

APPLICATION OF BIOWASTE MATERIALS FOR THE SORPTION OF HEAVY METALS IN CONTAMINATED AQUEOUS MEDIUM

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Biowaste materials were evaluated as metal ion adsorbents in aqueous medium. The biowastes used were black gram husk, wheat bran, *sheesham* (*Dalbergia sissoo*) sawdust, pea pod, rice husk and cotton and mustard seed cakes. All these biosorbents, except pea pod and rice husk, exhibited good adsorption potential for Cd, Pb, Cu, Zn and Ni. Black gram husk (bgh) was found to have the highest sorption capacity with 100, 99.4, 95.7, 98.2 and 93.1% removal of Cd, Pb, Cu, Zn and Ni, respectively. The metal ions adsorbed by bgh desorbed with 0.1 M HCl and the regenerated biosorbent was reused successfully for the sorption of metal ions in the next cycle. Concentration of the tested metals achieved at equilibrium in the contaminated aqueous medium was well below the maximum limits recommended by UNEP for sewage discharge. The study indicates the potential of bgh as a new, inexpensive and efficient biosorbent for the treatment of water contaminated with heavy metals.

Key words: Biosorption, Biowastes, Effluent treatment, Heavy metals, Black gram husk, *Cicer arietinum*.

Introduction

The discharge of industrial effluents laden with heavy metals is a significant contributory to environmental pollution. It is, therefore, desirable from the public health point of view that industrial effluents are treated to remove heavy metals to acceptable limits before the discharge into open spaces and water bodies. A number of methods used for the purpose include chemical precipitation, membrane filtration, ion exchange, evaporation and electrolysis (Aderhold *et al* 1996; Aksu *et al* 1998; Chong *et al* 2000). Limitations of operation are associated with each of these (Aderhold *et al* 1996; Atkinson *et al* 1996). This has led to the investigation of several biowastes for their ability to remove heavy metals from effluents. The biowastes studied for the purpose include coconut fibre (Espinola *et al* 1999), rice husk (Munaf and Zein 1997), petiolar felt-sheath of palm (Iqbal *et al* 2002) soybean and cotton seed hulls, rice straw and sugar cane bagasse (Marshall and Champagne 1995), rice bran (Verma and Rehal 1994), melon seed husk (Okieimen and Onyenkpa 1989), and oil palm fibers (Low *et al* 1993). Most of these biowastes, however, have to be chemically treated or modified to enhance their metal sorption capacity (Suemitsu *et al* 1986; Maranon and Sastre 1991; Low *et al* 1993). These lead to the problem of enhanced chemical burden on the biowaste sorbents, while the additional step to remove such chemicals may hinder the development of a continuous system in terms

of increased cost and operational time. The search for new sources of biowastes for the biosorption of heavy metals is, therefore, continuing. Present study reports the efficiency of a number of biowastes, *viz.*, black gram husk, wheat bran, *sheesham* saw dust, pea pod, rice husk, cotton and mustard seed cakes without any chemical treatment to biosorb Cd, Cu, Pb, Ni and Zn in the metal contaminated aqueous medium.

Experimental

Biosorbent materials. The biowastes studied for the biosorption of heavy metals were black gram (*Cicer arietinum*) husk, wheat (*Triticum aestivum*) bran, *sheesham* (*Dalbergia sissoo*) sawdust, pea (*Pisum sativum*) pod, rice (*Oryza sativa*) husk, cotton (*Gosypium hirsutum*) and mustard (*Brassica campestris*) seed cakes. These were collected from their respective processing mills, where these were generated as primary waste. These were then extensively washed in running tap water for 2-3 h to remove dirt and other particulate matter followed by washing and boiling in double distilled water, changed repeatedly, till clear of any colouration. The washed and boiled biowaste materials were oven dried at 80°C for 24 h, stored in desiccator, and used for biosorption studies as such or as ground material of different particle sizes sieved through British Standards sieves of mesh size 4, 5, 7, 8 and 12 with aperture size of 4, 3.35, 2.8, 2.0 and 1.4 mm, respectively.

Heavy metal solutions. Atomic absorption spectroscopy standard metal solutions (Merck) of Cd, Cu, Ni, Pb and Zn, concentration $1,000 \pm 2 \text{ mg l}^{-1}$ were diluted to 10 mg metal l⁻¹

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and adjusted to pH 5 with 0.1 M NaOH. Fresh dilutions were used for each biosorption study.

Determination of metal biosorption. Batch biosorption assays were carried out with 1 g of each biowaste material in 100 ml of 10 mg l⁻¹ metal solutions of nitrates of cadmium, copper, nickel, lead or zinc. The pH of the biowaste-metal ion suspension was maintained at 5.0 to avoid the precipitation of metals, which has been reported to occur at higher pH (Saeed and Iqbal 2002). The mixture was shaken on orbital shaker at 150 rpm in tightly stoppered flasks for 60 min at 30 ± 2°C followed by centrifugation at 5,000 rpm for 5 min to separate the biowaste material from metal solution. For the determination of equilibrium time, biowaste-metal suspensions were incubated for 60 min and samples were drawn at different intervals (5, 15, 30, 45 and 60 min), centrifuged and analyzed for metal concentration. Residual concentration of each metal in their respective solutions was determined using atomic absorption spectrophotometer (UNICAM-969). Solutions of each metal ion in the absence of biowaste, served as the control. All experiments were performed in triplicates. Statistical analysis of the data was done according to the Duncan's new multiple range test.

The metal biosorption capacity (q) of bgh biomass was calculated using the following equation and was reported as mg metal biosorbed per g of dry biomass:

$$q = V(C_1 - C_2)/M$$

where V is the volume of metal solution (ml), C₁ the concentration of metal in the control solution, C₂ the concentration of metal in solution incubated with bgh biomass and M is the dry weight of biomass (g).

Metal desorption. Biowaste material reusability was determined by washing the metal laden biosorbent with deionized water to remove any traces of free, non-adsorbed metal. The

biowaste material was then transferred to 12 ml screw capped Pyrex tubes containing 10 ml of 0.1 M HCl. These tubes were gently rotated in test tube rotator for 60 min at 30 ± 2°C. The biosorbent was removed by centrifugation at 5,000 rpm for 5 min. The amount of metal ion present in the supernatant indicated the extent of desorption achieved. The biosorbent was then washed with deionized water thrice, dried to constant weight, and reused for another cycle of metal sorption.

Chemical analysis. Black gram husk was analyzed for protein, fiber and lignin according to AOAC (1984), cellulose using the procedure of Kurschner and Hanak (1930) and hemicellulose by the method of Goering and Soest (1975).

Results and Discussion

Several agricultural and wood wastes, viz., black gram husk - a chickpea variant - (bgh), wheat bran (wb), sawdust of sheesham (*Dalbergia sissoo*) - a kind of furniture hardwood - (ss), pea pod (pp), rice husk (rh), and cotton (csc) and mustard seed cakes (msc), were investigated as low cost and easily available biowaste materials for the sorption of Cd, Cu, Ni, Pb and Zn in contaminated aqueous medium. All these materials were noted to have varying degree of affinity to biosorb the heavy metals tested (Fig. 1). It is evident from these observations, further, that bgh was the most efficient biosorbent of all metals, except Pb, which was biosorbed more efficiently by ss. The difference of biosorption efficiency of Pb by bgh and ss was, however, statistically insignificant (Duncan's multiple range test, p= 0.05). A comparison between the investigated plant wastes for the biosorption of various metals showed that rh and pp consistently adsorbed all metals significantly less than others (Table 1). On a statistical basis, the investigated plant wastes can be broadly categorized in order of decreasing biosorptive capacity as bgh (category A) >csc, msc, wb, ss (category B) >rh (category C) > pp (category D). Since bgh adsorbed all the five metals more efficiently and in

Table 1
Comparative adsorption ability of various bio-wastes towards heavy metals (within parenthesis is given the percentage of each metal biosorbed)

Contaminant* heavy metal	Order of sorption ability of different biowastes** (%)
Cd:	bgh(100)a> ss (98.5)ab>csc(97.9)ab>msc(96.8)b>wb (96.3)b >pp(60.7)c>rh(59.6)c
Pb:	ss (99.8)a>bgh(99.4)a > wb (94.2)b >csc(93.0)bc>msc(90.9)c>pp(83.0)d>rh(81.7)d
Cu:	bgh(95.7)a>msc(93.7)ab>wb (93.6)b >ss (93.1)b>csc (91.3)c>rh (70.2)d>pp(35.7)e
Zn:	bgh(98.2)a>msc(94.9)b >wb (91.6)c>csc(91.1)c >ss (88.4)d >rh (72.3)e>pp(45.2)f
Ni:	bgh(93.1)a>csc(83.5)b > cs (80.3)b >wb(80.0)b >msc(79.8)b>rh (35.7)c>pp(19.3)d

bgh, black gram husk; ss, sheesham wood sawdust; wb, wheat bran; pp, pea pod; rh, rice husk; csc, cotton seed cake and msc, mustard seed cake. a, b, c, d, e and f: values with different alphabets significantly different from each other at p=0.05 (Duncan's multiple range test).

* Metal concentration of 10 mg l⁻¹, pH 5.0.

** 1g biosorbent material dispersed in 100 ml metal solution incubated for 60 min at 30 ± 2°C.

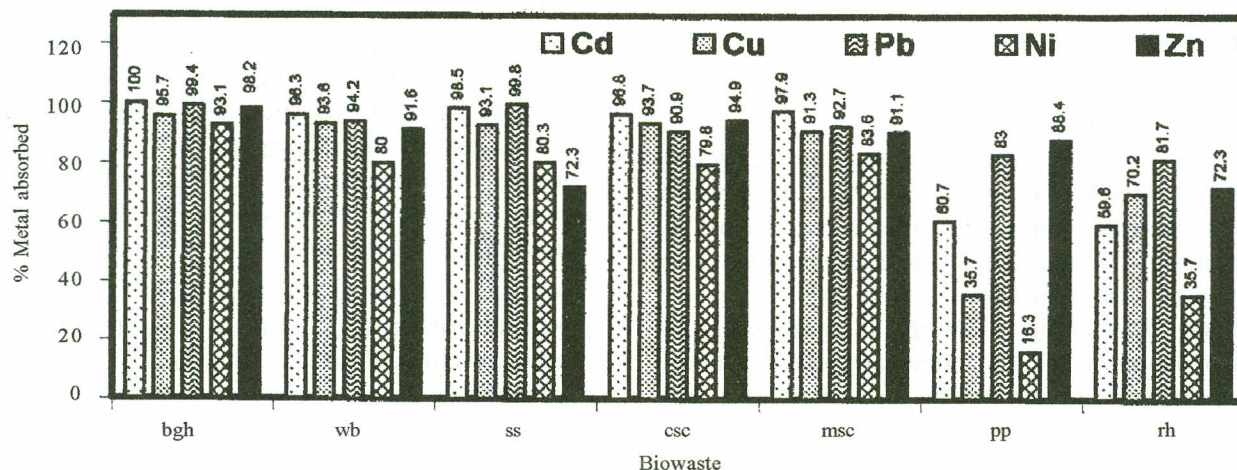


Fig 1. Biosorption of heavy metals by biowastes.

bgh, black gram husk; wb, wheat bran; ss, sheesham sawdust; pp, pea pod; rh, rice husk; csc, cotton seed cake and msc, mustard seed cake.

higher amount than other biowastes (except the statistically insignificant higher biosorption of Pb by ss), this material was selected for further studies for bioremoval of metals. No direct comparison of the biosorption efficiency of bgh, with others reported in literature, is possible due to variations in data presentation and the experimental conditions. Such a comparison, however, can serve as a useful indirect indicator. It is significant to point out, accordingly, on the basis of comparative efficiency of bgh with other biosorbents of plant origin reported in literature for the effective removal of Cd, Cu, Ni, Pb and Zn, that bgh was by far the better plant material than the others (Table 2). The only exceptions were the more efficient biosorption of Cu and Ni by soybean and cotton seed hulls (Marshall and Champagne 1995). The difference in comparative efficiency of bgh was, nevertheless, statistically insignificant. The ability of bgh to remove these metals was so effective that the contaminated water after treatment with this biosorbent met the maximum limits recommended by UNEP (1989) for the discharge of sewage water and by WHO (1993) for drinking water in respect of Cd, Cu and Zn (Table 3).

Morphologically, bgh is the seed coat, comprising testa and tegumen, of *Cicer arietinum*. It is generated as a waste during the seed splitting milling process. The particle size of bgh after the milling process ranged between 1.0 to 5.0 mm. The percentage distribution of various particle size fractions, when passed through different mesh size sieves, is given in Table 4. No significant difference was observed in the biosorption of Cd in 10 mg l⁻¹ solution by the complete mixture of all fractions of bgh generated after milling in comparison with individual fractions of different particle sizes (Fig. 2). From this it may be concluded that biosorption of Cd by bgh was independent of particle size. These observations are similar to those of Ebihara and Takeuchi (1991) who reported no difference in the

biosorption of Zn by different particle sizes of refined corn hull (rch). It is quite likely that fractions of different particle sizes of both bgh and rch provided sufficiently porous pack to have large external and internal surface areas. Such a matrix is suitable for facilitating the access of metal ions to functional groups involved in active biosorption.

The capacity of bgh to accumulate Cd, Cu, Ni, Pb and Zn from their respective metal solutions at different time intervals is presented in Fig. 3. The rate of adsorption of all the five metals was relatively fast, with more than 70% metal adsorption taking place during the first five min. Further biosorption of metals by bgh, after the initial phase of rapid uptake, occurred slowly achieving equilibrium within 20-30 min (Fig. 3). No obvious increase in the sorption of metals was observed thereafter.

The results presented in Table 1 and Fig. 3 clearly indicate that bgh has very high potential for the removal of all toxic metals, ranging between 93.1-100% biosorption from contaminated water. This high biosorption potential of bgh may be explained

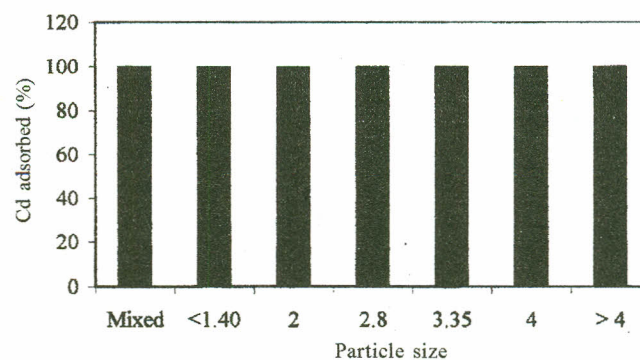


Fig 2. Effect of particle size of black gram husk (bgh) on the biosorption of Cd.

on the basis of its chemical composition, which is principally lignocellulosic in nature. The agrowaste contains: 3.32% protein and 51.9% total fibre consisting of 69% cellulose, 11.98% hemicellulose and 19.14% lignin. This composition indicates the presence of many hydroxylic (-OH) and carboxylic (-COOH) functional groups in the lignocellulosic moieties. It has been shown that the hydrogen of these groups is capable of ion

exchange with metal cations (Burba and Willmer 1983; Srivastava et al 1994; Marshall and Champagne 1995). Viraraghavan and Dronamraju (1993) have also linked the high biosorption of Zn, Cu and Ni from municipal wastewater by horticulture peat to about 82% lignocellulosic substances present in it.

For successful application of a biosorbent system to remove toxic metals from contaminated aqueous media, economical

Table 2
A comparison of metal adsorption capacity of biowaste materials

Biowaste	Biomass conc. (g l ⁻¹)	Metal conc. (mg l ⁻¹)	Sorption capacity (mg g ⁻¹ biomass)	Sorption efficiency (%)	Reference
Cd					
Black gram husk	10.0	10.0	1.0	99.99	Present Study
Waste tea	3.0	5.0	1.63*	98	Orhan and Buyukgungor 1993
Exhausted coffee	3.0	5.0	1.48*	89	Orhan and Buyukgungor 1993
Walnut skin	3.0	5.0	1.5*	90	Orhan and Buyukgungor 1993
Rice husk	6.0	n.m	n.m	85	Munaf and Zein 1997
Coconut fibre	10	n.m	1.0	99	Espinola <i>et al</i> 1999
Pb					
Black gram husk	10.0	10.0	1.0	99.4	Present Study
Polymerize corn cob	10	0.04**	8.6	92.5	Odozi <i>et al</i> 1985
Melon seed husk	10	100	2.4	24*	Okieimen and Onyenkpa 1989
Cu					
Black gram husk	10.0	10.0	0.94	95.7	Present Study
Polymerize corn cob	10	4.0**	15.1	59.1	Odozi <i>et al</i> 1985
Rice husk	6	n.m	n.m	80	Munaf and Zein 1997
Ricebran	10	10	0.76	76.3	Verma and Rehal 1994
Defatted rice bran	10	100	8.24*	82.4	Marshall <i>et al</i> 1993
Treated rice hulls	10	100	2.69*	26.9	Marshall <i>et al</i> 1993
Soybean hulls	50	100	1.99*	99.7	Marshall and Champagne 1995
Cotton seed hulls	50	100	1.97*	98.8	Marshall and Champagne 1995
Zn					
Black gram husk	10.0	10.0	0.98	98.2	Present Study
Polymerize corn cob	10	0.64**	3.0	71.8	Odozi <i>et al</i> 1985
Rice husk	6	n.m	n.m	85	Munaf and Zein 1997
Defatted rice bran	10	100	9.37*	93.7	Marshall <i>et al</i> 1993
Treated rice hulls	10	100	2.2*	22.0	Marshall <i>et al</i> 1993
Soybean hulls	50	100	1.93*	96.4	Marshall and Champagne 1995
Cotton seed hulls	50	100	1.93*	96.6	Marshall and Champagne 1995
Ni					
Black gram husk	10.0	10.0	0.91	93.1	Present Study
Polymerize corn cob	10	0.55**	2.36	74.5	Odozi <i>et al</i> 1985
Defatted rice bran	10	100	5.28*	52.8	Marshall <i>et al</i> 1993
Treated rice hulls	10	100	1.84*	18.4	Marshall <i>et al</i> 1993
Soybean hulls	50	100	1.91*	95.6	Marshall and Champagne 1995
Cotton seed hulls	50	100	1.93*	96.7	Marshall and Champagne 1995

n.m, not mentioned; *, values are calculated from the data given in the respective publication; **, meq g⁻¹

Table 3
WHO (1993) standards for drinking water and UNEP (1989) discharge limits for heavy metals in the industrial effluents, and the residual concentration of metals in contaminated water after adsorption by black gram husk (bgh).

Metal ions	Concentration		Limits recommended by WHO for drinking water (mg l ⁻¹)	UNEP maximum limits for effluent discharge (mg l ⁻¹)
	Before biosorption (mg l ⁻¹)	After biosorption by bgh (mg l ⁻¹)		
Cd (II)	10.02	0.001±0.002	0.003 ^a	0.1
Pb (II)	09.98	0.06±0.015	0.01 ^a	0.6
Cu (II)	10.04	0.43±0.041	2.00 ^b	3.3
Ni (II)	10.06	0.69±0.037	0.02 ^a	4.0
Zn (II)	10.36	0.19±0.002	3.0 ^c	2.6

a, Maximum acceptable concentration for health reasons; b, Provisional value for health reasons; c, Limit for aesthetic or consumer oriented reasons.

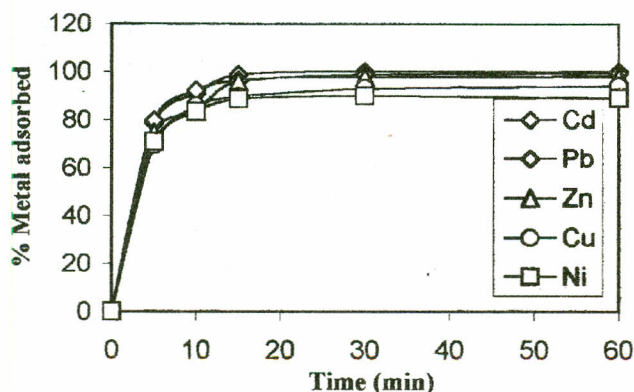


Fig 3. Effect of incubation time on the adsorption of various metals by black gram husk (bgh).

Table 4
Particle size distribution of black gram husk

	Particle size distribution (mm)					
	>4.0	4.0-3.35	3.35-2.8	2.8-2.0	2.0-1.4	<1.40
Percentage	8.27	14.43	27.46	33.74	11.66	4.44

efficiency of operation is of significant importance. A major determining factor is a simple method to regenerate the metal laden biosorbent for reusability. For this purpose, recovery of Cd, Pb, Cu, Ni and Zn from loaded bgh was investigated using the simple procedure of lowering pH of the biosorbent to less than 1 with the addition of 0.1 M HCl. This resulted in 92.54-99.19% desorption of all metals (Table 5). The desorbed bgh biosorbent when reused in the second cycle continued to show high degree of metal sorption efficiency. The pattern of sorption, however, was slightly different from that observed during the nascent use of the biosorbent in first cycle. There was no statistically significant difference between the first and second cycle sorption of Cd, Pb, and Cu. The sorption of Ni and Zn in the second cycle, compared with the first, decreased by 4.91% and 13%, respectively. The drop in the sorption of Zn relative to Ni, however, was very significant when desorbed bgh was used for the sorption of this metal. These observations clearly indicate that whereas bgh is a biosorbent that can be regenerated for reuse for Cd, Pb and Cu it is not so for Ni and Zn.

It may be concluded from the aforesaid observations that bgh in its natural form, without any additional chemical or

Table 5
Biosorption and desorption of heavy metals from metal laden black gram husk

Metal ion	First cycle adsorption (%)	Desorption efficiency (%)	Second cycle adsorption (%)	Standard deviation from the first cycle (%)
Cd (II)	99.9±0.026	99.19±0.86	98.18±0.146	1.22
Pb (II)	99.6±0.357	98.37±1.28	97.81±0.015	1.26
Cu (II)	95.6±0.072	93.36±0.77	98.19±0.278	1.83
Ni (II)	92.6±1.235	92.54±1.47	88.05±1.412	3.22
Zn (II)	98.2±0.156	97.65±0.44	85.43±1.510	9.03

physical treatment, is a highly efficient metal sorbent. The metal sorption, furthermore, is achievable within the short span of 20-30 min and the biosorbent is rechargeable in a simple procedure in a continuous sorption-desorption cycle. The material has thus shown application potential, as an inexpensive agrowaste, for the bioremoval of such toxic metals as Cd, Cu, Pb, Ni and Zn from contaminated effluents. Its efficiency to bring down metal levels below the maximum allowable limits recommended for sewage by UNEP (1989) indicates further investigation for the development of a water treatment plant based on bgh as the metal biosorbent in a continuous system.

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