adsorbent (tab. 2, fig. 5).

Table 2

Adsorption coefficient values

Ion	Conc.	50 mg/L	100 mg/L	150 mg/L	200 mg/L	250 mg/L
Copper	Final concentration	5.33	18.667	38.667	53.667	92.0
	Adsorption coefficient	89.333	162.667	222.667	292.667	316.0
	% of retained ion	94.50	81.333	74.222	73.167	63.20
Cobalt	Final concentration	2.75	6.083	10.25	20.05	50.25
	Adsorption coefficient	94.5	187.833	279.5	359.5	399.5
	% of retained ion	94.50	93.917	93.167	89.875	79.90

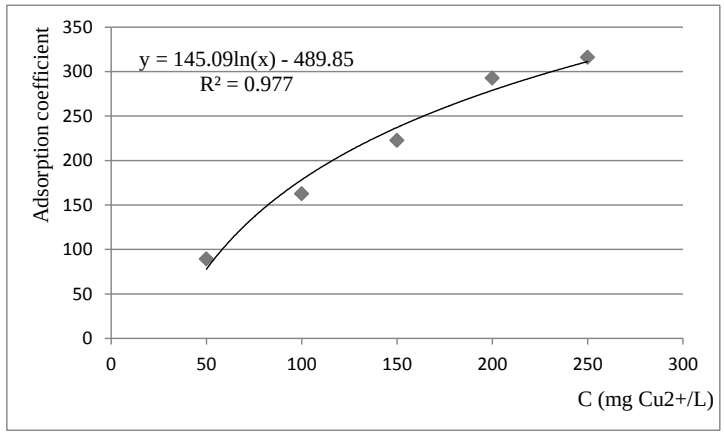

Fig. 3 Correlation between initial copper concentrations and adsorption coefficients

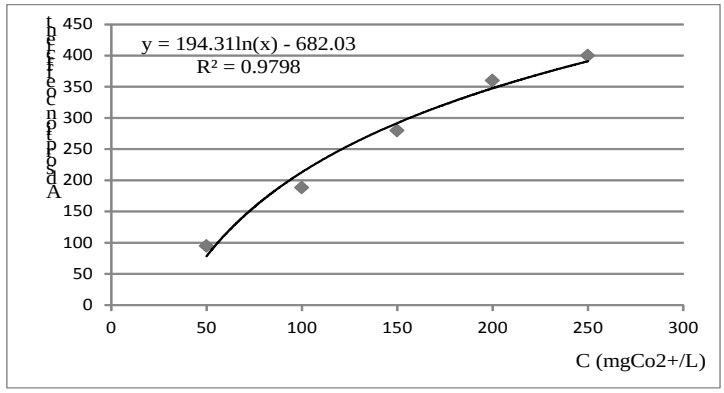

Fig. 4 Correlation between initial cobalt concentrations and adsorption coefficients

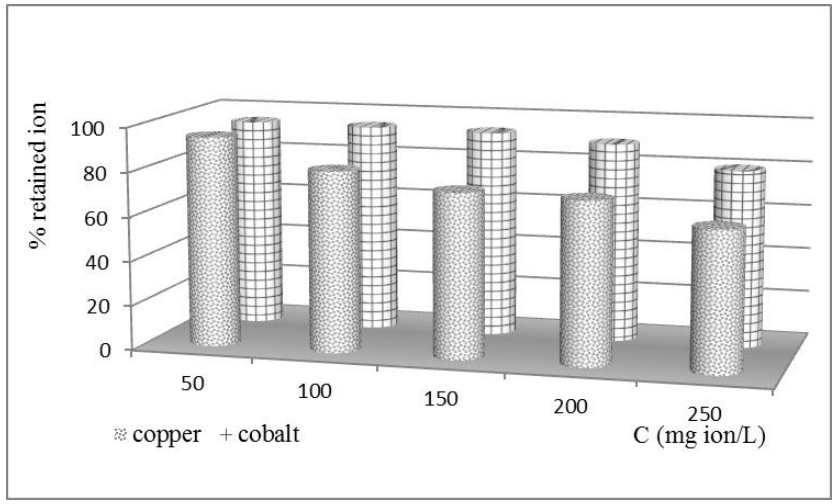

Fig. 5 Percentages of heavy metal ions removed by acid activated sawdust

The activation process with acidic solutions does not require high concentrations and long reaction time, being available for large-scale applications. The actual absorption process is very simple and efficient; working with small samples, we preferred stirring the adsorbent with the tested solutions, but for larger quantities the process can develop in continuous flow, in columns, under minor pressure or statically in large chambers filled with adsorbent sawdust.

CONCLUSIONS

1. Alder sawdust can serve as adsorbent material for divalent copper and cobalt ions from aqueous solutions;

2. The activation procedure, which proved to be increasing the adsorption capacity, is simple and quick;

3. Copper ions were adsorbed on sawdust in percentages from 94.5 (from 50 mg/L solution) to 63.2 (from 250 mg/L solution);

4. Cobalt ions were adsorbed on sawdust in percentages from 94.5 (from 50 mg/L solution) to 79.9 (from 250 mg/L solution);

5. The method proved effective for decreasing heavy metal ions levels in solutions and can develop in continuous flow or static conditions.

REFERENCES

1. Argun M.E., Dursun S., Ozdemir C., Karatas M., 2008 - *Heavy metal adsorption by modified oak sawdust*, Thermodynamics and kinetics. Journal of Hazardous Materials, 141: 77-85.

2. Bozić D., Stanković V., Gorgievski M., Kovacević R., 2009 - *Adsorption of heavy metal ions by sawdust of deciduous trees*, Journal of hazardous materials, 171(1-3):684-92..

3. Bulut Y., Tez Z., 2007 - *Removal of heavy metals from aqueous solution by sawdust adsorption*, Journal of Environmental Sciences, Vol 19 (2):160-166.

4. Šćiban M., Klašnja M., 2003 - *Removal of heavy metals from wastewaters by adsorption onto wood sawdust*, Central European Journal of Occupational and Environmental Medicine, Vol.9 (4): 337–343.

5. Yu B., ZhangY., Shukla A., Shukla S., Dorris K., 2000 - *The removal of heavy metal from aqueous solutions by sawdust adsorption — removal of copper*, Journal of Hazardous Materials, Vol. 80(1-3):33-42.

6. Yu B., Zhang Y., Shukla A., Shukla S., Dorris K., 2001 - *The removal of heavy metals from aqueous solutions by sawdust adsorption--removal of lead and comparison of its adsorption with copper*, Journal of Hazardous Materials, Vol. 84(1):83-94.