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Biosorption of Few Heavy Metal Ions Using Agricultural Wastes

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Abstract Since a few years a lot of interest has been shown in monitoring environmental pollution caused by heavy metals. Many methods such as precipitation, electroplating, evaporation, ion exchange etc. have been employed in the treatment of waste water, but have not proven to be much advantageous due to greater sludge production, higher reagent requirement etc. Biosorption which can be defined as the selective sequestering of metal soluble species, resulting in the immobilization of the metals is a striking technology for retaining heavy metals from dilute solutions with high efficiency. Several prior studies and research in environmental biotechnology have shown that many biosorbents occurring in the environment have the capacity to remove heavy metals from solutions. This paper presents the potential and result of studies carried out on economically cheaper natural materials like agricultural wastes such as peanut shells and banana peels as biological adsorbent for the removal of toxic heavy metal ions from waste water. The different metal ions studied were lead, copper, zinc and cadmium. The biosorption of the above metals was studied by various techniques such as Atomic Absorption Spectrophotometry, X-ray Difftaction and Scanning Electron Microscopy. Using peanut shells, adsorption of metal ions shown was in the order of lead > zinc > copper > cadmium, whereas using banana peels adsorption was in the order of cadmium > copper > lead > zinc. X-ray Difftaction results showed the presence of zinc, copper, mercury whereas the images obtained from Scanning Electron Microscope showed metal adsorption on the surface clearly at a magnification power of 500 µm and 200 µm.

Keywords: *bio-adsorption, heavy metal toxicity, Atomic Absorption Spectrophotometry, scanning electron microscopy*

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1. Introduction

Heavy metals are an important class of environmental pollutants. With the onset of fast developing industries and energy stations, metal wastes are getting discharged into the environment in many ways. There have been many instances when heavy metal toxicity has led to mass deaths. Removal of heavy metal ions from effluents can be achieved by various methods [1]. The existing technologies for waste water treatment have major problems. Costs involved in the construction of waste water treatment plants are un-economical, it consumes lot of space, and commercially they are unattractive and have disposal problems. The technologies are divided into three types namely biological, chemical and physical [2]. There were many merits and demerits caused due to high cost and disposal problems. The technologies like electro floatation, electro kinetic coagulation, coagulation combined with floatation and filtration, conventional oxidation methods by oxidizing agents, irradiation and electro chemical processes are the technologies which fall under chemical methods [3]. These chemical technologies are having many disposal problems. Ion exchange and membrane technologies are very costly. So there was a need for some alternative method which can overcome all these problems and treat the waste water in an appropriate way [4]. In bio-adsorption, removal of metal ions helps in the effective usage of bio-waste as metals stick on to the surface of biological components. Full scale biosorption process requires the biological materials which have high metal binding capabilities and specific heavy metal selectivity. It may involve one process or a blend of processes like adsorption, electrostatic interaction, chelation, micro-preciptation and ion exchange [4,5,6]. This study reveals about the importance of using an environmental pollution free approach for the removal of heavy metal ions from water. Dry peanut shells and banana peels are used as bio-adsorbents for the removal of heavy metal ions like lead, copper, zinc and cadmium. Routes of exposure to lead include contaminated air, water, soil, food, certain consumer products, lead smelters, metal processing plants and incinerators. The major sources of copper in water are corrosion of household plumbing systems, erosion of natural deposits, vehicle brake pads, architectural copper, copper-containing pesticides and marine antifouling coatings. The source of zinc contamination in water is insecticides, fungicides, exposed batteries, run off from rubber of vehicle tyres etc. The major sources of cadmium are products of industries such as metal plating, cadmium-nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, metallurgy, ceramics, photograph, textile printing, lead mining, sewage sludge, alkaline batteries and electroplating [7,8]. Banana peels have found to be best suited for copper removal from the waste water at pH 6 and adsorption capacity was found to be 27.78 mg/g. Studies also show that per gram of banana peel can remove 7.97 mg of lead ions at pH of 5.5 [9]. On the other hand, peanut shells were used to study biosorption of chromium ions and copper ions from aqueous solutions. Different kinetic models were used to study the kinetic data and it revealed that affinity of peanut shells towards copper [Cu(II)] and chromium [Cr(III)] ions were very high. The adsorption capacity of Cu(II) and Cr(III) was found to be 25.39 mg/g and 27.86 mg/g of peanut shells respectively [10]. The aim of the present work was to study the capacity of peanut shells and banana peels in adsorbing some heavy metal ions such as lead, cadmium, zinc and copper. The agricultural wastes were put up in metal complexes of known concentrations, left for some time in shaker and later washed to analyze the adsorption efficiency through Atomic Absorption Spectrophotometry (AAS) and X-ray Diffraction (XRD) method. Later the samples were observed under a Scanning Electron microscope to view its micro porous structure.

2. Materials and Methods

2.1. Sample Collection

This study was done during the months of January to April 2013. Peanut shells were collected from the oil and domestic industries of Tumkur village of Bangalore, as it is having a good production of the same. Peanut shells were selected on the basis of its freshness, dryness and hard structure. It contains 8.2% of protein, 28.8% of lignin, 37.0% of cellulose, 18.7% of hemicellulose and 2.5% of carbohydrates. Its bulk density was 120-140 kg/m^3 and ash melting point (K)>1200. The shells were thoroughly washed three to four times with distilled water to remove external dust particles, after which it was kept for sun drying under supervision for 9-11 days. Once it was completely dried, the shells were incompletely powdered using domestic mixer (Sujata mixer grinder- Dynamix model). The powdered peanut shells were subjected to sieve analysis for 15 minutes to separate peanut shells of different sizes. In a similar manner, fresh banana peels were collected from domestic wastes at home and various fruit juice centers from the surrounding areas of Chikkabanavara, Bangalore, as its availability and transportation was easy. Banana peel contains lipids (1.7%), proteins (0.9%), crude fiber (31%) and carbohydrates (59%). The various minerals present are potassium (78.10 mg/g), manganese (76.20 mg/g), sodium (24.30 mg/g), calcium (19.20 mg/g) and iron (0.61 mg/g). The peels were allowed to dry in shade for 7-8 days until all the moisture content was lost from it and the color change was observed from yellow to brownish black. Using the domestic mixer the peels were incompletely powdered and later using sieve analysis unit different fractions of peels was obtained.

Table 1. Biological components present in peanut shells and banana peel

Components	Peanut Shells	Banana Peels
proteins	8.2%	0.9%
carbohydrates	2.5%	59%
lipids	-	1.7%
lignin	28%	-
cellulose	37%	-
hemicellulose	18.7%	-
crude fibers	-	3.1%
minerals	-	potassium, manganese, iron, sodium, calcium.

2.2. Sample Processing

2.2.1. Sieve Analysis

It is a procedure used to assess the particle size distribution of the powdered samples. A typical sieve analysis involves a nested column of sieves with wire mesh cloth. The samples were shaken over nested sieves. Sieves were selected as per its specification. The sieves were nested in order of decreasing size from the top to the bottom and the sample. The samples were placed on the top sieve which has the largest screen openings and the sieves were shaken in a mechanical shaker for approximately 10 to 15 minutes, or the minimum time determined to provide complete separation for the sieve shaker being used. Each lower sieve in the column has smaller openings than the one above. At the base is a round pan, called the receiver. The powdered peanut shells and banana peels were subjected for sieve analysis. The samples were stored very carefully in air tight polythene pouches to prevent it from moisture and contamination

Figure 1. Sieve analysis column

The powdered samples weighing 2 gm was added to 100 ml metal solutions of different concentration and kept for shaking at around 140 rpm to 160 rpm at room temperature for different intervals of time. The samples of various sizes were used for study. Later the solutions were filtered using Whatman's filter paper No. 1 and was further dried and kept for further analysis.

2.2.2. Atomic Absorption Spectrophotometry (AAS)

200 ml of metal complex (lead acetate, copper sulphate, zinc sulphate and cadmium nitrate solution respectively)

containing 100 ppm of metal ion (lead, copper, zinc and cadmium ions respectively) was prepared and was used as stock solution. Dilutions were done using 100 ml volumetric flask such that the solutions contained 20, 40, 60, and 80 ppm of metal ions in it. Metal ion solution of 60 ppm was chosen for adsorption studies. 5 gm of dried and powdered peanut shells and banana peels of 425 mm and 600 mm fractions were chosen for the experiment. 5 g of both the adsorbents were added into 100 ml of 60 ppm lead solution. All the solutions were kept for shaking at 140 rpm for 12 hrs. The solutions were filtered using Whatman's filter paper. The adsorbents were collected and dried under shade and filtrate was collected to analyze for the presence of individual metal ions. The analysis was done using atomic absorption spectrophotometer (GBC 932 plus). By using an appropriate filter (lead, copper, zinc and cadmium filter respectively) in Atomic Absorption Spectrophotometry (AAS) the absorbance of metal solutions of 20 ppm, 40 ppm, 60 ppm and 80 ppm was obtained and a standard calibration curve was plotted. Now the absorbance of the filtrate was found out and from the standard graph the concentration of metal ions in the filtrate was obtained [11,12,13,14,15].

2.2.3. X-ray Diffraction (XRD)

The components of X-ray Diffraction (XRD) are X-Ray tube, X-Ray generator and Goniometer. The X-Ray tube is of sealed type with copper anode. The focus size is 1x 10mm (2.0 kw) or 2x 12 mm (2.7 kw) and rating is 2.0 kw or 2.7 kw. The X-Ray generator has a control with second side detection and uncontrolled first side detection. Goniometer has an angle 2θ and a scanning speed of 2°/ min. The angle range is from 0 to 80 and 5 to 80. A solution containing many heavy metal ions was treated with peanut shells and banana peels and after the experiment was completed, the peanut shells and banana peels were dried and then analyzed using XRD (Shimadzu, Maxima- 7000). The X-Ray Diffraction studies were done for the dried peanut shells and banana peels samples treated with synthetic waste water containing metal ions such as magnesium, zinc, copper and mercury. After metal treatment, the samples were kept in shaker, filtered and then thoroughly washed thrice to remove all metal traces and then it was re-filtered again and dried completely to be used for XRD analysis [16].

2.2.4. Scanning Electron Microscopy (SEM)

This technique is used for the high magnification of almost all biomaterials. The Scanning Electron Microscopy (SEM), Model: Hitachi SU-1500 was used for the study of ground nut shells and banana peels structure. The micrographs obtained before and after the adsorption of metal ions were compared to study the adsorption efficiency [12,17]. Data size was 1280 x 960, accelerating voltage 15000 V, deceleration voltage was 0 V and emission current was 86000 nA. The vacuum of 15 kV was maintained throughout and the magnification power was kept at 50, 100, 200, 400 and 500 µm. SEM analysis was used for the study of banana peels and peanut shell structures using high magnification, the micrographs obtained before and after the adsorption of metal ions were compared to study the adsorption efficiency. The study was done for the metal ions mercury, lead, copper, magnesium, chromium, zinc and cadmium.

3. Results

3.1. Sieve Analysis

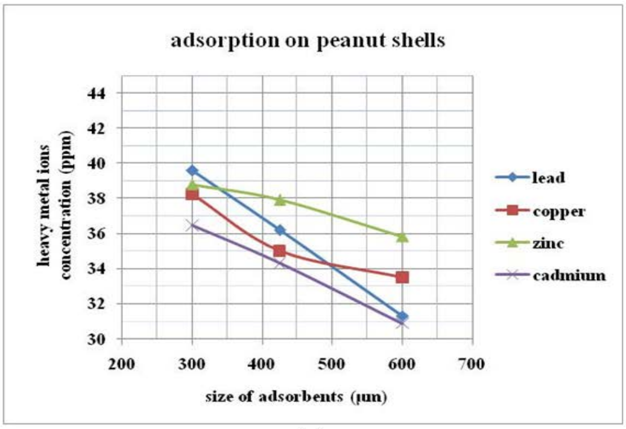
Out of all the fractions obtained after the sieve analysis, the different sample fractions of 2100µm, 1700µm, 850µm, 600µm, 425µm, 300µm, 212µm, 150µm, 106µm, 75µm and 53µm were obtained. The percentage of aggregate passing through each sieve, was found out by calculating the percent of samples retained in each sieve, which was done by using the following equation,

$$\% \text{ Retained} = \frac{W_{Sieve}}{W_{Total}} \times 100\ \%$$

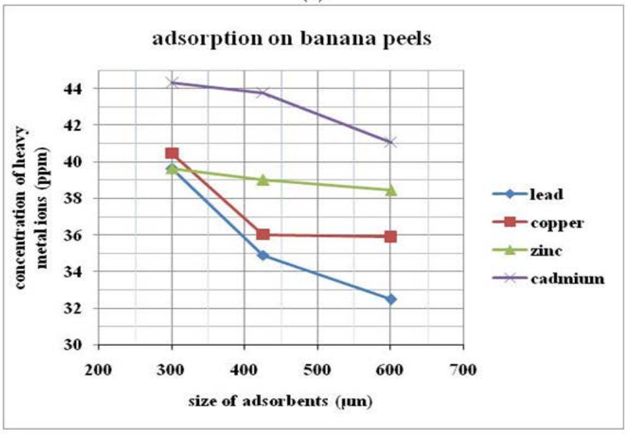
where W_{Sieve} was the weight of aggregate in the sieve and W_{Total} was the total weight of the aggregate [18].

3.2. Atomic Absorption Spectrophotometry (AAS)

Atomic absorption spectrophotometery analysis was done for the banana peels and peanut shells treated with metal solutions. Comparatively peanut shells showed better adsorption of heavy metal ions than banana peels. The results showed that peanut shells adsorbed metal ions in the order of lead > zinc > copper > cadmium where as banana peels showed adsorption in the order of cadmium > copper > lead > zinc [19].



(a)



(b)

Figure 2. (a) Adsorption of metal ions on peanut shells; (b) Adsorption of metal ions on banana peels

3.3. X-ray Diffraction (XRD)

The following graphs were obtained which were compared to the standard JCPDS card, after which the presence of metal ions was detected.

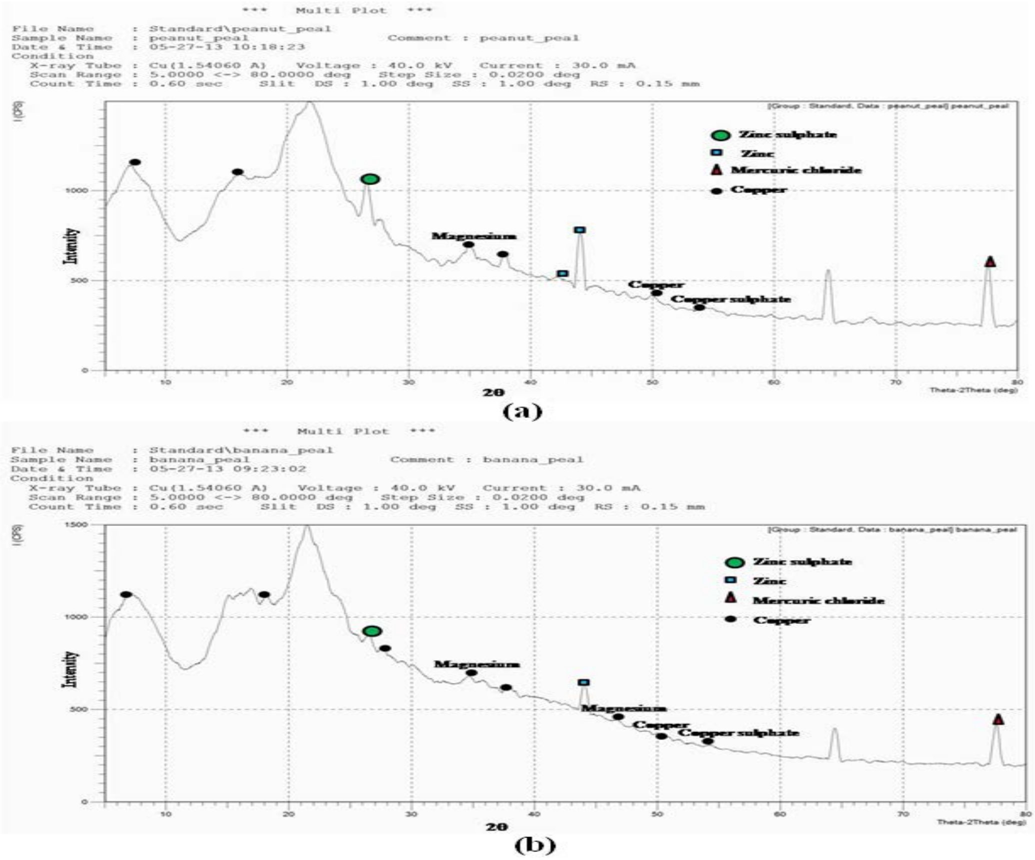


Figure 3. (a) XRD analysis of metal ions on peanut shells; (b) XRD analysis of metal ions on banana peels

3.4. Scanning Electron Microscopy (SEM)

SEM was used for studying the structure of peanut shells and banana peels. This study revealed the micro porous structure of peanut shells as well as banana peels. The SEM micrographs of peanut shells and banana peels are as shown below.

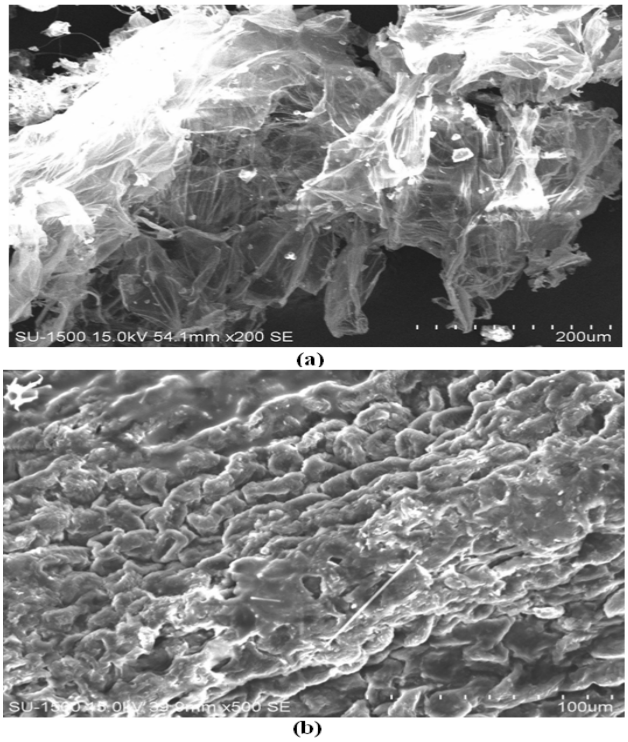


Figure 4. (a) Micrographs of peanut shells and banana peels; (b) Micrographs of peanut shells and banana peels

4. Discussion

4.1. Sieve Analysis

The powdered peanut shells and banana peels were subjected for sieve analysis, after which sizes of 600µm, 425µm and 300µm were used for adsorption studies. The powdered peanut shells and banana peels of maximum and minimum sizes, obtained after sieve analysis very not taken up for the experiment, as they will have either a lot of surface area for adsorption or not much surface. The fractions in between were selected. The cumulative percent of aggregate retained in each sieve was calculated by adding up the total amount of aggregate that was retained in each sieve and the amount in the previous sieves. The cumulative percent passing of the aggregate was found by subtracting the percent retained from 100%.

4.2. Atomic Absorption Spectrophotometry (AAS)

Atomic absorption spectroscopy is a spectro-analytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples employed in pharmacology, biophysics and toxicology research. The heavy metal ion removal by adsorption on peanut shells and banana peels from synthetic waste water are related to the size of the adsorbents, as the latter is related to the surface area of adsorbents for adsorption [20]. The samples were analyzed using AAS to check the concentration of metal ions left out in solution. It was done by keeping rising ppm level of samples for analysis. The sample in which the concentration of metal ions was to be measured was sprayed onto the flame generated in the AAS and the ions present in that solution got ionized and the absorbance of those ions at respective wavelength was obtained. The least size of peanut shells and banana peels obtained after sieve analysis showed the maximum removal of metal ions. A typical result from atomic absorption spectroscopy showed that as the size of the adsorbents increased the efficiency of metal ion removal decreased. Among the considered fractions of adsorbents, a size of 300µm showed effective removal of metal ions. The efficiency of adsorption varied for different metal ions. This method was found to less time consuming, accurate and more convenient [21,22].

4.3. X-ray Diffraction (XRD)

X-ray crystallography is a technique used to determine the atomic and molecular structure of a crystal. The atoms in the crystal cause the beam of X-rays to diffract in many directions. The crystallographer will produce a three-dimensional picture of the density of the electrons by measuring the angles and intensities of the diffracted beams. The position of each atom in the crystal also their chemical bonds, their disorder and various other information can be determined by making use of the density. By using Bragg's law the interference pattern of X-rays scattered by crystals can be studied. Diffraction has been developed to analyze the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest [23]. X-ray diffraction unit consists of a goniometer onto which the sample will be mounted. The samples are then bombarded with X-rays and then it is gradually rotated producing a diffraction pattern of regularly spaced spots. Two dimensional images are taken at different rotations which are then converted into three-dimensional model of the density of electrons using the mathematical method of Fourier transforms, combined with known chemical data of the sample. To confirm the adsorption of a particular heavy metal ion, X-Ray diffraction (XRD) studies were carried out [24].

4.4. Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The number of secondary electrons is a function of the tilt of the surface. On a flat surface, the plume of secondary electrons is mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the tilt of the surface is created [25]. At first, when the peanut shells and banana peels untreated with metal ions were seen under scanning electron microscopy at a magnification power of 500 µm and 200 µm, there were no traces of metal ions seen and the samples became unstable on the stage after sometime due to high energy beam of electrons. The samples were not able to stay solidified for a longer time. But with metal treated samples of peanut shells and banana peels, at a magnification power of 500µm clear micrographs were obtained from SEM which showed the presence of heavy metal ions at the pores of peanut shells and banana peels. At a lower magnification power of 200µm also, where the beam of electrons is of high energy, the samples did not move or get diluted and stayed fixed onto the stage, indicating the presence of metal ions which kept them intact. The micrographs of peanut shells and banana peels obtained from SEM represented a large surface area for heavy metal ion adsorption.

5. Conclusion

Making use of bio-adsorbents is an effective method to adsorb toxic heavy metals from effluents not polluting the ground water and at the same time utilizing the discarded open agricultural wastes in the environment for a useful purpose of waste water treatment. This method not only requires minimal energy input, less labour and low investment, but also proves to be very economical, biodegradable and effective compared to synthetic adsorbent and chemicals. The bio-adsorbents once used could be re-used through desorption methods for a certain period of time and this could be employed commercially in the future.

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