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Cauliflower Leaves, an Agro waste : Characterization and its Application for the Biosorption of Copper, Chromium, Lead and Zinc from aqueous solutions

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ABSTRACT

Cauliflower leaves being non-edible, is frequently discarded from vegetable markets and it forms a part of Municipal Solid Wastes. The present study focuses on using the cauliflower leaves as a biosorbent for the removal of heavy metals Copper, Chromium, Lead and Zinc from spiked solutions of known concentrations as well as from industrial effluents using batch method. The pH, bulk density, ash content, and iodine index of the cauliflower leaves powder were calculated and further characterizations of the leaves like surface morphology and functional groups present on the surface of the biosorbent were carried out using E-SEM and FT-IR respectively. The heavy metal concentrations in the solutions were found out using ICP-AES analysis. After the biosorption process, the removal of heavy metals was found to be 80.43%, 57.26%, 99.39% and 69.91% for Copper, Chromium, Lead and Zinc respectively from spiked solution at pH 7 after adding 1% adsorbent dose at 30°C temperature for 60 minutes. The biosorption was also carried out for effluents collected from industries like powder dusting, chemical, electroplating, paper mill and textile industry and removal of all four metals were found to be in the range of 26% to 100% after biosorption process. Characterization of the biosorbent by FTIR showed the presence of various functional groups like hydroxyl, aliphatic methylene group, aromatic groups, etc. which might have involved in interacting/ binding to metal ions. The SEM images of the material showed distinct changes in the surface morphology after interacting with the metal solutions which may be due to metal stress on the biosorbent.

Keywords: Biosorption, pH, bulk density, Ash content, Iodone Index, ICP-AES, FT-IR, SEM

I. INTRODUCTION

Most of the industries in India are situated along the banks of the river for easy source of water and also for discharge of their effluents. According to Central Pollution Control Board (CPCB) report, Maharashtra state has the largest number of polluted river water stretches in the country. The industries contributing to such pollution include petrochemical industries, sugar mills, distilleries, leather processing industries, paper mill, agrochemicals and pesticides manufacturing industries and pharmaceutical industries. The wastes often contain a wide range of contaminants such as petroleum hydrocarbons, chlorinated hydrocarbons, toxic metals, various acids, alkalis, dyes and other chemicals. Hence there is a need for extensive monitoring of discharged industrial effluents which has the potential to pollute the nearby water bodies like rivers or creeks [1]. Environmental pollution particularly from heavy metals and minerals in the wastewater is the most serious problem in India. Due to extensive anthropogenic activities such as industrial operations particularly mining, agricultural processes and disposal of industrial waste materials; their concentration has increased to dangerous levels [2]. In most wastewaters, the concentration of heavy metals present is much larger than the safe permissible limits [3]. The heavy metals from waterbodies may accumulate in the body of flora and fauna and later on may pass through the food chain into the plants, fishes and human beings. These toxic metals enter the human body mostly through food and water. However, it also enter through inhalation of polluted air, use of cosmetics, drugs, poor quality herbal formulations (herbo-mineral preparations) and Unani formulations. In humans, heavy metal toxicity can cause chronic degenerative diseases like mental disorders, pain in muscles and joints, gastro intestinal disorders and vision problems. Genotoxicity and cancer can also occur. Sometimes the symptoms are vague and difficult to diagnose at early stage [4].

Over the decades, several methods have been devised for the treatment and removal of heavy metals. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. But all these methods show disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal [5]. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. Biosorption can be a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents [6]. Several researchers have reported the removal of heavy metal through algae, marine algae, bacteria, yeast and higher plants in immobilized as well as in free state [7][8]. The fins of *Catla catla* fishes were found to be successful in adsorbing copper, chromium, lead and zinc from different industrial effluents [9]. The present work focusses on using one of the commonly discarded vegetable wastes, cauliflower leaves for the biosorption of heavy metals from industrial effluents.

II. MATERIALS AND METHODS

A. Preparation of Biosorbent

The Cauliflower Leaves (CL) was collected from local vegetable market situated in Andheri, Mumbai, M. S. India. The CL was washed with tap water for multiple times followed by thrice washing with distilled water to remove adhering dust particles. The washed leaves were then oven dried at 80^{o}C till crispy. The dried materials were grounded into fine powder using kitchen mixer grinder. The powdered CL was then stored in polythene bags till further use.

B. Preparation of metal solutions

Stock solutions (1000 mg/l) of heavy metals were prepared by dissolving analytical grade of respective metal salts like $CuSO_4.5H_2O$, K_2CrO_4, $Pb(NO_3)_2$ and ZnO, in deionized water. The working standard solution (50 mg/L) was prepared by diluting stock solution to appropriate volumes.

C. Treatment of metals solutions with CL powder

The biosorption process was carried out for four toxic heavy metals (Copper, Chromium, Lead, Zinc). 100 ml of 50 mg/L solution of each metal concentration were treated with 1% of biosorbent at pH 7 for 60 minutes at 30^{o}C with occasional stirring. The solution was then filtered using Whatmann filter paper No. 1. The metal concentration of the filtrate was then carried out using ICP-AES at SAIF Dept. IIT Bombay.

D. Treatment of industrial effluents with CL powder

The effluents samples were collected from different industries like paper mill, chemical industry, electroplating industry, powder dusting industry and textile industry situated in the Navi Mumbai MIDC areas. The effluent samples were stored in polythene bottles till further use. The metal concentration in the industrial effluents was found out using ICP-AES at SAIF Dept. IIT Bombay.

E. Calculation of efficiency of biosorption

Percentage of metal removal was calculated as follows:

$$\text{Metal Removal (\%)} = \frac{100\,(Co-Ce)}{Co}$$

Where Co is the initial metal concentration (mg/l), Ce is the final metal concentration after biosorption (mg/l).

F. Characterization of Cauliflower Leaves

The pH, bulk density, ash content and iodine index of cauliflower leaves were calculated as per protocols mentioned in [10].

1) pH of the biosorbent: One gram of biosorbent was added to 100ml of deionized water in a conical flask. The mixture was stirred for 15-20 minutes and filtered. The pH of the filtrate was determined using pH meter.

2) Ash Content: The ash content was determined by heating one gram of each sample in muffle furnace set at temperature of 500°C for two hours. The materials were allowed to cool in desiccators for several minutes. Then ash content (%) was estimated using following formula:

$$\text{Ash Content} = \frac{W_2 - W_0}{W_1 - W_0} \times 100$$

Where W_0 – Weight of empty crucible (gm)

W_1 – Weight of empty crucible + biosorbent (gm)

W_2 – Weight of empty crucible + ash (gm)

3) *Bulk Density:* The bulk density was determined by measuring the 10ml capacity of dried cylinder and sample was packed inside the cylinder and weighed. The difference in the weights gave the mass of the biosorbent. Bulk density of the sample was calculated using the following formula:

$$\text{Bulk density (gm/l)} = \frac{M_2 - M_1}{V}$$

Where M_2 – mass of cylinder + sample

M_1 – mass of empty cylinder

V – Volume of cylinder

4) *Iodine number (or iodine index)*: 0.1 g of biosorbent was placed with 25 mL of iodine solution in a 250 mL conical flask and was shaken for 1 min. After that the solution was filtered and 10 mL of the filtrate was taken in a conical flask. The solution was titrated with 0.01 N sodium thiosulfate solution until it become clear. The iodine number of the biosorbent was determined by using the formula as follows.

$$\text{Iodine number} = \frac{V * (Ti - Tf) * Ci * Mi}{Ti * g}$$

Where V- The volume of iodine solution (25 mL)

Ti-The volume of sodium thiosulfate solution used for the titration of 10 mL iodine solution

Tf -The volume of sodium thiosulfate solution used for the titration of 10 mL filtrate

g- Represents the weight of adsorbent (0.1 g)

Mi- the molar weight of iodine (126.9044 g/mol)

Ci is the concentration of iodine solution (0.01 N)

5) Fourier Transformed InfraRed (FT-IR) Spectroscopy: The FTIR study was carried by using potassium bromide (KBr) disc method over the wavelength region 4,000cm^{-1} to 400cm^{-1} to determine the presence of functional groups present on the biosorbent. The ratio of sample: KBr was maintained as 1:10. The FTIR spectra were recorded on a FTIR spectrophotometer – FT/IR – 4100 type A (C208161016) using a standard light source and TGS detector at Department of Chemistry, Birla College, Kalyan.

6) *Environmental Scanning Electron Microscopy (E-SEM):* The surface morphology of the biosorbent

before and after heavy metals adsorption were observed using Environmental Scanning electron microscopy (E-SEM) at IIT-Bombay. The powdered samples were placed on the sample stubs. The samples were then dried under IR light for 2-3 minutes followed by platinum coating for 600 seconds using JEOL JFC-1600 Auto fine Coater. Samples were then scanned using FEI QUANTA 200 E-SEM operating at 15 kV. The image analysis of the biosorbents were carried out under 2500x magnification.

III. RESULTS AND DISCUSSION

The cauliflower leaves (CL) as a biosorbent showed adsorption of all four metals (Cu, Cr, Pb and Zn) under the given conditions. The efficiency of CL for biosorption varied for all four metals which was calculated in the form of percent removal (Table 2). Also, the characteristics of Cauliflower leaves were as follows:

Table 1. Characterisitics Of Cauliflower Leaves

Characteristics	Cauliflower leaves
pH	7
Ash content (%)	10.5263
Bulk density (gm/ml)	0.2887
Iodine Index (mg/gm)	368.9081

Table 2. Percent Removal Of Heavy Metals From Spiked Samples And Industrial Effluents

Industry	% Removal of Heavy Metal			
	Copper	Chromium	Lead	Zinc
Spiked Sample	52.03	47.84	72.08	47.31
Powder Dusting	--	100	18.93	99.29
Electroplating	40.84	31.23	55.82	53.65
Paper Mill	100	--	19.68	84.02
Textile	100	97.44	54.12	44.54
Chemical	99.22	59.9	5.77	26.42

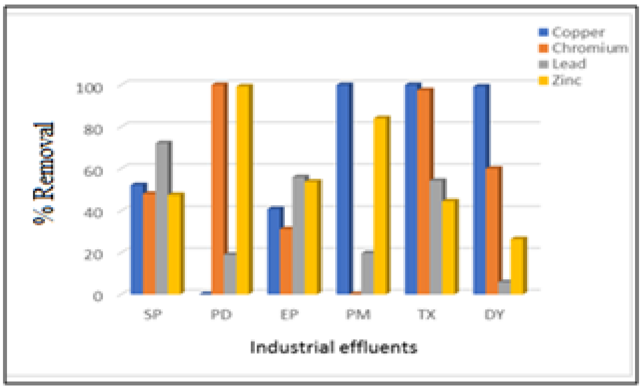

Figure 1. Figure showing percent removal of heavy metals from spiked solution and industrial effluents

The functional groups present on the surface of CL were found out using FT-IR (Table 3). Figure 2a shows the FTIR spectrum of biosorbent before the biosorption of heavy metals. The appearance of a broad peak at 3434.6- 3450.99 cm^{-1} is due to the stretching vibration of free-OH or -NH (str.) on the adsorbent surface. The peaks at 2924.52 cm^{-1} to 2852.2 cm^{-1} indicate the C-H stretching mode of aliphatic compounds. Peaks detected at 1639-1640cm^{-1}, and 1412-1414 cm^{-1} correspond to aromatic C=C bending, C-C stretching (in ring) aromatic respectively. The peak at 1020 cm^{-1} might be due to C-O stretching of alcohols, carboxylic acids, esters, and ethers present on the surface of the biomass. Figure 2b shows the spectra of biosorbent after the adsorption of heavy metals. The spectra of CL did not show considerable changes in the frequencies of functional groups after the adsorption of heavy metals at the surface of biosorbent which indicates that it is due to their involvement in sorption process through physical Vander Waals forces. Hence, shifting in the peaks at was not noticeable. This study indicates that there are functional groups *viz.* carboxyls, hydroxyl, phosphate, amino and amide, present on the biosorbent which may facilitate heavy metal binding on the cell surface.

Table 3. Ft-Ir Spectra Of Cauliflower Leaves

Sr. No	Location wave number (cm^{-1})		Vibration	Functional group
	Before Biosorption	After Biosorption		
1	3434.6	3450.99	0-H str.	Bonded and non bonded hydroxyl groups and water
2	2924.52	2924.52	C-H str. asymmetrical	Aliphatic methylene group
3	2853.17	2852.2	C-H str. symmetrical	Aliphatic methylene group
4	2347.91	2336.06	N-H Str.	Ammonium ions
5	1639.2	1640.16	C=O, COO- str. C=O str.	Amide I, carboxylates aromatic ring modes, alkenes
6	1561.09	1562.06	$-NO_2$ groups	Nitrogroups
7	1414.53	1412.6	C-C str. (in ring)	aromatic
8	-	1339.32	S=O	sulfone
9	1020.16	1020.12	-C-H plane bending	Aromatic
10	802.242	801.278	=C-H bend	Alkenes
11	644.108	643.144	S-O bending	sulphate

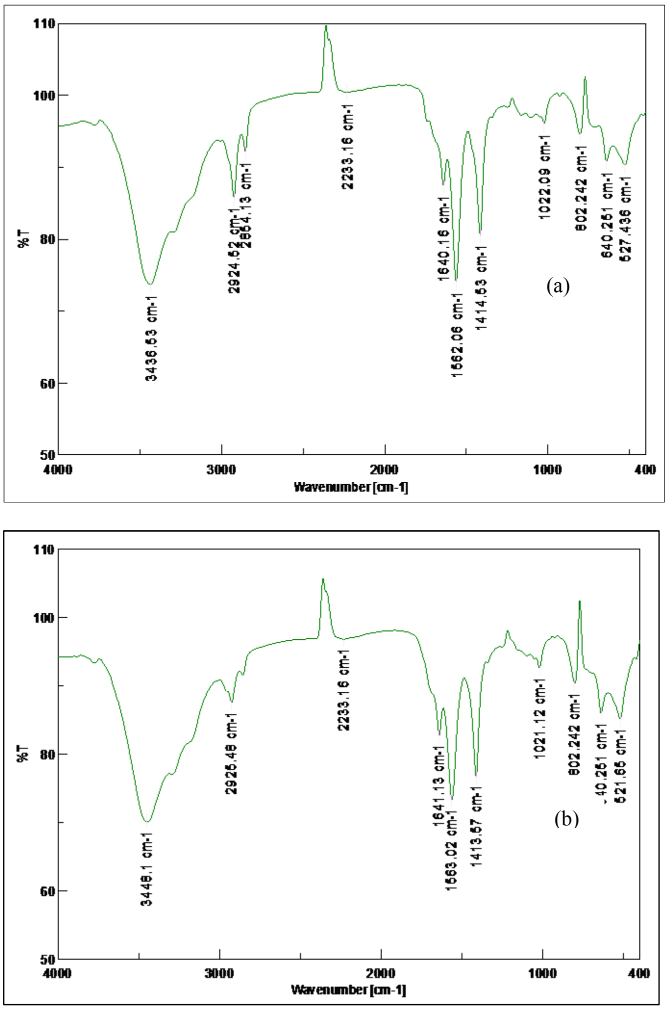

Figure 2. FT-IR Spectra of Cauliflower leaves (a)before treatment with heavy metals (b) after treatment with heavy metals

The SEM image of cauliflower leaves before biosorption shows longitudinal filaments which got circular after biosorption process. This may be due to heavy metal stress. Tubular pores and cavities increase the surface area of the biosorbent. Hence, SEM study showed that there is distinct change in surface morphology of the biosorbent after treatment with heavy metals.

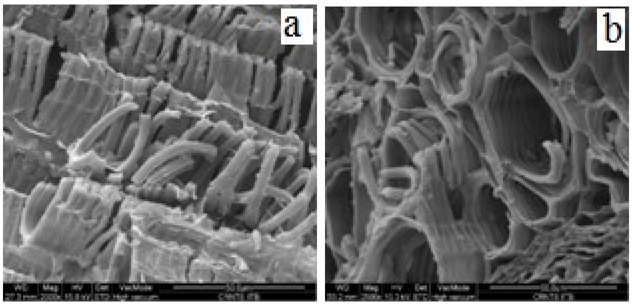

Figure 3. SEM Images of Cauliflower leaves (a) before treatment with heavy metals (b) after treatment with heavy metals

III. CONCLUSION

The cauliflower leaves powder was found to be efficient in adsorbing heavy metals from spiked metal solutions as well as from different industrial effluents. The characteristics of the CL powder like iodine number showed good value (i.e. 368.9081 mg/g) which may lead to its application as a commercial adsorbent of heavy metals. The FTIR spectra of the adsorbent did not show much difference before and after treatment with adsorbent which may indicate that adsorption is mostly physical in nature via Vander Waals force of attraction. This may lead to easy desorption of adsorbed metals and may help in recovery of metals. Hence, the cauliflower leaves which is discarded as wastes from markets can be considered as a good adsorbent for removal of heavy metals from industrial effluents.

IV. ACKNOWLEDGEMENT

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