Heavy Metal Removal from Wastewater using Ocimum Sanctum

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Abstract- Heavy metals are commonly released in the wastewater from various industries. These heavy metal ions are toxic to both human beings and animals. The toxic metals cause physical discomfort and sometimes life threatening illness and irreversible damage to vital body system. The present work investigates the potential use of Ocimum sanctum for the removal of iron and lead from wastewater. Ocimum sanctum (Tulsi) a medicinal plant, is used for the removal of heavy metals from wastewater.

Keywords- Adsorption, Biosorption, Biosorbents, Iron solution, Lead solution, Ocimum sanctum

I. INTRODUCTION

Water pollution caused due to the addition of heavy metals resulting from the industrial activities is increasing tremendously and is a matter of global concern. Mining, mineral processing and metallurgical operations are generating effluents containing heavy metals. The heavy metals present in the wastewater is persistent and nondegradable in nature. Moreover, they are soluble in aquatic environment and thus can be easily absorbed by living cells. Thus, by entering the food chain, they can be bio-accumulated and biomagnified in higher trophic levels also. The conventional methods for heavy metal removal from wastewater includes chemical precipitation, chemical oxidation, ion exchange, membrane separation, reverse osmosis, electrodialysis etc. These methods are not very effective, are costly and require high energy input. Adsorption has emerged out to be better alternative treatment method. It is said to be effective and economical because of its relatively low cost. The key benefit of adsorption method for heavy metal removal is less initial as well as operation cost, unproblematic design and less requirement of control systems. Generally the heavy metals are present in the wastewater at low concentrations and adsorption is suitable even when the metal ions are present at concentrations as low as 1 mg/l. This makes adsorption an economical and favourable technology for heavy metal removal from wastewater.

Biosorption is a property of certain types of inactive, dead microbial biomass to bind and concentrate pollutants from every aqueous solution. Biosorption is defined as the accumulation and concentration of organic and inorganic pollutants including metals, dyes and odor causing substances from aqueous solutions by the use of biological materials. The biosorption process involves a solid phase (sorbent or

 (sorbate, metal ions).Due to higher affinity of the sorbent for the sorbate species, the latter is attracted and bound there 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.
The main objective is to study the effect of Ocimum sanctum on removal of heavy metals- iron and lead. The biocarbon obtained from medicinal plant called Ocimum sanctum is

on removal of heavy metals- iron and lead. The biocarbon obtained from medicinal plant called Ocimum sanctum is considered as a cheap material for the removal of metal ions like lead, cadmium, copper, zinc, nickel etc. from aqueous solution. The activated biocarbon Ocimum sanctum was investigated as a replacement for the current expensive methods of removing metal ions from aqueous solutions.

biosorbent: biological material) and liquid phase (solvent,

normally water) containing a dissolved species to be sorbed

A. OCIMUM SANCTUM

Plants are important sources of medicine & a large numbers of drugs in use are derived from plants. The therapeutic uses of plants are safe, economical and effective ease of availability. Among the plants known for medicinal value, the plants of genus Ocimum belonging to family Lamiaceae are very important for their therapeutic potentials. Ocimum sanctum has two varieties i.e. black (Krishna Tulsi) and green (Rama Tulsi): their chemical constituents are similar. Tulsi is a Sanskrit word which means "matchless one". Several medicinal properties have been attributed to the Tulsi plant not only in Ayurveda and Siddha but also in Greek, Roman and Unani systems of medicine. The medicinal use of plants is very old. Literatures indicate that therapeutic use of plants is as old as 4000-5000 B.C and Chinese used first the natural herbal preparations as medicines. Earliest references are available in Rigveda which is said to be written between 3500-1600 B.C. Tulsi (Ocimum sanctum), Queen of Herbs and the Legendary, "Incomparable One" is one of the holiest and most cherished of the many healing and health giving herbs distributed mainly in the oriental region. Tulsi a widely grown, sacred plant belongs to the Lamiaceae family. It is called by names like Rama Tulsi, Krishna Tulsi in Sanskrit and Holy Basil in English. The natural habitat of Tulsi varies from sea level to an altitude of 200 m. It is found growing naturally in moist soil nearly all over the globe. In Nepal,

Aryan people grow Tulsi as a religious plant in their homes, temples and their farms. They use Tulsi leaves in routine worship.

1) Plant profile: Ocimum belongs to family Lamiaceae and is very important for their therapeutic potentials. Ocimum sanctum is a strongly scented small annual herb, up to 18 inches tall, grows into a low bush and is commonly known as holy basil, Tulsi or Tulasi. Three varieties of Tulsi are

- Rama or Light Tulsi (Ocimum sanctum)
- Shyama or Dark Tulsi (Ocimum sanctum)
- Vana Tulsi (Ocimum gratissimum)

Scientific classification:

- Kingdom: Plantae
- Division: Magnoliophyta
- Class : Magnoliopsida
- Order : Lamiales
- Family : Lamiaceae
- Genus : Ocimum
- Species : O.Tenuiflorum
- Binomial name: Ocimum Tenuiflorum or Ocimum Sanctum L (Siva M. et.al, 2016).

2) Properties: Ocimum sanctum (OS) or Tulsi extracts are used in ayurvedic remedies for common colds, headaches, stomach disorders, inflammation, heart disease, various forms of poisoning and malaria. Traditionally, Ocimum sanctum is taken in many forms, as herbal tea, dried powder or fresh leaf. Several recent investigations using these extracts indicates anti-inflammatory, antioxidant and immune modulatory and antistress properties. In addition, it has been reported to have radio protective and anti-carcinogenic property. Several medicinal properties have been attributed to Ocimum sanctum. Ocimum sanctum is known as a general vitalizer and increases physical endurance.

Different parts of Ocimum sanctum like leaves, flowers, stem, root, seeds etc. are known to possess therapeutic potentials and have been used by traditional medicinal practitioners, as expectorant, analgesic, anticancer, antiasthamatic, antiemetic, diaphoretic, antidiabetic, antifertility, hepatoprotective, hypotensive, hypolipidmic, antistress agents. Ocimum sanctum has also been used in treatment of fever, bronchitis, arthritis, convulsions etc. Ocimum sanctum has been well documented for its therapeutic potentials and described as antiasthmatic and antikaphic drugs. Indian Materia Medica describe the use of aqueous, hydro alcoholic and methanolic extract of Ocimum sanctum leaves in variety of disorders, like bronchitis, rheumantism and pyrexia.

B. Iron

Iron is a chemical element with symbol Fe (from Latin: ferrum) and atomic number 26. It is a metal in the first transition series. It is by mass the most common element on Earth, forming much of Earth's outer and inner core. It is the fourth most common element in the Earth's crust. Its abundance in rocky planets like Earth is due to its abundant production by fusion in high mass stars, where it is the last element to be produced with release of energy before the violent collapse of a supernova, which scatters the iron into space. Like the other group 8 elements, ruthenium and osmium, iron exists in a wide range of oxidation states, -2 to +6, although +2 and +3 are the most common. Elemental iron occurs in meteoroids and other low oxygen environments, but is reactive to oxygen and water. Fresh iron surfaces appear lustrous silvery-gray, but oxidize in normal air to give hydrated iron oxides, commonly known as rust. Unlike the metals that form passivating oxide layers, iron oxides occupy more volume than the metal and thus flake off, exposing fresh surfaces for corrosion. Iron metal has been used since ancient times, although copper alloys, which have lower melting temperatures, were used even earlier in human history. Pure iron is relatively soft, but is unobtainable by smelting because it is significantly hardened and strengthened by impurities, in particular carbon, from the smelting process. A certain proportion of carbon (between 0.002% and 2.1%) produces steel, which may be up to 1000 times harder than pure iron. Crude iron metal is produced in blast furnaces, where ore is reduced by coke to pig iron, which has a high carbon content. Further refinement with oxygen reduces the carbon content to the correct proportion to make steel. Steels and iron alloys formed with other metals (alloy steels) are by far the most common industrial metals because they have a great range of desirable properties and iron bearing rock is abundant. Iron chemical compounds have many uses. Iron oxide mixed with aluminium powder can be ignited to create a thermite reaction, used in welding and purifying ores. Iron forms binary compounds with the halogens and the chalcogens. Among its organometallic compounds is ferrocene, the first sandwich compound discovered. Iron plays an important role in biology, forming complexes with molecular oxygen in haemoglobin and myoglobin; these two compounds are common oxygen transport proteins in vertebrates. Iron is also the metal at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals. A human male of average height has about 4 grams of iron in his body, a female about 3.5 grams. This iron is distributed throughout the body in hemoglobin, tissues, muscles, bone marrow, blood proteins, enzymes, ferritin, hemosiderin and transport in plasma. As per IS 10500-2012, acceptable limit for iron in drinking water is 0.3 mg/l.

1) Sources of iron: Sources of iron ore include iron and steel production, cement industry, coal washery, and ferro-

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alloys/alloy steel industry. Automobile and other basic industries, manufacturing pumps main body are the main sources of cast iron. Wrought iron is produced by furniture industries and many other basic industries.

C. Lead

Lead is a chemical element with atomic number 82 and symbol Pb (from Latin: plumbum). It is a soft, malleable and heavy metal. Freshly cut lead has a bluish-white color that soon tarnishes to a dull gravish color when exposed to air; as a liquid, it has a shiny chrome-silver luster. Lead's density of 11.34 g/cm3 exceeds that of most common materials. It has the second highest atomic number of all practically stable elements. As such, lead is located at the end of some decay chains of heavier elements, which in part accounts for its relative abundance: it exceeds those of other similarly numbered elements. Lead is a post transition metal and is relatively inert unless powdered. Its weak metallic character is illustrated by its general amphoteric nature: lead and lead oxides react with both acids and bases. Lead also displays a marked tendency towards covalent bonding. Its compounds are most commonly found in the +2 oxidation state, rather than +4, unlike the lighter group 14 elements. Exceptions are mostly limited to organolead compounds, where the positive charge on lead is dispersed and stabilized. Like the lighter group 14 elements, lead shows a tendency to bond to itself, forming complicated chain, ring, or polyhedral structures. Lead has several properties that make it useful: high density, low melting point, ductility and relative inertness to oxidation. Combined with its relative abundance and low cost, these factors have led to its wide spread employment. Lead is used in building construction, lead acid batteries, bullets and shot, weights, as part of solders, pewters, fusible alloys and as a radiation shield. Lead was established as poisonous in the late nineteenth century and this is why it is being phased out for some applications. If ingested or inhaled, lead and its compounds are poisonous to animals and humans. Lead is a neurotoxin that accumulates in soft tissues and bones, damaging the nervous system and causing brain disorders. Lead can also cause blood disorders in mammals. As per IS 10500:2012, acceptable limit for lead in drinking water is 0.01 mg/l.

1) Sources of lead: Sources of lead include old lead pigment paints, batteries, industrial smelting and alloying, some types of solders, ayurvedic herbs, some toys and products from China, glazes on (foreign) ceramics, leaded (antiknock compound) fuels, bullets and fishing sinkers, artist paints with lead pigments and leaded joints in some municipal water systems.

II. METHODOLOGY

A. Bioadsorbent

The Tulsi leaves were collected from a few residences in Thrissur, Kerala. The collected leaves were washed with distilled water, then the washed samples were drenched in 3M NaOH solution for 24 hrs. After 24 hours the drenched samples were washed with distilled water and the washed samples were kept in hot air oven for overnight at 60° C. Then the samples were crushed (N.V.Ravi Shekhar and Supriya Biswas, 2015).

B. Stock iron solution

Add slowly 20 ml concentrated H_2SO_4 to 50 ml distilled water and dissolve 1.404 g ferrous ammonium sulphate [Fe (NH4)₂ (SO4)₂ 6H₂O]. Add 0.1 N KMnO₄ drop wise until a faint pink colour persists. Dilute to 1 litre with iron free distilled water. Each 1 ml of this solution contains 200 µg iron (Fe).

C. Stock lead solution

Dissolve 0.1598 g lead nitrate $Pb(NO_3)_2$ in a minimum amount of 1+1 HNO₃,add 10 ml concentrated HNO₃ and dilute to 1000 ml with water. Each ml of this solution contains 100 µg lead (Pb).

D. Experimental procedure

50 ml of heavy metal solution were taken in 250 ml conical flask and add the adsorbents in to the conical flask (0.5g, 1 g, 1.5g, 2g, 2.5g and 3g). It is then shaken well for 3 hours. Then samples were taken at different time interval. The samples were filtered with the whatman filter paper (N.V.Ravi Shekhar and Supriya Biswas, 2015).

III. RESULTS

A. Tests for iron

The phenanthroline method is the preferred standard procedure for the measurement of iron in water. The method depends upon the fact that 1, 10 phenanthroline combine with Fe⁺⁺ to form an orange-red complex. Its colour conforms to Beer's law and is readily measured by visual or photometric comparison. Using phenanthroline method, initial iron content was determined and it was found to be 1.82 mg/l.

1) Effect of biosorbent dosage for iron: The amount of iron removal showed adsorbent dosage dependence. This attributes to the increased adsorbent surface area and availability of more adsorption sites resulting from the increase of dosage. Table shows the concentration of 3g/50 ml was sufficient for maximum biosorption.

TABLE. 1
Absorbance readings for different dosages in iron solution

Dosage (g)	Absorbance at 508 nm(Fe)
0.5	0.155
1	0.162
1.5	0.170

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2.0	0.200
2.5	0.246
3.0	0.272
3.5	0.272

2) Effect of contact time for iron: 3g of biosorbent was added to 50 ml of iron solution and shaken well. At different time intervals, adsorbance readings were noted. Biosorption continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. It was observed that sorption percentage increased with the increase of time up to 210 minutes.

TABLE. 2 Absorbance readings for different time intervals in iron solution

Time(min)	Absorbance at 508 nm (Fe)
30	0.182
60	0.189
90	0.196
120	0.210
150	0.260
180	0.272
210	0.278
240	0.259

3) Final iron content determination: Absorbance obtained for optimum dosage and contact time was used for final iron content determination. 3g of biosorbent was added to 50 ml of sample and was kept for 210 minutes and final iron content corresponding to 0.278 absorbent was obtained as 0.48 mg/l.

4) Determination of percentage of biosorption

Percentage of biosorption

Therefore, percentage of iron removed = $1.82 - 0.48 \times 100$ 1.82

B. Tests for lead

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It requires standards with known analyte content to establish the relation between the measured absorbance and the analyte concentration and relies therefore on the Beer-Lambert Law. Initial lead content was noted as 110 ppm by atomic adsorption spectroscopy. 1) Effect of biosorbent dosage for lead: The amount of lead removal showed adsorbent dosage dependence. This attributes to the increased adsorbent surface area and availability of more adsorption sites resulting from the increase of dosage. Table shows the concentration of 3g/50 ml was sufficient for maximum biosorption.

TABLE. 3 Absorbance readings for different dosages in lead solution

Dosage (g)	Absorbance at 510 nm(Pb)
0.5	0.005
1	0.007
1.5	0.008
2	0.009
2.5	0.011
3	0.012
3.5	0.012

2) Effect of contact time for lead: 3g of biosorbent was added to 50 ml of lead solution and shaken well. At different time intervals, adsorbance readings were noted. Biosorption continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. It was observed that sorption percentage increased with the increase of time up to 180 minutes.

TABLE. 4 Absorbance readings for different time intervals in lead solution

Time(min)	Absorbance at 510 nm(Pb)
30	0.006
60	0.008
90	0.009
120	0.01
150	0.011
180	0.012
210	0.009

3) Final lead content determination: Absorbance obtained for optimum dosage and contact time was used for final lead content determination.3g of biosorbent was added to 50 ml of sample and was kept for 180 minutes. Atomic absorption spectroscopy showed an adsorption reading of 0.012 and concentration of 0.48.Since the sample was diluted 10 times to avoid sodium error,

Final lead content = $0.48 \times 10 = 4.8 \text{ ppm}$.

4) Determination of percentage of biosorption

Percentage of biosorption

= Initial-final metal concentration x 100Initial metal concentration

Therefore, percentage of lead removed = $\frac{110-4.8}{110}$ x 100

=95.63%

C. Comparsion of percentage removal efficiency of metals using Ocimum sanctum

Results showed that Ocimum sanctum was more effective in removing lead than iron. Percentage removal efficiency of iron and lead was found to be 73.62 % and 95.63 %.

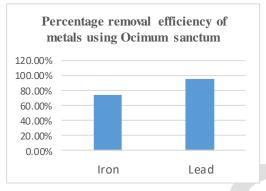


Fig.1 Comparison of percentage removal efficiency of metals using Ocimum sanctum.

D. Water quality criteria for irrigation

As per Indian standards, recommended maximum permissible concentration of iron and lead in irrigation water is 5.0 mg/l. The final concentration of iron and lead after addition of optimum coagulant dosage and contact time is 0.48 mg/l and 4.8 mg/l. Therefore, the samples after addition of biosorbent can be used for irrigation purposes.

E. Effect on pH

TABLE. 5 pH values of various samples

Sample	рН
Ocimum sanctum	7.2
Ocimum sanctum dipped in NaoH	10.8
Iron solution	1.1
Iron solution mixed with Ocimum sanctum	2.0
Lead solution	1.8
Lead solution mixed with Ocimum sanctum	8.0

Optimum pH of water to be used for irrigation purposes is 6.5-8.5. It was observed that when Ocimum sanctum dipped in sodium hydroxide solution was added to iron solution, its pH changed from 1.1 to 2.0 .Hence neutralization methods must be employed to remove its acidity. But when Ocimum sanctum dipped in sodium hydroxide was added to lead solution, its pH changed from 1.5 to 8.0.Hence additional methods to remove acidity need not be employed.

F. Colour

Addition of Tulsi leaves to iron and lead solution imparts colour. Since colour is objectionable, all efforts must be taken to remove colour as far as practicable.



Fig. 2 Green colour imparted to metal solution

IV. CONCLUSIONS

Wastewater from various industries like metallurgical industry, iron and steel production, cement industry, chemical industry, automobiles, furniture industry, paint industry etc. shows adverse percentage release of heavy metals like chromium, lead, iron, cadmium, nickel, copper etc. It can be removed by various conventional methods like physicochemical methods, chemical precipitation, coagulation and flocculation, electrochemical treatments, ion exchange, membrane filtration, electrodialysis etc. Use of natural adsorbents are more eco-friendly when compared to other conventional methods. In this investigatory work, Ocimum sanctum has been selected for the removal of heavy metals like iron and lead, as an adsorbent. Stock metal solutions of iron and lead has been prepared as samples of wastewater containing these metals. The parameters affecting the biosorption of lead using Tulsi leaves were studied. Biosorption was confirmed to be controlled by redox, ion exchange and coordination reaction, of which alcohol, carboxylamino and sulphonic groups play important role. The amount of metal removal showed adsorbent dosage dependence. The percentage of metal removal increased with the increase of Tulsi leaves dosage. This attributes to the increased adsorbent surface area and availability of more adsorption sites resulting from the increase of the dosage. It was observed that for both iron and lead 3g /50 ml was sufficient for maximum biosorption. The process continues till equilibrium is established between the amount of solid bound sorbate species and its portion remaining in the solution. The sorption percentage increased with the increase of time up to

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210 minutes for iron and 180 minutes for lead. Percentage of biosorption for iron and lead was found to be 73.62 % and 95.63 %.Since final metal concentrations of iron and lead after addition of biosorbent is less than 5 mg/l it can be used for irrigation purposes. pH remained acidic even after addition of Tulsi leaves in iron solution, whereas in lead solution pH changed from acidic to slightly alkaline. Hence neutralisation methods must be adopted for iron solution. Colour produced due to addition of Tulsi leaves poses a problem. Additional cost will be required for adopting colour removal techniques. So, considering percentage removal efficiency and pH, it can be concluded that Ocimum sanctum is more efficient in removing lead than iron (refer fig. 1). Intensive interdisciplinary collaboration in basic and applied research is expected to be beneficial in the near future. Mixture of natural adsorbents can also be verified and investigated which will be more eco-friendly and cost effective. Removal of other heavy metals can also be tried for further research work using Ocimum sanctum.

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