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Removal of Lead from Periyar River Water Using Citrus Sinensis and Mangifera Indica

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Abstract— **Heavy metals are major toxic pollutants with severe health effects on humans. They are released into the environment from a variety of industrial activities. Cadmium, lead, zinc, chromium and copper are the most toxic metals of widespread use in industries such as tanning, electroplating, electronic equipment manufacturing and chemical processing plants. Heavy metals contribute to a variety of adverse health environmental effects due to their acute and chronic exposure through air, water and food chain. Periyar River, the longest river of Kerala state is considered to be the life line of central Kerala. Angamaly to Kochi occupies the most industrialized zone of the Periyar River basin. Citrus sinensis (orange) peel and Mangifera indica (mango) peel are naturally occurring and abundant biomass can offer an economical solution for metal removal.**

Keywords— **Adsorption, heavy metals, Citrus sinensis, Mangifera indica**

I. INTRODUCTION

Water pollution due to development in technology, continues to be of great concern. With increasing generation of heavy metals from technological activities, many aquatic environments face metal concentrations that exceed water quality criteria designed to protect the environment, animals and humans. Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water and is toxic or poisonous even at low concentrations. Some well known toxic metallic elements are arsenic, (specific gravity 5.7); iron.(7.9); chromium.(7.19); cadmium,(8.65); lead,(11.34); and mercury,(13.54). Heavy metals are highly dispersed in a wide variety of economically important minerals. They are released to the environment during mineral extraction process. Therefore, mining activities are considered as the primary anthropogenic source of heavy metals.

The rivers of Kerala also have been increasingly polluted from the industrial and domestic waste and from the pesticides and fertilizers used in agriculture. Industries discharge hazardous pollutants like phosphates, sulphides, ammonia, fluorides, heavy metals and insecticides into the downstream reaches of the rivers. It is estimated that, nearly 260 million liters of industrial effluents reach the Periyar daily from Kochi industrial belt (Green Peace, 2003).

Preliminary report of the trace/heavy metal concentration in the pollution affected areas of Periyar River was reported by Paul and Pillai (1976). According to their report higher concentrations of trace elements in the downstream locations were observed than in the upstream regions. Elevated concentrations of copper, zinc and cadmium near Binani Zinc and Travancore Cochin Chemical Ltd (TCC) were some of the highlights of the data.

The global heavy metal pollution of water is a major environmental problem. Due to this reason the preservation and maintenance of our natural water resources is a very difficult task. Rivers play a major role in assimilating or carrying of industrial and municipal waste water, runoff from agricultural fields, roadways and street which are responsible for river pollution. Among various organic and inorganic water pollutants, metal ions are toxic, dangerous and harmful because of their tissue degradation in nature. Toxic metals are also bio accumulative and relatively stable as well as carcinogenic and require close monitoring. Most of the rivers are deteriorating in quality gradually and

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the maintenance of the quality of the river water will be a severe problem in the years to come.

A. *Health Effects Due To Heavy Metals*

Heavy metal toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term exposure may result in slowly progressing physical, muscular, and neurological degenerative processes. Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g., beryllium, chromium), neurotoxicity (e.g., lead), nephro toxicity (e.g., mercuric chloride, cadmium chloride), and cancer (e.g., arsenic, hexavalent chromium). Humans are often exposed to heavy metals in various ways—mainly through the inhalation of metals in the workplace or polluted neighborhoods, or through the ingestion of food (particularly seafood) that contains high levels of heavy metals or paint chips that contain lead.

B. *Methods For Removal Of Heavy Metal From Water*

Several technologies have been used to treat metal containing aqueous solution, for the last few decades. The conventional methods to remove heavy metal from water includes Membrane process (Reverse osmosis technique), Precipitation and clarification techniques, Activated carbon process, and Ion exchange process. Adsorption has emerged as promising technique for metal removal. The processes can occur at an interface between any two phases, such as, liquid-liquid, gas-liquid, or liquid-solid interfaces.

II. NATURAL ADSORBENTS

Most of the adsorption researches have been concentrated on the use of bacteria and fungi for the removal of heavy metals. Both viable and inactive cells have been studied. This generally involves culturing of these microorganisms using chemicals. A potential economical alternative would be to use, naturally abundant materials such as waste biomass. These natural materials can be easily processed and used for metal removal, and hence can offer an economical solution to the problem of heavy metal pollution. Low cost naturally available adsorbents like peels of orange, mango, neem barks or leaves coconut shell, etc can be used. The adsorption technique using agricultural wastes, fruit peels or natural biomass are low cost and effective. Metabolisms of adsorbent (fruit peels or agricultural wastes) helps in the heavy metal removal.

III. STUDY AREA

Periyar river , the longest river of Kerala state is considered to be the life line of Central Kerala. It originates from the Sivagiri peaks (1800m MSL) of Sundaramala in Tamil Nadu. The total length is about 300kms (244kms in Kerala) with a catchment area of 5396sq.kms (5284sq.kms in Kerala). The total annual flow is estimated to be 11607cubic meters.

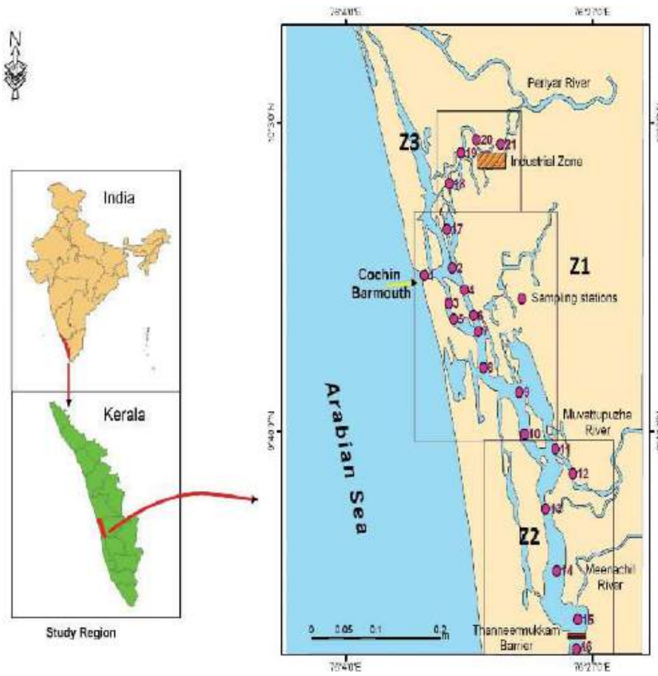

Fig.1. Study Area

Angamaly to Kochi occupies the most industrialized zone of the Periyar River basin. There are over 50 large and medium industries and over 2500 small scale industries in this region. The industries located in Edayar – Eloor area consumes about 189343cum per day water from the day and discharge about 75% as used water along with large quantity of effluents and pollutants. The major type of these industries are fertilizers, pesticides, chemicals and allied industries, petroleum refining and heavy metal processing, radioactive mineral processing, rubber processing units, animal bone processing units, battery manufacturers, mercury products, acid manufacturers, pigment and latex producers etc. The wide spectra of pollutants that adversely affect the natural environmental quality of water of the river include toxic and hazardous materials such as heavy metals, phenolics, hydrocarbons, pesticides, radio nucleides, ammonia, phosphates, domestic and untreated waste water. Two study sites were identified in the river for the collection and analysis of the selected trace metals in water.

A. Site I (Kuzhikundam Creek)

Eloor is the most industrialized zone of the Periyar River. There are around 250 factories in this area, 125 of which are chemical factories, like Binani Zinc, Travancore Cochin Chemicals Ltd, United Catalysts India Ltd, Kanyakumari Polymer. These factories discharge effluent directly to the Kuzhikundam creek, a tributary to the Periyar.

B. Site II (Kalady)

Kalady situated 48 km north-east of Kochi, on the banks of Periyar River. Water from the river is drawn for the purpose of irrigation as well as drinking. Small deltas have also been formed during recent years in the river at Kalady due to the ruthless unauthorized sand mining.

IV. MATERIALS AND METHODS

A. Preparation Of Adsorbents

Low cost naturally available adsorbents like peels of Citrus sinensis (orange) and Mangifera indica (mango) are used. The adsorption technique using agricultural wastes, fruit peels or natural biomasses are low cost and effective. Metabolism of adsorbent (fruit peels or agricultural wastes) helps in removal of heavy metal.

Fig.3. Orange peel

Fig.4. Mango peel

The peels of orange and mango were collected from local juice shops. They were then washed thoroughly with double distilled water to remove dust and other impurities. Then it was sun dried and cut into small pieces and ground to 250 mesh size. After screening they were again washed with double distilled water several times to remove color. Finally they were dried in an oven at 80^0Cfor 24 hours.

B. Collection Of River Water Samples

Water samples were collected from just below the surface (about 2 litres). It is Mixed and stored in bottles for the determination of heavy metals and physicochemical variables. Samples were collected from two points i.e. Site I and Site II. Site I is the downstream point, where heavy metal concentrations are high. Site II is the upstream point where pollution is considerably low. 100 ml of sample were transferred to a clean glass bottle &

acidified with Nitric acid (10%) so as to prevent precipitation and to promote sample digestion.

C. Determination Of Physicochemical Parameters

Various physical and chemical parameters of the river water sample have to be determined. These parameters indicate the pollution load of the river water. The physical parameters include Colour, odour and temperature. The chemical parameters include pH, Total Dissolved Solids (TDS), Turbidity, conductivity, BOD, phosphate and nitrate.

D. Determination Of Heavy Metals Present

The heavy metals present in the river water sample were obtained by analyzing in Atomic Absorption Spectrophotometer. Samples were analysed for the metals, iron, copper, manganese, lead, cadmium and zinc in an atomic absorption spectrophotometer. For calibration, standard is prepared at a concentration of 10 mg/l in an acid matrix of 5% HCl acid.

TABLE I

HEAVY METALS PRESENT IN THE SAMPLE

Heavy Metal (mg/l)	Site I	Site II
Cadmium	1.5	0.5
Iron	8.4	2.05
Copper	3.12	0.141
Manganese	4.01	9.23
Lead	3.18	0.10
Zinc	12.32	1.23

E. Batch Studies

Adsorption experiments were carried out by adding 0.5gm dried adsorbent per 100ml samples in a volumetric flask. Samples are shaken in a temperature controlled incubator shaker at 30°C with 200rpm speed. The pH of the sample was maintained at 5.5±0.5 and the contact time of 120min was used for batch tests. To study the effect of pH, the pH of the metal solution was adjusted to different values ranging from 2 to 7. The desired pH was adjusted by 0.1N HCl and 0.1 N NaOH solutions. After that the samples were taken and filtered and analyzed using Atomic Adsorption Spectrophotometer. Then the procedure is repeated with adsorbent dosage of 1, 1.5, 2 and 2.5 grams.

F. Equilibrium Studies

Adsorption equilibrium studies were conducted to determine the nature of the adsorption isotherms and the adsorption capacity of the adsorbent for the removal of metal ions. The adsorption flasks were agitated in an incubator shaker at 200rpm and samples were collected at specified time intervals and were analyzed for the residual metal concentration followed by separation of the biomass by filtration. During adsorption a rapid equilibrium is established between adsorbed metal ions and adsorbent. The equilibrium metal uptake q is calculated using the following equation:

$$q = \frac{(C_i - C_f)\, V}{M}$$

Where, V is the volume of the solution,
C_i and C_f are initial and equilibrium concentrations
and M is the dry mass of adsorbent

The Freundlich and Langmuir isotherms were plotted and the best fit isotherm was noted. The effects of various parameters like pH, adsorbent dosage and contact time on the removal efficiency were also noted.

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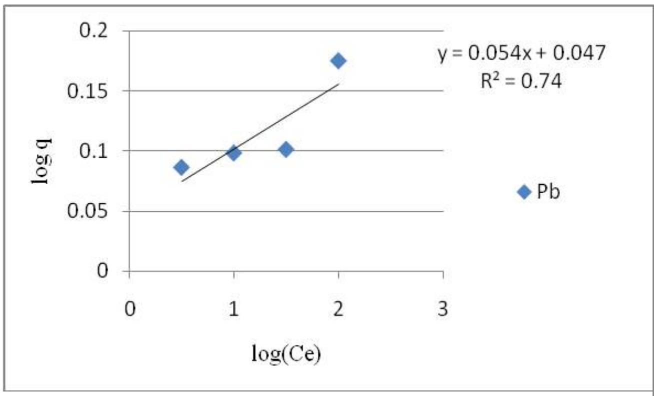


Fig.5. Freundlich Isotherm For Site I

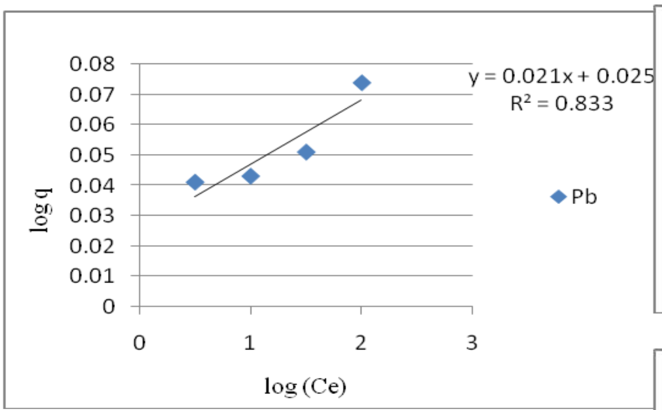


Fig.6. Freundlich Isotherm For Site II

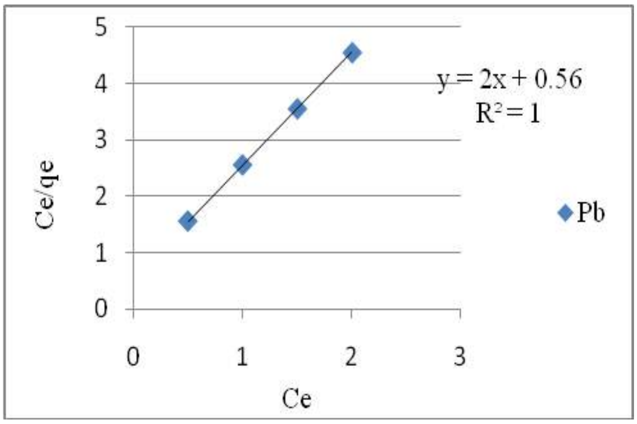


Fig.7. Langmuir Isotherm For Site I

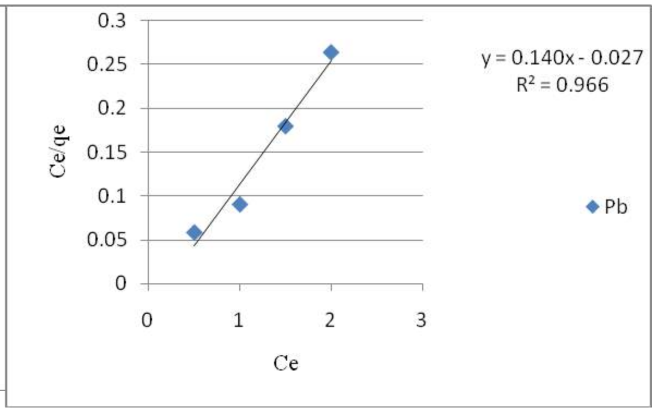


Fig.8. Langmuir Isotherm For Site II

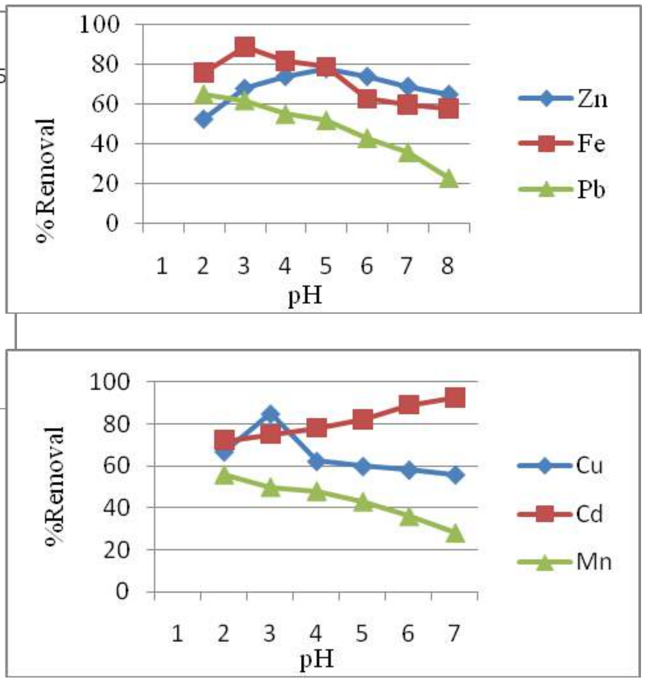
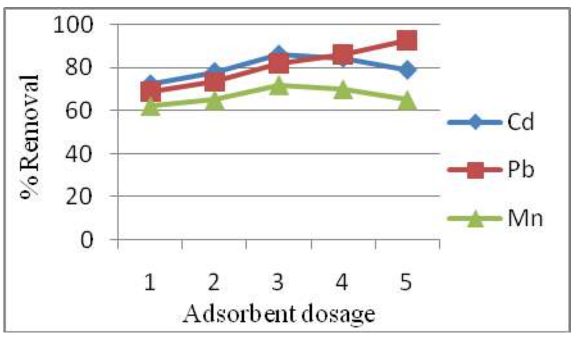


Fig.9. Effect Of pH



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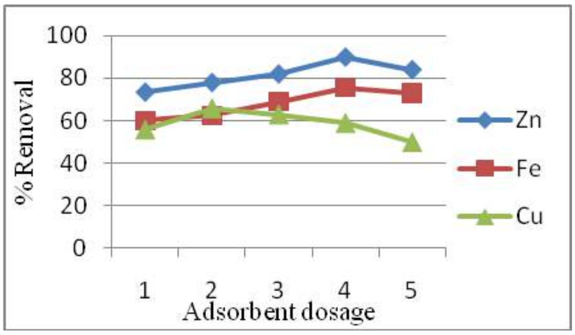

Fig.10. Effect Of Adsorbent Dosage

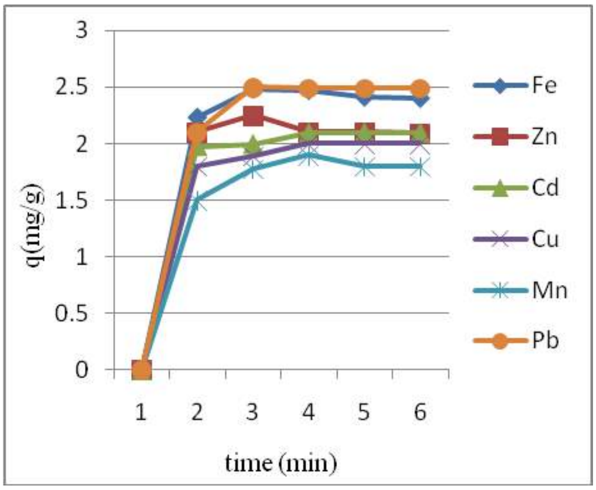

Fig.11. Effect Of Contact Time

V. RESULTS AND DISCUSSIONS

Orange peel has greater removal efficiency for lead with 92.6 % at conc. 2.5 at site I and 92% at conc. 2.5 at site II. The higher the b, the higher is the affinity of the adsorbent for metal ions.

Hence, the affinity order of orange peel is Cd>Pb> Fe> Zn> Mn> Cu in Site I and Cd> Zn> Pb> Mn> Cu> Fe in Site II. Thus, orange peel has higher adsorption capacity towards Lead. Also it requires less pretreatment. It also has 89% removal efficiency towards Zinc.

The effects of contact time, pH and adsorbent dosage on the metal uptake/ removal efficiency were studied. The optimum contact time of 60-75 minutes were obtained. The maximum removal efficiency was obtained with adsorbent dosage of 2.5 gram in pH range 6 to 7.

VI. SUMMARY AND CONCLUSIONS

In view of the values of the linear regression coefficients, Langmuir model fits very well to the sorption data in the studied concentration range studied. Also based on the value of constant b, orange peel has greater affinity towards Lead removal.

The mango peel has been prepared and the removal efficiency of mango peel in removal of lead has to be determined. The removal efficiencies of both mango and orange peel in lead removal have to be compared. The comparison between orange and mango peel as an adsorbent in the removal efficiency of heavy metals (Lead) from the Periyar river water is to be done.

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