# Spectroscopic characterization for remediation of copper, cadmium and mercury using modified palm shell powder

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A B S T R A C T

Palm shell powder (PSP) has been modified with formaldehyde (MPSP) to protonate the surface functional groups and to induce polymerization of the color imparting functionalities. The potential of MPSP for the removal of $Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$ was studied. The process was investigated spectroscopically using FT-IR, XPS techniques and mechanistically using kinetic and sorption isotherm models to find out the mechanism involved in the sorption process.

The maximum sorption capacity by MPSP was found to be 153.9, 45.3 and 60.2 mg/g for $Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$, respectively. EDTA was used for quantitative recovery of copper after sorption while HCl was used for $Cd^{2+}$ and $Hg^{2+}$. Multiple binding mechanisms involved in the sorption process, includes reduction, ion-exchange, complexation, coordination and micro-precipitation to different extents. However, spectroscopic studies revealed that ion exchange is the predominant mechanism during sorption of $Cu^{2+}$ and $Cd^{2+}$ while sorption of $Hg^{2+}$ is accompanied by reduction mechanism.

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## 1. Introduction

Industrial uses of metals and other domestic processes (e.g., burning of fossil fuels, incineration of wastes, automobile exhausts, smelting processes and the use of sewage sludge as landfill material and fertilizer) have introduced substantial amounts of potentially toxic heavy metals into the atmosphere and into the aquatic and terrestrial environments. Heavy metal ions, such as mercury, cadmium and copper, have to be removed from industrial wastes because of their potential threat to the environment and to all living systems. Mercury and cadmium are the most toxic transition metals. Mercury affects the nervous and renal systems while cadmium is known to be carcinogenic and teratogenic [1]. Copper also has been classified as priority pollutant by US EPA as it could be toxic as well as carcinogenic at high concentrations though it is an essential micronutrient at low concentrations [2]. Despite strict environment regulations, water pollution due to toxic heavy metals still remains a serious environmental and public problem.

Removal of metal ions from wastewater in an effective manner has thus become an important issue today. Recent promising approach has been the use of biosorbents like chitosan, algae, fungi and agricultural by-products [3]. Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups [4]. These groups have the ability to bind heavy metals by the replacement of hydrogen ions for metal ions in solution or by donation of an electron pair from these groups to form complexes with the metal ions in solution [5].

However, many plant materials can leach organic compounds like chlorophyll and carotene into aqueous solutions. In using these materials for metal sorption, this organic leachate produces a secondary pollutant in the water. Therefore, the material must be chemically treated to remove or immobilize the organic components [6].

Anirudhan and coworkers [7] reported the use of banana stem as a precursor material for the preparation of adsorbent with sulfonic acid functionality by grafting formaldehyde onto banana stem. Barrera-Diaz and coworkers [8] used formaldehyde treated orange peel for sorption of lead. Saka [9] reported the sorption characteristics of $Pb^{2+}$ prepared from pre-boiled and formaldehyde-treated onion skins.

Palm shell (obtained as an agrowaste from palm fruit (Borassus flabellifer) and available throughout coastal Asia) and its modified forms have been investigated as a biosorbent for the removal of pollutants in our laboratory [10–12]. Preliminary investigations on

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the use of formaldehyde modified palm shell (MPSP), for the removal of $Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$ have shown encouraging results [13].

Although previous preliminary studies have highlighted the sorption ability of MPSP for several metal ions, in depth mechanistic studies have not been performed. This study aims to investigate the influence of pH, sorption kinetics, isotherm and thermodynamics for the sorption of $Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$ on MPSP as well as the binding mechanism. Spectroscopic techniques have been a valuable aid in determining functional groups that are responsible for metal binding to MPSP. FT-IR and XPS provide good insight into sorption process and have been adopted to identify the major functional groups of sorbents and elucidate their interaction with metal ions. However, to predict adsorption behavior of ions as a function of environmental parameters we have resorted to the application of isotherm and kinetic models to our adsorption data.

## 2. Materials and methods

### 2.1. Preparation of biosorbent material

The shell of palm fruit (B. flabellifer) was collected from coastal Andhra Pradesh, India. The collected palm shells were cut into small pieces, washed extensively with running tap water for 30 to 40 min followed by double distilled water and then dried in an air oven at 70°C. The dried biomass was ground in a laboratory blender and sorted using standard test sieves and termed as palm shell powder (PSP). Modification of PSP with formaldehyde was done in order to protonate the functional groups present and to polymerize the color imparting components of PSP. One gram of PSP was soaked in 100 mL of 0.2% formaldehyde solution for 24 h. The resulting modified palm shell powder (MPSP) was then filtered, washed with 300 mL of distilled water several times, and dried overnight in an oven at 60°C and sieved through 20Φ mesh. From our earlier studies it was observed that MPSP was found to have low surface area (0.505 m²/g) but relatively higher ion exchange capacity (0.5 meq/g) and iodine value 312.5 mg/g [13].

### 2.2. Spectroscopic characterization

The FT-IR spectra for MPSP and metal-loaded MPSP were obtained using a Perkin Elmer RX1 model in the wave number range of 400 to 4000 cm$^{-1}$. The samples were first mixed with KBr and then ground in a mortar at an appropriate ratio of 1/100 for the preparation of the pellets. The resulting mixture was pressed at 10 t for 5 min and 16 scans with 8 cm$^{-1}$ resolution were applied for recording the spectra. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra.

The surface of the samples was analyzed using a KRATOS AXIS 165 X-ray photoelectron spectrometer. Peak fitting and presentation output are produced by an integrated VISION control and information system. The deconvolution process of C1s spectra as well as the elemental composition evaluation may result in an error of up to 5%. All spectra are presented charge balanced and energy referenced to C1s at 284.6 eV.

### 2.3. Batch uptake

To study the effect of pH, 25 mL of known concentration of each metal ion solution ($Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$) under study was separately taken in 100 mL stoppered conical flasks containing known amount of MPSP. The pH of the solution was varied in the range 1–10 for $Cd^{2+}$ and $Hg^{2+}$, while for copper the pH was varied from 1 to 5 (to avoid precipitation), by using 0.1N NaCl or 0.1 N NaOH. The contents of the flasks were agitated in a thermostated rotary mechanical shaker at ambient temperature (~30°C) for

180 min. The metal content in the supernatant liquor was estimated by using AAnalyst 200 Perkin-Elmer atomic absorption spectrophotometer (AAS). The uptake of metal by the sorbents under study ($q_e$) was calculated from the difference between the initial and final concentration as follows:

$$q_e = \frac{(C_i - C_e)}{m} \tag{1}$$

where $C_i$—initial concentration of metal ion mg/L; $C_e$—equilibrium concentration of metal ion mg/L; $m$—mass of sorbent g/L; $q_e$—amount of metal ion (mg) sorbed per gram of sorbent. Each experimental result was obtained by averaging the data from three parallel experiments.

The adherence of the equilibrium isotherm and kinetic data obtained from experimental results was tested graphically to different sorption isotherm and kinetic models (Table S1).

Values of correlation coefficients and standard deviation (S.D.) were used to compare the models. SD was calculated using the equation.

$$SD = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(X_i - \bar{X})^2} \tag{2}$$

where $\{x_1, x_2, \ldots, x_N\}$ are the observed values of the sample items and $\bar{X}$ is the mean value of these observations, while the denominator $N$ stands for the size of the sample.

### 2.4. Desorption studies

0.1 g of metal loaded sorbents under study was treated with 10 mL of 0.1 M EDTA, 0.1 M NH$_3$ and 0.1 M HCl for a period of 30 min in a thermostated rotary mechanical shaker. After 30 min the amount of metal desorbed from the sorbents under study was determined by AAS. The sorption–desorption experiments were repeated for three cycles using the same sorbent. The sorbent was washed repeatedly with distilled water before it was subject to the subsequent metal loading cycle.

## 3. Results and discussion

### 3.1. Spectroscopic investigation

#### 3.1.1. Fourier transform infra-red spectroscopy

Infrared spectra of the pristine and metal-loaded sorbents are shown in Fig. S1. The corresponding infrared absorption bands of functional groups on PSP, MPSP and metal-loaded MPSP are summarized in Table 1.

The band at 3361 cm$^{-1}$ represents –OH and –NH groups on PSP which has been shifted to 3389 cm$^{-1}$ in MPSP suggested that the basic structure is still retained but modified. The shift in the bands to 3496, 3304 and 3343 cm$^{-1}$ in $Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$ loaded MPSP indicates metal –OH and –NH interaction during sorption onto MPSP. The presence of bands at 1732 and 1254 cm$^{-1}$ for PSP indicate the presence of aldehydic or ether linkages while their shift to 1727 and 1284 cm$^{-1}$ in MPSP suggests protonation and formation of carboxylic groups. The bands were further shifted to 1716, 1738 and 1735 and 1237, 1268 and 1260 cm$^{-1}$ respectively in $Cd^{2+}$, $Cu^{2+}$ and $Hg^{2+}$ loaded MPSP which could be due to the association of the carbonyl group with metal ions. The bands at 1101 cm$^{-1}$ in PSP can be attributed to etheric and C–OH vibrations of lignin and cellulose which decreased considerably in MPSP. The absence of these bands in Cu-MPSP and Hg-MPSP, suggests the oxidation of ether linkages to carboxyl and alcoholic groups in these materials. The simultaneous appearance of sharper and much intense bands at 1640 and 1450 cm$^{-1}$ attributed to