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Removal of Copper from aqueous solution using local agricultural wastes as low cost adsorbent

N.N Bandela[1*], M.G. Babrekar[1], O.K. Jogdand[1], Geetanjali Kaushik[2]

[1]*Department of Environmental Science,*
Dr.BabasahebAmbedkarMarathwada University, Aurangabad, 431004 (M.S.) India.
[2] *Mahatma Gandhi Mission's, Jawaharlal Nehru Engineering College, N-6 CIDCO, Aurangabad, 431004 Maharashtra, India.*

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**Corresponding author. E-mail: geetanjaliac@gmail.com (N.N. Bandela); Phone: +91 9823207519*

Abstract
Human activities have caused extensive contamination of both surface and ground water with toxic heavy metals. On account of their toxicity, bio-accumulation and persistency in the environment these metals are of specific concern. In this research, toxic metal ion biosorption on inexpensive and efficient biosorbents from agricultural waste materials were investigated. It was found that the carbons made from wheat, corn, sugarcane and *bajra* agro-wastes can be effectively used in the reduction of copper from aqueous solution. *Bajra* was one of the most efficient wastes with an ability to reduce copper by approximately 98 percent. Hence, agro-wastes being abundantly available can prove to be a low cost solution for removal of toxic copper ions.

Keywords: Copper, waste water, biosorption, agro-wastes

1. Introduction
Over the last few decades environmental pollution caused by anthropogenic activities has increased exponentially and has reached alarming levels in terms of adverse effects on living organisms [1]. Human activities such as mining, waste accumulation, industrial activities, road traffic and the use of agro-chemicals (fertilisers and pesticides) have caused extensive contamination of both surface and ground water with toxic heavy metals [2]. Heavy metal discharge into aquatic ecosystems is a matter of concern. It is known that 11 metals namely Pb, Cr, Hg, Ur, Se, Zn, As, Cd, Co and Ni out of the 20 classified metals are referred to as toxic and are released into the environment in quantities which pose serious risks to human health [3]. On account of their toxicity, bio-accumulation and persistency in the environment these metals are of specific concern [4]. Various episodes of heavy metal toxicity such as Minamata in Japan due to methyl mercury contamination in streams and Itai-Itai resulting from cadmium contamination have been reported in the literature [5].Therefore; even at low concentration the heavy metals discharged from industries into water bodies pose a significant risk to animal health as well as the environment [6]. Copper is a hazardous heavy metal that is used in various industries such as smelting, plating, electroplating, manufacture of brass and copper based agro-chemicals. Though copper at a lower concentration is essential for living organisms, at a higher concentration it becomes potentially toxic. Copper toxicity, also called copperiedus, refers to the consequences of excess of copper in the body. Copper toxicity can occur as a result of intake of food and water containing excess copper. Further copper does not degrade in the environment and its presence in the soil adversely impacts the activities of micro-organisms thereby slowing down the decomposition of organic matter [7]. In living organisms copper

intake in excess causes its accumulation in the liver and leads to gastrointestinal disorders, damage to kidneys and anemia. It has been reported that increased incidences of lung cancer among industrial workers has been blamed on the inhalation of copper containing sprays [8]. Hence, it is necessary to ensure that copper is removed from waste waters prior to its discharge into water bodies as water is essential to human life and necessary for almost all domestic, agricultural and industrial activities. Various technologies have been applied and found effective in heavy metal removal. Such technologies include electrochemical precipitation, membrane separation, ion exchange, adsorption [9, 10]. However, these conventional techniques are associated with their limitations which include sensitive operating conditions, low efficiency, sludge production and also the disposal is expensive [11]. Amongst these methods, adsorption has been found to be promising on account of its simplicity, feasibility and economic viability [5]. Application of moulds, seaweeds, dead microbial biomass and agro-wastes has been successfully undertaken in removal of heavy metals [12, 13, 14, and 15]. In recent times attention has been focused on biomaterials that are generated as by-products or wastes at large scale either from industrial or agricultural operations. The main advantages associated with such materials include low cost, high process efficiency, low sludge production and the possibility of metal recovery. Studies reveal that a wide variety of agro-wastes such as sawdust, wheat shells, lentil shells, wheat straw, rice shells, rubber leaves, palm leaf powders have been successfully tried as low cost adsorbents.

It has been reported that in India about 600 MT (million tonnes per year) wastes are generated primarily from agricultural sources. The major types of wastes which are generated from agricultural sources include sugarcane baggase, straw and husk from paddy and wheat, vegetable wastes, tea, groundnut shell, jute fibre, coconut husk, wooden mill waste etc. Around 90 MT of sugarcane bagasse, 20 MT rice husk, 12 MT rice wheat straw and 11 MT groundnut shell are generated in India on an annual basis [16, 17]. State of Maharashtra ranks second in the production of sugarcane and cotton whereas production of food grains is somewhat lower than other states. Marathwada being a large producer of these agricultural products, the agro wastes of these products are available easily at low cost. The use of these agro-waste materials is one step ahead in the process of solid waste management. The rapid uptake and high capacity of chalf, rice husk, sesame, sunflower and tea waste have indicated that these could be a better alternative for the removal of Pb (II) from real wastewater by sorption process [18].

Several studies have investigated the removal of heavy metals by adsorption on agricultural wastes. A study [19] concluded that bagasse was a better adsorbent for Cd^{2+} and Fe^{2+} (at 5 mg/ℓ concentration). The high sorption capacity of bagasse was attributed to the presence of negative charge on the surface of bagasse that makes it capable of adsorbing the positively charged metals Cd^{2+} and Fe^{2+}. The adsorption of copper (II) ions on to dehydrated wheat bran was investigated as a function of initial pH, temperature, initial metal ion concentration and adsorbent dosage. The percent adsorption of copper (II) ions by dehydrated wheat bran was obtained as 96.4% due to increase in the surface area of the wheat bran resulting from acid treatment while 12% of the copper (II) ions in solution were removed by using the raw wheat bran, at optimum adsorption conditions [20].

It is evident from the above discussion that heavy metal pollution particularly caused by copper is harmful to the environment and living organisms on account of its toxic effects. It is imperative that simple cost effective techniques be evolved for dealing with this issue especially for developing countries which lack sophisticated removal techniques and finances for it. Biosorption is a suitable process to remediate waste water containing copper. India's Marathwada region in the state of Maharashtra is a top producer of agricultural produce and hence, agrowastes are also generated in high quantities. Numerous studies have investigated the potential of agro-wastes in heavy metal removal. Therefore, to reduce environmental risks associated with copper pollution it is essential to develop low cost adsorption techniques with the use of various agricultural wastes. In this study we report the potential of 4 types of local agricultural waste materials in copper removal from aqueous solution. The activated carbons of wheat, *bajra*, sugarcane baggase and corn were used (Table 1).

Table 1: Agricultural waste materials used for the study

SNo.	Scientific names	Common names
1.	*Triticumaestivum*	Wheat
2.	*Pennisetumglaucam*	Bajra
3.	*Saccharumofficinarum*	Sugarcane
4.	*Zea mays*	Corn

2. Materials and Methods

2.1Material collection and preparation:

Agro wastes of wheat, *bajra*, sugar cane and corn were collected from the agricultural field of Phulambri Taluka of Aurangabad District (M.S.). 5 Kg of agro-wastes were collected respectively and kept in a dry place at room temperature. For each experiment 100 g of material of particular waste was used for making activated carbon. Agro wastes were initially washed with water and then dried for 24 hour in an open environment, followed by cutting the pieces of waste in smaller parts and allowed for drying in a muffle furnace, i-Therm (Model- AI-7741) at 300^0C-400^0C to acquire carbon. Later, the carbons of wheat, *bajra* and corn were washed with 2% hydrochloric acid (HCl)where as carbon of *bajra* was washed with 1% sulphuric acid (H_2SO_4) solution and kept in oven (Quality Instruments & Equipments- Model –DTC-72) for 2 hours for the activation of carbon. The activated carbons so acquired were rinsed thoroughly with distilled water and dried at 100^0C for 1 hour and further ground by Mortar and Pestle method then preserved at room temperature (25^0C) in plastic containers with proper labelling for further use [21].

2.2 Preparation of Stock Solutions:

Copper solution of 1000 ppm was prepared as 1g of copper metal was dissolved in 50 ml of 5M nitric acid. Then it was diluted to 1 litre in a volumetric flask with deionised water, this was the stock solution of 1000 ppm of copper solution. Finally, sets of 5 ppm and 10 ppm concentrations were prepared by dilution of 1000 ppm copper solution which was used as adsorbate in the experimental work.

2.3 Adsorption studies:

Pilot studies were done for estimation and reduction of copper ions through activated carbon by applying adsorption process. The adsorbing column i.e glass rod column of 50ml capacity was used for the study. Preliminarily 5g of activated carbon was filled in each adsorption column. Then, 50 ml of Copper solutions of 5 ppm and 10 ppm concentrations were passed through these adsorbing columns. The retention of 30 min was recorded for the 1st pass of the concentrations. This process was repeated thrice to obtain maximum % adsorption of heavy metals by the adsorbents [22].

The amount of heavy metal reduction was calculated from the amount of heavy metals adsorbed on the adsorbent and amount of metal ions available in the adsorbate solutions,
the equation of % reduction of heavy metals is shown as below:

$$\% \, Reduction \ = 100 - \frac{\text{Concentration of adsorbate}}{\text{Initial concentration of adsorbing solution}} x100$$

2.4 Atomic Adsorption Spectrophotometer – Elico-Model SL-163

Entire experimental work was done on Atomic Adsorption Spectrophotometer (Elico-SL-163). The calibration curves were made using standard solution of the metal ion by following the procedure given in the manual using appropriate detector in the wavelength range suitable for the concentration range.

3. Results and Discussion

The % removal of 5 ppm of copper solution with agro-wastes was found in the order *Bajra*>Wheat> Corn> Bagasse were found 98>74>71>70 as shown in (Table 2). It is evident that *Bajra* agro-waste was more efficient as compared to the other agro-wastes in terms of % reduction for 5 ppm copper solution.

Table 2: Copper removal by agro-wastes (5 ppm concentration)

SNo.	Activated carbon Sources	pH	Initial Cu Conc. (ppm) (A)	Cu Conc. after adsorption (ppm) (B)		% Reduction (100-C)
1	Wheat	5.0	5.55	1.43	25.76	74.23
2	*Bajra*	5.6	5.55	0.07	1.26	98.74
3	Sugarcane	5.8	5.55	1.67	30.09	69.91
4	Corn	5.6	5.55	1.57	28.29	71.71
					Average	78.64

Agricultural waste materials mainly are composed of lignin and cellulose. Other constituents include hemicelluloses, lipids, sugars, proteins, water, starches, ash and various other compounds which contain several functional groups. Functional groups which are present in these molecules include carbonyl, acetamido, phenolic, amido, carboxyl, amino, alcohols, esters and sulphydryl [23, 5]. It is these groups which possess affinity for complexation with metals. During biosorption studies various researchers have confirmed the presence of functional groups and their complexation with heavy metals through spectroscopy [24]. From figure 1 presented below it is evident that agro-wastes were effective in removing copper from the aqueous solution.

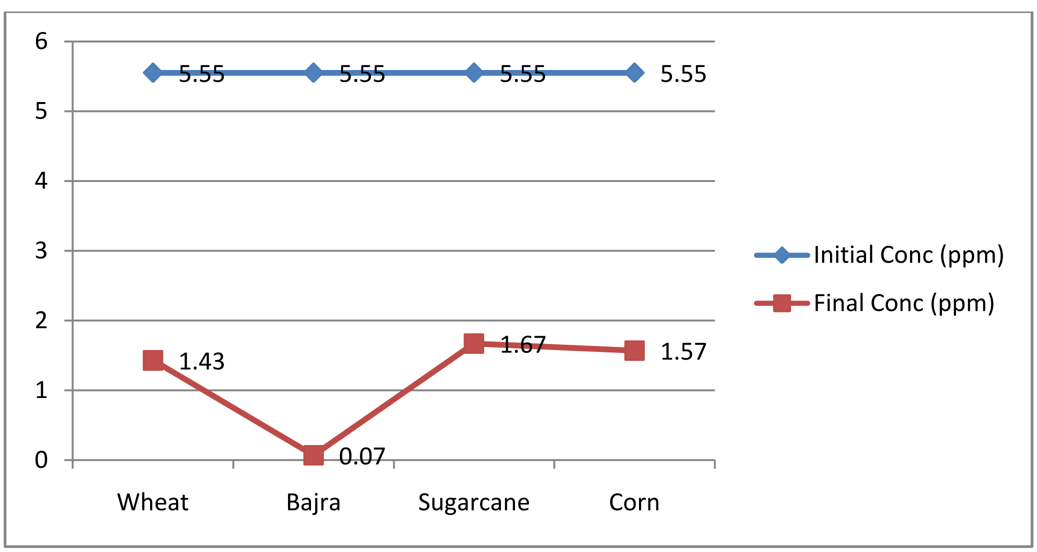

Figure 1: Copper removal by agro-wastes (5 ppm concentration)

Table 3: Copper removal by agro-wastes (10 ppm concentration)

SNo.	Activated carbon Sources	pH	Initial Cu Conc. (ppm) (A)	Cu Conc. after adsorption (ppm) (B)	% of Cu Obtained (C = B/A x 100)	% Reduction (100-C)
1	Wheat	5.3	11.52	0.79	6.86	93.14
2	*Bajra*	5.5	11.52	0.69	5.99	94.01
3	Bagasse	5.5	11.52	0.26	2.26	97.74
4	Corn	5.7	11.52	0.53	4.61	95.39
					Average	95.13

For 10 ppm copper solution the % reduction by agro-wastes was higher for all the materials used. It followed the order Bagasse (98%)> Corn (95%)> *Bajra* (94%)> Wheat (93%) (Table 3). Other studies have also shown that the adsorption of Cu (II) metal ion by husk of green gram seeds (*Phaseolus aureus*) was better at higher metal ion concentration [25].

Other studies have also concluded that bagasse, corn and *bajra* are effective in removal of heavy metals. Modified bagasse fly ash removed Cr (VI) by 67% [26]. Bagasse was efficient in removing Cd (II) and Zn (II) by up to 90–95% [27]. Pre-treated bagasse with NaOH and CH_3COOH removed Cr (VI) and Ni (II) by 90% and 67% respectively [28].Wheat shell was highly efficient in removing Cu (II) up to 99% [29]. Bagasse fly ash removed Cd (II) and Ni (II) by 90.0% [30]. Bagasse fly ash was highly efficient in Cr (VI) removal by up to 96–98% [23]. Chemically treated bagasse was able to remove Cr (VI) by 50–60% [31]. A maximum removal of about 99% was observed at an adsorbent dosage of 5g/100 ppm of *bajra* powder. The increase in adsorption was attributed to increase in availability of active sites on account of increase in effective surface area of adsorbent. Similar trend was also observed for Ni (II) and Fe (II) [32]. Sugarcane bagasse, maize corn cob, jatropha oil cakes were quite effective in removal of Cr (III) by up to 97% [24].Figure 2 shows copper removal by agro-wastesat 10 ppm copper solution. It is clear that activated carbon (adsorbent) made from agro-wastes can effectively reduce the percentage of 5 ppm and 10 ppm copper.

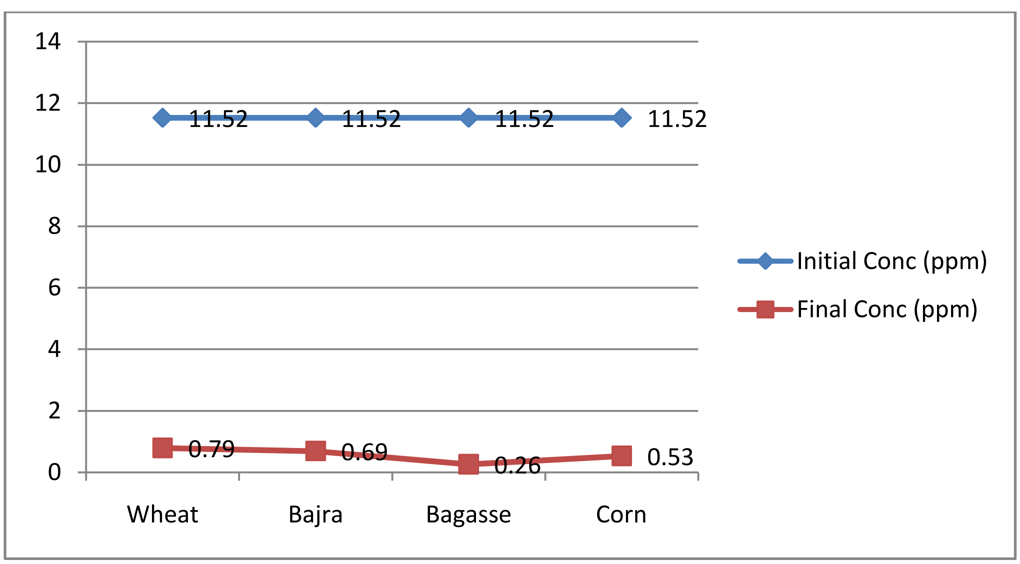

Figure 2: Copper removal by agro-wastes (10 ppm concentration)

The present investigation reveals that the low cost adsorbents like wheat, *bajra*, sugarcane bagasse and corn can be used as an effective adsorbent for the treatment of wastewaters containing metal ions of copper.

Limitations of the study

1. In this research authors were able to study only copper however, other heavy metals such as nickel, chromium, mercury and cadmium which are part of industrial effluent also deserve attention in this regard.
2. In addition the effect of different pH and dosage levels on adsorption process also need to be carefully examined in future studies.

Future Scope

1. Adsorption by agro-wastes is significantly enhanced by giving suitable treatments to the agro-wastes with acids etc. Future studies must explore this dimension.
2. In this study agro-wastes were taken singly however, a combination of such wastes might have better adsorption with regard to heavy metals. This aspect also deserves attention in future.

Conclusions

Human activities such as mining, waste accumulation, industrial activities, road traffic and the use of agro-chemicals (fertilisers and pesticides) have caused extensive contamination of both surface and ground water with toxic heavy metals. On account of their toxicity, bio-accumulation and persistency in the environment these metals are of specific concern. Biosorption is a relatively new process that has shown significant potential in the removal of contaminants from aqueous effluents. In this research toxic metal ion biosorption on inexpensive and efficient biosorbents from agricultural waste materials was investigated as an alternative strategy for existing conventional systems. It was found that the carbons made from wheat, corn, sugarcane and *bajra* agro-wastes can be effectively used in the reduction of copper from aqueous solution. *Bajra* is one of the most efficient wastes having a capacity to reduce copper by approximately 98 percent. The use of these low cost biosorbents is recommended since they are relatively cheap, easily available, renewable and show highly affinity for heavy metals. Hence, agro-wastes being abundantly available can prove to be a low cost solution for the removal of toxic copper ions.

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