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Editorial

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Editorial Note

The first issue of the first volume of SAJMR received good response from the readers. The feedback received from the readers made us to improve the present issue.

The present issue has broader scope than the earlier, yet we have kept the true spirit of the journal. In this issue we have included articles from the Computer Studies and Environmental Management field as well. As we have stated earlier, the objective of the journal is to provide a common platform for the practicing managers and academicians to share their research knowledge through this journal.

In future, we also welcome articles related to different pedagogical approach in management teaching. Many courses including management discipline everywhere use more of a traditional approach of lecturing to share the knowledge. Lecturing method is more passive in nature. Case study comes next to lecturing method in imparting knowledge. But not much has been done in developing experiential approach as a pedagogy of teaching in management field, particularly in India.

Experiential learning is more active rather than passive. The readers can contribute case studies and teaching material in experiential learning approach in different management fields such as marketing, human resources, organization behaviour, organizational change and development, strategic management, etc.

I am grateful to all the authors, reviewers and editorial members of the journal for their contribution and support in bringing out the second issue of first volume of the journal successfully.

Dr. Babu Thomas
Editor

Management of thiocyanate pollution using a novel low cost natural waste biomass

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Abstract

Environmental pollution caused due to the release of toxic and hazardous (T&H) chemical wastes from industrial processes is an issue of major environmental concern. 'Thiocyanate', one such T&H chemical, is encountered in several industrial effluents. Owing to its toxicity, its proper management by removal from liquid wastes using suitable cost-effective and efficient technology is the key. Management/removal by sorption using biomass is one such technology. Waste biomass (powdered dried leaves) of various photosynthetic plants (consisting of big trees and weeds) were screened for the removal of thiocyanate from the aqueous solutions. Among the tested biomaterials, *Mangifera indica* (Mango) biomass was found to be highly efficient biosorbent of thiocyanate. Biosorption of thiocyanate from solutions took place optimally in the pH range of 4 to 6 and biosorbent quantity of 3% (w/v). Loading capacity of *Mangifera indica* biomass (10.5 mg/g) was comparable with that of activated charcoal (11 mg/g), which was used as a reference material. Kinetic study showed that the process of biosorption was rapid and for maximum thiocyanate sorption the contact time required was 60 minutes. The experimental data showed that thiocyanate uptake values could well be fitted to the Langmuir and Freundlich adsorption isotherms models. When the process of biosorption was carried out under standardised conditions, a 10-17 fold concentration of thiocyanate could be achieved using sodium hydroxide as an eluting agent. Laboratory experiments thus, clearly indicate that thiocyanate could effectively be managed by its removal from aqueous solutions using low-cost natural waste biomass.

Keywords: Biosorption, Low-Cost, *Mangifera indica*, Pollution Management, Thiocyanate, Waste Biomass

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1. Introduction

A surge in science and technology in the eighteenth century resulted in the industrial revolution beginning in England and France, which spread elsewhere from the mid nineteenth century worldwide during 1850. In the latter half of the twentieth century, the industrial sector expanded substantially thereby positively impacting economic growth in almost every nation. However, it also resulted in a significant depletion of natural resources with simultaneous deterioration of the quality of environment. In the past few decades, rapid industrial development and growth have taken theirs toll by increasing environmental pollution. The contamination of various environmental segments owing to the release of hazardous and toxic chemical wastes is one of the major problems faced by mankind. Often these chemicals prove to be highly toxic to plants, animals and humans, if improperly managed.

Industrial effluents can broadly be classified as wastes rich in organic matter on the one hand; and wastes rich in inorganic matter on the other. Cyano-group of chemicals and heavy metals (viz. copper, cadmium, chromium, iron, nickel, etc.) form a significant part of the latter type of wastes. One of the important family members of cyano-group of chemicals known is 'Thiocyanate'. Chemically, it is toxic in nature, negatively charged species (SCN^-) and contains one-carbon along with sulphur and nitrogen. Moreover, thiocyanate is linear, polyatomic ion and a good example of pseudohalides because of the similarity of its reactions to that of halide ions (Hughes, 1975).

Sources of thiocyanate include plants, biotic and abiotic decomposition and *in vivo* detoxification. Thiocyanate occurs naturally in plants like cauliflower, turnips and cabbage present in the wastes. Therefore, removal of precious/important anionic species like thiocyanate and their metal-complexes from wastes requires immediate attention of scientists and technologists. The challenge is not limited only to their removal, but also extends to finding efficient and economical ways of possible recovery and recycling. It was thought by us that if an efficient process for removal/recovery could be developed, thiocyanate could be conserved, which in our opinion would be a novel approach of resource recovery. Since thiocyanate is an anionic species, in principle, well established physico-chemical methods can be used for removal/recovery of thiocyanate.

Overview on thiocyanate removal mainly focuses on (bio)degradation of thiocyanate and (bio)adsorption of metal "cations". Far less attention has been paid on biosorption of "anions" like thiocyanate, cyanide and their metal complexes using low-cost natural waste biomaterials. Microorganisms capable of metabolising/degrading cyano-compounds like cyanide and metal-cyanides are well documented and have been studied for a long time (Karavaiko *et al.*, 2000; Patil and Paknikar, 2000). Use of metabolically inactive (dead) microorganisms for the removal and recovery of metal-cyanides have also been reported (Patil and Paknikar, 1999). Successful attempts to set-up large scale biological treatment plant for the removal of cyanide, metal-cyanides and thiocyanates from mining effluents have been made on commercial scale (Whitlock, 1990).

In the light of the above background, the researchers in the present paper focussed on the use of a novel low-cost natural waste material (viz. powedered biomass of mango leaves) for the management (i.e. removal) of thiocyanate from aqueous solutions.

2. Experimental

2.1. Collection and processing of waste biomass

The biomass used in the present study comprised mainly of natural waste, dried leaves of various tree species viz. *Eucalyptus* sp. (Nilgiri), *Tectona grandis* (Sag), *Mangifera indica* (Mango), *Azadirecta indica* (Neem), *Casurina* sp. (Suru); *Jambulana* sp. (Jamun), *Delonix regia* (Gold Mohar) and *Artocarpus heterophyllus* (Jackfruit). Biomass of some commonly occuring weeds (i.e. unwanted plants) like *Parthenium* sp. (Congress grass), *Lantana camera* (Ghaneri), *Calycopteris floribunda* (Ukshi) and *Eicchornia* sp. (Jalparni) were also used for the study. All the biomass samples were collected from various locations in and around Kudal city of Sindhudurg District, located in the Southern parts of Maharashtra, India. Conventional sorbents like activated charcoal, saw dust and fly ash were used as reference materials. All the waste biomass samples were collected in polythene bags and transported to the laboratory. The biomass samples were then washed several times with distilled water (DW) to remove the dirt and other contaminants, if any, present on the sample. After washing, the samples were subjected to drying in oven at 50-60°C for 2-3 days till the constant weight was obtained. Later, the dried biomass was ground using mortar and pestle and was sieved so as to get uniform particles of 14-16 BSS mesh (1.2-1.4 mm) size.

2.2. Thiocyanate sorption/uptake studies

A batch equilibration method was used to determine the sorption of thiocyanate using ground tree leaves. Biosorbent (1 g) was contacted with 50 ml thiocyanate solution having concentration of 100 mg/l of desired pH in a set of 150 ml capacity conical flasks. The contents of the flasks were stirred gently by sparging air using electrical aerator units and incubated at room temperature (30±2C) for 0.5 – 5 h. The contents of flasks were filtered and analysed for residual thiocyanate content.

In order to evaluate the effect of pH on biosorption of thiocyanate, 5 g of powdered biomass obtained from each plant/tree species was conditioned in DW at desired pH of 2, 3, 4, 5, 6, 7, 8, 9 and 10. Other experimental conditions were similar to those mentioned earlier. Thiocyanate loading capacity (mol thiocyanate bound per gram weight of biomass) of each biosorbent material was determined by contacting 1 g powdered biomass several times with fresh batches of 50 ml thiocyanate solution (100 mg/l) till the saturation was reached. These experiments were carried out at optimum pH value obtained for the respective biomass. For determining optimum biosorbent amount, 0.5 to 5% (w/v) sorbent was contacted with target compound i.e. thiocyanate. Rate of thiocyanate uptake was studied by contacting the biosorbent for a period ranging 0 - 5 h. This experiment was carried out at optimum pH and biosorbent concentration. Other experimental conditions were similar to those mentioned earlier. All the experiments were performed in duplicates and repeated twice to confirm the results. Appropriate controls were run simultaneously to test the stripping of thiocyanate, if any, from solutions.

2.3. Glassware, chemicals and analyses

All the glassware used in the present study was made of borosilicate material. Chemicals used were of analytical grade. Potassium thiocyanate (KSCN) was obtained from Loba Chem, Mumbai. All the stock solutions and reagents were prepared in glass-distilled water (DW) and stored in refrigerator at 8-10°C. Thiocyanate in the liquid samples was estimated colorimetrically (Equiptronics, India) by ferric nitrate method as described in Standard Methods (APHA-AWWA-WEF, 1998). pH of the solutions were measured using pH meter (Equiptronics, India).

2.4. Adsorption isotherm models

Thiocyanate solutions of varying concentrations (ranging from approximately 1 to 17 mM, corresponding to approximately 50 to 1000 mg/l) were used to study the effect of initial thiocyanate concentration on it adsorption. The amount of thiocyanate sorbed at equilibrium, Q (mol/g), which represents the thiocyanate uptake, was calculated from the difference in thiocyanate concentration in the aqueous phase before and after adsorption, according to the following equation:

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

Where, Q is the thiocyanate uptake (mol per gram biomass); V is the volume of thiocyanate solution (ml); C_i is the initial concentration (mg/l); C_f is the final concentration (mg/l); m is the mass of biosorbent (g).

To examine the relationship between sorbed and aqueous concentration at equilibrium, sorption isotherm models viz. Freundlich and Langmuir were used for fitting the data.

2.5. Freundlich adsorption model

The Freundlich model (Freundlich, 1926) habitually gives a better fit particularly for adsorption from liquids and can be expressed as:

$$\text{In}\ Q = \text{In}\ K + \frac{1}{n} C_{eq} \tag{2}$$

Where, C_{eq} is the liquid phase concentration of thiocyanate; K is the constant; 1/n is the intensity of adsorption and Q is the specific metal uptake.

In this model, the mechanism and the rate of adsorption are functions of the constants 1/n and K. Many researchers have used this model to interpret their sorption data for various systems (Patil and Paknikar,1999).

2.6. Langmuir adsorption model

The Langmuir adsorption isotherm (Langmuir, 1918) is given by the following equation:

$$\frac{C_{eq}}{Q} = \frac{1}{bQ_{max}} + \frac{C_{eq}}{Q_{max}} \tag{3}$$

Where, C_{eq} is the liquid phase concentration of thiocyanate; b is the Langmuir constant; Q is the thiocyanate uptake (mol/g biomass) Q_{max} is the maximum thiocyanate uptake.

In this model, Q_{max} (mg/g) is the amount of adsorption corresponding to complete monolayer coverage i.e. the maximum adsorption capacity. A host of research workers have applied this model to interpret their sorption data (Puranik and Paknikar, 1997).

2.7. Adsorption/Desorption of thiocyanate

Biosorbent (1 g) loaded with thiocyanate was eluted using 0.1 - 1 N sodium hydroxide (NaOH) in concentrated form and analysed. Following the elution, the biosorbent was washed with DW and then conditioned to appropriate pH to use it in next adsorption/desorption cycle. At each stage, one set was removed as a control.

Table 1: Biosorption of thiocyanate by waste biomass at optimum pH

Sr. No.	Biosorbent (Vernacular Name)	Q (mg thiocyanate sorbed per gram biomass)	Optimum pH for maximum sorption
1.	*Azadirecta indica* (Neem)	2.1	5, 6
2.	*Casurina* sp. (Suru)	2.0	5
3.	*Calycopteris floribunda* (Ukshi)	2.3	5
4.	*Eicchornia sp.* (Jalparni)	2.7	5, 6
5.	*Eucalyptus* sp. (Nilgiri)	1.8	5, 6
6.	*Artocarpus heterophyllus* (Jackfruit)	1.5	5, 6
7.	*Delonix regia* (Gold Mohar)	1.9	5, 6
8.	*Jambulana* sp. (Jamun)	2.4	5, 6
9.	*Lantana camera* (Ghaneri)	3.2	5, 6
10.	*Mangifera indica* (Mango)	3.8	4, 5, 6
11.	*Parthenium* sp. (Congress Grass)	2.7	5, 6
12.	*Tectona grandis* (Sag)	2.9	5, 6
13.	Activated charcoal*	4.6	4, 5, 6
14.	Fly ash*	1.4	6
15.	Saw dust*	2.8	4, 5, 6

All the values presented in table are average of two readings; *Reference materials used as control

3. Results

3.1. Screening of plant/tree biomass for thiocyanate sorption at optimum pH

The results obtained for thiocyanate sorption under optimal pH conditions are summarised in Table 1. It was observed that optimum sorption of thiocyanate (100 mg/l) for most of the sorbents tested were at pH 5.0 and 6.0 with the exception of *Casurina* sp. and *Calycopteris floribunda* biomass. For both the biomass, maximum sorption was observed only at pH 5. However, in case of *Mangifera indica* leaf biomass, activated charcoal and saw dust, pH optimum of 4 was also observed for thiocyanate sorption along with pH 5 and 6. For all the tested biomass, biosorption of thiocyanate did not take place above pH 6.0; while at pH below 4, sorption significantly decreased (data not shown). The table also shows that other than activated charcoal and saw dust (which were used as reference materials) biomass of *Mangifera indica, Lantana camera, Tectona grandis, Parthenium* sp. and *Eicchornia sp.* were efficient sorbents of thiocyanate. The Q values thus observed for these sorbents were in the range of 2.7 to 4.6 mg/g. The control flasks run simultaneously along with the experimental flasks showed no loss of thiocyanate.

On the basis of maximum thiocyanate uptake values (Q) obtained under optimum pH conditions, *Mangifera indica, Lantana camera, Tectona grandis, Parthenium* sp. and *Ecchornia* sp. were selected for further experiments on thiocyanate biosorption. Activated charcoal and saw dust were used as reference materials.

3.2. Thiocyanate loading capacity

Table 2 depicts the data on thiocyanate loading capacity of sorbent/biosorbents selected on the basis of maximum sorption under optimum pH. It is seen that *Mangifera indica* biomass had the maximum loading capacity for thiocyanate (10.5 mg/g) among the tested biomass; and was followed by *Lantana camera* (9.4 mg/g), *Parthenium* sp. (8.0 mg/g), *Ecchornia sp.* (7.8 mg/g) and *Tectona grandis* (7.1 mg/g). Loading capacity values of *Mangifera indica* biomass were comparable with activated charcoal (11 mg/g), which was used as reference material.

Table 2. Thiocyanate loading capacity of various biosorbents

Sorbent / Biosorbents	Loading capacity (mg/g of biomass)
Ecchornia sp.	7.8
Lantana camera	9.4
Mangifera indica	10.5
Parthenium sp.	8.0
Tectona grandis	7.1
Activated charcoal	11.0
Saw dust	9.5

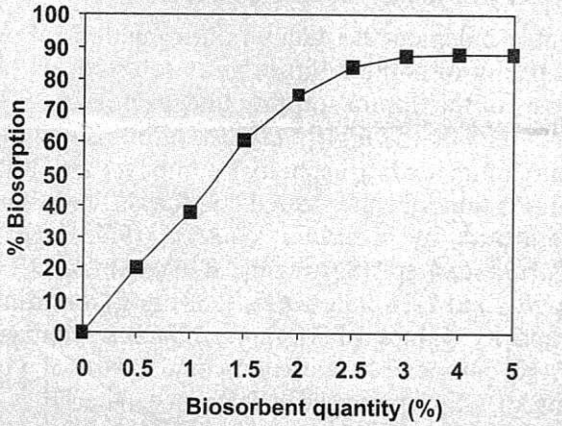
All the values presented in table are average of two readings

Considering these results, selection of the biosorbent was further narrowed down to *Mangifera indica* leaf biomass for thiocyanate biosorption.

3.3. Influence of biosorbent/biomass quantity on thiocyanate biosorption

The effect of biomass quantity [% biomass in 50 ml thiocyanate solution (w/v)] on the thiocyanate biosorption was studied at room temperature (30±2°C) and at optimum pH of 5. Various amount of biomass like 0.5, 1, 1.5, 2.0, 2.5, 3, 4 and 5 g were used keeping the volume of thiocyanate solution constant i.e. 50 ml; thereby giving the solid-to-liquid ratio in the range of 0.01 to 0.1 and the results are shown in Fig. 1. The results indicate that as the biomass quantity increased the % biosorption of thiocyanate also increased. Maximum uptake (~87%) was observed at 3% (w/v) of *Mangifera indica* biomass quantity with 100 mg/l of thiocyanate. With 2% and 1% biomass amount, uptake decreased to 75% and 39%, respectively (Fig. 1).

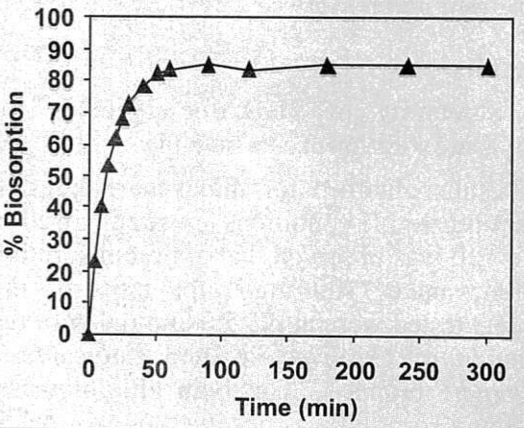
Fig. 1. Influence of biosorbent quantity on thiocyanate biosorption by *Mangifera indica*



3.4. Influence of contact time

The effect of contact time on thiocyanate biosorption was studied at optimum pH of 5, room temperature (30±2°C) and biomass quantity of 3% (w/v). 50 ml of thiocyanate solution having concentration 100 mg/l was contacted with 1.5 g of grinded *Mangifera indica* biomass for the period up to 300 min. The time intervals chosen to study the effect of contact time were 5, 10, 15, 20, 30, 40, 50, 60, 90, 120, 150, 180, 240 and 300 min. Periodically the flask content were removed by filtration and the filtrate were analysed for thiocyanate concentration. Curve in the Fig. 2 representing the kinetics of thiocyanate sorption showed that the rate of thiocyanate uptake was maximum in the first 20-30 minutes with over 60% of biosorption. Later, the sorption rate slowed down until it reached a plateau after 60 min, indicating equilibration of the system. Maximum sorption of thiocyanate observed at 60 min was 85% (Fig. 2).

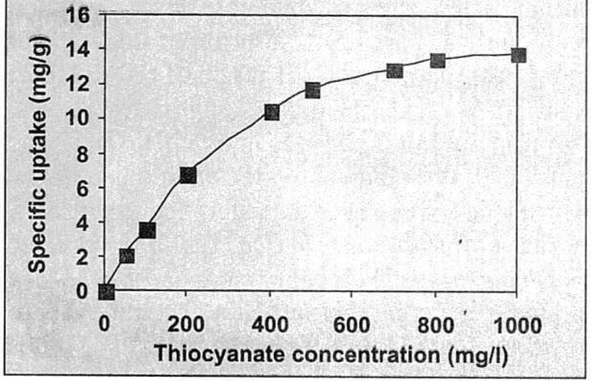
Fig. 2. Rate of thiocyanate uptake by *Mangifera indica* biomass



3.5. Adsorption isotherm models

The effect of initial concentration provides an important driving force to overcome all mass transfer resistance of target ion between the aqueous and solid phases. The biosorption of thiocyanate was carried out at different initial thiocyanate concentrations ranging from 50 to 1000 mg/l (corresponding to approximately 1 to 17 mM) at pH 5.0 using 3% of ground *Mangifera indica* leaf biomass. Fig. 3 depicts the thiocyanate uptake by the ground *Mangifera indica* leaf biomass. It can be seen that the equilibrium sorption capacity of the sorbent increased with increasing initial concentration of thiocyanate from 50 to 1000 mg/l due to the increase in the number of ions competing for the available binding sites in the biomass. The uptake of thiocyanate by the sorbent reached a plateau at 700-800 mg/l. There was a significant increase in the specific uptake of thiocyanate upto 500 mg/l. Later the specific uptake of thiocyanate decreased with increased concentration. The specific uptake was 2 and 12 mg/g for thiocyanate concentration of 50 and 500 mg/l, respectively.

Fig. 3. Effect of initial thiocyanate concentration on uptake of *Mangifera indica* biomass



3.6. Equilibrium models to fit experimental data

To examine the relationship between sorption, isotherm models are widely employed for fitting the data. Langmuir and Freundlich models were used to describe the equilibrium between the thiocyanate sorbed on the ground *Mangifera indica* leaf biomass and thiocyanate ions in the solution. Fig. 4 and 5 show that thiocyanate uptake values could be fitted to the Langmuir and Freundlich isotherm models with the regression value of>0.96.

3.7. Adsorption-desorption of thiocyanate

The loaded thiocyanate could be desorbed with more than 90% efficiency using 0.1 - 1 M sodium hydroxide solution. Final concentrations of thiocyanate in the eluant were in the range of 800 to 1000 mg/l (14 to 18 mM) using *Mangifera indica* leaf biomass. These values represented an approximately 8 to 10 fold concentration of thiocyanate as compared to the original concentration of 100 mg/l (1.72 mM) that was used for sorption. However, during the second cycle of thiocyanate adsorption, the loading capacity of the biosorbent decreased by 35-40%.

Fig. 4. Langmuir adosption isotherm for thiocyanate biosorption by *Mangifera indica*

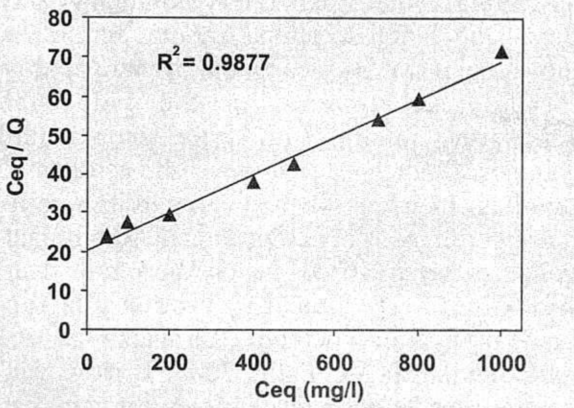
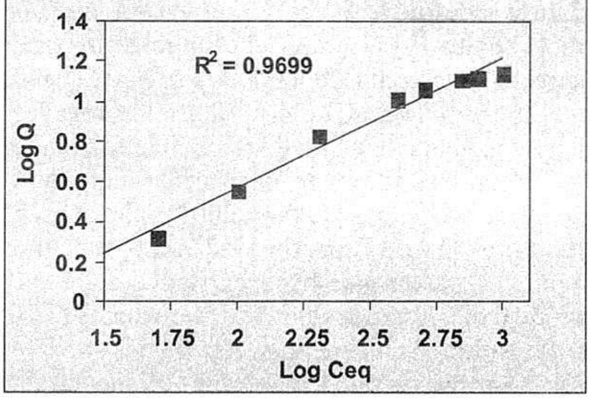


Fig. 5. Freundlich adsorption isotherm for thiocyanate biosorption by *Mangifera indica*



4. Discussion

Biosorption of heavy metal cations from aqueous solutions have been studied extensively by several researchers world wide (Modak and Natrajan, 1995; Paknikar *et al.*, 2003). A number of research papers have also been published on the sorption and removal of anionic metal species like chromates (Basha *et al.*, 2008), free cyanide (Azab *et al.*, 1995) and metal-cyanides (Patil and Paknikar, 1999) using microbial biomass (especially fungal cultures) procured either from fermentation industry or by cultivating it under laboratory conditions and then using it for sorption. Another important known chemical species is 'thiocyanate' that is normally encountered in the industrial wastewaters along with free- and metal-cyanides. Thiocyanate is one of the active and important members of the cyano-group family that occur in the water environment. Significant work has been carried out on the removal of thiocyanate species by biodegradation /biodetoxification method (Karavaiko *et al.*, 2000; Patil, 2008a; Patil, 2008b). However, scanty information is available on the removal and recovery of anionic species like thiocyanate using sorption technology from aqueous wastes. Much of the work carried out previously is mainly confined to the removal of metal-thiocyanates using anion exchange resins and activated charcoal (Kononova *et al.*, 2007) and polyurethane foam (Hasany, 2002). Removal of metal-thiocyanate using low-cost materials like agricultural solid waste has been reported in recent times (Namasivayam, 2007). The overall literature review clearly indicates that no significant work has been carried out on the removal of anionic species like thiocyanate from waste solutions using low-cost materials like plant biomass. Since all the cyano-group chemicals like free cyanide and thiocyanate, metal-cyanides and metal-thiocyanates are toxic to all classes of living organisms their removal from waste prior to discharge in the environment becomes the key.

In the light of the above background, the core objective of the present research work was to study the feasibility of biological removal and recovery of thiocyanate from aqueous industrial waste solutions for possible recycling in the industry using ground waste leaves obtained from various photosynthetic trees. It was thought that, if an efficient process for removal/recovery could be developed, thiocyanate could be conserved, which in our opinion would be a novel approach of resource recovery. Free cyanide and thiocyanate, metal-cyanides and metal-thiocyanates can occur in the waste waters in various forms depending upon the chemical nature of the compounds and the concentration of metal, cyanide and thiocyanate, provided the 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. Therefore, it was thought worthwhile to explore the possibility of their recovery by adsorption on low-cost material like ground plant leaf biomass procured from various photosynthetic trees. Known sorbents such as activated charcoal, saw dust and fly ash were used for obtaining comparative data.

It is well known that the process of biosorption is governed by the solution pH (Puranik and Paknikar, 1997). For this reason, the first selection step used during the present studies was determination of optimum solution pH. It was found that the biosorption of thiocyanate by all the biomass increased with the increase in pH and then declined rapidly with further increase in pH (data not shown). As seen from Table 1, maximum sorption of thiocyanate could take place in the pH range of 5.0 to 6.0 in most cases; and pH 4.0 to 6.0 in few cases. Sorption did not take place above pH 6.0. It was found that other than activated charcoal and saw dust (which were used as reference materials), biomass of *Mangifera indica*, *Lantana camera*, *Tectona grandis*, *Parthenium* sp. and *Ecchornia* sp. were efficient biosorbents for thiocyanate sorption. The Q (i.e. specific uptake) values observed for these sorbents were in the range of 2.7 to 4.6 mg/g. There was no loss of thiocyanate in the control flasks (flasks devoid of any biosorbent) confirming that biosorption is the only mechanism by which thiocyanate is being removed from the aqueous solution. Previous studies carried out by Namasivayam (2007) found that the optimum pH for maximum adsorption of thiocyanate by modified coir pith (an agricultural waste) was 2.0; while Lazaridis (2003) has reported a pH optimum of 7.0 - 7.5 using hydrocalcite-500.

The increase in sorption of thiocyanate in acidic conditions may be due to the protonation of biosorbent surface (i.e. the functional groups) acquiring net positive charges. Therefore, probably the formation of species such as HSCN on the biomass might have taken place. Thus, relatively more thiocyanate species could have accommodated on the biosorbent sites. Leaves from the plant biomass are well known to contain large number of surface functional groups viz. hydroxyl, carbonyl, carboxyl, sulphydryl, amine, imine, amide, phosphonate, phosphodiester, etc (Basha *et al.*, 2008; Gardea-Torresdey *et al.*, 1998). Probably some of these functional groups might have played the role in the sorption of thiocyanate from aqueous solution. It is known that the pH dependence of cations and anionic adsorption can largely be related to type and ionic state of these functional groups and also the chemistry of target compound in solution (Matheickal and Yu, 1996). Thiocyanate, although a non-metal and anionic chemical species, could be compared with anionic metal species like hexavalent chromium (an oxyanion). 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 metal-cyanides from aqueous solutions using *Cladosporium cladospoiroides* biomass.

It is worthwhile to mention that HCN gas is not formed under acidic conditions (as it happens easily in case of free cyanide i.e. KCN/NaCN and up to certain extent in metal-cyanides) because SCN^- is known to have high stability under acidic conditions (APHA-AWWA-WEF, 1998). Biosorption, therefore, under acidic conditions would be a safe procedure. Cyanide and thiocyanate containing industrial wastewaters generally have pH ranging from 5.5 to 12.5. Obviously, appropriate pH adjustments of the effluents will have to be carried out prior to biosorption. On the basis of maximum thiocyanate uptake values obtained under optimum pH conditions, *Mangifera indica*, *Lantana camera, Tectona grandis, Parthenium* sp. and *Ecchornia* sp. were selected for further experiments on thiocyanate biosorption. Activated charcoal and saw dust were used as reference material.

The thiocyanate loading capacity of the biosorbent could be taken as an equivalent measure of binding sites present. It could be seen that *Mangifera indica* biomass had the maximum loading capacity for thiocyanate (10.5 mg/g) among the tested biomass; and was followed by *Lantana camera* (9.4 mg/g), *Parthenium* sp. (8.0 mg/g), *Ecchornia sp.* (7.8 mg/g) and *Tectona grandis* (7.1 mg/g). Loading capacity value of *Mangifera indica* biomass was comparable with activated charcoal (11 mg/g); which opens up new possibilities of developing an efficient bisorption technology for the recovery of anionic speceis like thiocyanate and other similar species from wastewaters. In the previous study by Patil (1999), it was found that the biomass of *Cladosporium cladosporoides* had higher loading capacity (34 - 40 μmol/g) than activated charcoal (27.5 - 30 μmol/g) for the sorption of metal-cyanides viz. copper- and nickel-cyanide. This result clearly indicates that more such programmes for biomass screening should be carried out in search for the right candidate for efficient sorption. Considering the results from our experiments on powdered plant leaf biomass, selection of the biosorbent was further narrowed down to *Mangifera indica* leaf biomass for thiocyanate biosorption.

For the cost-effective treatment of industrial wastewaters for thiocyanate removal, it is necessary to know the biomass quantity (i.e. solid-to-liquid ratio) required. In our experiments, it was found that as the biomass quantity increased the percentage biosorption of thiocyanate also increased. Maximum uptake (~87%) was observed at 3% (w/v) of *Mangifera indica* biomass quantity with 100 mg/l of thiocyanate giving the solid-to-liquid ratio of 0.03. With 2% and 1% biomass amount, uptake decreased to 75% and 39%, respectively (Fig. 1). However, as the concentration of biomass was further increased the thiocyanate sorption did not increase but remained constant. No specific thiocyanate uptake at increased biomass loading is attributable to the interference between binding sites at higher quantities (deRome and Gadd, 1987).

The process of sorption/biosorption is essentially a surface interaction and is characterised by rapid uptake of ions by biomass surfaces. Rapidity of the process makes it a good candidate for use in effluent treatment on a large scale. Kinetics of thiocyanate sorption showed that the rate of thiocyanate uptake was more in the first 20-30 minutes with over 60% of biosorption. Later, the sorption rate slowed down until it reached a plateau after 60 min, indicating equilibration of the system. Maximum sorption of thiocyanate (up to 85%) was observed at 60 min (Fig. 2). The rapid kinetics has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy.

The effect of initial thiocyanate concentration on biosorption by ground *Mangifera indica* leaf biomass showed that the equilibrium sorption capacity of the sorbent increased with increasing initial concentration of thiocyanate from 50 to 1000 mg/l. This was due to the increase in the number of ions competing for the available binding sites in the biomass. Uptake of thiocyanate at various concentrations reached a plateau when the concentration was in the range of 700 to 800 mg/l. This might be due to the saturation of binding sites, which clearly showed that thiocyanate uptake by *Mangifera indica* biomass was a chemically equilibrated and saturable phenomenon. The higher initial concentration provides 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 thiocyanate ions and the sorbent. This results in higher uptake of the target compound. Moreover, biomass cell membranes contain polysaccharides as basic building blocks, which have ion exchange properties, and also proteins and lipids and therefore offer a host of functional groups capable of binding to thiocyanate ions.

Biosorption of target ions (both cations and anions) is a dynamic process. Immediately after contact of biosorbent with the target compound solution, the rate of sorption (forward reaction) is very high as compared to the rate of desorption (backward reaction). Sorption slows down as binding sites are progressively occupied, until the rates of both the forward and backward reactions are exactly balanced. At this point the biomass is saturated with target ions and no net uptake of these ions occurs. 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 valuable information for selection of an adsorbent and facilitate evaluation of adsorption process for a given application (Weber, 1985). The isotherm indicates the relative affinity of biosorbent for target ions and the adsorption capacity of biosorbent. Also, the sensitivity of biosorption changes in target compound concentration can be determined by the relative steepness of the isotherm line. Important equilibrium models developed to describe adsorption isotherm relationships include single layer adsorption (Freundlich, 1926; Langmuir, 1918) and multilayer adsorption (Branauer *et al.*, 1938).

Langmuir (1918) developed this model on the assumptions that: (i) Adsorption energy is constant and independent of surface coverage; (ii) Adsorption occurs on localised sites with no interaction between adsorbate molecules; and (iii) Maximum adsorption occurs when the surface is covered by a monolayer of adsorbate. The Freundlich (1926) isotherm model is originally empirical in nature, but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data (Patil, 1999; Puranik, 1998). It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation.

Despite the complexity of the adsorption process, which can include several mechanisms, adsorption isotherms have been used to characterise target compound uptake and they appear to be of use for projected industrial applications (Tsezos and Volesky, 1981). Hence, it was decided to fit the available thiocyanate 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 thiocyanate adsorption capacities. Experimental data obtained in the studies were found to obey basic principles underlying these models, that is, heterogeneous surface adsorption and monolayer adsorption at constant adsorption energy respectively (Freundlich, 1926; Langmuir, 1918).

Recovery of target compound from industrial effluents is desirable when the target compound is costly and rare. Although the concentration of target compounds in the effluents may not be very high (< 25 – 50 mg/l), the total amount of target compound may be quite significant considering the large volumes of effluent generated daily. 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 include mainly mineral acids, alkalis, organic acids, etc. In the present studies on sorption/desorption the loaded thiocyanate on *Mangifera indica* leaf biomass could be desorbed with more than 90% efficiency using 0.1 - 1 M sodium hydroxide solution. Final concentrations of thiocyanate in the eluant were in the range of 800 to 1000 mg/l (14 to 18 mM). These values represented an approximately 8 to 10 fold concentration of thiocyanate as compared to the original concentration of 100 mg/l (1.72 mM) that was used for sorption. Such highly concentrated solution of recovered thiocyanate may be recycled in the user industry. Thus, it can be concluded that natural waste biomass (like dried leaves of photosynthetic plants) has immense potential "as biosorbents" for the removal/management of variety of industrial pollutants, as evident from the example of thiocyanate 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.

Management of industrial pollutants in the 21st century is completely changing its face and orientation. In the present day scenario, a pollutant is no way considered as a pollutant or waste but is rather regarded as a 'resource' that could be recovered or extracted from the effluents using suitable technologies. Therefore, in a real sense, concepts like reuse, recycle and recovery of waste materials are gaining remarkable importance in today's so called Technological Society. Applications of concepts similar to this work will ultimately reduce/minimize the demand for natural resources by the industries, thereby increasing their overall profit margin and prolonged sustenance of both natural and manmade resources. In this regard, the present research work is an advancement of knowledge in the field of resource management, waste minimization, pollution management and help profitability of business community at large.

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