

# COMPARISON OF REMOVAL OF COPPER (II) IONS FROM AQUEOUS SOLUTIONS BY BIOSORPTION ONTO OLIVE STONE AND PINE BARK

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## Abstract

Olive stone (OS) and pine bark (PB), two agricultural solid waste by-products have been used as effective and efficient biosorbents for the removal of Cu(II) from aqueous solutions. Batch adsorption experiments were carried out as a function of initial metal ion concentration. Equilibrium data agreed well with Langmuir isotherm model. The biosorption capacities of pine bark and olive stone for Cu(II) were determined at 25 °C with the Langmuir model as 11.94 mg/g and 1.97 mg/g, respectively. Specially, pine bark was shown to be a promising biosorbent for Cu(II) removal from aqueous solutions.

## Introduction

Industrial effluents are the major sources for contamination of water resources by heavy metals. The presence of these heavy metals in the aquatic environment has been of great concern because of their toxicity and non-biodegradable nature. Copper is one of the most widely used heavy metals. Its waste sources include mining wastes, drainage discharge, plating baths, fertilizer industry, paints and pigments, etc. Intake of excessively large doses of copper by man leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, central nervous system irritation followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney (Ajmal *et al*, 1998; Yao *et al*, 2010).

There are several methods available to achieve the reduction of heavy metals in wastewater (Hsu *et al*, 2008). These methods are relatively expensive, involving either elaborate and costly equipment or high costs of operation and energy requirements. To achieve wide-spread removal of heavy metals from water sources, a more efficient and low-cost process is needed. Recently, biosorption has attracted growing interest. Using inexpensive sorbents, biosorption can achieve high purity in treated wastewater.

In the present work, Cu(II) was chosen as a model pollutant in aqueous solution to carry out an investigation on olive stone and pine bark biosorption action.

## Methods

**Biosorbent preparation:** Olive stone (OS) was provided by an oil extraction plant “Cooperativa Nuestra Señora del Castillo” located in Vilches, province of Jaen (Spain). The stones were obtained from the separation process of the olive cake with an industrial pitting machine. Pine bark (PB) was provided by the company Carsan Biocombustibles, S.L. located in Padúl, province of Granada (Spain). The two solids were milled with an analytical mill (IKA MF-10) and <1.000 mm fraction was chosen for the biosorption tests without any pre-treatment.

**Preparation of Cu (II) solutions:** The aqueous solutions of Cu<sup>2+</sup> were prepared using CuSO<sub>4</sub>·5H<sub>2</sub>O. A stock solution (500 mg/L) of Cu<sup>2+</sup> was prepared by dissolving the required quantity of CuSO<sub>4</sub>·5H<sub>2</sub>O in distilled water. It was further diluted to obtain standard solutions. For all of the biosorption experiments, a Cu<sup>2+</sup> solution containing 10–300 mg/L was prepared and used. The pH of the solution was adjusted using HCl and NaOH solutions.

**Batch biosorption experiments:** Equilibrium isotherm studies were conducted at 25 °C with a constant amount of biosorbent (10 g/L), at a constant pH 5 for over 100 minutes, and for an initial metal concentration between 10 and 300 mg/L to evaluate the copper biosorption capacity of PB and OS. Then the mixture was centrifuged and filtrated and finally, the Cu<sup>2+</sup> in the remaining solution was then analyzed in an Atomic Absorption Spectrometer.

The amount of metal uptake was obtained by the following equation:  $q_e = \frac{(C_0 - C_e)}{m} \cdot V$

where  $q_e$  (mg/g) is the amount biosorbed,  $C_0$  (mg/L) and  $C_e$  (mg/L) are the initial and the equilibrium concentration, respectively while  $m$  (g) is the mass of biosorbent and  $V$  (L) is the volume of solution.

## Results and discussion

The biosorption isotherm indicates how the sorbate molecules distribute between the liquid phase and the solid phase at equilibrium. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. In this research, biosorption isotherm study was carried out on one well-known two-parameter isotherm: Langmuir isotherm.

The Langmuir isotherm represents the equilibrium distribution of metal ions between the aqueous and solid phases following the equation (Langmuir, 1918):

$$q_e = \frac{b q_m C_e}{1 + b C_e}$$

where  $C_e$  is the equilibrium copper solution concentration (mg/L),  $q_e$  is the amount of copper biosorbed onto the solid at equilibrium (mg/g),  $q_m$  is a Langmuir constant of the maximum copper uptake (mg/g) and  $b$  is also a Langmuir constant of the ratio of the biosorption rate constant to the desorption rate constant, which is related to the energy of sorption through the Arrhenius equation.

As seen from Figure 1, both sorbents fit quite well into the Langmuir model. The correlation coefficients were extremely high as shown in Table 1. The maximum biosorption capacity of the OS and PB biomass regarding copper ions are found to be 1.97 and 11.94 mg/g, respectively. The value of  $b$  for OS and PB are 0.0208 and 0.0247 L/mg, respectively.

Table 1. The comparison of the Langmuir constants obtained from biosorption isotherms of Cu(II) ions by OS and PB.

Biosorbent	$q_m$ , mg/g	$b$ , L/mg	$R^2$
OS	1.965	0.0208	0.961
PB	11.935	0.0247	0.983

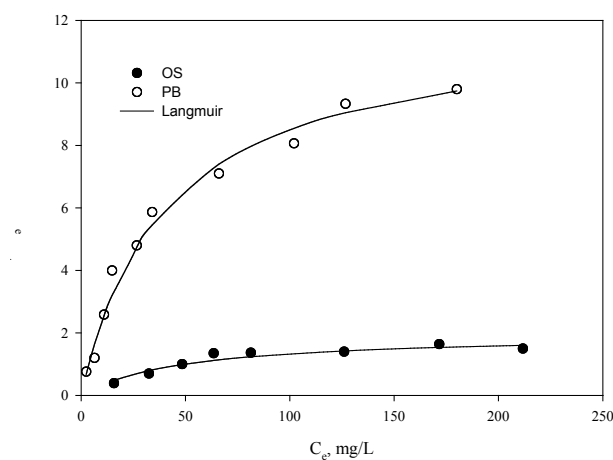


Figure 1. Langmuir plots for copper(II) ion sorption by OS and PB ([biosorbent] 10 g/L; temperature 25°C; pH 5).

## Conclusions

The results showed that OS and PB can be used as sorbents for the effective removal of Cu (II) from aqueous solutions. The maximum biosorption capacity of Cu(II) was 1.97 mg/g and 11.94 mg/g at an optimum pH 5 and at 15 °C for OS and PB, respectively. The adsorption isotherms followed the Langmuir model of isotherms ( $R^2 > 0.99$ ). Taking into consideration the above results, it can be concluded that OS and PB are two suitable biosorbents for the removal of Cu (II) ions from aqueous solutions in terms of low-cost and its natural and abundant availability.

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