Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2016, 5 (2): 488-496

(International Peer Reviewed Journal)

Studies on the Reduction of Lead And Cadmium From Aqueous Solutions Using Citrus Pennivesiculata (Gajanimma) Peel

M. Munichandran, Battala Gangadhar*, P. Latha and Gurijala Ramakrishna Naidu

*Department of Environmental Sciences, S.V. University, Tirupati – 517 502, **INDIA**

Email: gangadhar.battala@gmail.com

Accepted on 19th March 2016

ABSTRACT

Currently there are numerous methods for the removal and recovery of toxic metals from waste water. Adsorption is one of the alternative purification and separation technique used in industry especially for water and waste water treatment. Cost is also an important parameter for comparing the adsorbent materials. In the present study reduction of lead and cadmium from aqueous solutions has been investigated using low cost and eco-friendly biosorbent derived from Citrus Pennivesiculata (Gajanimma) peel. The influence of pH, contact time, metal concentration, adsorbent dosage on the selectivity and sensitivity of the removal process was investigated. The adsorption efficiencies were found to be good at pH 5. The equilibrium time was attained at 120 min and the maximum removal percentage was achieved at an adsorbent loading weight of 125 mg L^{-1}.

Keywords: Biosorption, Lead, Cadmium.

INTRODUCTION

Rapid development of industries such as metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc., heavy metals are directly or indirectly discharged into the environment increasingly, especially in developing countries [1]. Unlike organic pollutants, heavy metals are non-biodegradable in the environment. Heavy metals can accumulate in living tissues particularly in human bodies causing significant physiological disorders such as damage of central nervous system and blood composition, production of energy and irreversible damage of vital organs of body [2]. Nowadays heavy metals are the environmental priority pollutants and are becoming one of the most serious environmental problems. Heavy metals such as Pb, Cd, Cr, Ni, Zn, Cu and Fe are present in industrial wastewater, these heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in for stomach of the rodent [3].

Among the different heavy metals, lead is one of the common and most toxic pollutants into the natural waters from various industrial activities. There are various industries those are pertaining lead such as pulp and paper, petrochemicals, refineries, printing, pigments, photographic materials and explosive manufacturing, ceramic, glass, oil, metal, phosphate fertilizer, electronic, wood production, combustion of fossil fuel, forest fires, mining activities, sewage wastewater, automotive, coating, painting, storage batteries, aeronautical, alloy and steel industries. Lead is accumulated into body via inhalation, ingestion or skin adsorption. Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anemia, kidney disease, nervous disorder and sickness even death. The high level of lead damages cognitive development especially in children. In drinking water maximum allowable limit of total Pb of 50 g L^{-1} is considered safe by the World Health Organization, whereas less than 0.015 g L^{-1} in potable water is adopted by the United States Environmental Protection Agency [4].

Cadmium is one of the heavy metals, which is highly toxic to human, plants and animals. The metal is of special concern because it is non-degradable and therefore persistent. The main anthropogenic pathway through which cadmium enters environment is via wastes from industrial processes such as electroplating, smelting, alloy manufacturing, pigments, plastic, cadmium-nickel batteries, fertilizers, pesticides, mining, pigments and dyes, textile operations and refining. All over the world cadmium contaminated waste waters and effluents are being generated either directly due to Cd production or through secondary sources. A major past disaster 'Itai-Itai' due to contamination of cadmium in Jintsu river of Japan is well known. According to WHO's recommendation Cd (II) limit in drinking water is 0.005 mg L^{-1} [5].

Table 1. Effect of Cadmium and lead on Human Health

Pollutant	Major Sources	Effect on human health	Permissible level mg/L
Cadmium	Welding, electroplating, Pesticide, fertilizer, Cd and Ni batteries, Nuclear fission plant	Renal dysfunction, Lung disease, lung cancer, bone defects (Osteomalacia, Osteoporosis), increased blood pressure, Kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer.	0.05
Lead	Paint, pesticide, smoking, automobile emission, mining, burning of coal.	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness and acute or chronic damage to the nervous system, epilepticus, liver, kidney, gastro intestinal damage.	0.1

There are various technologies involving in the removal of toxic heavy metals from water and waste water, out of them biosorption has attained kind attention and based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake [6]. In industrial sector, Biosorption has distinct advantages over expensive clean up technologies which were used for the treatment of water and waste water. The major advantages of biosorption, includes reusability of biomaterial, low operating cost, and high efficiency of metal removal from dilute solution. There is no need of additional nutrient requirement. Operation time is also short. [7]. The process of biosorption involves a solid phase which is a sorbent or biosorbent / biological material and a liquid phase which is a solvent, normally water containing a dissolved species to be sorbed which is sorbate or metal ions. Due to higher affinity of the sorbent for the sorbate species the sorbate is attracted and removed by different mechanisms. The process continues till equilibrium is established between the amount of solid bound sorbate species and its portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases [8].

The removal of metal ions from industrial wastewaters using different adsorbents is always of great interest [9]. Treatment of industrial effluents with sorbents of biological origin is simple, comparatively inexpensive and friendly to the environment. Biosorption of heavy metals is very effective, versatile, powerful, most efficient and cost effective technologies involved in the removal of heavy metals from industrial effluents. Heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms, which leads to several health problems in animals, plants and human beings [10]. Because of the various problems associated with the toxicity of heavy metals, their concentration has to be reduced in water and waste water. Many methods that are being used to remove heavy metal ions include chemical precipitation, ion-exchange, adsorption, membrane filtration, electrochemical treatment technologies, etc. The present research article deals with the reduction of heavy metals in aqueous solutions using citrus pennivesiculata peel.

MATERIALS AND METHODS

Chemicals: All the chemicals used in the present study were of Analytical Grade (AR). Double distilled water was used in all preparations. $CdCl_2$ and Pb $(NO_3)_2$ are obtained from Merck.

Adsorbent: The Citrus Pennivesiculata (Gajanimma) peel was obtained from fruit stalls, washed with deionized water to remove dirt and cut in to small pieces. These small pieces were air dried for one day and then dried in hot oven for 12 h at 105 ^{0}C. and powdered using mixer grinder. The powdered peel was sieved using mesh and washed several times with double distilled water to remove unwanted suspended dust particles. Then the biosorbent material was dried in oven for 6 h at 105 ^{0}C to remove the moisture content in the material. Then the material is taken out from oven and powdered using mortar and pestle and stored for characterization.

Adsorbate: Standard cadmium (II) solution (1000 µg mL^{-1}), was prepared by weighing 1.7911 g of $CdCl_2$ and standard lead (II) solution 1000 µg mL^{-1}), was prepared by weighing 1.60 g of Pb $(NO_3)_2$ dissolving in double distilled water to give a volume of 1000 mL. Working standard solutions are prepared from these standard solutions at appropriate volumes.

Glassware and Apparatus used: All glass wares used in the present study were of Borosil. The instruments and apparatus used throughout the experiment are listed in table 2.

Table 2. List of instrument used during experimentation

S. No.	Instrument	Make
1.	Flame Atomic Absorption Spectrophotometer	Model 6300, Shimadzu (Japan)
2.	Digital pH Meter	Elico (India)
3.	Digital Electronic Balance	Shimadzu AUX 320
4.	FT-IR	Nicolet IR-200 (USA)

Batch mode adsorption studies: The adsorption of lead and cadmium on to Citrus Pennivesiculata (Gajanimma) peel was studied by batch technique. In all sets of experiments, fixed volume of metal solution i.e. 100 mL was stirred with desired biosorbent dose (50 – 200 mg) for a period of 120 min. Different conditions of pH (3-8), initial metal ion concentrations (1 – 6 µg m L^{-1}) and contact time (30 – 150 min) were evaluated during the study. In order to regulate pH of the medium, 0.1 N of HCl and NaOH was used. The solutions are separated from the biomass by filtration through Whatman 40 filter paper. The initial and final concentrations of the metal ions in the solution are measured using Flame Atomic Absorption Spectroscopy. The results of these studies were used to obtain the optimum conditions for maximum removal of lead and cadmium from aqueous solutions.

$$\text{Metal ion removal (\%)} = [(C_0 - C_e)/C_0] \times 100$$

Where C_0: Initial metal ion concentration of test solution, mg/L, C_e : Final equilibrium concentration of test solution mg L^{-1} [11].

RESULTS AND DISCUSSION

FT-IR (Fourier transform infrared) spectral analysis: FTIR spectroscopy was used to show the functional groups present on the surface of the peels. Both Citrus Pennivesiculata peel (CPP) and metal loaded CPP were analyzed by using FTIR spectra and the results are shown in fig. 1. CPP exhibits a number of adsorption peaks indicating the complex nature of the material examined. The broad absorptions between 3000 and 3500 cm^{-1} confirm the existence of carboxylic O–H groups and free COOH's of CPP. The doublet peaks appeared in all the spectra at wave number 2902 cm^{-1} and 2931 cm^{-1}, respectively, due to the asymmetric and symmetric stretch of aliphatic chains (–CH) [25]. The peak around 1,612 cm^{-1} is due to the C=C stretching that can be attributed to the aromatic C-C bond, and the peak at 1,018 cm^{-1} can also be associated with either C-O symmetric or asymmetric stretching vibration (-C-O-C-ring). The absorption band at 1743 cm^{-1} is attributed to C=O of carboxylic group. The comparative study of FT-IR spectra of CPP (Figure 1a) and metal loaded CPP (Figure 1b,1c) revealed that the CPP has functional groups such as alcoholic, ketonic, and carboxylic groups. These groups can be involved in complexation reactions with Cd (II), Pb (II) and CPP could be viewed as a natural ion-exchange material that primarily contains weak acidic and basic groups on the surface [12]

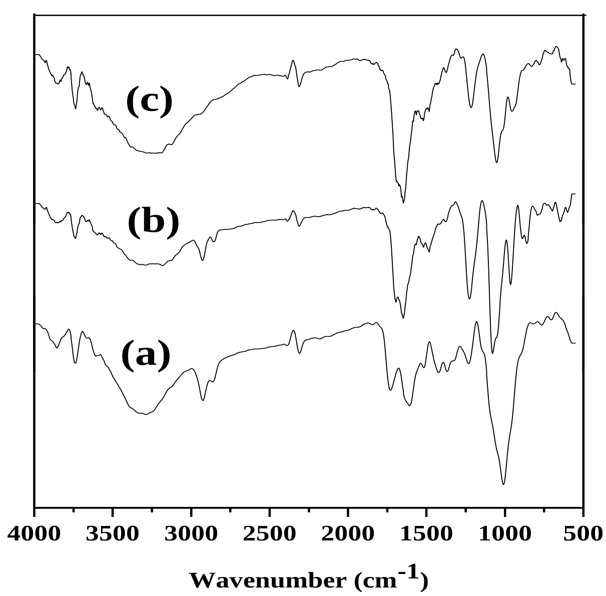

Fig 1. FT-IR spectra of (a) CPP (b) Cd-CPP (c) Pb-CPP

Effect of pH: In adsorption process hydrogen ion concentration is considered as one of the most important parameters that influence the adsorption behavior of metal ions in aqueous solution. It affects the solubility of the metal ions in the solution, replaces some of the positive ions found in the active sites, and affects the degree of ionization of the adsorbate during the reaction [13]. The results of table 3 indicated that Cd (II) and Pd (II) removal was increased to maximum and then decreased with pH variation from 5 to 8. The maximum percent removal of Cd (II) was 89% and Pb (II) 90% at pH 5 (Fig. 2). The per cent removal of metal ions with the increase in pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions

Table 3. pH studies for the biosorbent Citrus Pennivesiculata (Gajanimma) peel for the removal of metal ions Cd (II) and Pb (II)

Cd(II)		Pb(II)	
pH	**% Removal**	**pH**	**% Removal**
3	60	3	63
4	65	4	68
5	89	5	90
6	73	6	72
7	75	7	73
8	76	8	75

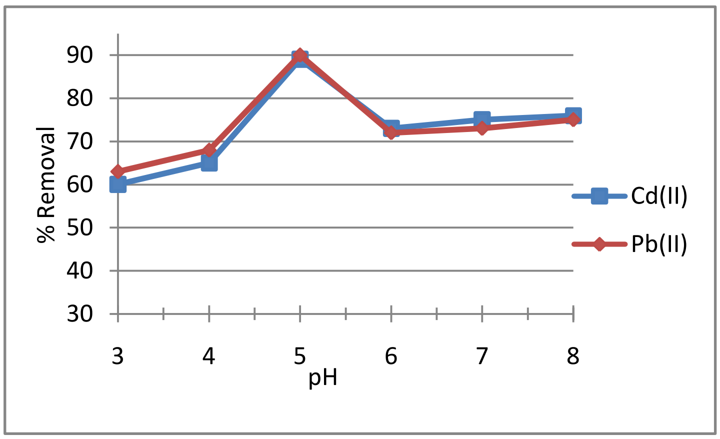

Figure 2. Effect of pH on adsorption of Cd ((II) and Pb (II)

Effect of Adsorbent Dosage: The results for adsorptive removal of lead and cadmium with respect to adsorbent dosage are shown in fig. 3 (Table 4). Adsorption efficiency of cadmium and lead was studied by varying the amount of adsorbent dosage from 50 to 200 mg keeping other parameters (pH, and contact time) constant. The removal efficiency of the cadmium and lead has improved on increasing adsorbent dose. This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. The maximum percent removal of cadmium and lead was about 92% and 93% at the dosage of 125 mg. The results suggests that after a certain dose of adsorbent, the equilibrium conditions reached and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent [14].

Table 4. Removal of metal concentration using Citrus Pennivesiculata (Gajanimma) peel with various dosages

Biosorbent Dosage in mg/L	Cd(II)	Pb(II)
	% Removal	**% Removal**
50	70	71
75	80	88
100	91	90
125	92	93

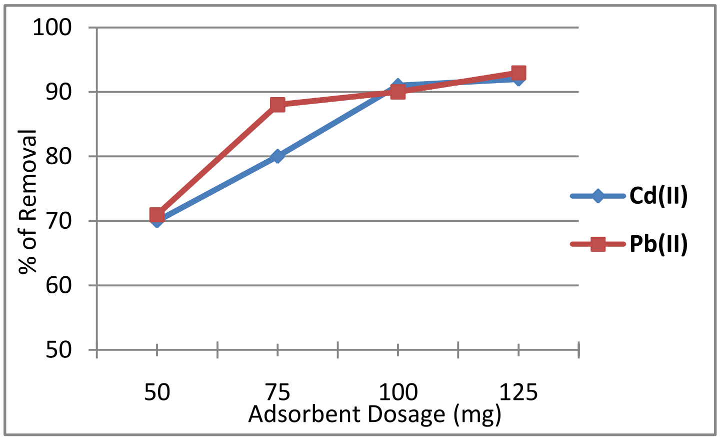

Figure 3. Effect of adsorption dosage on adsorption of Cd ((II) and Pb (II)

Effect of contact time: Metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as dose of adsorbent and pH of solution were kept constant. The results of table 5 (Fig.4) indicated that Cd (II) removal was increased from 42 to 92%with the contact time variation from 30 to 120 min and Pb (II) removal was increased from 44 to 91%with the contact time variation from 30 to 120 min, the percentage removal of Cd (II), Pb (II) remains constant, which showed that equilibrium was reached at 120 min itself. Thus the results illustrated that the optimum contact time for maximum removal (92%) of Cd (II), and (91%) of Pb (II) was 120 min. This result is important because equilibrium time is one of the important parameters for an economical wastewater treatment system [15].

Table 5. Removal of Cd (II) and Pb (II) concentration with time

Contact time	Cd (II)	Pb (II)
	% Removal	% Removal
30	42	44
60	77	73
90	88	87
120	92	91

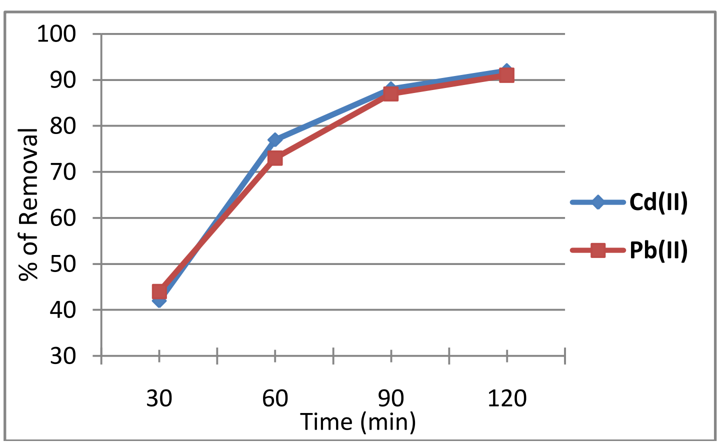

Figure 4. Effect of contact time on adsorption of Cd ((II) and Pb (II)

Effect of initial metal ion concentration: The effect of initial metal ions concentration on the adsorption rate was studied in the range (1-6mg L^{-1}) at constant pH, and constant contact time. It was observed from the results of table 6 (Fig. 5) that the percentage of removal decreased with increasing in initial cadmium and lead concentration. The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of moles of lead and cadmium to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial lead and cadmium concentration. Therefore it was evident from the results that lead and cadmium adsorption was dependent on the initial metal concentration [16]

Table 6. Remval of Cd ((II) and Pb (II) concentration with metal ion concentration

Cd(II)		Pb(II)	
Intial con	**% Removal**	**Initial con**	**% Removal**
1	75	1	70
2	77	2	74
3	80	3	79
4	88	4	90
5	50	5	55
6	40	6	42

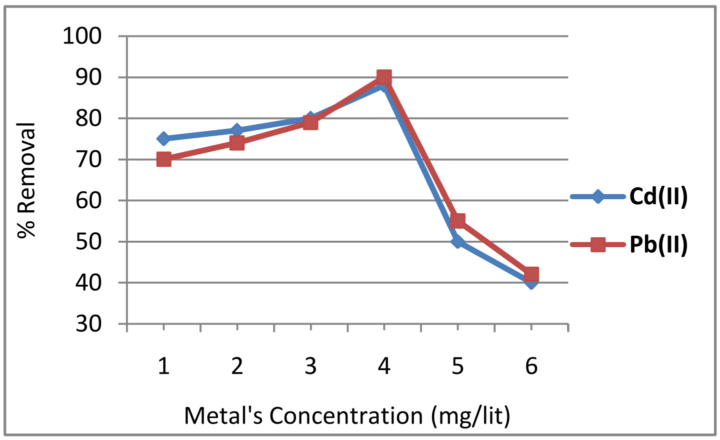

Figure 5. Effect of initial metal on concentration on adsorption of Cd ((II) and Pb (II)

Equilibrium studies of cadmium and lead: Removal of lead (II) and cadmium (II) were obtained at 120 min. Hence, 120 min equilibrium time was considered in the experiments. Citrus Pennivesiculata (Gajanimma) peel in present investigation has immense potential of lead (II) and cadmium (II) removal from wastewater. Removal of lead (II) and cadmium (II) from the liquid media was 92 and 93 % respectively at 125 mg L^{-1} of initial adsorbate concentration. Removal of lead and cadmium was 89 and 90% at pH 5 respectively.

APPLICATIONS

The low cost and eco-friendly biosorbent derived from Citrus Pennivesiculata (Gajanimma) peel is inexpensive and acts as an excellent material for the reduction of cadmium and lead from aqueous solutions.

CONCLUSIONS

The present research work examined the usage of Citrus Pennivesiculata (Gajanimma) peel as an inexpensive sorbent for the sorption and reduction of lead and cadmium from aqueous solutions. Usage of biosorbent for metal sorption bears a lot of advantages compared to classical methods such as chemical precipitation, membrane filtering, chemical oxidation or reduction, etc. From the present investigation, we can conclude that the low-cost natural adsorbent Citrus Pennivesiculata (Gajanimma) peel acts as an excellent adsorbent and can efficiently remove cadmium and lead ions present in the aqueous solutions.

The present work also explores a new cheaper, economical and selective adsorbent as an alternative to costly adsorbents for the reduction of lead and cadmium from aqueous solutions [17]

ACKNOWLEDGEMENTS

One of the Authors Dr.BGR is thankful to UGC for the award of Post Doctoral Fellowship, File No. F./PDFSS-2014-15-SC-AND-7541.

REFERENCES

[1] Fenglian Fu and Qi Wang, *Journal of Environmental Management*, **2011,** 92, 407-418.

[2] Naeema H. Yarkandi, *Int.J.Curr.Microbiol. App.Sci*, **2014,** 3 (4), 207-228

[3] E. Bernard, A. Jimoh, J.O. Odigure, *Research Journal of Chemical Sciences,* **2013**, 3 (8), 3-9.

[4] Sumeth Khaoya and Ura Pancharoen, *International Journal of Chemical Engineering and Applications,* **2012**, 3 (2), 98-103.

[5] K.S.Rao, M. Mohapatra, S.Anand and P. Venkateswarlu, *International Journal of Engineering Science and Technology***, 2010**, 2 (7), 81-103.

[6] E. Fourest, J. C. Roux, *Applied Microbiology and Biotechnology,* **1992**, vol. 37, 399-403.

[7] Jagruti N. Jadav, Sandip D. Maind, Satish A. Bhalerao, *J. Applicable Chem.*, **2015**, 4 (6): 1700-1715.

[8] Nilanjana Das, R. Vimala, P. Karthika, *Indian Journal of Biotechnology*, **2008**, 7, 159-169.

[9] M. Mustaqeem, M. Sharif Bagwan and P. R. Patil, *J. Applicable Chem,* **2014**, 3 (1), 275-282.

[10] Shweta Shukla, Jyoti V. Mani and Amit Chattree, *J. Applicable Chem,* **2014**, 3 (5): 2004-2010.

[11] S. Babel, T.A. Kurniawan, *J. Hazard. Journal of hazardous Material*. **2003,** 97, 219–243.

[12] M.N.Pons, S.L. Bonte, O. Potier, Spectral analysis and finger printing for biomedia characterization, *J. Biotechnol.* **2007,** 113, 211–230.

[13] Mona E. Ossman, Moustapha S. Mansour, *International Journal of Industrial Chemistry,* **2013**, 4 (13), 1-7.

[14] Jagruti N. Jadav, Sandip D. Maind, Satish A. Bhalerao, *J. Applicable Chem*, **2015**, 4 (6), 1700-1715.

[15] N. Kannan and R. Pagutharivalan, *J. Applicable Chem,* **2012**, 1 (1), 22-38.

[16] N.S. Rajurkar and Dipali Mahajan, *J. Applicable Chem,* **2015**, 4 (4), 1206-1217.

[17] G. Annadurai, R.S. Juang, D.J. Lee**,** *Water Science and Technology,* **2003**, 47 (1), 185–190.

AUTHORS' ADDRESSES

1. **Mr. M. Munichandran**
Research Scholar, Department of Environmental Sciences
S.V. University, Tirupati - 517 502, Andhra Pradesh, India
Mobile: 91-9703406713, E-mail: munichandranm@gmail.com

2. **Dr. B. Gangadhar**
Post Doctoral Fellow (UGC), Department of Environmental Sciences
S.V. University, Tirupati - 517 502, Andhra Pradesh, India
Mobile: 91-9347894951, E-mail: gangadhar.battala@gmail.com

3. **P. Latha**
Research Scholar, Department of Environmental Sciences
S.V. University, Tirupati - 517 502, Andhra Pradesh, India
Mobile: 91-9441572639

4. **Dr. G. Ramakrishna Naidu**
Professor Emeritus, Department of Environmental Sciences
S.V. University, Tirupati - 517 502, Andhra Pradesh, India
Mobile: 91-9393620557, E-mail: naidugrk@gmail.com