MINING AND METALLURGY INSTITUTE BOR
TEHNICAL FACULTY BOR, UNIVERSITY OF BELGRADE


## 47th International October Conference on Mining and Metallurgy

# PROCEEDINGS

**Editors:**

**Ana Kostov**
**Milenko Ljubojev**

**4th – 6th October 2015**
**Hotel "Jezero" Bor Lake, Serbia**

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**and**

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# BIOSORPTION OF HEAVY METALS USING THE AGRO WASTE BIOMASS

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## ABSTRACT

*Heavy metals pollution of wastewater has become an important issue with respect to the environmental and human health. Biosorption, using the agro waste materials is observed as the low-cost and eco-friendly method for removal of heavy metals from wastewater. This paper promotes the biosorption process as a potential alternative to the conventional methods for t removal of heavy metals from wastewater. The biosorption capacity of different agro waste materials has been also discussed with focus to the operating parameters, which affected the biosorption process. Mechanisms involved in biosorption of heavy metals from wastewater include the ion exchange, chemisorption, microprecipitation, complexation and chelatation.*

***Keywords**: biosorption, agro waste, heavy metals, operating parameters, mechanism*

## 1 INTRODUCTION

Rapid industrialization and technological advice thought the world has generated large amount of wastes. Industrial wastewater is the major sources for contamination the environmental water by heavy metals (HV). Heavy metals are non-biodegradable and very toxic, even at trace levels. However, heavy metals are the essential elements for living organisms and play an important role for maintenance the normal biological activities. On the other hand, an excessive intake of heavy metals can cause many diseases. Thus, it is necessary to remove the heavy metals from wastewater.

Different conventional methods have been used for removal the heavy metals from wastewater such as extraction, coagulation and chemical precipitation, ion exchange and membrane filtration [1,2]. Numerous methods have several disadvantages such as low efficiency, high operating costs, low selectivity and production of large quantities of sludge. This situation has leaded many researchers to the use of cheap, easy available and eco-friendly adsorbent, which might efficiently remove heavy metals from wastewater.

Over the few last years, the agro waste materials as adsorbent of heavy metals from wastewater have attracted extensive attention. The main compounds of agro waste biomass are lignin and cellulose which consists of different functional groups make agricultural wastes the proper material for adsorbing metals from wastewater [3]. A lingo cellulosic waste material adsorbs metal ions on their surface binding sites through interaction with the chemical functional groups. Large number of agro wastes has been used as heavy metals adsorbents such as agave bagasse [4], rice straw [5], rice husk [6], wheat stem [7], olive pumice [8], olive stone [9], barley straw [10], coconut shell [11], corn cob [7,12], apricot stone [12], cashew nut shell [13], grapefruit peel [14], etc. The major advantages of adsorption of heavy metals using the agro waste materials over conventional methods are low operating cost, high efficiency, minimization of chemical and/or biological sludge, regeneration of biosorbent and possibility of metals recovery.

This literature review presents recent studies of using low cost agro waste biomass for heavy metals removal from wastewater. The main aim of this work is to provide a summary of literature data concerning the use agro waste biomass and to compare results found in the literature. This paper presents a comprehensive review with focused discussions on some sections: factor affecting biosorption process; biosorption mechanism and maximum adsorption capacities.

### 1.1 Factors affecting the biosorption process

A number of physico-chemical factors influenced the biosorptive capacity of heavy metals ions [15]. Important factors include:

- For biosorption of HM, pH which is the most important parameter of biosorption process affecting the solution chemistry of the pollutants themselves, the activity of functional groups in the biosorbents, and competition with coexisting ions in solution [12]. The biosorptive capacity of HM increases with increasing of pH but too high pH value may cause precipitation of metal complexes. The low biosorptive capacity of heavy metals on the biosorbents at low pH value is evidently because of the presence of the high concentration of available $H^+$ ions which compete with heavy metals ions for the sorption sites on the biosorbents surface.
- The increased biosorbent dosage reduces the biosorption capacity of biosorbent, but increases removal efficiency by competing with the metal for binding sites on the biosorbent [12]. The decrease of biosorption capacity with increasing the biosorbent dosage may be attributed to the formation of aggregates of adsorbent due to its high concentration.
- The increased initial metal concentration increases the biosorption capacity of biosorbent, but decreases the removal efficiency [12]. This may be attributed to the initial metal concentration which provides an important driving force to the mass transfer of metal ions between the solution and biosorbent.
- Temperature usually enhances biosorption capacity when it is increased by increasing surface activity and kinetic energy of the biosorbent, and also damages the physical structure of biosorbent [15].
- The decreased biosorbent size increases the biosorption capacity of biosorbent. This was due to the particles with smaller particle size allowed a faster contact between the metal ion and the binding sites on the biosorbent and the increase in surface area provided more sorption sites for metal ion [16].

### 1.2 Mechanisms of the biosorption process

The biosorption process involves the solid phase (biomaterial) and liquid phase (solution of metal ions). Metal ions are attracted and bound to the biomaterial by different mechanisms. Mechanisms affecting the biosorption process include the ion exchange, complexation and chelation, micro precipitation, surface adsorption etc. The maximum biosorption capacities of different types of agro waste materials and proposed mechanism for heavy metal removal are summarized in Table 1.

**Table 1** *The performance of different agro waste biomass for heavy metal ion removal*

| Agro waste biomass | Metal | $q_{max}$ (mg/g) | Proposed mechanism | Ref |
|---|---|---|---|---|
| Agave bagasse | Pb | 35.6 | Ion exchange, complexation | [4] |
| Corncob | Pb | 16.22 | | [7] |
| Coconut shell | Pb | 54.62 | | [11] |
| Barley straw | Cu | 4.64 | Ion exchange, chelation | [10] |
| Olive stone | Cu | 20.2 | | [9] |
| Agave bagasse | Cd | 13.27 | Ion exchange, complexation | [4] |
| Rice straw | Cd | 13.89 | Ion exchange, chelation | [5] |
| Wheat stem | Cd | 11.6 | Complexation | [7] |
| Grapefruit peel | Ni | 46.13 | Ion exchange | [14] |
| Agave bagasse | Zn | 7.84 | Ion exchange, complexation | [4] |
| Olive pomace | Cr | 13.95 | Ion exchange | [8] |

In order to study the mechanisms of biosorption process, it is important to have information about the structure of biomaterial as well as solution chemistry. Different techniques that have been used to study the biosorption process such as atomic absorption spectrophotometry (AAS), UV–VIS spectrophotometry, scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM–EDX), potentiometric titration, Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), nuclear magnetic resonance (NMR) and thermo gravimetric analysis (TGA) [15,16]. These techniques may complement each other in giving insights into the mechanisms of biosorption [15]. Mechanism of biosorption process is shown in Figure 1.

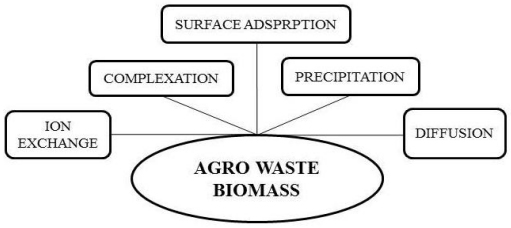


**Figure 1** *Mechanism involved in metal ion removal from aqueous solution*

### 1.3 Biomass modifications

The use of untreated biomass as biosorbent can cause several problems such as low adsorption capacity, high chemical oxygen demand, biological chemical demand as well as total organic carbon due to the release of soluble organic compounds contained in these materials. Thus biomass needs to be modified before being applied for the biosorption of heavy metals. In general, the raw biomass is modified by various methods to increase their sorption capacities because metal ion binding by these biosorbents is believed to take place through chemical functional groups such as carboxyl or phenolics [17]. Several researchers have used different modifying agents such as: sodium hydroxide, calcium hydroxide, and sodium carbonate; mineral and organic acid solutions – hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, and thioglycollic acid; organic compounds – ethylenediamine, formaldehyde, epichlorohydrin, and methanol; oxidizing agent – hydrogen peroxide to remove the soluble organic compounds and to eliminate coloration of the aqueous solutions thus increasing metal adsorption efficiency.

## 2 CONCLUSIONS

Millions tones of biomasses such as corn cob, olive stone, coconut shell, cashew nut shell, grapefruit peel, barley straw, rice straw are discarded as a waste every year. This material holds potentials to be used for heavy metals removal as cheap adsorbents. Most recent studies of agro waste biomass as abundant and low-cost adsorbent for heavy metal ion from aqueous solutions have been reviewed. Agro waste biomasses reveal their potential for heavy metal removal from high-volume industrial wastewater due to high adsorption capacities, cheap source and easy availability. It is important to note that the heavy metal removal from contaminated wastewater depends on some basic parameters such as pH, biosorbent dosage, initial metal concentration, temperature, biosorbent nature and size. Ion exchange and complexation are the two major important mechanisms involved in metal uptake by different biosorbents.

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