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Biosorption of Cu (II) and Zn (II) from Real Wastewater onto *Cajanus cajan* Husk

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***Abstract*—**In this preliminary work, locally available husk of *Cajanus cajan* (commonly known in India as Tur or Arhar), a bio-waste, has been used in its physically treated and chemically activated form for the removal of binary Cu (II) and Zn(II) ions from the real waste water obtained from an electroplating industry in Bangalore, Karnataka, India and from laboratory prepared binary solutions having almost similar composition of the metal ions, for comparison. The real wastewater after filtration and dilution for five times was used for biosorption studies at the normal pH of the solutions at room temperature. Langmuir's binary model was used to calculate the metal uptake capacities of the biosorbents. It was observed that Cu(II) is more competitive than Zn(II) in biosorption. In individual metal biosorption, Cu(II) uptake was found to be more than that of the Zn(II) and a similar trend was observed in the binary metal biosorption from real wastewater and laboratory prepared solutions. FTIR analysis was carried out to identify the functional groups in the industrial wastewater and EDAX for the elemental analysis of the biosorbents after experiments.

***Keywords*—**Biosorption, *Cajanus cajan*, multi metal remediation, wastewater.

I. Introduction

COPPER and zinc are known to be essential to living things but they can have adverse effects if their limit in the effluent water exceeds certain threshold values. According to the World Health Organization (WHO), maximum acceptable concentrations of Zn(II) and Cu(II) in drinking water are 5.0 ppm and 1 ppm, respectively. Cu(II) and Zn(II) are among the most common and abundant heavy metal pollutants in landfill leachate and these are potentially toxic to plants and animals [1]. Mixed Cu(II) – Zn(II) can come into the environment mainly from electroplating industries. In humans toxicity of copper causes itching, keratinization of hands and soles, even may damage pancreas, liver, lungs and kidney when consumed in large dose [2], [3]. Symptoms of zinc toxicity include irritability, muscular stiffness, loss of appetite and nausea [4].

Biosorption is relatively a new method for the removal of heavy metal ions from aqueous solutions and it is economically attractive, clean, and technically feasible as compared to other methods such as precipitation, reverse osmosis, electrolysis, ion exchange, etc. for the removal of heavy metals from contaminated effluents [5]-[12]. Electroplating industry generates a huge amount of wastewater and has been declared as a major polluting industry in India by the central pollution control board. The industry of metal finishing and electroplating are one of the major source of heavy metals (Cu, Zn, Cr) and cyanide.

Industrial metal-bearing wastewater contains materials such as supplementary cations, chelating agents, and other organic materials, besides heavy metals. All these can produce three possible types of behavior: synergism (the interaction of two different ions to produce an effect greater than the sum of their individual effects), antagonism (two or more different ions in combination have an overall effect which is less than the sum of their individual effects) and non-interaction. Thus, any study of biosorption characteristics of biosorbents in single metal solutions may only be considered as preliminary. Also, the literature is still scarce to cover the problem of multi-metal biosorption from real wastewaters.

As several metal ions are present in the wastewater, there may be interference and competition for biosorption sites [13]. In this work Cu(II) and Zn(II) were removed from laboratory and real wastewaters containing these metals using *Cajanus cajan* husk. *Cajanus cajan* is an important pulse crop in India commonly called as red gram and as Arhar or Tur locally. India is the largest producer and consumer of this pulse in the world. The husk of this pulse is available abundantly as a bio-waste.

II. Materials and Methods

A. Chemicals and Instruments

Copper (II) sulphate-5-hydrate [$CuSO_4.5H_2O$] (Central Drug House (P) Ltd., Mumbai) and Zinc chloride [$ZnCl_2$] (HIMEDIA Laboratories Pvt. Ltd., Mumbai) were used to prepare laboratory simulated binary metal solutions in double distilled water. Sodium hydroxide [NaOH] (SD Fine, Mumbai), Calcium chloride [$CaCl_2$] (SD Fine, Mumbai) and Ethanol [C_2H_5OH] (Changshu Yangyuan Chemical, China) were used for the chemical activation of the *Cajanus cajan* husk.

The instruments used were: an atomic absorption spectrophotometer (Elico-167 model, India), orbital shaker (Kemi, Kerala, India), hot air oven (Kemi, Kerala, India), precision electronic weighing balance (Essae Teraoka Ltd.), pH meter (Elico-LI 612 model) and an all-glass water double distillation unit (Borosil make). All glass wares used for experiments were of Borosil make.

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B. Preparation of Biosorbents

1.Physical Preparation of Biosorbant:

Cajanus cajan husk was collected from Chidri Dall Mill, Humnabad, Bidar District, Karnataka, India. The husk was ground in a mixer-grinder and boiled in water for many times to remove the color. It was then dried in a hot air oven at 85°C for 24 h and the dried material was screened and the size fraction of average size 0.5125 mm was stored in air tight polythene bags and designated as CC(N).

2.Chemically Activated Biosorbent:

For chemical activation, 500 ml absolute ethanol, 250 ml of NaOH (0.5 mol/L) and 250 ml of $CaCl_2$ (1.5 mol/L) were added to 100 g of CC(N), and kept aside with intermittent shaking for 24 h. The supernatant liquid was drained out and the husk was thoroughly washed with distilled water to remove residual chemicals until the pH of washed water reached 7. It was then dried in a hot air oven at 85°C for 24 hand designated as CC(CA).

C. Equilibrium Studies

Batch biosorption experiments were carried out for laboratory prepared solutions having initial 50 ppm Cu(II) and 50 ppm Zn(II) concentration with CC(N) and CC(CA). 50 ml solutions were dosed with different amounts of biosorbents (0.1 to 0.5 g) and shaken in an orbital flask shaker at 180 rpm for 3 h for the attainment of equilibrium at the normal pH of the solutions. The solutions were then filtered and the residual Cu(II) and Zn(II) concentrations were determined by using atomic absorption spectrophotometer.

The same procedure for equilibrium studies with CC(N) and CC(CA) was repeated for a real wastewater obtained from an electroplating industry in Bangalore, Karnataka, India, which contained 62.73 ppm of Cu(II) and 49.68 ppm of Zn(II) after dilution for five times.

Single metal batch biosorption equilibrium experiments were also carried out with Cu(II) and Zn(II) for obtaining Langmuir parameters for use in binary biosorption models.

Individual biosorption constants may not define exactly the multi-component biosorption behavior of metal ion mixtures. For that reason, better accuracy may be achieved by using modified isotherm models.

The equilibrium data obtained were analyzed using the modified Langmuir isotherm [14] given by:

$$q_{e,i} = \frac{q_{m,i} K_{L,i} C_{e,i}}{1+\sum_{i=1}^{2}(K_{L,i} C_{e,i})} \text{ for i = Cu, Zn} \quad (1)$$

The parameters $q_{m,i}$ and $K_{L,i}$ for the biosorption of individual metal ions were determined using Langmuir isotherm model [15] given by:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad (2)$$

where, q_e and q_m are in mg/g, C_e is in ppm.

III. Results and Discussion

The industrial wastewater was filtered and the chemical oxygen demand (COD) was determined by dichromate method [16] and the biochemical oxygen demand (BOD) by standard method [17]. The characteristics of the wastewater after filtration are given in Table I. The wastewater was filtered and diluted (5×) so as to reduce the Pb(II) concentration to a low level and used for biosorption studies.

TABLE I
CHARACTERISTICS OF WASTEWATER

Parameter	Value
pH	2.6
COD (mg O_2/L)	675
BOD (mg O_2/L)	292
Zn (ppm)	248.4
Cu (ppm)	313.6
Pb (ppm)	18.2
Total dissolved solids (ppm)	445

FTIR (Fourier Transform Infrared Spectroscopy) was carried out to identify the functional groups in the industrial wastewater. The spectrum is in the range of 400 to 4000 cm^{-1}. The spectrum of the wastewater showing the major absorption bands with the relevant assignments is given in Fig. 1. At 3267 cm^{-1} it is OH stretching, 2073 cm^{-1} indicate the presence of nitrates, at 1644 cm^{-1} H-O-H stretching takes place and 769 cm^{-1} indicates Cu-OH deformation.

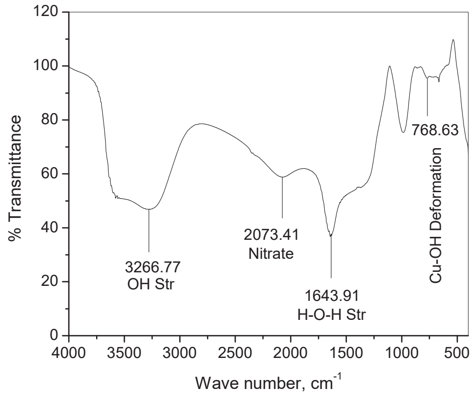

Fig. 1 FTIR of wastewater

The experimental data for the simultaneous biosorption of Cu(II) and Zn(II) from real wastewater and laboratory prepared solutions onto CC(N) and CC(CA) is shown in Fig. 2, which indicates gradual decrease of residual metal concentrations in most cases as the biosorbent dose is increased. However, in the case of Zn(II) on CC(CA) in real wastewater (RW) and Zn(II) on CC(N) in laboratory prepared solutions(LP), gradual decrease of residual metal concentrations was not observed, which may be due to more competitive nature of Zn(II) in biosorption in the binary metal solution.

The binary Cu(II)-Zn(II) biosorption data on CC(N) and CC(CA) for real wastewater and laboratory prepared solutions

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were modeled using the binary isotherm model given by (1).

In (1) $q_{m,i}$ and $K_{L,i}$ are the isotherm parameters for the biosorption of single metal by CC(N) and CC(CA). The isotherm parameters were determined by non-linear fitting of the equilibrium data to Langmuir model, with the initial metal concentrations taken as 50 ppm and are given in Table II.

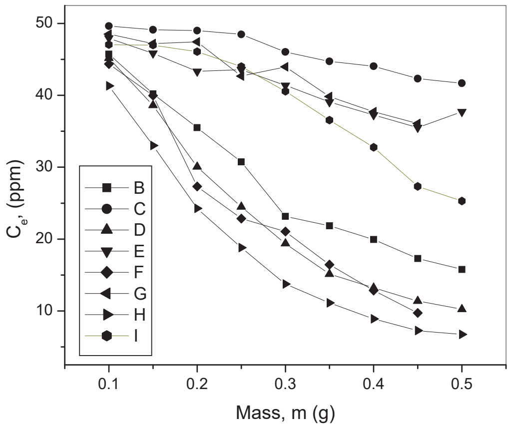

Fig. 2 Effect of biosorbent dose on the residual metal concentrations Legend: B: Cu(II) – CC(N) – RW; C: Zn(II) – CC(N) – RW; D: Cu(II) – CC(CA) – RW; E: Zn(II) – CC(CA) – RW; F: Cu(II) – CC(N) – LP; G: Zn(II) – CC(N) – LP; H: Cu(II) – CC(CA) – LP; I: Zn(II) – CC(CA) – LP

TABLE II
LANGMUIR ISOTHERM PARAMETERS FOR THE INDIVIDUAL BIOSORPTIONOFCU(II) AND ZN(II) BYCC(N) AND CC(CA) C_0 = 50 PPM CU(II) AND ZN(II)

Metal Ion	Biosorbent	q_m	K_L
Cu(II)	CC(N)	11.0446	1.3618
Cu(II)	CC(CA)	16.4348	0.2423
Zn(II)	CC(N)	03.4763	1.3973
Zn(II)	CC(CA)	06.1643	0.2796

The equilibrium uptake of Cu(II) and Zn(II) by CC(N) and CC(CA) from the binary metal solutions (real wastewater and laboratory prepared) calculated using (1) is shown in Fig. 3.

Wastewaters contain more than one metal ions. Hence interference of ions and competition for biosorption occurance lead to complex biosorption equilibrium. Therefore, competitive isotherm models express relationships between the biosorbed quantity of one component and the concentrations of all other components, either in solution or already biosorbed. One of the isotherms proposed to describe the equilibrium and competitive biosorption for such a system is the Langmuir model based on the hypotheses as for the single-component Langmuir model and also assumes identical saturation capacities for all components. The extension of the basic Langmuir model to competitive biosorption of multi-component mixture is given in (1).

Fig. 3 indicates favorable isotherms for Cu(II), signifying Cu(II) is more competitive than Zn(II) for biosorption, at the experimental conditions for both the real wastewater (RW) and the laboratory prepared solutions (LP).

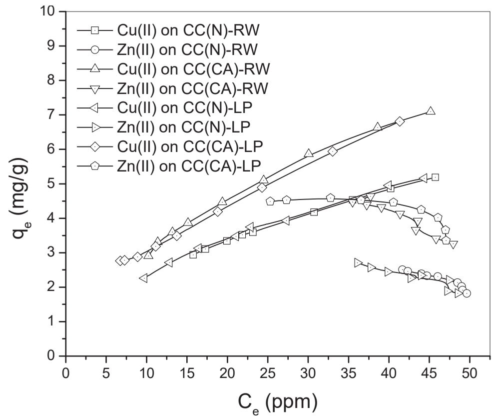

Fig. 3 Equilibrium uptake of Cu(II) and Zn(II)

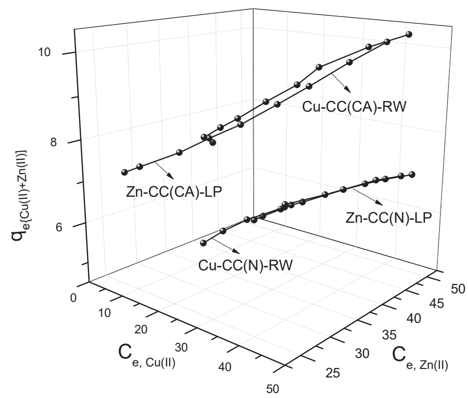

Fig. 4 Cu(II), Zn(II) and total uptake as a function of equilibrium concentration in Cu(II)-Zn(II) binary solution

Figs. 4 and 5 represent equilibrium metal uptake by the biosorbents as a function of residual equilibrium metal ion concentrations. It has been observed that CC(CA) shows better metal uptake capacity than CC(N).

EDAX (Energy Dispersive Analysis of X-rays) spectrums of the biosorbents after the metal uptake in the experiments are shown in Fig. 6 (after biosorption of metals in industrial wastewater by CC(N)) and Fig. 7 (after biosorption of metals in industrial wastewater by CC(CA)). EDAX is a powerful technique particularly in contamination analysis. The data generated by EDAX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the specimen being analyzed. These figures indicate successful biosorption of Cu(II) and Zn(II).

In this case of binary Cu(II) – Zn(II) system, antagonistic competitive effects were obvious for the biosorption in multi-metal solutions, as the maximum sorption capacity for one metal decreased in the presence of another metal in the solution. This is also confirmed by the data using the modified Langmuir model for the biosorption in binary metal systems. Additionally, a competitive mechanism seems to be dominant during biosorption in binary systems.

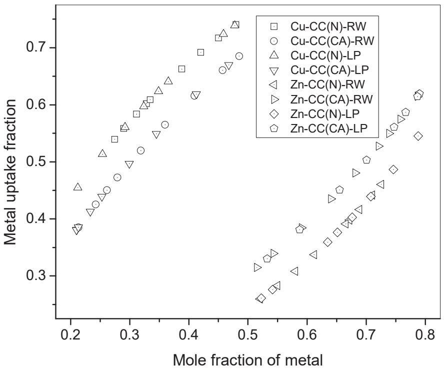

Fig. 5 Plot of metal mole fractions versus metal uptake fraction

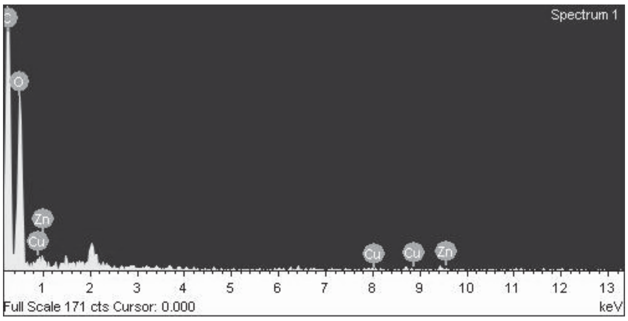

Fig. 6 EDAX of CC(N) after biosorption

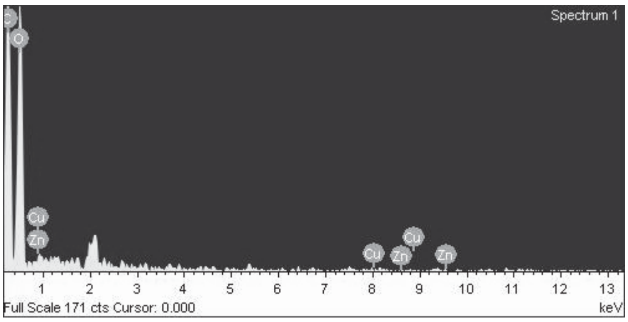

Fig. 7 EDAX of CC(CA) after biosorption

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