SCREENING OF SOME LOW-COST WASTE BIOMATERIALS FOR THE SORPTION OF SILVER-CYANIDE COMPLEX [Ag (CN)$_2$]$^-$ FROM AQUEOUS SOLUTIONS

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ABSTRACT

Low-cost waste biomaterials/biomass from different categories (viz. Agricultural by-products, Industrial waste, Municipal solid waste, Fungal waste, Algal biomass and Photosynthetic plants waste) were collected from diverse sources and habitats were screened for the removal of precious silver-cyanide complex [Ag (CN)$_2$$^-$] (Dicyanoargentate-DCAG) from aqueous solutions. Among the tested biomaterials, *Eicchornia* root and tea powder waste biomass were found to be highly efficient biosorbents of DCAG. It was observed that biosorption of DCAG took place optimally at pH 6 for majority of the biomaterials tested. Loading capacity of *Eicchornia* root biomass (9.74 µmol/g) was higher than that of tea powder waste biomass (9.41 µmol/g), but was marginally lower than that of conventional activated charcoal (9.95 µmol/g). Results showed that low-cost biomaterials have tremendous potentials for their applications in environmental clean-up.

Key words: Biosorption, Dicyanoargentate, Low-cost biomaterials, Silver-cyanide, Waste biomass

INTRODUCTION

Industries like electroplating, jewelleries, printed circuit board manufacturing and mining (mainly gold and silver) emanate large-volume low-tenor effluents containing anionic metal-cyanide (MCN) complexes like silver-cyanide i.e. [Ag(CN)$_2$]$^-$ (Dicyanoargentate – DCAG). The total cyanide and Ag content in these effluents ranges from 5-25 and 5-10 mg/L, respectively. The discharge limits for total cyanide is 0.2 mg/L, while for Ag the standards are not defined[1]; although National Secondary Drinking Water

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Standards of Environmental Protection Agency (EPA), U.S. has reported the limit of 0.1 mg/L. Since cyanide is toxic and Ag being precious metals, non-renewable and finite resource; their complete removal from effluents is the key. At low concentration, Ag and Ag-cyanide recovery by conventional means is either not possible and/or very expensive. Biological methods like biodegradation using live microorganisms although reported[2], but are subject to toxicity of cyanide and Ag. Therefore, removal of precious metal like Ag and their complexes with cyanide from wastes requires immediate consideration of scientists and technologists. MCN in wastewaters can occur in various forms depending upon the concentration of metal and cyanide. For example, Cu-cyanide can occur in various anionic forms such as $[Cu(CN)_2]^-$, $[Cu(CN)_3]^{2-}$ and $[Cu(CN)_4]^{2-}$. Dissociation of MCN in water forms anionic moieties. Therefore, in principle, a well established physico-chemical methods can be used for removal/recovery of Ag-cyanide. A few physico-chaimical methods have been tried for the adsorption of Ag-cyanide[3], metal-cyanide using activated carbon and inorganic chemically active adsorbents[4], by foam fractionation[5] and modified ground sulphur[6]. However, practical utility and cost-effectiveness of these processes are not yet established. Biosorption of metal cations have been studied extensively[7]. Very few attempts have been made to adopt this technology for possible removal and recovery of "anions" such as metal-cyanides[8]. Review of literature indicates that far less attention have been paid on sorption of anionic species like Ag-cyanide using low-cost waste biosorbents/materials. The present research paper focusses on the screening of some low-cost biomaterials capable of removing Ag-cyanide ions efficiently from aqueous solutions.

EXPERIMENTAL

Biomaterials

The biomaterials used in the present study comprised of variety of low-cost biomaterials (as given below) collected from diverse sources and habitats. They were:

(i) **Agricultural by-products:** Coconut fibers, Cow-dung cakes, Groundnut shells, Rice husk and Rice straw.

(ii) **Industrial waste/by-products:** Dairy waste sludge, Saw dust, Tea powder waste and Sugarcane bagasse.

(iii) **Solid waste:** Vegetable waste, Nirmalya (Waste flowers).

(iv) **Fungi:** *Ganoderma* sp., *Mucorheimal is*, *Penicillium* sp., *Streptomyces* waste, *Streptoverticillium* waste and Wood rotting fungi.

(v) **Algae:** Mixed algal biomass.

(vi) **Plants:** *Parthenium* sp., *Eicchornia* leaves, *Eicchornia* roots, *Eicchornia* stem, Runners and *Tectonagrandis* dried leaves.

(vii) **Adsorbents as reference materials:** Activated charcoal, Fly ash, Bacterial consortium (capable of degrading cyanide and thiocyanate available in our laboratory).

All the biomass samples were collected from different sites in and around Kolhapur city. Sample were collected in polythene bags and transported to the laboratory. The biomass were washed several times with tap water to remove the dirt and other contaminants, if any, present on the sample. Finally the biomass samples were washed with deionised water. After washing, the samples were subjected to drying in oven at 50-60°C for 48-72 h till the constant weight was obtained. Later the dried biomass was crushed using electric mixer and sieved so as to get uniform particles size of $\leq$ 500 μm (0.5 mm).

Preparation of anionic silver-cyanide solution

The stock solution of Ag-cyanide i.e. $[Ag(CN)_2]^-$ (Dicyanoargentate - DCAG) was prepared stoichiometrically by combining silver nitrate solution with sodium cyanide solution in molar proportion of 1 : 2[9]. Spectral properties of prepared DCAG solution was checked and confirmed periodically using UV-visible spectrophotometer. The prepared Ag-cyanide solution was stored at 5-10°C.

Chemicals and analyses

Analytical grade chemicals were used for all the experiments. Glassware used were of borosilicate material. All the stock solutions and reagents were prepared in RO water having electrical conductivity of less than 5 μS and stored in refrigerator (5-10°C). Silver metal in the solutions was analysed by Atomic Absorption Spectrophotometer (Elico, India SL-173). Total cyanide content was estimated by pyridine-barbituric acid method as described in standard methods[10]. pH and electrical conductivity were measured by the respective meters (Elico Ltd., India).

Ag-cyanide (DCAG) biosorption studies

A batch equilibration method was used to determine the sorption of DCAG (0.1 mM). Biosorbent (0.1 g) was contacted with 5 mL solution of DCAG of desired pH in a set of 50 mL capacity bumper test tubes. The test tubes were incubated on rotary shaker at 150 rpm at 30°C for 0.5 h. Contents of flasks were filtered and then analysed for residual metal and total cyanide. All the experiments were performed in duplicates and repeated twice to confirm the results. In order to evaluate the influence of pH on biosorption of DCAG, 10 g

of powdered biomass was conditioned in DW at pH 4, 5, 6, 7, 8, 9 and 10 prior to testing the sorption of DCAG. Appropriate controls were run simultaneously.

The amount of DCAG sorbed at equilibrium, Q (mol/g), which represents the Ag-cyanide uptake, was calculated from the difference in DCAG concentration in the aqueous phase before and after adsorption, according to the following equation:

$$Q = \frac{V(C_i - C_f)}{1000\,m} \qquad\qquad …(1)$$

Where, Q is the DCAG uptake (mM per gram biomass); V is the volume of DCAG solution (mL); C_i is the initial concentration of DCAG (mM); C_f is the final concentration of DCAG (mM) and m is the mass of sorbent (g).

RESULTS AND DISCUSSION

Screening of low-cost biomaterials for Ag-cyanide (DCAG) sorption at optimum pH

Table 1 depicts the results obtained for DCAG sorption under optimal pH conditions. The results showed that optimum sorption in terms of Q (i.e. µmol DCAG sorbed per gram biomass) of 0.1 mM DCAG for most of the waste biomass/sorbents tested were at pH 6.0. Biosorption of DCAG was significantly low above pH 7.0 for all the biomass tested; while in acidic pH conditions, the sorption of DCAG was significantly increased.

The table also shows that other than activated charcoal (which was used as a reference material) which showed highest sorption capacity (5.00 µmol/g), biomass of *Eicchornia* roots and tea powder waste were most efficient biomaterials for DCAG among all the biomass screened. The Q values obtained for *Eicchornia* root and tea powder waste biomass was 4.76 and 4.73 µmol/g, respectively. These Q values of efficient biomass were marginally below the Q value obtained for activated charcoal (5.00 µmol/g). The optimum pH for maximum DCAG biosorption by *Eicchornia* root biomass and tea powder waste biomass was in the range of 6.0 to 9.0 and 5.0 to 9.0, respectively. Other than *Eicchornia* root and tea powder waste biomass, the next best candidate for DCAG sorption was dairy waste sludge (4.71 µmol/g). Also, among the different category of waste biomass tested, almost all the candidates from agricultural by-products category (viz. Coconut fibers, Cowdung cakes, Groundnut shells, Rice husk and Rice straw) showed good biosorption capacity efficiency (> 4.6 µmol/g). Biomass like saw dust, nirmalya, *Eicchornia* leaves, *Eicchornia* stem, runners and *Tectonagrandis* leaves were also found to be an efficient biosorbents of DCAG (> 4.6 µmol/g). Lowest sorption of DCAG sorption in terms of Q was

shown by a fungal biomass namely *Mucorhiemalis* (> 2.29 µmol/g). There was no loss of DCAG in the control tubes without sorbent during the tested time period.

Table 1: Biosorption of DCAG by various categories of low-cost biomaterials/biomass at optimum pH values

Sr. No.	Biosorbent/Biomaterials	Q (µmol DCAG sorbed per gram biomass)
(A)	**Agricultural by-products**	
1.	Coconut fibers	[a]4.62(5.0)
2.	Cowdung cakes	4.64 (6.0)
3.	Groundnut shells	4.62 (6.0)
4.	Rice husk	4.68 (6.0)
5.	Rice straw	4.69 (6.0)
(B)	**Industrial waste/by-products**	
6.	Dairy waste sludge	4.71 (6.0)
7.	Saw dust	4.64 (6.0)
8.	Sugarcane bagasse	4.03 (6.0)
9.	Tea powder waste	4.73 (5.0-9.0)
(C)	**Municipal solid waste**	
10.	Nirmalya (Waste flowers)	4.60 (6.0)
11.	Vegetable waste	3.88 (6.0)
(D)	**Fungal waste**	
12.	*Ganoderma* sp.	4.07 (6.0)
13.	*Mucorheimali*	2.29 (6.0)
14.	*Penicillium* sp.	3.99 (6.0)
15.	*Streptomyces* waste	2.78 (6.0)
16.	*Streptoverticillium* waste	3.52 (6.0)
17.	Wood rotting fungi	4.21 (6.0)

(E)	**Algal biomass**	
18.	Mixed algal biomass	4.16 (6.0)

(F)	**Photosynthetic plants waste**	
19.	*Parthenium* sp.	4.22 (6.0)
20.	*Eicchornia* leaves	4.62 (6.0)
21.	*Eicchornia* roots	4.76 (6.0-9.0)
22.	*Eicchornia* stem	4.66 (6.0)
23.	Runners	4.67 (6.0)
24.	*Tectonagrandis* leaves	4.63 (6.0)

(G)	**Reference materials**	
25.	Activated charcoal	5.00 (6.0)
26.	Bacterial consortium	4.00 (6.0)
27.	Fly ash	4.70 (6.0)
28.	Control (without biomass)	0 (6.0-9.0)

[a]All the values presented in table are average of two readings;
Values in the parentheses indicates optimum pH

It is well known that the process of biosorption is governed by the solution pH[11]. It was found that the biosorption of DCAG was maximum in acidic conditions (Table 1). The increase in sorption of DCAG under acidic conditions may be attributed to the protonation of biosorbent surface (i.e. the functional groups) acquiring net positive charges. Therefore, probably the formation of species such as $H^+ - Ag\ CN_2^-$ on the biomass might have taken place. Thus, relatively more DCAG species could have accommodated on the biosorbent sites. Most of the waste biomass from the natural origin contains large number of surface functional groups viz. hydroxyl, carbonyl, carboxyl, sulphydryl, amine, imine, amide, phosphonate, phosphodiester, etc. Probably some of these functional groups might have played the crucial role in the sorption of DCAG from the aqueous solution. Patil and Paknikar[8] have reported the optimum pH of 4.0 for the sorption of copper- and nickel-cyanides from aqueous solutions using *Cladosporium cladospoiroides* biomass and many other fungal cultures that were subjected to screening procedure. Further, in their studies they have attributed biosorption with the probable formation of species such as $H_2Cu\ (CN)_4$ and $H_2Ni\ (CN)_4$ that might have taken place on the biomass[8]. During our experiments, we found that there was no loss or auto-oxidation of DCAG in the controls tubes without

sorbent/biomass confirming that biosorption was the only mechanism by which DCAG is being removed from the aqueous solutions.

Biosorption process is similar to an ion-exchange process and therefore pH of solution influences the nature of biomass binding sites and metal solubility. At low pH (< 2.0), there is negligible metal uptake. The metal uptake increases as the pH increases from 3.0-5.0. At optimum pH, metal sorption is highest and it decreases with further increase in pH. At very acidic conditions, the proton concentration in solution is high. Metal ions have to compete with H^+ ions for surface binding sites[12]. At low pH, wall ligands associated with H_3O^+ restrain the access of metal ions due to repulsive forces[7]. The increase in metal binding with increase in pH could be due to less ionic competition. Also, increase in pH would expose more negatively charged ligands with subsequent increase in attraction for positively charged metal ions. However, at high pH, solubility of metal ions decreases, reducing the free metal ions available for binding. The pH (4.0-8.0) is optimal for metal uptake for almost all types of biomass[13]. However, Balkrishnan et al.[14] has reported higher uptake of precious metals at alkaline pH (8-10). Metals as anions in aqueous solutions, viz. CrO_4^{2-}, $AuCl_3^-$, $Ag(CN)_2^-$ exhibit higher uptake in the acidic pH[7]. In the present study, we found that DCAG uptake was at acidic pH and the results obtained corroborates with the study of Pethkar and Paknikar[15].

It needs to be mentioned that hydrogen cyanide (HCN) gas is not formed under acidic conditions (which happens readily in case of free cyanide ions i.e. KCN/NaCN) because DCAG under acidic conditions is very stable metal-cyanide complex having log K of 20.8[16] as against the log K of 9.2 of potassium/sodium cyanide[17]. Therefore, biosorption under acidic conditions would be an innocuous procedure. Cyanide and metal cyanide containing industrial wastewaters generally have pH ranging from as low as 5.5 to as high as 12.5. Obviously, appropriate pH adjustments of the effluents will have to be carried out prior to biosorption. On the basis of maximum MCN uptake values obtained under optimum pH conditions, *Eicchornia* root and tea powder waste biomass were selected for further DCAG loading capacity experiments. Being an efficient sorbent, activated charcoal was selected as reference material.

Loading capacityof DCAG

Table 2 depicts the data on loading capacity of sorbent/biosorbents selected on the basis of maximum sorption under optimum pH. It could be seen that *Eicchornia* root biomass showed highest loading capacity of 9.74 µmol/g followed by tea powder waste biomass (9.41 µmol/g). Loading capacity values of *Eicchornia* root biomass is highly competitive and was marginally below activated charcoal (9.95 µmol/g).

Table 2: DCAG loading capacity of selected biosorbents

Biosorbents	Loading capacity (µmol/g of biomass)
Eicchornia root biomass	9.74
Tea powder waste biomass	9.41
Activated charcoal	9.95

All the values presented in table are average of two readings

The loading capacity of the biosorbent could be taken as an equivalent measure of binding sites present. Loading capacity values of *Eicchornia* root biomass was highly competitive and comparable with activated charcoal (9.95 µmol/g), which was used as reference material (Table 2). This opens up new possibilities of developing an efficient biosorption technology for the recovery of anionic species like silver-cyanide, gold cyanide and similar other species from wastewaters. In the previous study carried out by Patil[8,9], it was found that the biomass of *Cladosporium cladosporoides* had higher loading capacity (34-40 µmols/g) than activated charcoal (27.5-30 µmol/g) for the sorption of metal-cyanides viz. copper- and nickel-cyanide. These results also indicate that more such biomass screening programmes are needed to be carried out in search of a right candidate for efficient sorption of precious contaminants.

Interactions of low-cost biomaterials/biomass with heavy metals and their complexes offer numerous opportunities for its application in environmental clean-up. The biosorption phenomena are the combinations of 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 metals (both cationic and anionic species). The overall interactions are a result of complexity of biomass surfaces and chemical/physical properties of metal ions. The phenomenon of biosorption could be exhibited by active (i.e. living) as well as passive (i.e. non-living) biomass. There are several advantages of biosorption process. They are: (i) non-living biomass is not subject to toxicity limitations; (ii) costly nutrients and aseptic conditions are not required for their growth; (iii) waste biomass from natural habitats, man-made activities and industry could be the cheap source of biomass; (v) biosorbent could be operated at wider range of pH, temperature and metal concentration; (vi) well established theories, conventions and formulae could be applied to the adsorbent, etc. Thus, it could be concluded from our screening studies that low-cost biomass like *Eicchornia* root was found to be a highly efficient biomaterial for the removal of precious silver-cyanide from solutions.

ACKNOWLEDGEMENT

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