

## **Biosorption of Chromium ion in Aqueous Solution Using Biomass of Wheat Shell and *Cantharellus lateritius* (Berk), a Nigerian Mushroom**

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### **Abstract**

*The biosorbents used in this study were biomass of wheat shell (an agricultural waste) and biomass of *Cantharellus lateritius*, a mushroom, at various concentrations of 0.125, 0.25, 0.5 and 1.0g. The effects of varying the metal ion concentration at constant value of biosorbents and vice versa were examined on metal uptake. The highest value of absorption of 154.42mg/g was recorded at the highest initial metal concentration of 400mg/l by the agricultural waste, after 60 minutes of contact. This was followed by the absorption of the metal by fungal biomass also at the highest initial metal concentration of 400mg/l, after 60 minutes of contact at the rate of 139.96mg/g. For each treatment of varying concentration of biosorbent, using wheat shell, the peak absorption in each case was reached within 90 minutes of contact. This trend was largely observed in case of *Cantharellus lateritius* only at the experiment of varying metal concentrations. Comparatively, wheat shell biomass turned out to be a better biosorbent of chromium (VI) oxide than the biomass of *Cantharellus*, with Freundlich constant,  $n$ , of 2.0 as compared to 1.9 of fungus. However the rate of absorption was observed to increase with increasing metal concentration for both biosorbents, but increase in time of exposure after two hours had no considerable positive effects on the metal uptake. These findings indicate wheat shell and *Cantharellus lateritius* as promising materials for Cr (VI) absorption, especially the mushroom, if grown to protect soils exposed to pollution from industrial effluents.*

**Keywords:** *Biosorbents, *Cantharellus lateritius*, Wheat shell, Biomass, Absorption, Chromium.*

**Proposed theme:** Soil protection and climate change with impacts of agrochemicals in the environments

### **Introduction**

The discharge of heavy metals into ecosystem is of great concern over the ages. The pollutants of serious concern include Cadmium, Lead, Copper, Chromium, Mercury, Uranium and Nickel due to their carcinogenic and mutagenic nature (Ahalya *et al.* 2005). These toxic metals or materials may be derived from mining operations, refining ores, sludge disposal, manufacture of electric equipment, paints, agricultural activities such as application of fertilizers and pesticides. However, mining activities, agricultural run-off, industrial and domestic effluents are mainly responsible for the increase of metallic species released into the environment (Ahalya *et al.*, 2005). Toxic metals are widely spread in the environments, naturally occurring in air, in soil and in waste waters as a result of both industrial and human activities. When they are released into the environment and persist indefinitely, they circulate and eventually accumulate through the food chain, thus becoming serious threat to the environment (Atkinson *et al.* 1998).

Moreover, inorganic salts and minerals arising from irrigation which is twice as high as combination of animals and artificial fertilizers as wastes are used for ecological farming to enhance crop growth. Furthermore, infestation of forest and agricultural sector by several phytopathogens and consequential use or overuse of harmful chemical such as herbicides, insecticides and pesticides is also a concern to present day consumer.

Microbial biomass generally has emerged as an alternative for developing economic, eco-friendly wastewater, and soil treatment process. Non living and dead microbial biomass such as fungi, bacterial, yeast, algae, have been employed to remove metals from dilute solution in biosorption due to their charge group present in them (Trivedi *et. al.* 2007). Among this microbial biomass, the cell wall of fungi, bacterial and yeast, and algae have made this possible to uptake metal ion from their native site. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metals to low levels, by the use of inexpensive materials (Holan and Volesky, 1994; Kratochvil and Volasky, 1998).

Fungi can exert strong influence on the fate of heavy metals within their biomass, translocate those metals to other parts of the ecosystem and then release them at other locations. The presence of a pollutant within the mycelium of the fungus can lead to changes in the chemical and physical state of the pollutant, making it more or less toxic to fungal consumers. Biosorption of metals by fungi relies on the ion exchange between the metals and the reactive group of the cell wall. The process is greatly influenced by environmental conditions (Byrne 1979). However Eneida *et. al.* (2002) reported that the biosorbent size of *Sargassium* sp. did not affect chromium biosorption rate and capacity.

Chromium is a common and very toxic pollutant, which usually comes from several industries such as leather tanning, chromate preparation, ore and petroleum refining processes. Chromium occurs most frequently as Cr(VI) or (III) in aqueous solution. It causes lung carcinoma in humans, irritation on skin and corrosion of respiratory tracts. The maximum allowed amount of chromium (VI) ion in natural water is only 0.05mg/l by the United State Environmental Protection Agency (USEPA), (APHA 1998). Thus, Cr (VI) should be removed from waste water before being discharged into the environments.

Natural biopolymers are industrially attractive because of their capability of lowering transition metals ion concentration to part per billion concentrations. Natural materials that are available in large quantities or certain wastes from agricultural operations may be of great potential, to be used as low biosorbent, as they represent unused resources (Fasidi and Olorunmaye 1994, Fasidi and Ekuere 1993).

Agricultural waste gives an alternative use to microbial biomass because they are readily and easily available and collected since there will always be a waste from agricultural products such as wheat shell, palm shell, rice husk, cotton seed waste, groundnut husks which can be effectively used as biomass (Ahalya *et al* 2005). However, when palm shell was combined with natural chitosan, it increased the sorption capacities (Saifudin *et al.*, 2005). In this context, agricultural waste and microbial biomass have been used to study their biosorbent capacity of chromium ion to a very low concentration in aqueous solution.

## Materials and methods

### Biosorbents

*Cantharellus lateritius* was obtained from the department of Plant Science and Biotechnology, Adekunle Ajasin University, Akungba, Nigeria and cultured on Malt Extract Agar (OXOID). The growth of the culture was further enhanced on sucrose medium, for biomass production. The

sucrose medium composed of the following sugar and salts in grams per litre. Sucrose 100g/l, NaNO<sub>3</sub> 6.5g/l, KH<sub>2</sub>PO<sub>4</sub> 0.5g/l, Yeast extract 1.6g/l, KCl 0.025g/l, MgSO<sub>4</sub> 0.025g/l, and were all dissolved in distilled water. The pH of the medium was maintained using a pH meter to be 7.5.

Biomass of *Cantharellus lateritius* was harvested eight days after incubation using Whatman filter paper No 42 ash less, and allowed to oven dry for 8 hours at 80°C, grinded and preserved for biosorption experiment.

### Preparation of agricultural waste

Wheat shell (agricultural waste) was also used as biosorbent and this was collected from a mill farm at Ikare, Akoko North East local Government, Ondo State. The wheat shell was carefully screened and dried in the oven, grinded and preserved for biosorption experiment.

### Preparation of stock solution

1000mg Chromium salt, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, was weighed and dissolved in 1litre of distilled water. From this standard stock solution, the varying concentrations of 50,100,200,400mg/l were taken and fresh dilutions were prepared as explained below.

**Table 1:** Dilution series

Metal concentrationon Mg/l	Volume of stock L	Volume of Distilled water (L)
50	50	950
100	100	900
200	200	800
400	400	600

### Biosorption experiment

One gram of biomass was suspended in 100ml of metal solution taken in 250 Erlenmeyer flask. Samples were withdrawn at periodic intervals and filtered using Whatman No 1 filter paper. The concentration of chromium remaining in the filtrate was analysed using Atomic Absorption Spectrophotometer (A.A.S) (Eneida *et. al.* 2002).

### Time depended studies

Samples were withdrawn at 30-minute intervals for the first four readings, and lastly after four hours, during the biosorption experiments and analysed for chromium.

### Effect of biomass concentration

Biomass concentration of 0.5, 1.0, 2.0 and 4.0 % (w/v) of *Cantharellus lateritius* were added to 25ml test solution taken in a series of 250-ml Erlenmeyer flasks, while 250, 500, and 1000mg of wheat shell were added to 100ml test solution, and biosorption experiments were carried out.

### Effect of chromium concentration

Test solutions containing 50, 100, 200 and 400mg of chromium/l were subjected to biosorption, maintaining the biomass concentration at 0.25%, for both biosorbents.

### Calculation of chromium uptake

Chromium uptake by biomass was calculated using the following mass balance equation for the biosorbents (Vieira and Volesky, 2000):

$$q = \frac{V(C_i - C_f)}{S}$$

S

where q is the chromium uptake (mg metal/g cell dry weight), V the volume of metal bearing solution contacted with the biosorbent, C<sub>i</sub> the initial concentration of metal in solution (mg/l), C<sub>f</sub> the final concentration of metal in solution (mg/l), and S the dry weight of biosorbent added (g).

### Biosorption isotherm

Freundlich isotherm was used for interpreting the process equilibria. The Freundlich equation is given below:

$$q = K_f C_e^{1/n}$$

where q is the heavy metal adsorbed on the biomass (mg/g dry weight), C<sub>e</sub> the final concentration of metal (mg/l) in the solution, K<sub>f</sub> is an empirical constant that provides an indication of the adsorption capacity of biomass, and n is an empirical constant that provides an indication of the intensity of adsorption.

### Results and discussion

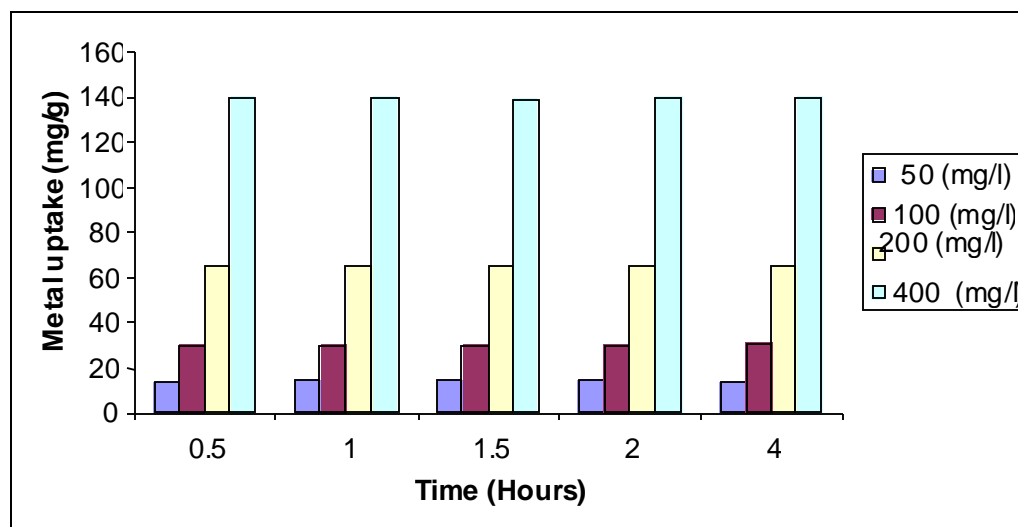
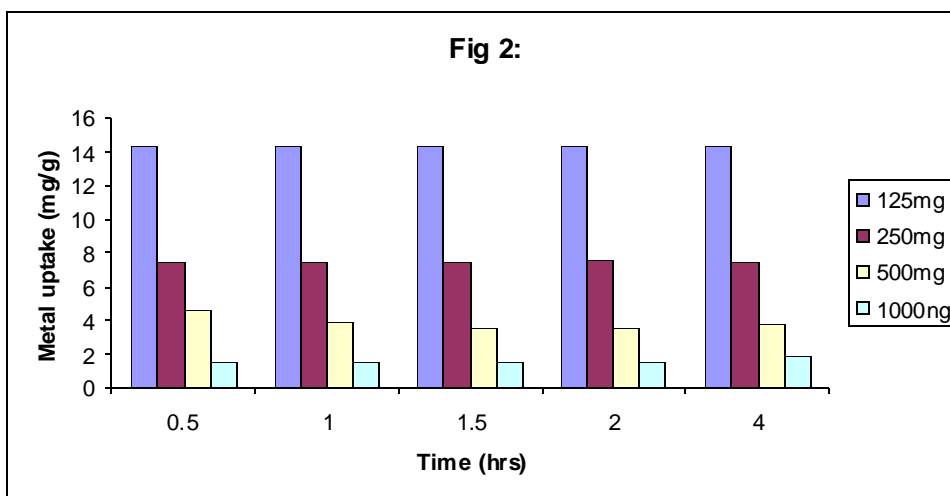


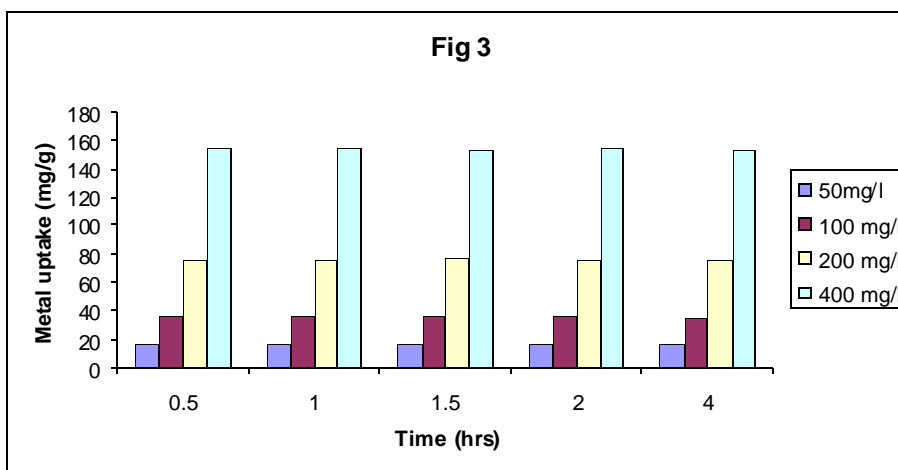
Fig 1: Effect of varying metal concentration at constant Biomass of *C. lateritius* on Chromium uptake

Using a constant mass of 0.25g of *Cantharellus lateritius*, it was observed that as the metal ion concentration increased from 50 to 400mg/l, the metal uptake increased from 13.83 to 139.96mg/l corresponding to adsorption percentage of 28.74 to 34.99. Similar performance by *Aspergillus niger* and *Saccharomyces cerevisiae* during studies on chromium biosorption has been reported (Parvathi *et al.* 2007). Hany *et al.* (2003) and Nikarzar *et al.* (2007) also reported separately that increases in concentration of metal from 50mg/l to 400mg/l could be attributed to the increases in electrostatic interaction between metal binding at the site of sorption.



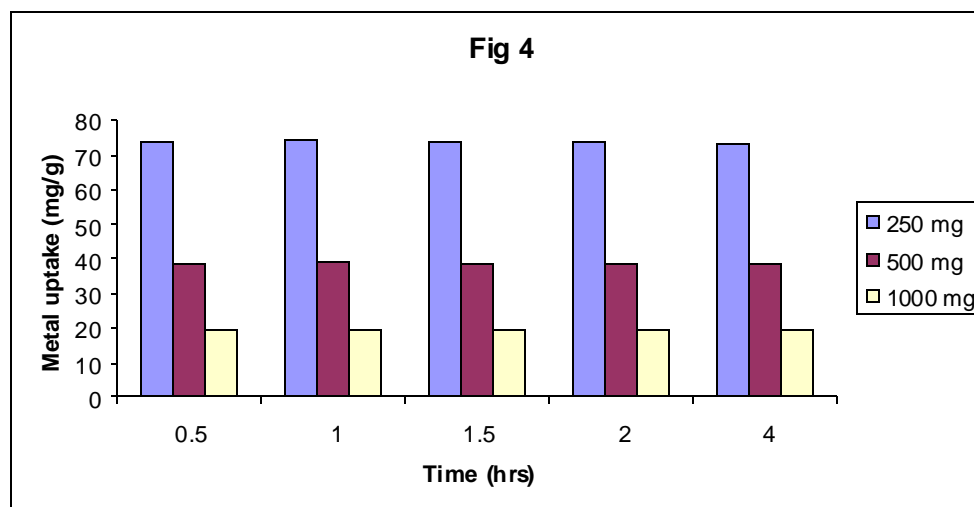
**FIG 2: Effect of varying Biomass of *C. lateritius* at constant metal concentration on chromium uptake**

Fig 2 shows effect of varying *C. lateritius* dose on metal uptake at constant metal concentration of 100mg/l. The highest metal adsorption capacity of 14.41% was reached at the lowest dosage of the fungus and the agricultural waste (125mg), regardless of the time. The time taken for about the maximum chromium biosorption of 14.38mg/g by *C. lateritius* and 74.12mg/g by wheat shell (fig 4) was 60 min for both biomass. Based on a similar result, Parvathi *et al.* (2007) suggested that the total adsorption is dependent upon the number of available sites, and as such specific uptake is calculated as the amount of metal adsorbed per weight biosorbent.



**FIG 3: Effect of varying metal concentration at constant Biomass of wheat shell on chromium absorption.**

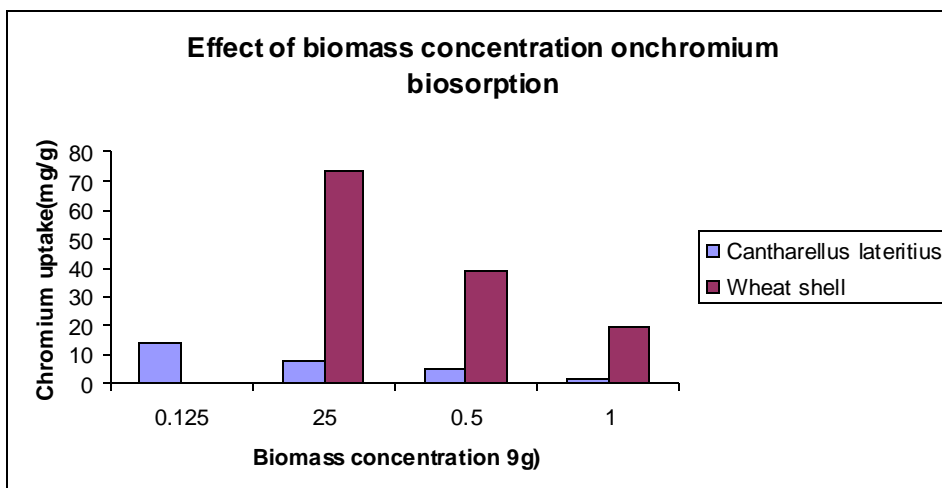
The same trend was also observed from the biosorbent capacity of wheat shell which was determined by varying the metal concentration from 50, 100, 200 to 400mg/l. Fig 3 summarizes the trend of the increases of metal uptake which increased from 17.78mg/g to 154.42, with increase in metal concentration. The highest adsorption capacity was recorded to be 38.6 after the first 30 minutes of contact at 400 mg/l concentration. This result is in agreement with the suggestion of Parvathi *et al.*(2007), who recorded the best time of sorption of Cr (VI) at the first 60 minutes of contact, from a similar experiment using a fungus BDT 14(DSM 15396). Concentration of metal provided an increase in driving force to overcome mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collision between Cr (VI) ions and the sorbents which result in higher metal uptake. (Nikarzar *et al.* 2007)



**FIG 4: Effect of varying concentration of wheat shell biosorbent at constant metal concentration of chromium biosorption**

Fig 4, shows the effect in varying wheat shell of 250, 500, 1000mg at 200mg/l of metal concentration. The highest metal uptake was recorded to be 74.12mg/g after 60 minutes of contact: The percentage adsorption was 37.06. Further increase in dosage of biosorbent from 500mg to 1000mg caused decrease in metal uptake. The percentage absorption declined from 9.68 to 1.51. This trend agreed with the report of Ahalya *et al.*, 2005 who explained that the decline could be due to interaction between metal ions binding at the site of sorption.

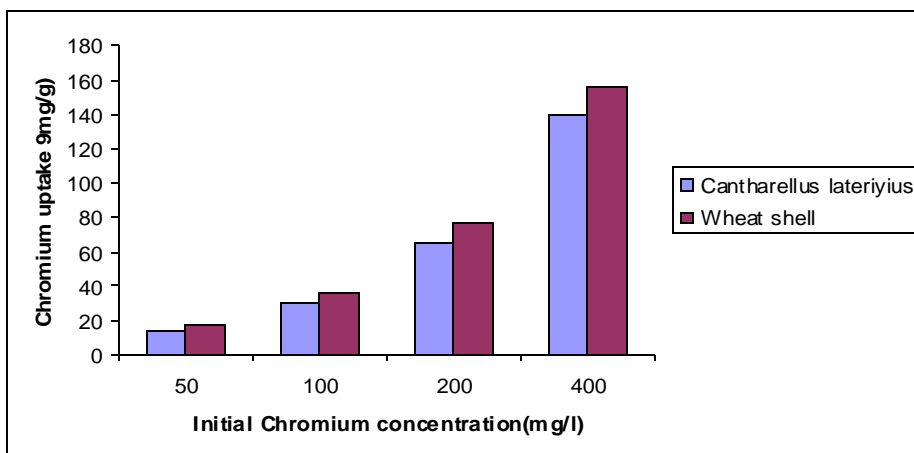
Fig 5 shows the effect of biomass concentration on chromium biosorption at initial concentrations of 100 and 200mg/l for *C. lateritius* and wheat shell respectively.



**Fig 5: The effect of biomass concentration on chromium biosorption**

The result supports the suggestions of Trevedi and Patel (2007) that initial metal ion concentration plays an important role in determining the adsorption capacity of a biosorbent. Doubling the initial concentration of wheat shell over *C. lateritius* resulted in over 9 fold sorption of chromium at 0.25g biomass concentration, over 8 fold at 0.5g and over 12 fold at 1.0g.

Chromium uptake of 14.09, 30.60, 65.49 and 139.30mg/g were recorded with *C. lateritius* at the metal concentration of 50, 100, 200 and 400mg/l respectively (Fig 6). The corresponding uptakes by wheat shell were 17.78, 36.43, 76.07 and 154.42mg/g respectively.



**Fig 6 ; Effect of initial metal concentration on chromium biosorption after thirty minutes of contact.**

The linearized forms of the Freundlich adsorption isotherm was used to evaluate adsorption data. The values of n were calculated from the slope of the Freundlich plots, and were found to be 1.9 and 2.0, while the Kf values were 5.8115 and 6.0398 for the fungus and agricultural waste respectively, at the experiment of varying the metal concentration. These Kf values indicated high capacities of both biomass to biosorb chromium (VI) ion.

According to Kadirvelu and Namasivayam (2000), n values between 1 and 10 represent beneficial adsorption.

## Conclusion

Chromium biosorption efficiency of *C. lateritius* and wheat shell was evaluated under laboratory conditions. The chromium biosorption equilibration time for both biomass was 60 min. with uptakes of 139.96mg/g for the fungus and 154.12mg/g for the agricultural waste, though maximum uptake was almost attained at 30min. Increasing trend in biosorption was observed with rise in chromium concentrations, while the trend was reversed with increase in biomass concentrations. Freundlich constants determined from the adsorption isotherms revealed that wheat shell is a better biosorbent of chromium ion than *C. lateritius*.

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