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Resource Recovery from Industrial Effluents Containing Precious Metal Species Using Low-Cost Biomaterials — An Approach of Passive Bioremediation and Its Newer Applications

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1. Introduction

Industrial wastes can generally be classified as wastes rich in organic matter on one hand and wastes rich in inorganic matter on the other. Cyanide (CN^-) and heavy metals (viz. copper, nickel, iron, zinc, cadmium, chromium, silver, gold, etc.) form a significant part of the latter type of wastes. Free cyanide (CN^-) is industrially important chemical because of its some unique properties of binding various transition metals to form metal-cyanides (M_xCN) complexes of variable stability and toxicity (Sharpe 1976). Therefore, cyanide finds enormous applications in variety of industrial processes. Industries like gold and silver mining, electroplating, printed circuit board manufacturing and jewellery units emanate large-volume low-tenor effluents containing anionic M_xCN complexes like gold-cyanide i.e. $[\text{Au}(\text{CN})_2]^-$ and silver-cyanide i.e. $[\text{Ag}(\text{CN})_2]^-$ (Vapur et al 2005). The total cyanide, gold (Au) and silver (Ag) content in these effluents ranges from 5-25, 1-2 and 5-10 mg/L, respectively (Patil 1999). The discharge limits for total cyanide is 0.2 mg/L, while for Au and Ag the standards are yet to be set and currently not available. Apart from Au and Ag many other heavy metals normally occur in the effluents in low quantity and concentrations. If inappropriately managed, cyanide and metals or their complexes can be mobilised and carried into the food web as a result of leaching from waste dumps, contaminated soils and waters. At each level of food chains, the concentration of metals increases which results into a phenomenon called biomagnification.

Since cyanide is toxic and Au and Ag being precious metals, non-renewable and finite resource; their complete removal from effluents is the key.

The conventional methods adopted for the treatment of M_xCN contaminated effluents is alkaline chlorination oxidation process (Ganczarczyk et al 1985). Although this method of treatment can be very efficient in detoxifying free cyanide bearing wastes, it is not effective when challenged with anionic metal species such as M_xCN (Eckenfelder 1989). Other methods, such as copper catalyzed hydrogen peroxide oxidation, ozonation, electrolytic decomposition, etc. requires large inputs of energy, cost intensive materials and are rarely used for treatment of M_xCN containing wastes. Furthermore, at low concentration, metal-cyanide recovery by conventional means is either not possible and/or very expensive. Thus, there is a big technological breach, which needs to be bridged immediately.

Biological treatment systems (i.e. bioremediation) for the detoxification of toxic and hazardous wastes has immense potential of becoming an effective alternative because of their several advantages over conventional methods; and therefore being explored by the researchers all over the world (Patil et al., 2012; Patil and Paknikar, 1999b). However, biological methods like biodegradation / biotransformation using live microorganisms are subject to toxicity of cyanide and metals. Therefore, removal of precious metal-cyanides species from wastes requires immediate attention of scientists and technologists. The challenge is not limited only to their removal, but also extends to finding competent and inexpensive ways of possible recovery and recycling. It was assumed that if a competent process for removal/recovery could be established, M_xCN could be conserved, which in the authors opinion would be an innovative strategy of resource recovery. Since M_xCN are anionic chemical species, therefore in principle, a well established physico-chemical methods can be used for removal and recovery of precious metal species. A few physico-chemical methods have been tried for adsorption of Au- and Ag-cyanide (Niu and Volesky 2001) and M_xCN using activated carbon or inorganic chemically active adsorbents (Lee et al 1998). However, the practical utility and cost-effectiveness of these processes are not yet established. Biosorption of metal "cations" have been studied extensively (Paknikar et al 2003). However, very few attempts have been made to adopt this technology for possible removal and recovery of "anions" such as M_xCN (Patil 2012; Patil and Paknikar 1999); especially Au- and Ag-cyanide (Niu & Volesky 2001). Literature clearly shows the paucity of references on the removal/recovery of precious Au- and Ag-cyanide using low-cost waste biomass.

It is known that biomass like bacteria, fungi, algae, plants, agricultural biomass and different agro-based industrial waste and byproducts have the ability to bind metals, in some cases selectively, from aqueous solutions (Paknikar *et al.*, 2003). This phenomenon is named as 'metal biosorption' and the biomass responsible for the process are known as 'biosorbents'. Biosorption is combination of the processes such as electrostatic interactions, ion exchange, complexation, formation of ionic bonds, precipitation, nucleation, etc. Biomass surfaces are usually charged. The functional groups like phosphoryl, carboxyl, sulphahydryl and hydroxyl of membrane proteins, lipids and of other cell wall components are responsible for adsorption of metal (both cationic and anionic species). The overall interfaces are a result of complexity of biomass surfaces and chemical/ physical properties of metal ions (Modak and Natarajan,

1995). The advantages of passive bioremediation (i.e. biosorption) are: (i) non-living biomass is not subject to toxicity limitations; (ii) costly nutrients and aseptic conditions not required; (iii) the process is very rapid; (iv) waste biomass from fermentation and many other natural and industrial sources could be a cheap source of biomass; (v) biosorbent could be operated at wider range of pH, temperature and metal concentration; (vi) established theories, conventions and formulae could be applied to the adsorbent and many others (Paknikar et al. 2003). Although biosorption of metal cations have been studied extensively, however, very little is known about the removal and recovery of anionic metal species (viz. M_xCN) from aqueous wastes.

With the above background in mind, investigations were aimed at screening diverse range of low-cost biomass obtained from different sources for the removal and recovery of precious anionic metal species like gold- and silver-cyanide from aqueous wastes with the emphasis on the development of a laboratory / pilot scale technology.

2. Materials and methods

2.1. Low-cost biosorbents

The low-cost biosorbents in the present study were collected from diverse sources (as given below). Some of these biosorbents are reported for the removal of diverse metal species from aqueous solutions (Mohan & Pittman, 2006), while some of them have been employed for the first time.

- i. **Agricultural wastes/by-products:** Coconut fibres, Cow dung cakes, Groundnut shells, Rice husk and Rice straw
- ii. **Industrial wastes/by-products:** Dairy waste sludge, Saw dust, Sugarcane bagasse and Tea powder waste.
- iii. **Municipal solid waste components:** Nirmalya (waste flowers), Compost and Vegetable waste.
- iv. **Fungal and Bacterial (waste) biomass:** *Ganoderma lucidum*, Yeast waste biomass, *Mucor heimalis*, *Penicillium* sp., *Streptomyces* waste biomass, *Streptoverticillium* waste biomass, Wood rotting fungal waste and Bacterial consortium (capable of degrading cyanide and thiocyanate). Biomass of the fungal cultures viz. *Mucor heimalis* and *Penicillium* sp. available in our laboratory were obtained by cultivating them aseptically in Sabouraud's medium (Composition: Glucose 20 g; Peptone 10 g; Distilled water 1000 ml; pH 4.5-5.0) for 4-5 days at 30°C on rotary shaker incubator (150 rpm). Biomass was harvested after growth by filtering through muslin cloth and washed with distilled water 3-4 times in order to remove the organic traces. After washing, the biomass was subjected to drying in oven at 50-60°C for 2-3 days till the constant weight was obtained. Biomass was then ground using electric mixer in order to obtain particle size of $\leq 500 \mu\text{m}$ (0.5 mm). Later the biomass were stored in glass bottles with suitable air tight caps for further use.

- v. **Algae:** Mixed algae biomass obtained from lake Rankala, Kolhapur
- vi. **Terrestrial and aquatic plant species:** *Parthenium* sp., *Eichhornia* root biomass, *Eichhornia* stem biomass, *Eichhornia* leaf biomass, Runners, *Tectona grandis* waste leaves and *Lantana camara*.
- vii. **Reference material:** Activated charcoal was employed as a reference material in order to obtain comparative data.

Biomass samples were collected in polythene bags and transported to laboratory. The samples were washed several times with tap water to remove the dirt and other contaminants, if any, and was then finally washed with deionised water ($< 5 \mu\text{S}$). Biomass were then subjected for drying at 50°C for 48-72 h to a constant weight and powdered. Dried biomass was pulverized employing electric mixer and sieved; so as to get uniform particle size of $\leq 500 \mu\text{m}$ (0.5 mm).

2.2. Synthesis of stock anionic M_xCN solutions

The stock solutions of Au-cyanide i.e. $[\text{Au}(\text{CN})_2]^-$ (Dicyanoaurate-DCAU) and Ag-cyanide i.e. $[\text{Ag}(\text{CN})_2]^-$ (Dicyanoargentate - DCAG) were prepared stoichiometrically by combining their respective salts with sodium cyanide in the molar proportion of 1:2 (Patil & Paknikar, 2000a; Patil and Paknikar, 2000b; Rollinson et al., 1987). Spectral properties were checked and confirmed periodically using UV spectrophotometer. The synthesized DCAU and DCAG solutions were refrigerated at $8-10^\circ\text{C}$.

2.3. Chemicals and analyses

Chemicals used for all experiments were of analytical grade (AR). Glassware used were made of borosilicate material. Stock solutions and reagents were prepared in deionized water ($< 5 \mu\text{S}$) and stored in refrigerator ($8-10^\circ\text{C}$). Gold (Au), silver (Ag), nickel (Ni), copper (Cu), zinc (Zn) and iron (Fe) in the experimental solutions and effluents were analysed using Atomic Absorption Spectrophotometer (Elico, India SL-173). Total cyanide and chemical oxygen demand (COD) content in the solutions were estimated by pyridine-barbituric acid and reflux method, respectively as described in Standard Methods (APHA-AWWA-WEF, 1998). Phosphates (PO_4^{3-}) from effluents were analysed by phenol- disulphonic acid method; sulphates (SO_4^{2-}) were determined by barium chloride method while chlorides (Cl⁻) were determined by argentometric method, as per the methods prescribed in Standard Methods (APHA-AWWA-WEF, 1998). Colour and turbidity were recorded by visual observations. pH and electrical conductivity from solutions was measured by their respective meters.

In order to determine the inherent/actual pH of each powdered unconditioned biomass, the biomass sample and RO water were mixed and serially diluted in the ratio of 1:20, 1:30, 1:40 and 1:50 (w/v) in conical flasks. The contents were stirred vigorously and kept for one hour in stationary conditions and was followed by determining the pH of each dilution ratio. pH value obtained for each dilution was then plotted on graph of "pH against water-to-biomass ratio (v/w)". The straight line obtained after joining all the points was extrapolated backwards so as to intersect with Y-axis (i.e. the pH scale).

2.4. Gold-cyanide (DCAU) and silver-cyanide (DCAG) biosorption studies

A batch equilibration method was used to determine the sorption of DCAU (0.02 mM i.e. 3.94 mg/l Au and 2.08 mg/l CN⁻) and DCAG (0.1 mM i.e. 10.78 mg/l Ag and 5.2 mg/l CN⁻). Biosorbent (0.05 to 0.2 g) was contacted with 10 ml solution of DCAU or DCAG of desired pH in a set of 50 ml capacity conical flasks. The flasks were incubated on rotary shaker incubator adjusted to a speed of 150 rpm at 30°C for 1 h. Contents of flasks were filtered using ordinary filter paper and then analysed for residual Au, Ag and cyanide. All experiments were performed in duplicates and repeated twice to confirm the results. Appropriate controls were run simultaneously to detect the air stripping of cyanide, if any, to confirm biosorption.

Influence of pH on biosorption of DCAU/DCAG was checked in the range of 4-10 with pre-conditioned biomass. On the basis of maximum DCAU/DCAG uptake values obtained under optimum pH conditions, efficient biosorbents were selected for further studies. DCAU/DCAG loading capacity (μmol DCAU/DCAG bound per gram weight of biosorbent) of each biosorbent was determined by contacting 0.1 g powdered biomass several times with fresh batches of 10 ml DCAU/DCAG solution till saturation was achieved. To determine optimum biosorbent amount, DCAU/DCAG was contacted with varying amounts of biomass powder, ranging from 0.1 to 5% (w/v). Rate of DCAU/DCAG uptake was studied by contacting the biosorbent for a period ranging between 0 to 5 h. Under optimised conditions, effect of various competing cations viz. Cu²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Pb²⁺, Fe²⁺, Ag⁺, etc. (0.01-0.1 mM) and anions viz. SO₄²⁻, NO₃⁻, Cl⁻, PO₄³⁻, etc. (0.1-1 mM) on biosorption of DCAU/DCAG was also checked. In order to test the effect of pre-treated biomass on uptake of DCAU/DCAG, the biosorbent were treated for one hour using L-cysteine, boiling water, sodium hydroxide, formaldehyde, acetone, acetate, methanol and acetic anhydride prior to sorption.

2.5. Adsorption isotherms

To study the impact of initial concentration on adsorption, varying concentration of DCAU/DCAG was used in the range of 0.01 to 1 mM. In order to obtain sorption data, uptake value (Q) was calculated using the following equation:

$$Q = V (C_i - C_f) / 1000 m \quad (1)$$

Where, Q is DCAU/DCAG uptake (mmol per gram biomass); V is the volume of DCAU/DCAG solution (ml); C_i is the initial concentration (μmol); C_f is the final concentration (μmol); m is mass of sorbent (g). Based on the 'Q' value obtained adsorption isotherms were plotted according to Freundlich and Langmuir equations (Freundlich, 1926; Langmuir, 1918):

$$\ln Q = \ln K + (1/n) C_{eq} \quad \text{Freundlich equation} \quad (2)$$

$$C_{eq} / Q = (1 / b Q_{max}) + (C_{eq} / Q_{max}) \quad \text{Langmuir equation} \quad (3)$$

Where, C_{eq} is the liquid phase concentration of DCAU/DCAG; b is Langmuir constant; Q_{max} is maximum DCAU/DCAG uptake; K is constant; n is the number of metal reactive sites and Q is the specific metal uptake.

2.6. Adsorption/desorption of DCAU and DCAG

Samples of 1 g biosorbent loaded with target M_xCN was eluted using desorbing agent (1-3 N NaOH) in concentrated form and analysed. Following the elution, biosorbent was washed with DW and then again conditioned to appropriate optimum pH to use in next adsorption/desorption cycle.

2.7. Biosorption of Au- and Ag-cyanide from industrial wastewaters

Two types of effluents were procured from silver and gold plating industry. Both effluents were subjected to characterization using Standard methods (APHA-AWWA-WEF, 1998). The proximate analysis of the samples is shown in Table 8 and 9. Batch equilibration method was followed as mentioned earlier. Rice husk (0.1 g) and *Eichhornia* root (0.1 g) biomass was contacted with 10 ml of gold-cyanide and silver-cyanide effluents, respectively. Prior to sorption, the gold- and silver-cyanide effluents were adjusted to desired optimum biosorption pH. All the batch sorption experiments were carried out under optimum conditions as given in Table 1. After contact, the contents of the flasks were filtered and then analysed for residual metal (i.e. gold and silver) and cyanide. Appropriate controls were run simultaneously.

Parameters	For DCAU experiments	For DCAG experiments
Biomass	Rice husk (L-cysteine treated)	<i>Eichhornia</i> root biomass (L-cysteine treated)
pH	4.0	6.0
Temperature (°C)	30	30
Biomass quantity (w/v)	1.0	2.0
Contact time (min)	60	60
Rotation speed (rpm)	150	150

Table 1. Optimum conditions used for biosorption experiments

2.8. Continuous biosorption studies using fixed bed column at laboratory level

Scale-up studies in fixed bed continuous mode at laboratory level for biosorption of gold- and silver-cyanide was carried out in two separate fabricated glass columns of height 44 cm, internal diameter 1.3 cm and filter media height being 30 cm. The total volume of the column was 58.37 cm³, while the working volume was 39.80 cm³ (figure not shown). Glass column no. 1 was filled with 21 g rice husk biomass pretreated with L-cysteine, while the glass column no. 2 was filled with 24 g *Eichhornia* root biomass also pretreated with L-cysteine. The target effluents were passed through the columns in upward direction in continuous mode at a flow

rate of 40 ml/h using programmable peristaltic pump (Enertech-Victor, India). All connecting silicon tubings used in the experiments were of 0.5 cm outer diameter and 0.3 cm inner diameter. Gold-cyanide effluent was passed through the column no. 1 upto 50 bed volumes, while silver-cyanide effluent was passed upto 34 bed volumes till the breakthrough curve (S-shaped) was obtained. Samples were collected periodically after every two hours and analysed for Au, Ag and total cyanide content.

2.9. Biodegradation of residual M_xCNs

Unrecoverable (residual) gold-cyanide and silver-cyanide in the solutions after biosorption treatment (in batch studies) were subjected to biodegradation using "live chemoheterotrophic bacterial consortium". The consortium (comprising of three *Pseudomonas* sp. in a proportion of 1:1:1) capable of degrading free cyanide and thiocyanate as the source of nitrogen was isolated by enrichment culture technique (Patil, 2008) and was available in my laboratory. Biodegradation experiment were conducted under aerobic and optimum conditions of pH (7.0), temperature (30°C), inoculum size (10^7 cells/ml) and glucose concentration (1 mM). The biodegradation process was used as a polishing step to clean the effluent containing traces of cyanide in order to meet the requirements of statutory agencies.

3. Results

3.1. Screening of low-cost waste biomass for DCAU and DCAG sorption

Data in Table 2 summarizes the results obtained for DCAU and DCAG sorption under optimal pH conditions. The results showed that optimum sorption in terms of Q (i.e. $\mu\text{mol } M_xCN$ sorbed per gram biomass) of 0.02 mM DCAU and 0.1 mM DCAG for most of the waste biomass/sorbents tested were at pH 4.0 and 6.0, respectively. It was observed that biosorption of DCAU and DCAG was less above pH 7.0 for all the biomass tested. In acidic pH conditions, sorption of DCAU and DCAG increased significantly. The table also shows that other than activated charcoal (chosen as reference material) which showed highest biosorption capacity, biomass of Rice husk (3.65 $\mu\text{mol/g}$) and *Eichhornia* roots (3.56 $\mu\text{mol/g}$) were efficient biosorbents for DCAU sorption; while *Eichhornia* roots (4.76 $\mu\text{mol/g}$) and Tea powder waste (4.73 $\mu\text{mol/g}$) were efficient biosorbents for DCAG. The overall Q values observed for all the waste sorbents tested for DCAU and DCAG were in the range of 2.69 - 3.65 $\mu\text{mol/g}$ and 2.74 - 4.76 $\mu\text{mol/g}$, respectively. The observed Q values for efficient biomass were found to be marginally below the Q values obtained for activated charcoal (3.80 - 5.00 $\mu\text{mol/g}$). As far the optimum pH for sorption was concerned, DCAU uptake was maximal at pH 4.0 for all the biomass tested, while DCAG uptake for majority of the biomass was at pH 5.0 to 6.0. There was no loss of DCAU or DCAG in the control flasks without sorbent during the tested time period.

Table 2 also shows the data on pH values of all unconditioned biomass. Other than the reference materials, the lowest pH observed was that of coconut fibers (pH 4.24), while the highest pH was of mixed algae biomass (pH 7.61). pH of unconditioned Rice husk, Tea powder waste and *Eichhornia* root biomass observed were 5.94, 4.94 and 7.01, respectively, while their

optimum pH of biosorption was 4.0 (for DCAU biosorption), 5.0 - 9.0 (for DCAG biosorption) and 4.0 (for DCAU biosorption) and 7.0 – 9.0 (for DCAG biosorption).

On the basis of maximum DCAU/DCAG uptake values obtained under optimum pH conditions, Rice husk and *Eichhornia* root biomass were selected for DCAU sorption, while *Eichhornia* root and Tea powder waste biomass were selected for DCAG sorption for further experiments. Activated charcoal acted as a reference material.

3.2. Influence of temperature on biosorption of DCAU and DCAG

It was observed that biosorption of DCAU and DCAG by the selected biomass did not had any significant impact with the change in temperature of the system from 5-45°C.

3.3. DCAU and DCAG loading capacity

Table 3 and 4 depicts the data on DCAU and DCAG loading capacity of pre-conditioned (at pH 4.0 for DCAU and pH 5.0-7.0 for DCAG) biosorbents selected on the basis of maximum sorption under optimum pH, as described earlier. Also the results were compared with the unconditioned biomass (i.e. the original pH of the biomass itself). It could be seen that Rice husk biomass had the maximum loading capacity for DCAU (7.63 $\mu\text{mol/g}$) sorption among the two tested biomass; and was followed by *Eichhornia* root biomass (7.04 $\mu\text{mol/g}$). It was also observed that the loading capacity of activated charcoal was found relatively lower when compared with the Rice husk. While the loading capacity of unconditioned biomass dropped by 7.6% and 43% for Rice husk and *Eichhornia* root biomass, respectively.

In case of DCAG, *Eichhornia* root biomass showed highest loading capacity (9.74 $\mu\text{mol/g}$) followed by Tea powder waste (9.41 $\mu\text{mol/g}$). Loading capacity values of *Eichhornia* root biomass was highly competitive and comparable with activated charcoal (9.95 $\mu\text{mol/g}$), which was used as reference material. Furthermore, the loading capacity of unconditioned biomass was not affected when compared with the conditioned biomass (Table 4).

Sr. No.	Biosorbent	pH of unconditioned biomass	Q ($\mu\text{mol M}_x\text{CN}$ sorbed per gram biomass)	
			DCAU	DCAG
(A) Agricultural waste/by-products				
1.	Coconut fibers	4.24	3.32 (4.0)*	4.62 (5.0)*
2.	Cow dung cakes	7.73	3.07 (4.0)	4.64 (6.0)
3.	Groundnut shells	5.49	3.22 (4.0)	4.62 (6.0)
4.	Rice husk	5.94	3.65 (4.0)	4.68 (6.0)
5.	Rice straw	6.13	3.25 (4.0)	4.69 (6.0)
(B) Industrial waste/by-products				

Sr. No.	Biosorbent	pH of unconditioned biomass	Q ($\mu\text{mol M}_x\text{CN}$ sorbed per gram biomass)	
			DCAU	DCAG
6.	Dairy waste sludge	6.88	2.91 (4.0)	4.71 (6.0)
7.	Saw dust	5.59	3.52 (4.0)	4.64 (6.0)
8.	Sugarcane Bagasse	5.92	3.16 (4.0)	4.03 (6.0)
9.	Tea powder waste	4.94	2.94 (4.0)	4.73 (5.0-9.0)
(C) Municipal solid waste components				
10.	Nirmalya (Waste flowers)	6.20	3.43 (4.0)	4.60 (6.0)
11.	Compost	7.28	3.09 (4.0)	3.22 (6.0)
12.	Vegetable waste	6.77	2.91 (4.0)	3.88 (6.0)
(D) Fungal and Bacterial waste/biomass				
13.	<i>Ganoderma</i> sp.	6.04	3.01 (4.0)	4.07 (6.0)
14.	Yeast biomass	4.39	2.69 (4.0)	3.06 (5.0)
15.	<i>Mucor heimalis</i>	4.45	1.97 (4.0)	2.29 (6.0)
16.	<i>Penicillium</i> waste	4.26	3.08 (4.0)	3.99 (6.0)
17.	<i>Streptomyces</i> waste	4.86	3.00 (4.0)	2.78 (6.0)
18.	<i>Streptoverticillium</i> waste	4.67	2.77 (4.0)	3.52 (6.0)
19.	Wood rotting fungi	6.04	3.18 (4.0)	4.21 (6.0)
20.	Bacterial consortium	6.83	3.12 (4.0)	4.00 (6.0)
(E) Algae biomass				
21.	Mixed algae biomass	7.61	3.29 (4.0)	4.16 (6.0)
(F) Photosynthetic trees/plants waste				
22.	<i>Parthenium</i> sp.	6.69	3.07 (4.0)	4.22 (6.0)
23.	<i>Eichhornia</i> leaves	5.57	3.20 (4.0)	4.62 (6.0)
24.	<i>Eichhornia</i> roots	7.01	3.56 (4.0)	4.76 (7.0-9.0)
25.	<i>Eichhornia</i> stem	5.58	3.38 (4.0)	4.66 (6.0)
26.	Runners	6.52	3.06 (4.0)	4.67 (6.0)
27.	<i>Tectona grandis</i> leaves	5.40	3.42 (4.0)	4.63 (6.0)
28.	<i>Lantana camara</i> leaves	6.59	2.98 (4.0)	2.74 (5.0)
(G) Reference materials				
29.	Activated charcoal	5.59	3.80 (4.0)	5.00 (6.0)

Sr. No.	Biosorbent	pH of unconditioned biomass	Q ($\mu\text{mol M}_x\text{CN}$ sorbed per gram biomass)	
			DCAU	DCAG
30.	Bagasse Fly ash	8.75	3.40 (4.0)	4.70 (6.0)
	Control (without biomass)	-	0 (2.0)	0 (6.0)

All the values in table are average of two readings; *Values in parentheses indicates optimum pH (Gaddi and Patil, 2011; Patil, 2012)

Table 2. Biosorption of DCAG and DCAU at optimum pH

Sorbent / Biosorbent	Loading capacity ($\mu\text{mol/g}$ of biomass)		
	Conditioned biomass (at optimal pH)	Unconditioned biomass (at original biomass pH)	Remarks
Rice husk	7.63 (4.0)	7.05 (5.94)	Moderately affected
<i>Eichhornia</i> roots	7.04 (4.0)	4.38 (7.01)	Significantly affected
Activated charcoal	7.61 (4.0)	7.58 (5.59)	Not affected

All the values presented in table are average of two readings

Table 3. DCAU loading capacity of selected biosorbents

Sorbent / Biosorbent	Loading capacity ($\mu\text{mol/g}$ of biomass)		
	Conditioned biomass (at optimal pH)	Unconditioned biomass (at original biomass pH)	Remarks
<i>Eichhornia</i> roots	9.74 (7.0)	9.77 (7.01)	Not affected
Tea powder waste	9.41 (5.0)	9.40 (4.94)	Not affected
Activated charcoal	9.95 (6.0)	9.94 (5.59)	Not affected

All the values presented in table are average of two readings

Table 4. DCAG loading capacity of selected biosorbents

Considering the above results, selection of the biosorbent was further narrowed down to Rice husk and *Eichhornia* root biomass for DCAU and DCAG biosorption, respectively, (using conditioned biomass) for further experiments.

3.4. Influence of biosorbent quantity

The effect of biomass quantity (% w/v) on DCAU and DCAG biosorption was studied at optimal pH values. Varying amount of biomass ranging from 0.1 to 5.0 g were used keeping the volume of both the metal-cyanides (M_xCNs) solution constant (10 ml); thereby giving the solid-to-liquid ratio in the range of 0.01 to 0.5. The results showed that the biomass quantity increased the % biosorption of both DCAU and DCAG also increased. Maximum uptake in terms of Q (3.84 $\mu\text{mol/g}$) was observed at 1% (w/v) of Rice husk biomass for DCAU sorption. However, from 1 to 5 % (w/v) there was no significant increase. In case of DCAG sorption, *Eichhornia* root biomass showed highest Q for biomass quantity from 2.0 to 5.0% (w/v).

3.5. Rate of DCAU and DCAG uptake

The effect of contact time on DCAU and DCAG biosorption was studied at their optimum pH (pH 4.0 and pH 6.0 for DCAU and DCAG sorption, respectively), temperature (30°C) and biomass quantity of 1% (w/v) and 2% (w/v) for DCAU and DCAG, respectively. 10 ml of precious M_xCN solution having concentration 0.02 mM (in case of DCAU) and 0.1 mM (in case of DCAG) was contacted with respective biomass (Rice husk and *Eichhornia* root biomass for DCAU and DCAG, respectively) for the period upto 180 min. The time intervals chosen for study were 0 to 180 minutes. Periodically the flask contents were removed by filtration and the filtrates were analyzed for Au, Ag and cyanide concentration.

It was observed that rate of both the M_xCN uptake was maximum in the 15-20 minutes, with over 80% of biosorption. Later, the sorption rate slowed down until it reached a plateau after 30-40 min, indicating equilibration of the system. Maximum sorption of both the precious M_xCNs was observed at 40 min (88.2% for DCAU and 94.3% in case of DCAG).

3.6. Adsorption isotherm models

The effect of initial concentration provides an important driving force to overcome all mass transfer resistance of target inorganic ion between the aqueous and solid phases. The biosorption of both DCAU and DCAG were carried out at different initial concentrations ranging from 0.01 mM to 1.0 mM (corresponding to approximately 10 to 1000 μmol) at pH 4.0 and 6.0 using 1 and 2% (w/v) of Rice husk and *Eichhornia* root biomass, respectively. It was found that the equilibrium sorption capacity of the sorbent increased with increasing initial concentration of M_xCNs from 0.01 mM to 1.0 mM, due to the increase in the number of ions competing for the available binding sites in the biomass. The uptake of M_xCNs approached towards plateau above 0.5 mM. There was a significant increase in the specific uptake of both M_xCNs

3.7. Equilibrium models to fit experimental data

To examine the relationship between sorption isotherm models are widely employed for fitting the data. Langmuir and Freundlich were used to describe the equilibrium between the two M_xCNs sorbed on Rice husk and *Eichhornia* root biomass and M_xCNs in solution. Data obtained show that M_xCNs uptake values could be well fitted to the Langmuir and Freundlich isotherm models with the regression value >0.98 .

3.8. Influence of cationic and anionic moieties on DCAU and DCAG sorption

It was observed that biosorption of both the metal-cyanides were not significantly affected by the presence of various metal cations and anions in majority of the cases. Biosorption of DCAU was affected by zinc, chromium and cadmium up to certain extent (33-40%). In case of DCAG, biosorption was affected significantly by the presence of cadmium, zinc, iron and chromium (37-67%). Biosorption in the presence of other metals cations (copper, nickel and silver) and anions (phosphates, sulphates and chlorides) was consistently above 80%.

When the low-cost biomass was pre-treated with different chemicals, it was found that (Table 5 and 6) there was greater degree of variation in the biosorption of DCAU and DCAG using Rice husk and *Eichhornia* root biomass, respectively. Rice husk and *Eichhornia* root biomass treated with 1% L-cysteine enhanced the biosorption capacity of both the M_xCNs . In contrast, the NaOH pretreated biomass significantly hampered the biosorption process. It was 0% in case of DCAU sorption and 2.5% in case of DCAG biosorption.

DCAU + Chemicals used for pre-treatment	% DCAU biosorption	Relative % biosorption
DCAU without sorbent (control)	0	0
DCAU + Rice husk without pretreatment	90.1	100
DCAU + Rice husk (treated with boiled water)	86.5	96.0
DCAU + Rice husk (treated with 1% L-cysteine)	100	110.9
DCAU + Rice husk (treated with 1 N NaOH)	0	0
DCAU + Rice husk (treated with 1 N Formaldehyde)	87.2	96.7
DCAU + Rice husk (treated with acid i.e. HCl)	79.0	87.7
DCAU + Rice husk (treated with acetate)	73.6	81.7
DCAU + Rice husk (treated with methanol)	27.1	30.1
DCAU + Rice husk (treated with acetic anhydride)	49.2	54.6
DCAU + Rice husk (treated with acetone)	53.7	59.6

Table 5. Impact of pretreatment on DCAU biosorption by Rice husk

The experiment on pretreatment of biomass with L-cysteine clearly showed enhanced biosorption of DCAU and DCAG from solutions. It was therefore thought worthwhile to find out the loading capacity of both the biomass pretreated with L-cysteine. Experiment on loading capacity of Rice husk and *Eichhornia* root biomass was performed as mentioned earlier (section 2.4). It could be seen from Table 7 that the loading capacity of Rice husk and *Eichhornia* root biomass enhanced the biosorption of DCAU and DCAG up to 175% and 140%, respectively compared to untreated biomass (i.e. in absence of L-cysteine loaded biomass).

DCAU + Chemicals used for pre-treatment	% DCAG biosorption	Relative % biosorption
DCAU without sorbent (control)	0	0
DCAU + <i>Eichhornia</i> root without pretreatment	94.0	100
DCAU + <i>Eichhornia</i> root (treated with boiled water)	83.0	88.3
DCAU + <i>Eichhornia</i> root (treated with 1% L-cysteine)	100	106.4
DCAU + <i>Eichhornia</i> root (treated with 1 N NaOH)	2.5	0.5
DCAU + <i>Eichhornia</i> root (treated with 1 N Formaldehyde)	89.4	95.1
DCAU + <i>Eichhornia</i> root (treated with acid i.e. HCl)	81.7	86.9
DCAU + <i>Eichhornia</i> root (treated with acetate)	64.9	69.0
DCAU + <i>Eichhornia</i> root (treated with methanol)	34.5	36.7
DCAU + <i>Eichhornia</i> root (treated with acetic anhydride)	56.6	60.2
DCAU + <i>Eichhornia</i> root (treated with acetone)	59.0	62.7

Table 6. Impact of pretreatment on DCAG biosorption by *Eichhornia* root biomass

Biosorbent	Loading capacity (µmol/g of biomass)	
	Biomass without pretreatment	L-cysteine treated biomass
Rice husk (for DCAU biosorption)	7.60 (100%)	13.34 (175%)
<i>Eichhornia</i> roots (for DCAG biosorption)	9.72 (100%)	13.62 (140%)

All the values presented in table are average of two readings

Table 7. Loading capacity of untreated and L-cysteine treated biomass

3.9. Adsorption-desorption of DCAU and DCAG

The loaded DCAU and DCAG on Rice husk and *Eichhornia* root biomass, respectively, could be desorbed with more than 97% efficiency using 1 N sodium hydroxide solution. Final concentrations of M_xCNs in the eluent were 28-30 folds of initial concentration of DCAU and 22-25 fold of the initial concentration of DCAG. However, during the second cycle of M_xCN adsorption, the loading capacity of the biosorbent decreased by 10-15%.

3.10. Biosorption of DCAU and DCAG from industrial wastewaters

The gold-cyanide and silver-cyanide from the effluents procured from the industries could be effectively biosorbed/treated by Rice husk and *Eichhornia* root biomass which were pretreated with L-cysteine. Table 8 and 9 depicts the data on gold-cyanide and silver-cyanide before and after biosorption along with their percentage removal. Gold and cyanide removal efficiency from gold-cyanide effluent was 91.53% and 82.69%, respectively. However, the cyanide content in the treated effluent after biosorption although very less (0.59 and 0.78 mg/l for Au- and Ag-cyanide effluents, respectively) but was not complying with the prescribed Indian

Sstandards (0.2 mg/l). Overall, the results indicated that both Rice husk and *Eichhornia* root biomass were very effective in treating the effluents by biosorption process.

Physicochemical parameters	Before biosorption	After biosorption	% Removal efficiency
Color	Colorless	Colorless	-
Turbidity	Clear	Clear	-
pH	6.87	4.12	-
Total cyanide	3.41	0.59	82.69
Gold	1.30	0.11	91.53
Silver	0.48	0.03	93.75
Copper	0.95	0.18	81.05
Nickel	BDL	-	-
Zinc	0.50	0.10	80.00
Iron	0.11	BDL	100.00
Phosphates	97.9	76.1	22.26
Sulfates	63.5	61.3	3.46
Chlorides	173.0	155.2	10.28
Chemical oxygen demand (COD)	42	31	26.19

All the figures given in the table are in mg/l, except pH; BDL: Below detectable limits

Table 8. Biosorption of gold-cyanide from industrial effluent in batch mode using rice husk pretreated with L-cysteine

In order to treat the residual (unrecoverable) cyanide remaining in the solutions after biosorption were subjected to biodegradation process using bacterial consortium under optimized conditions in further experiments.

3.11. Biodegradation of unrecoverable (residual) metal-cyanides

Typical residual concentrations of gold and cyanide in gold-cyanide effluent after biosorption were 0.11 and 0.59 mg/l, respectively. Similarly, the residual silver and cyanide concentration in the silver-cyanide effluent were 0.98 and 0.78 mg/l, respectively. When these solutions were subjected to biodegradation using bacterial consortium under optimum conditions as mentioned earlier, it was observed that the consortium could degrade the said cyanide from both effluents with an efficiency exceeding 90% within a period of 3-4 h. pH, cyanide and chemical and oxygen demand (COD) of the treated effluent were within the permissible limits prescribed by statutory agencies in India (Table 10). Percent cyanide removal efficiency was >90% for both types of effluents. Gold and silver metals were not detected in bacterial free treated solutions. Findings indicated that biodegradation could be used as a polishing step in the treatment of M_xCNs containing wastewaters.

Physicochemical parameters	Before biosorption	After biosorption	% Removal efficiency
Color	Colorless	Colorless	-
Turbidity	slightly turbid	Clear	-
pH	7.16	6.44	-
Total cyanide	5.02	0.78	85.0
Gold	-	-	-
Silver	7.29	0.98	86.55
Copper	1.56	0.31	80.12
Nickel	BDL	-	-
Zinc	0.92	0.27	70.65
Iron	0.18	BDL	100.0
Phosphates	117.5	115.0	2.12
Sulfates	94.1	95.2	0
Chlorides	199.6	193.3	3.15
Chemical oxygen demand (COD)	47	29	38.29

All the figures given in the table are in mg/l, except pH; BDL: Below detectable limits

Table 9. Biosorption of silver-cyanide from industrial effluent in batch mode using *Eichhornia* root biomass pretreated with L-cysteine

Parameter	Biodegradation		*BIS Standards	% Removal Efficiency
	Before	After		
Gold-cyanide				
pH	6.99-7.04	7.05-7.12	5.5 – 9.0	-
Total cyanide	0.59 mg/l	0.04	0.2	93.22%
Chemical oxygen demand (COD)	102 mg/l	23 mg/l	250	77.45%
Gold	0.11	BDL	NA	-
Silver-cyanide				
pH	6.95-7.03	7.07-7-11	5.5 – 9.0	-
Total cyanide	0.78 mg/l	0.05	0.2	93.58%
Chemical oxygen demand (COD)	98 mg/l	19 mg/l	250	80.61%
Silver	0.98	BDL	NA	-

*BIS- Bureau of Indian Standards; BDL-Below Detectable Limits; NA-Not Available; All the values presented in table are average of two readings

Table 10. Treatment of residual gold-cyanide and silver-cyanide by a cyanide and thiocyanate degrading heterotrophic bacterial consortium

3.12. Biosorption of gold- and silver-cyanide effluent in packed bed column

Biosorption studies on gold-cyanide and silver-cyanide effluents were performed in continuous mode in two separate packed bed glass columns consisting of Rice husk (column 1) and *Eichhornia* root biomass (column 2), respectively. Biosorption results showed that breakthrough point observed for gold and cyanide in column 1 was 60 h, while the breakthrough time observed for silver and cyanide in column 2 was 40 h (figures not shown). The total effluent passed through the column 1 and 2 was equivalent to 50 and 34 bed volumes, respectively. Column 1 and 2 got completely saturated after 90 and 70 h, respectively.

4. Discussion

Review of literature show that biosorption of heavy metal cations from aqueous solutions have been studied widely (Paknikar *et al.*, 2003). Studies have also been carried out on biosorption of anionic metal species like chromates (Basha *et al.*, 2008; Itankar and Patil, 2012), free cyanide (Azab *et al.*, 1995) and metal-cyanides (Patil and Paknikar, 1999a) using microbial biomass, especially the waste fungal biomass obtained from fermentation industry and laboratory cultivated biomass. In contrast, biotransformation of metal-cyanides and thiocyanate using live bacterial consortium was also studied (Patil, 2006; Patil, 2008a; Patil, 2008b; Patil, 2011; Patil and Paknikar, 2000; Patil and Paknikar, 2001). Safety aspects of cyanide use in mining industries have been well emphasized by Patil and Kulkarni (2008). Prashanth and Patil (2007) have also studied the impact of free cyanide on edible fish *Catla catla*.

Another important and precious chemical species that are normally encountered in the industrial effluents emanating from mining, electroplating, printing circuit board manufacturing, photography units, etc. are gold-cyanide and silver-cyanide. These species are active and important members of cyano-group chemicals that occur in water environment. Some research has been carried out on the removal of gold-cyanide and silver-cyanide species by biodegradation/biotransformation method (Karavaiko *et al.* 2000; Kiruthika and Shrinithya, 2008). However, very little information is available on the removal and recovery of gold-cyanide and silver-cyanide from high volume low tenor effluents (Gaddi and Patil, 2011). Much work has been restricted to the removal of metal-cyanides and thiocyanates using anion exchange resins and activated charcoal (Kononova *et al.*, 2007) and polyurethane foam (Hasany, 2001). Some papers on removal of free thiocyanate and metal-thiocyanate have also been published using low-cost materials (Namasivayam, 2007; Thakur and Patil, 2009). Overall literature survey shows that very little work has been carried out on the removal of anionic species like Au-cyanide i.e. $[\text{Au}(\text{CN})_2]^-$ (Dicyanoaurate-DCAU) (Niu and Volesky, 2000) and Ag-cyanide i.e. $[\text{Ag}(\text{CN})_2]^-$ (Dicyanoargentate-DCAG) (Gaddi and Patil, 2011) from waste solutions using low-cost materials emanated either by natural or manmade activities. Since all the cyano-group chemicals like free cyanide and thiocyanate, metal cyanides and metal thiocyanate are toxic to all classes of living cells their removal and recovery from waste prior to discharge in environment is the key.

In the light of above, the present research work was focused to study removal and recovery of Au- and Ag-cyanide from effluents using low-cost biosorbents (using waste biomass from various sources); followed by biodegradation (using active bacterial consortium). It was contemplated that if an efficient process for removal and recovery could be developed, then precious M_xCN or metals could be conserved, which according to the project investigators opinion would be an innovative approach of resource recovery.

It is well-known that certain type of microbial or waste biomass has high degree of competency to adsorb heavy metals. This sorption is solely due to the chemical composition of biomass (Volesky, 2003). With biosorption applications in mind it makes sense to screen variety of biomass types that are readily available in large quantities. There are basically two types of biomass sources that can practically be considered with low costs and availability in mind. First, the industrial waste biomass generated as a by-product of large scale (for example fermentation industry) with virtually no uses for it and disposal is a problem. Secondly, the biomass generated in large quantities from water environment (for examples unwanted plants like *Eichhornia* sp. and algae). It can be easily collected or harvested as raw material for biosorbents. Also, there are many other sources from where low-cost biomass could be procured especially in a developing country like India. These include the vegetable waste, yard wastes, waste flowers and coconut fibres from temples, etc. Energy generation potential from biomass and MSW have been reported by Saini et al (2012). In order to find the right biosorbent candidate, it is imperative to screen variety of biomass occurring in human environment.

Free cyanide and thiocyanate, metal-cyanides and metal-thiocyanates can occur in the wastewaters in various forms depending upon the chemical nature of the compounds and the concentration of metal, cyanide and thiocyanate, provided if metal moiety is bound to cyanide and thiocyanate. For example, free cyanide and thiocyanate can occur in the waters in its anionic form like CN^- and SCN^- , respectively. While metal-cyanide like for example - copper-cyanide occur in water in various forms such as $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Cu(CN)_4^{2-}$, etc. Similarly, copper-thiocyanate complex occur in waste waters in various forms like $Cu(SCN)_2^-$, $Cu(SCN)_3^{2-}$, $Cu(SCN)_4^{2-}$, etc. Therefore, it was thought worthwhile to explore the possibility of their recovery by adsorption on low-cost biomass procured from various places. Activated charcoal, a conventional material, was used for obtaining comparative data.

It is well known that the process of biosorption is regulated by aqueous solution pH (Puranik and Paknikar, 1997). The first step in present study was therefore determination of optimum solution pH for biosorption of gold-cyanide and silver-cyanide. It was found that biosorption of both the M_xCNs (for all the low-cost biomass) increased with pH and then declined rapidly with further increase in pH. As seen from the Table 2 that maximum sorption of DCAU was at pH 4.0 while DCAG sorption by most of the biomass was at pH 6.0. Sorption decreased in the alkaline pH. It was found that other than activated charcoal (which was used as reference material) biomass like Rice husk & *Eichhornia* roots and *Eichhornia* roots and Tea powder waste were efficient biosorbents for DCAU and DCAG sorption. There was no auto-oxidation loss of both the M_xCNs in controls without sorbent confirming that (bio)sorption is the only mechanism by which M_xCNs are being removed from solution. In the previous study carried out by Niu and Volesky (2000) found that the maximum adsorption of DCAU by biomass was

in the acidic pH ranging from 2.0 to 4.0. These results corroborates with the results obtained in our studies.

Increased sorption under acidic conditions may be due to the protonation of the functional groups acquiring net positive charges. Probably therefore, the formation of species such as $H^+AuCN_2^-$ and $H^+AgCN_2^-$ on the biomass might have taken place thereby accommodating more number of M_xCN species on the biosorbent sites. Waste biomass from natural origin contains large number of surface functional groups like hydroxyl, carbonyl, carboxyl, sulphhydryl, amine, imine, amide, phosphonate, phosphodiester, etc. Probably some of these functional groups might have played the crucial role in the sorption of DCAU and DCAG from aqueous solution.

Matheickal and Yu (1996) have reported that pH dependence of cationic and anionic adsorption can largely be related to type and ionic state of these functional groups and the chemistry of target compound in solution. DCAU and DCAG in our studies could be compared with anionic metal species like hexavalent chromium (an oxyanion) and arsenic. At low pH values, cell wall ligands are protonated and compete significantly with metal binding. With increasing pH, more ligands such as amino and carboxyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption on to cell surface (Aksu, 2001). As the pH increased further, the overall surface charge on the cells could become negative and biosorption decreased (Aksu, 2001). Patil and Paknikar (1999) have reported the optimum pH of 4.0 for the sorption of copper- and nickel-cyanide from aqueous solutions using *Cladosporium cladosporioides* biomass.

Free cyanide (CN^-) bearing effluents are highly alkaline in nature and have pH ranging from 9.5 to 12.5, whilst M_xCN effluents have pH in range of 6.0 to 10.0. Obviously, suitable pH alterations of the effluents would be required before biosorption. Unlike free cyanide, M_xCN s does not evolve potent hydrogen cyanide (HCN) gas because of their high stability constants (APHA-AWWA-WEF, 1998; Sharpe, 1976). Therefore, biosorption under acidic conditions would be a safe procedure. On the basis of screening studies under optimum pH conditions, Rice husk and *Eichhornia* root biomass were selected for DCAU sorption, while *Eichhornia* roots and Tea powder waste biomass were selected for DCAG sorption for further experiments.

The DCAU and DCAG loading capacity of the biosorbent could be taken as an equivalent measure of binding sites present. It was found that Rice husk biomass had the maximum loading capacity for DCAU (7.63 $\mu\text{mol/g}$) sorption among the two tested biomass; and was followed by *Eichhornia* root biomass (7.04 $\mu\text{mol/g}$). Loading capacity of Activated charcoal was less (7.61 $\mu\text{mol/g}$) when compared with Rice husk. In case of DCAG biosorption, *Eichhornia* root biomass showed highest loading capacity (9.74 $\mu\text{mol/g}$) followed by Tea powder waste (9.41 $\mu\text{mol/g}$). Loading capacity of *Eichhornia* root biomass though marginally less, but was highly competitive and comparable with that of activated charcoal (9.95 $\mu\text{mol/g}$). This unlocks newer opportunities of developing an efficient biosorption process for the removal and recovery of anionic species like gold-cyanide and silver-cyanide from low tenor waste solutions. In the study carried out by Patil (1999) it was found that the biomass of *C. cladosporioides* had higher loading capacity (34-40 $\mu\text{mol/g}$) than activated charcoal (27.5-30 $\mu\text{mol/g}$) for the sorption of metal-cyanides viz. copper- and nickel-cyanide. These results also indicate

that more such biomass screening programmes are needed in search of right candidate for efficient sorption.

In the present study loading capacity of conditioned biomass was also compared with that of unconditioned biomass (Table 3 and 4). For DCAU sorption, the unconditioned biomass showed lowered loading capacity compared to conditioned biomass. This reduction in loading capacity might be due to pH at which the loading capacity was determined. For conditioned biomass, the optimum pH for sorption was 4.0 as against the pH of sorption of unconditioned biomass i.e. the pH of original biomass (pH of Rice husk 5.94; pH of *Eichhornia* root biomass 7.01). In case of DCAG biosorption, it was observed that pH of unconditioned and conditioned biomass did not have any effect on the loading capacity of *Eichhornia* root and Tea powder waste biomass. This could be illustrated by the fact that original pH (unconditioned) of both *Eichhornia* root (pH 7.01) and Tea powder waste (pH 5.94) were similar to the obtained optimum pH values of our experiments. This result is very important from the view point of actual use of the biosorption process at commercial scale is concerned. Use of unconditioned biomass at commercial scale will save both time and money thereby making the cost of treatment economical which otherwise would have required for conditioning the biomass. Considering these results, selection of biosorbent was further narrowed down to Rice husk and *Eichhornia* root biomass for DCAU and DCAG biosorption, respectively.

For cost effective treatment of industrial effluents, it is imperative to discern the biomass quantity (i.e. solid-to-liquid ratio) required. In our experiments, it was found that as the biomass quantity increased the % biosorption of both the M_xCNs also increased. Maximum uptake in terms of Q ($3.84 \mu\text{mol/g}$) was observed at 3% (w/v) of Rice husk biomass for DCAU sorption. However, from 1 to 5 % (w/v) there was no significant increase. In case of DCAG sorption, *Eichhornia* root biomass showed highest Q value for the biomass-to-sorbent quantity from 2.0 to 5.0% (w/v). However, as the concentration of biomass was further increased the M_xCN uptake did not increase the biomass loading which is attributable to the interference between binding sites at higher quantities (de Rome and Gadd, 1987).

Process of biosorption is fundamentally a surface interaction and is characterized by rapid uptake of ions by biomass surfaces. Rapidity of the process makes it a worthy candidate for use in effluent treatment on a commercial scale. Kinetics showed that rate of uptake of both the M_xCN was maximum in first 15-20 minutes with over 80% of biosorption. Later, the sorption rate slowed down until it reached a plateau after 35-40 min, indicating the equilibration of system. Maximum sorption of DCAU and DCAG was 88% and 94% in 40 min. The quick equilibrium time may be attributed to the particle size. The effective surface area is high for small particles. Such type of result is typical for biosorption of metals involving no energy-mediated reactions, where metal removed from solution is due to purely physico-chemical interactions between the biomass and metal in solution. Basha *et al.* (2008) observed similar results in case of biosorption of oxyanion species viz. chromium using seaweed *Cystoseira indica*. The rapid kinetics has significant practical importance as it will facilitate smaller reactor/column volumes ensuring efficiency and economy.

The influence of starting DCAU and DCAG concentration on biosorption by Rice husk and *Eichhornia* roots biomass showed that equilibrium sorption capacity of the sorbent increased

with increasing starting concentration of M_xCNs from 0.01 to 1 mM (10 to 1000 μmol). This might be due to the increase in number of ions competing for available binding sites in the biomass. Uptake of M_xCNs at various concentrations reached a plateau when the concentration was in the range of 0.5 mM (500 μmol). This might be due to the saturation of binding sites, which clearly showed that M_xCN uptake by Rice husk and *Eichhornia* root biomass was a chemically equilibrated and saturable phenomenon. The higher starting concentration of target compound offers increased driving force to overcome all mass transfer resistance of target chemical ions between the aqueous and solid phases resulting in higher probability of collision between M_xCN ions and the biosorbent. This results in higher uptake of the target compound. Moreover, the biomass cell membrane comprises host of functional groups made of polysaccharides, proteins, lipids that have the potential of binding to M_xCN ions.

It is well known that biosorption resembles physical adsorption process and follows an adsorption type isotherm (Tsezos, 1990). Adsorption isotherms are the plots of solute concentration in the adsorbed state as a function of its concentration in the solution at constant temperature. Equilibrium sorption isotherms give useful evidence for selection of an adsorbent and facilitate evaluation of adsorption process for a given application (Weber, 1985). Isotherm indicates the relative affinity of biosorbent for target ions and the adsorption capacity of biosorbent. Also, the sensitivity of biosorption to changes in target compound concentration can be determined by the relative steepness of the isotherm line. Some of the important equilibrium models developed to describe adsorption isotherm relationships include single layer adsorption (Langmuir, 1918; Freundlich, 1926) and multilayer adsorption (Branauer *et al.*, 1938).

Adsorption isotherms are known to have been largely used for projected industrial applications (Tsezos and Volesky, 1981). In the present study, it was decided to fit the DCAU and DCAG sorption data with two most widely accepted adsorption models viz. Freundlich and Langmuir. Linear transformation of the adsorption data using Freundlich and Langmuir models ($R^2 = >0.96$) allowed computation of the M_xCN adsorption capacities. Experimental data was found to obey the basic principles underlying these models, that is, heterogeneous surface adsorption and monolayer adsorption at constant adsorption energy, respectively (Langmuir 1918; Freundlich 1926).

Other than the M_xCN species many additional cations and anions are normally encountered in the effluents emanated from industries like metal mining, electroplating, photofinishing units, printed circuit board manufacturing, etc. These species might inhibit the removal of DCAU and DCAG from aqueous solutions. The impact of commonly occurring cations and anions was therefore studied on biosorption of DCAU and DCAG by Rice husk and *Eichhornia* root, respectively. It was observed that M_xCNs were not significantly affected in most of the cases. However, biosorption of DCAU reduced by 33-40% in the presence of zinc, chromium and cadmium. In case of DCAG, sorption reduced by 37-67% by the presence of cadmium, zinc, iron and chromium. Biosorption in the presence of other metals cations (copper, nickel and silver) and anions (phosphates, sulphates and chlorides) was consistently above 80%.

Pretreated Rice husk and *Eichhornia* biomass with variety of chemicals showed greater degree of variation in the biosorption of DCAU and DCAG. Pretreatment of Rice husk and *Eichhor-*

nia root biomass with 1% L-cysteine enhanced the biosorption capacity of both the M_xCNs , while the NaOH pretreated biomass significantly hampered the biosorption process. Based upon the results obtained, it was thought worthwhile to determine the loading capacity of L-cysteine pretreated biomass as well. It was observed that the loading capacity of Rice husk and *Eichhornia* root biomass enhanced the biosorption of DCAU and DCAG upto 175% and 140%, respectively compared to untreated biomass (i.e. in absence of cysteine loaded biomass). These result corroborated with the findings obtained by Niu and Volesky (2000). This could be explained by the fact that in the acidic pH (pH 4.0 to 6.0 in our study), weak base groups either on cysteine or on the biomass becomes protonated and acquires a net positive charge. Roberts (1992) had reported the pK ranging from 3.5 to 6.0 of the positively charged weak base amine groups. Carboxyl group on the biomass could be protonated in their neutral for as the pKa is in the range of 3 to 5 (Buffle, 1988). In acidic pH range of 2.0 to 6.0, some of the carboxyl groups on cysteine may still be dissociated since the dissociated constant of carboxyl group on cysteine is 1.90, whereas the amino group is protonated and with a positive charge. This allows the cysteine binding to biomass through the integration/combination of negative cysteine carboxyl groups with some of the positively charged biomass functional groups. Thus, the positively charged cysteine amino group were available for binding of anionic M_xCN species like $[Au(CN)_2^-]$ and $[Ag(CN)_2^-]$ which are the target compounds in our studies. In other words, the anionic species $[Au(CN)_2^-]$ and $[Ag(CN)_2^-]$ adsorbed by ionizable functional groups on cysteine loaded biomass carrying a positive when protonated.



When the target compound is rare and costly, it is always desirable to recover the target compound from industrial effluents having low concentration and high volumes. For an effective and viable biosorption technology, elution methods for the recovery of target compound should be highly efficient, economical and should not cause damage to the biomass. Several eluting agents have been reported in the literature which includes mainly mineral acids, alkalis, organic acids, etc. In the present study, the loaded DCAU and DCAG on Rice husk and *Eichhornia* root biomass, respectively, could be desorbed with more than 95% efficiency using 1 N sodium hydroxide solution. Final concentration of DCAU and DCAG in the concentrated eluent was 28-30 and 22-25 folds, respectively, of the starting concentration. Such high tenor solution of recovered gold-cyanide and silver-cyanide may be recycled back to the user industry.

The next major task in the study was to test the selected biomass viz. Rice husk and *Eichhornia* root biomass for the removal of gold-cyanide and silver-cyanide from their respective industrial effluents in batch mode. As mentioned earlier that the project investigator encountered great difficulty in procuring the effluent samples from industries. In the end, third party intervention helped the investigator to get the sample. In developing country like India, most of industrial personnel are reluctant to give any information regarding toxic chemical waste like cyanide. Moreover, they don't allow the outsider to invade into their industry mainly due to the risk and threat that is associated with cyanide disposal. With the stricter statutory limits imposed by statutory agencies, the conventional physic-chemical methods for the treatment

of metal-cyanide bearing effluents are proving to be expensive and also inadequate to meet the required standards. This techno-economic impasse has led to closure of several industries especially the plating industries.

The gold-cyanide and silver-cyanide from the effluents procured from the industries could be effectively biosorbed by Rice husk and *Eichhornia* root biomass which were pretreated with L-cysteine. Gold and cyanide removal efficiency from gold-cyanide industrial effluent was 91.53% and 82.69%, respectively. However, the cyanide level in the biosorbed treated effluent although very less (0.59 mg/l) but was not below the standard limits prescribed by Indian statutory agencies, which is 0.2 mg/l. Similarly, the cyanide concentration after biosorption treatment to silver-cyanide effluent was also not complying with the standards prescribed by Indian statutory agencies. Overall, the studies on industrial effluents indicated that both the biomass viz. Rice husk and *Eichhornia* root biomass were very effective in treating both the effluents by biosorption process. Therefore, it is possible to employ Rice husk and *Eichhornia* root biomass for the treatment of industrial effluents on commercial scale. The residual (unrecoverable) cyanide remaining in the solutions after biosorption were subjected to biodegradation process using bacterial consortium under optimized conditions.

When the residual gold-cyanide and silver-cyanide biodegradation experiment was run under optimized conditions in batch mode, it was found that the live bacterial consortium previously isolated by Patil (2008) could degrade the cyanide present in the solution within a period of 5 h with an efficiency of >90% for both types of effluents. The resulting treated solution could comply with the disposal standards prescribed by statutory agencies in India. These findings indicated that biodegradation could be used as a polishing step in the treatment of precious M_xCNs containing industrial waste waters.

In process applications, the most effective apparatus for sorption/desorption and making the most effective use of the reactor volume, is a fixed-bed column. The column makes optimum use of the concentration gradient between the solute sorbed by the solids and that remaining in the liquid phase thereby providing the driving force for the biosorption process. The process of biosorption (metals and their related species) is governed by three key regimes: (i) the sorption equilibrium, (ii) the sorption particle mass transfer and (iii) the flow pattern through the packed bed. These three regimes determine the overall performance of the sorption column which is judged by its 'service time'. Service time is the length of time until the sorbed species breaks through the bed to be detected at a given concentration in the column effluent. The breakthrough point indicates that the column is saturated practically and could be taken out of operation for some kind of its regeneration (Volesky, 2003).

The column bed is being saturated at inflow concentration which represents equilibrium concentration for the part of the bed upstream from the transfer zone. The saturation of the bed/column varies from zero to the full saturation. This zone of partial saturation moves the column in the direction of the flow at a certain velocity which is predominantly determined by the biomass loading, sorbent capacity and the feed rate to column. The column is operational until this zone reaches the end of the column. Until that time the effluent leaving the column has no trace of the sorbate in it. When the transfer zone reaches the column end, the sorbate concentration in the effluent starts to gradually increase and for all practical purposes, the

working life of the column is over and the “breakthrough point” occurs marking the usable column “service time”. These two parameters are very important from the process design point of view because they directly affect the feasibility and economics of the sorption process (Volesky, 2003).

After successfully treating both the industrial effluents in batch mode using Rice husk and *Eichhornia* root biomass, further biosorption studies were carried out in continuous mode using packed bed column. It was found that the service time offered by the column beds for gold-cyanide (from column 1) and silver-cyanide (from column 2) effluents were 60 h and 40 h, respectively. In other words, these itself were the breakthrough points. For both the columns the transfer zone observed was of 30 h each. The total effluent passed through the column 1 and 2 was equivalent to 50 and 34 bed volumes, respectively, while the complete saturation occurred after 90 and 70 h, respectively. Continuous study clearly showed that both the effluents were biosorbed and treated successfully in the packed bed columns for the removal of both precious and toxic species. Further, in these studies the project investigator did not immobilized any of the biomass primarily because the present work was focused on low tenor effluents containing precious gold and silver and toxic chemical species like cyanide (all below 10 mg/l). Secondly, the results obtained through batch and continuous studies showed that both the biomass were efficient enough to sorb and treat the effluents and therefore the project investigator felt that immobilization of the biomass probably is not required in this case.

Thus, it could be concluded that the waste biomass used in the present study has immense potential “as biosorbents” for the removal/management of low tenor precious and toxic pollutants, as evident from the example of gold-cyanide and silver-cyanide management in the present study. Further, biosorption technology used could also become an economical, non-destructive and reliable alternative to the conventional processes for the management of industrial effluents employed on the commercial scale.

5. Application of biosorption to some newer wastes and products

Apart from the removal and recovery of precious heavy metal species from industrial effluents, passive bioremediation technology (PBT) can also be employed for some newer type of wastes and products that have emerged in the recent times.

A novel approach of combined biosorption-biodegradation processes was used by Patil and Paknikar (1999) for the removal and recovery of copper- and nickel-cyanide from electroplating effluents. *Cladosporium cladosporioides* biomass was found to be highly efficient sorbent in this case. The unrecoverable (residual) metal-cyanides after biosorption was subjected to biodegradation process using bacterial consortium. The treated effluent was free of cyanide and metals and complied with the statutory limits (Patil and Paknikar, 1999).

The problem of waste photovoltaic cells was addressed by Paknikar et al (1997) by way of recovering and recycling of expensive metals like silver, cadmium and tellurium. In this study, the researchers used scrapings of waste photovoltaic cells, which were dissolved in suitable

mineral acid and was diluted to obtain desired metal concentration. The metal solution was then subjected to biosorption column consisting of inactive granulated biomass of *C. cladosporioides* #1 for selective removal of silver. Similarly, in the next step, cadmium was removed by biosorption process by passing the solution through biosorbent column. The silver and cadmium free solution after treatment was then fed to tellurium reducing bioreactor consisting *P. mendocina*. The overall removal and recovery efficiency of these metals was >90%. With the rising demand and shift towards renewable energy sources, the number of photovoltaic cells producing units/industries will increase in the years to come; and so the use of non-renewable resources like metals and its wastages in the form of rejections. Although the economic feasibility of the process was not studied by the researchers) but the study certainly add to the advancement of knowledge by employing combined passive and active bioremediation (Paknikar et al 1997).

Pethkar et al. (2001) reported an interesting study on the removal of toxic metals like lead and cadmium from fruit juices of carrot, grapes and oranges, and extracts of Jatamansi herb and raisin by passive bioremediation using the biomass of *C. cladosporioides* #2. With a growth rate of 15%, the annual turnover of herbal medicinal industry in India is Rs. 75,000 million. As per ASSOCHAM (Associated Chamber of Commerce and Industry), the turnover of herbal industry is projected to double to Rs.1,50,000 million (USD 3 billion) by 2015. However, the business is getting severely affected by the presence of toxic heavy metals into food and herbal products thereby making them unacceptable in foreign markets because of their stringent statutory norms. Therefore, removal of these toxic metals from such products using biosorption process is crucial and has great prospectus. Sun et al (2007) had reported sorption of heavy metal ions by polyaspartyl polymers from Chinese herbal medicines. However, there is paucity of literature on biosorption of toxic metals from herbal medicines and food products.

Bhat et al (2012) had proposed a novel integrated model for the recovery of gold/silver from e-waste using an integrated hydrometallurgical (chemical) and biometallurgical (low cost biomass) processes. Feasibility study was conducted to explore the possibility of removal/recovery of silver-cyanide using low-cost biosorbents. *Eichhornia* root biomass and Waste tea powder were found to be an efficient low-cost biosorbents for leached silver-cyanide from electronic scrap. The concentrated silver-cyanide recovered had the potential for its further use as input material for electroplating industry (Bhat et al, 2012). Awareness among the urban population regarding disposal and management e-waste has also been studied by Bhat and Patil (2012).

In the twenty-first century, entire world is witnessing a paradigm shift in the overall waste management practices, which is rapidly changing its face and orientation. Waste is no more considered as waste but is recognized as a 'Resource'. This lost resource could potentially be recovered from the wastes using suitable strategies and technologies. Therefore, in a real sense, model like recovery and recycling of waste resource is gaining remarkable importance in today's so called 'Technological Society'. Application of concepts similar to this work will ultimately reduce the demand for natural resources thereby extending its sustenance. In view of this, the present chapter on passive bioremediation will certainly add to the advancement of knowledge in the field of resource recovery and industrial pollution management, waste

minimization and will help profitability of business community at large. It has not escaped through authors mind that the recovered resource from the waste of one industry has all the potential for its use as an input material for other industry thereby strengthening the emerging discipline of 'Industrial Ecology'.

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