SAWDUST AS LOW-COST NATURAL ADSORBENT FOR REMOVAL OF Cu(II) IONS FROM AQUEOUS SOLUTIONS

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ABSTRACT

Nowadays heavy metals are reported as priority pollutants, due to their mobility in natural water ecosystems and their toxicity; they are among the most important pollutants in source and treated water, and are becoming a severe public health problem. Cellulose can adsorb heavy metals from solution. In this paper, the inexpensive and effective metal ion (Cu^{2+}) adsorbent from wood-waste materials (sawdust) was investigated using the biosorption process, which is a relatively new process that has proven very promising in the removal of metals ions from aqueous effluents. The results show that the biosorbtion of copper ion occurs with higher yields in alkaline solution (pH= 8.5), the adsorption equilibrium is quickly reached (after 15-30 minutes) and copper ions can be removed extensively from aqueous solution after successive adsorption stages.

INTRODUCTION

Since the industrial revolution, anthropogenic impacts have caused many hazardous substances releasing to environment. Heavy metal pollution is today one of the most important environmental and public health problem caused by heavy metals toxicity and other adverse effects on water bodies. Various industries produce and discharge wastes containing different heavy metals into the aquatic environment such as mining and smelting of metalliferous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, etc. [1÷3].

Conventional methods for removal of metal ions from aqueous solutions include chemical precipitation, electrochemical treatment, ion exchangers, reverse osmosis, electro-dialysis, membrane technologies, etc. Since 1990's the adsorption of heavy metal ions by low cost renewable organic materials has gained momentum [4]. The process of adsorption implies the presence of an "adsorbent" solid that binds molecules by physical attractive forces, ion exchange, and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap [5]. Biosorption can be defined as the removal of metal or metalloid species, compounds and particulates from solution by biological material [6]. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical or biological sludge, no additional nutrient requirement, and regeneration of biosorbents and possibility of metal recovery. The sorption capacity of lignocellulosics for metal ions is generally described as adsorption and this is the most attractive method due to its simplicity, convenience and high removal efficiency [7÷9].

One metal that is targeted for the development of new removal techniques is copper. Copper is a bio-essential element, e.g. the adult daily requirement for human beings estimated to be 2 mg; however, ecological impacts may be observed when copper concentrations exceed 0.2 mg/ L [5]. Utilization of sawdust also played significant role in removal of copper and

other metal ions [10-13]. The main component of sawdust is cellulose (Fig 1) with proven adsorbtion properties.

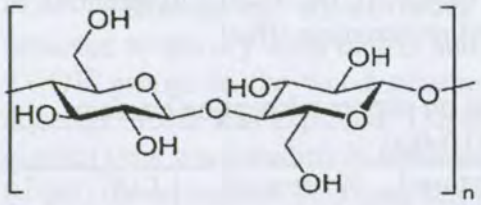

Figure 1. Structure of cellulose, an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units

Sawdust is a forestry by-product, composed of fine particles of wood. In countries with strong forestry industry such as Romania, sawdust is produced in large quantities but at this moment, less valorized. For this reason we have proposed to study the adsorption capacity of sawdust for copper ions, first in synthetic aqueous solutions.

MATERIALS and METHODS

- Batch studies were conducted using synthetic Cu^{2+} solution to assess adsorption studies. Working solution was prepared by successive dilutions from stock solution (solution I) of Cu^{2+} with concentration 0.4 moles Cu^{2+} /L (0.4 M respectively 25.400 ppm) obtained by dissolving in a volumetric flask of 1000 mL a 100 g CuSO4*5H2O in distilled water; 1 mL of this solution was diluted to100 mL obtaining the solution II (254 ppm). 10 mL of solution II was diluted with water in a volumetric flask to 250 mL and the final solution (III) containing 10.16 ppm Cu^{2+} ($1.6*10^{-4}$M) was prepared.
- Sawdust samples were obtained from some wood factories located in Faget area, Timis County. It has been used without being crushed before.
- Determination of Cu^{2+}: a volumetric method was used, respectively: over 0.1 ml of sample 50 ml distilled water was added 3 ml acetic acid (1M) and 0.1 ml of indicator solution alcohol (PAN). Titration was done with complexone solution III EDTA (0.01 M), turn indicator is red-orange to greenish yellow. Factor solution is verified daily. [14].

RESULTS

In laboratory experiments we have used two types of oak sawdust samples from different source. Their adsorption capacity was evaluated comparatively in two ways: without preliminary draying (series A) and after drying at 105 ^{0} C, to constant weight (series B; humidity of sawdust samples was between 9.5 and 10%).
The results are presented in Table 1. It can be seen that:

- sawdust adsorb quickly copper ions; 15 minutes are sufficient; after 45 minute (sample 1) and about 30 minute (sample 2) , sawdust efficiency decreases slightly;
- there are differences between the two samples of oak sawdust on adsorption capacity of Cu^{2+} ions, probably because of different degree of crushing, age of the trees, chemical composition;
- the drying process of sawdust is not advantageous because the adsorption capacity of copper ion decreases by 8.7-16.7% for sample 1 and by 30-50% for oak sawdust, sample 2;
- 1 g of undried sawdust can retain 10.16÷11.10 mg/L Cu^{2+} (sample 1) or 12.10-12.74 mg/L Cu^{2+} (sample 2).

The pH effect was investigated as well. Determinations of adsorbtion capacity were made after 15 and 30 minutes and could be observed differences depending on the pH of

aqueous solution. The most favorable pH is the alkaline one (pH 8.5) when the results increased by 30-40%. At a higher pH copper ions precipitate. A Cu^{2+} solution with pH 5 lead to slightly better results than those obtained at pH 6.4; at lower pH, percentage of retention of copper ions significantly decreases probably due to sorbent protonation effect.

Table 1. Effect of adsorption time and sawdust drying on cupper adsorption capacity (synthetic solution Cu^{2+} $1.6*10^{-4}M$)

Sawdust sample	Experimental conditions	Adsorption ratio mL aq. Cu^{2+}/ weight of sawdust (g)	Adsorption time, minute	% removal, 100 (C_i-$C_{f)}$/C_i,	Cu^{2+} (mg/L) adsorbed by 1 g sawdust
A1.	Undried oak chips, sample 1, 25^{0}C, magnetic stirring (500rpm), pH = 6.4	500:1	15	50.03	10.16
			30	51.87	10.54
			45	54.62	11.10
			60	53.89	10.84
			75	53.12	10.74
			90	52.65	10.62
A2	Undried oak chips, sample 2, 25^{0}C, magnetic stirring (500rpm), pH = 6.4	500:1	15	58.25	11.84
			30	60.60	12.32
			45	63.10	12.82
			60	62.15	12.74
			75	61.75	12.18
			90	61.50	12.10
B1	Dried oak chips, sample 1, 25^{0}C, magnetic stirring (500rpm), pH = 6.4	500:1	15	49.35	10.06
			30	47.32	9.50
			45	44.38	8.94
			60	45.63	9.20
			75	44.38	8.94
			90	43.78	8.82
B2	Dried oak chips, sample 2, 25^{0}C, magnetic stirring (500rpm), pH = 6.4	500:1	15	32.08	6.58
			30	32.13	6.68
			45	30.20	6.12
			60	30.62	6.14
			75	30.97	6.26
			90	28.72	5.86

Taking into consideration the findings so far we have tried to retain the Cu^{2+} ions in three successive adsorption stages. The results are shown in Figure 2. Retention percentage after the first cycle of adsorption of ions is 52% and in the following two cycles 67.68 % and 73% respectively, which would allow the removal of heavy metal ions by using batteries of adsorption.

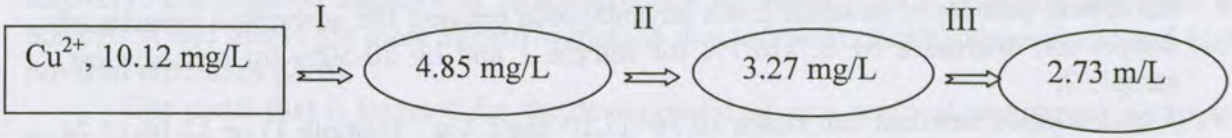

Figure 2. Concentration of Cu^{2+} solution after successive adsorption stages on cellulosic material (oak sawdust)

CONCLUSIONS

Cellulose can adsorb heavy metals from solution. The polar solvent molecules are attracted to the dry solid matrix and held by hydrogen bonding forces between the –OH or –COOH groups in the wood structure. Sorption potential of untreated sawdust copper from aqueous media was explored. The effects of pH, initial concentration, biosorbent dosage and contact time were studied in batch experiments. The results show that:

- the adsorbtion of copper ion occurs with higher yields in alkaline solution (pH 8.5);
- the adsorption equilibrium is quickly reached, after 15-30 minutes working at room temperature (25^0C);
- 73% of copper ions can be removed from the solution after three adsorption stages.

ACKNOWLEDGEMENTS: *This paper was partially supported by Romania-Republic of Serbia IPA Cross-border Cooperation Programme, within project MIS-ETC Code 464, subsidy contract from IPA No 8518.*

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