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Application of Chitosan, Ferric Chloride and Aluminium Sulphate in the Removal of Heavy Metals from Coastal, Estuarine and Industrial Wastewater

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Abstract— Water quality in water bodies is subjected to the natural degradation process of eutrophication and has adverse effect on social development. Most of the water bodies in Kochi, Alappuzha and Kottayam shrunk considerably due to the aggressive rapid urbanization process and overpowering invasion. This study aims at assessing the physic-chemical parameters of coastal, estuarine and industrial wastewater samples and application of chitosan in removal of heavy metals. A study was conducted to determine the physico-chemical parameters of water of 5 different water bodies and 2 industries in Ernakulam, Kottayam and Alappuzha named Periyar River, Fort Kochi beach, Poonithura Canal, Vembanadu Lake, Vettikattumukku pond in Kottayam, and two seafood industries in Cochin from March to May, 2021. The selected parameters were water temperature, color, salinity, pH, Dissolved Oxygen (DO), concentration of nutrients (Nitrite, Phosphate and Silicate) and concentration of alkali metals (Sodium, Potassium and Calcium). This analytical study would improve the socio eco features of these water bodies by employing utility-based restoration plans. Heavy metals are naturally occurring elements, which are found throughout the earth's crust, most environmental contamination and human exposure and majority of them are carcinogenic.

We removed the heavy metals for reducing the toxicity of wastewater in eco-friendly and cheaper way using chitosan, aluminium sulphate and ferric chloride. Under different pH conditions, adsorption of chromium and copper ions by chitosan was investigated. Amount of chromium and copper absorbed or the efficiency of heavy metal removal by chitosan, alum and ferric chloride were determined using ICP-AES. Among Chromium and Copper, Cu can be efficiently removed from the water using chitosan at higher pH. Ferric chloride is more efficient in removing heavy metals than Aluminium sulfate at the same pH.

Index Terms— Aluminium sulphate, chitosan, heavy metal removal, wastewater

I. INTRODUCTION

The distribution of water on the Earth's surface is not even. Only 3% of water on the surface is fresh. That is, only one percent of the water on the Earth's surface is usable by humans, and 99% of the usable quantity is located underground. As a result, water quality has received a lot of attention in the scientific community. The most popular definition of water quality is "it is the physical, chemical, and biological characteristics of water". . The major types of water quality parameters are physical, chemical, and biological [12]. Physical parameters of water quality include Turbidity, Temperature, Color, Taste and Odor and Electrical Conductivity. pH, Acidity, Alkalinity, Chloride, Sulfate, Nitrogen, Phosphate, Silicate, Fluoride, Dissolved Oxygen (DO), Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Hardness and Toxic substances are coming under chemical parameters. Biological parameters are Bacteria, Fungus, Virus, Algae, etc [6].

Water pollution occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment [4]. The fast expansion of urban, agricultural and industrial activities driven by rapid population growth has produced vast amounts of solid wastes. Although there are more than 20 heavy metals, 4 are particular concern to human health and environment (Lead, Cadmium, Mercury and Arsenic [5]. Discharge of wastewaters and sewage into rivers has been a significant source of heavy metals into aquatic environment. They easily adsorb to suspended particles in water, settling down in the riverbed, and are later released into the water column, where they become a potential secondary source of contamination, threatening ecosystems [5].

Small amounts of hazardous compounds dissolved in water that never settles out can also be removed through physical treatment. Chitosan is commonly used in wastewater purification plants in order to remove oil, grease, heavy metals and fine particulate matter that cause turbidity. Coagulation and flocculation are a crucial part of drinking water treatment and wastewater treatment. Al (III) and Fe (III) coagulants are two main inorganic compounds used in water treatment plants. The most common coagulants used are ferric sulfate, aluminum sulfate, and ferric chloride. The present study investigated al efficiency of the heavy metal remove chitosan, ferric chloride and aluminium sulphate under different pH conditions. The physico-chemical parameters of samples collected from different water bodies of Kerala were also studied.

II. MATERIALS AND METHODOLOGY

Kerala is located between the Arabian Sea in the West and the Western Ghats in the East with an area of 38863 sq km, which is between 8° 8' and 18° 48' North latitude and 74° 4' to 77° 50' East longitude,

Samples for analyzing Heavy Metals were collected from 7 locations in Kerala. They include Periyar River, Poonithura canal, Vembanadu Lake, Fort Kochi beach, Vettikkattumukku Pond, two seafood industries in Cochin.

Temperature and pH were measured with a mercury filled Celsius thermometer and digital PH meter respectively. The Salinity was evaluated using Refractometer. The Dissolved Oxygen (DO) was determined using Iodometric titration (Winkler's method) and the Nutrients (Nitrite, Phosphate and Silicate) were estimated using spectrophotometer (Klaus Grasshoff., 1999).The Alkali Metals were determined using Flame Emission Spectroscopy (FES). Detection and estimation of Heavy Metals were carried out using Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES) (Klaus Grasshoff 1999) .

The sample was collected in polyethylene bottles and filtered the sample under vacuum through a 0.45-μm membrane filter. Then preserved samples by adding 1.5 mL concentrated HNO_3 to 1L of sample to give pH<2. When handling samples, be extremely careful not to introduce contamination during sampling, handling, storage, or treatment. Use the highest purity HNO_3 available in the laboratory and analyze water, filter and acid blanks regularly [3].

Coagulation is useful to remove removes colloids and suspended solids from the water [2]. After that during flocculation, the particles are attracted together by van der Waal's forces, forming floc [1] [16]. Aluminium sulfate and Ferric chloride were tested as conventional coagulants [11]. Chitosan is used as an excellent flocculent due to its large numbers of NH_3 groups, which can interact with negatively charged colloids [15].

This study investigated the metals Chromium, Copper, Iron and Lead. As the raw waste water samples did not contain detectable quantities of dissolved metals, the water samples collected from Fort Kochi beach were spiked with metals (copper and chromium) to obtain suitable concentrations of metals in waste water [10].

10 mM copper solution was prepared using analytical grade copper nitrate, $Cu(NO_3)_2$ powder and this solution was kept as stock solution of Copper. Similarly, 0.1942g analytical grade potassium chromate, K_2CrO_4 powder was taken and made up to100 mL. This solution was kept as stock solution of Chromium. 10 milligram chitosan powder was weighed into a small glass beaker, dissolved with minimum amount of 0.05M Acetic acid and kept for about 30 minutes to dissolve. Initial pH of the samples was adjusted to 2 and 7. Subsequently 10 mg of chitosan solution were added to each flask [14]. 2.5 mL of 10mM $Cu(NO_3)_2$ solution was added to each flask and made up to 25 mL with the sample solution. Similarly chromium spiking was done by adding 2.5 mL of 10 mM K_2CrO4 solution to the sample solution of pH 2 and 7 respectively and made up to 25 mL with the sample solution having appropriate pH value. And similarly, Initial pH of samples were adjusted to 7. Subsequently 10 mg of aluminium sulphate and 10 mg of ferric chloride [7] were separately added to each flask. 2.5 mL of 10 mM $Cu(NO_3)_2$ solution was added to each flask and made up to 25 mL with the sample solution [7]. Similarly chromium spiking was done by adding 2.5 mL of 10 mM K_2CrO_4 to each flask and made up to 25 ml with the sample solution (Agarwal 2017).

All the samples along with blank were shaken vigorously for 6 hours in molecular orbital shaker at room temperature [8]. It is followed by centrifugation for 15 minutes and once the equilibrium is achieved, the samples were withdrawn from supernatant [13]. Then, the sample solutions were filtered and filtrate was digested with the aid of concentrated Nitric acid. Once the digestion step was completed, the solution was filtered and the filtrate was analyzed for heavy metals using Inductively Coupled Plasma- Atomic Emission Spectroscopy ICP-AES [17].

III. RESULTS AND DISCUSSION

The physico-chemical parameters were measured for a total of seven samples were obtained from seven different places in Kerala (Table 1). The distribution and variation of physico-chemical parameters such as temperature, pH, Electrical Conductivity, salinity, dissolved Oxygen and alkali metals as well as the heavy metals in water samples, were studied.

Among the stations, wastewater from seafood industry 1 (Figure 2) shows maximum nitrite content (43μmol/L) due to the high protein content of fish and marine invertebrates, and minimum nitrite content is observed in Kottayam Pond water (1.2μmol/L) (Figure 1) due to the influx of fresh water. The wastewater from seafood industry 1 shows higher phosphate (440μmol/L) content, which may originate from the seafood, but can also be introduced with processing and cleaning agents and the lowest concentration was shown in Vembanadu Lake (1.1μmol/L). In this study, the maximum silicate concentration was found in wastwater from seafood industry 1(25μmol/L) because, this seafood industry mainly focused on crustaceans and siliceous seafood. The seawater collected from Fort Kochi also showed higher silicate value (16.86 μmol/L) as the seawater contains in suspension a wide spectrum of finely divided siliceous materials. Many of them have been formed by the weathering of rocks on land and have been transported to the sea by rivers and by wind [9]. Minimum content of silicate is found in Vembanadu Lake (1.44μmol/L).

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Table 1: Physicochemical parameters of water samples collected from different locations in Kerala

Station	Color	Temperature (°C)	pH	Salinity (ppt)	EC (4)	DO (mg/L)
Vembanadu Lake	Pale green	34	7.33	20	0.2	6.4
Kottayam Pond	Light green	27	6.5	3	0.7	10.4
Fort Kochi Beach	Colorless	29	7.8	30	0.9	7.2
Poonithura Canal	Blue-greenish	32.4	7.1	5	0.4	7.2
Periyar River	Colorless	32	6.27	2	0.1	7.2
Seafood Industry 1	Brown	27	7.24	10.3	_	ND
Seafood Industry 2	Grey	26	6.1	3	_	ND

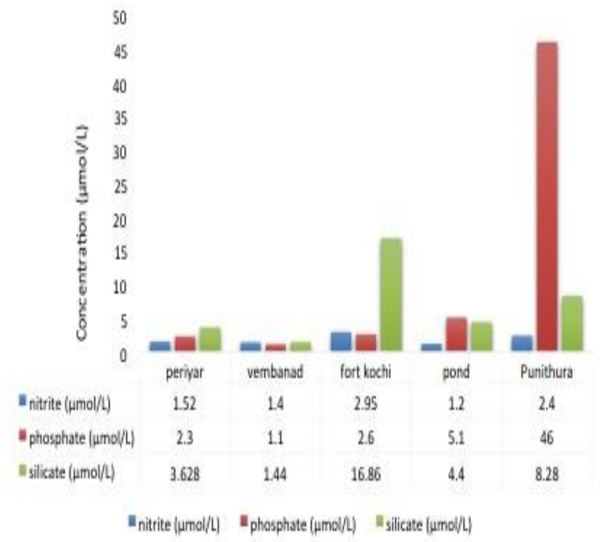

Fig. 1 Concentration of nutrients obtained from different water bodies. The X axis represents the different locations and Y axis shows corresponding concentrations of nitrite, phosphate and silicate present in the water samples.

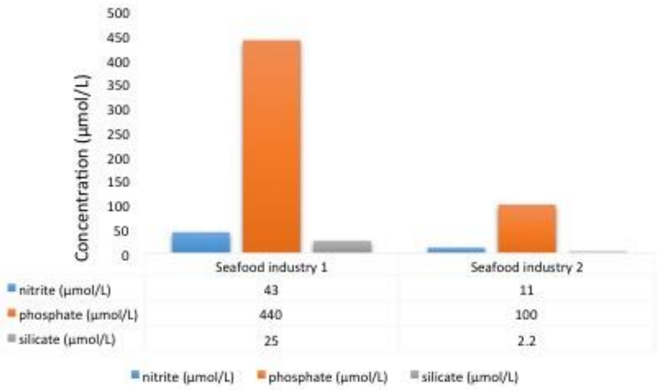

Fig. 2 Concentration of nutrients obtained from two different seafood industries. The X axis represents the different locations and Y axis shows corresponding concentrations of nitrite, phosphate and silicate present in the water samples.

The highest DO value obtained from Kottayam Pond (10.4 mg/L) shows that it is less polluted by human activity and the lowest value in Vembanadu Lake (6.4 mg/L) (Table 1). DO concentration was not detected in both seafood industries. For seafood- processing, the waste water is comes after treatment which include screening, sedimentation, dissolved air flotation and activated sludge treatment etc. [18]. These unit operations will generally remove up 85% dissolved oxygen in the water.

Analysis of alkali metals revealed (Figure 3) that the highest sodium concentration was in Fort Kochi seawater (157.3ppm) and the lowest in Kottayam Pond water. There are a number of sources of Na that can contribute substantial quantities to surface water including water treatment chemicals and sewage effluents. Fort Kochi water showed higher concentration of potassium (31.2ppm) and a minimum in Vembanadu lake water (4.9 ppm). Main cause for increase in potassium levels in water bodies is due to agricultural activities. Water softeners that regenerate using KCl can also raise the level of K in water significantly. Calcium is abundant in water bodies because of the presence of its mineral in the Earth crust. Among this Periyar River water shows a maximum Ca concentration (78 ppm) and a minimum value at Kottayam pond water (0.82 ppm). The water and effluents from industrial complex with giant fertilizer plant and oil refinery were dumped into the Periyar River at certain locations.

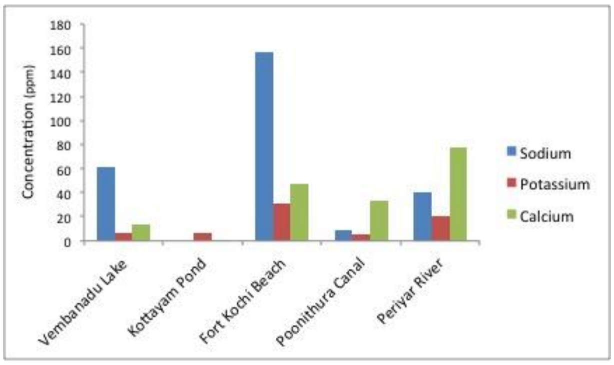

Fig. 3 Concentration of alkali metals (ppm) from different stations

Table 3: Removal efficiency of heavy metals using chitosan, aluminium sulphate and ferric chloride; Sample 1 and 2 : Fort Kochi sample spiked with 1 mM Cu under pH 2 and pH 7 respectively; Sample 3 and 4: Fort Kochi sample spiked with 1 mM Cr under pH 2 and pH 7 respectively

Samples	Removal Efficiency (%)					
	Chitosan		Aluminium Sulphate		Ferric Chloride	
	Copper	Chromium	Copper	Chromium	Copper	Chromium
Sample 1	20.21	-----	-----	-----	-----	-----
Sample 2	9.185	-----	25.81	----	-----	-----
Sample 3	-----	8.395	-----	-----	-----	-----
Sample 4	-----	8.49	-----	7.105	-----	7.04

In the sample collected from Fort Kochi, after spiking with 1mM Cu solution the value of Cu was 63.5 ppm (Table 3). After adding chitosan to this solution, the value of Cu became 20.21 in pH=2 and 9.185 in pH=7. Thus the efficiency of removal of Copper using chitosan is 68.17% in pH=2 and 85.54% in pH= 7 respectively. Similarly in the case of Cr, after spiking with 1 mM Cr solution the value of Cr was 52 ppm. After adding chitosan to this solution, the value of Cr became 8.395 in pH=2 and 8.49 in pH=7. Thus the efficiency of Cr removal using chitosan is 83.85% in pH=2 and 83.67% in pH=7.Removal efficiency of Cu using aluminium sulfate is 59.3% and efficiency of Cr using aluminium sulfate at pH 7 is 86.3% (Table 3).

IV. CONCLUSION

It is observed that Poonithura Canal (Ernakulam) is the most polluted water body among the samples taken. The value of nutrients (nitrite, phosphate and silicate) higher here is due to municipal and sewage waste disposal. This increase in the value of nutrient may lead to algal bloom which eventually results in eutrophication. From the study, the sample collected from a pond in Kottayam is observed to be the least polluted water body among the samples collected. This may be due to the low anthropogenic activities. The samples collected from both industries showed high nutrient value and below detection value for Dissolved Oxygen. For the samples collected from the Fort Kochi Beach, the removal of heavy metals using chitosan is done for both pH, 2 and 7. It is observed that the removal of heavy metal using chitosan is more efficiently done in pH=2. And also among Chromium and Copper, Cu can be efficiently removed from the water using chitosan at higher pH. Ferric chloride is more efficient in removing copper from the water samples. Ferric chloride and aluminium sulfate are almost equally efficient for the removal of chromium. For the water sample collected from the Fort kochi beach, the removal of heavy metals (Cr and Cu) using Aluminium sulfate and Ferric chloride was done at pH 7. It is found that ferric chloride is more efficient in removing heavy metals than Aluminium sulfate at the same pH.

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