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A Green Pathway for Purification of Surface Water by Removing Heavy Metals

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Abstract:

The removal of turbidity and heavy metals from surface waters for potabilization is a topic of research in many regions of the world since it has emerged as a public health issue. Numerous researchers create methods for removing heavy metals, however because of the risks involved in using chemical reagents by people with little to no education; these methods are typically challenging to apply in rural areas. In order to find low-cost, low-tech techniques for potabilizing surface waters in small towns, this chapter will undertake a thorough literature study and include an original research project created by our working group. It also seeks to offer information for improved comprehension. By employing plants and their extracts to remove turbidity and other heavy metals, these cost-effective, environmentally friendly, and effective techniques will contribute to the improvement of surface water treatment for human use. This chapter's suggested techniques for potabilizing natural water represent advancement in green analytical chemistry. Presenting metals, removal methods, and assessing the effectiveness of Fe and Mn removal during phytoremediation procedures are the goals of this chapter. Three steps were taken into consideration in order to complete this task. The amount of plant material needed for the procedure is chosen in the first step.
The second step involves determining the metal removal capacity using the chosen mass, and the third step is to compare the removal levels of extracts from *Hylocereus triangularis* and *Opuntia ficus-indica* with *Hydrilla verticillata* (L.f.) Royle. Atomic absorption spectroscopy was used to determine the metals using a previously approved technique. Fe and Mn were completely removed from the *Hydrilla,* while turbidity and colour were reduced by 92% and 94%, respectively. Plants such as *Opuntia ficus-indica* and *Hydrilla verticillata* (L.f.) Royle can be used to remove colour, turbidity, Mn, and Fe from natural waterways. In natural waters, the *Hylocereus triangularis* did not demonstrate effective removal of these metals. Opuntia is important for rural populations because, like *Hylocereus* and *Hydrilla*, it may be used to remove turbidity from natural waters.

Keywords: *Turbidity, Phytoremediation, Green Analytical Chemistry, Potabilization, Turbidity.*

1. Introduction:

Heavy metals, which are a big problem in developing nations because of the substantial pollution they cause to surface waters, are among the many toxins that plague aquatic ecosystems that are vital for human consumption (1). Anthropogenic activities are the cause of this degree of contamination. Although there are many different ways to treat water, many of them are expensive but effective (2). Therefore, the removal of such contaminants requires the use of suitable and affordable methods. It is crucial to emphasize the many techniques utilized for pollution removal because rural areas in developing nations lack the capability for costly water treatments. Additionally, it is crucial to demonstrate practical and affordable techniques that make heavy metal removal possible.

Many different types of heavy metals are of interest because they can be harmful to human health. These include iron (Fe), manganese (Mn), chromium (Cr), arsenic (As), copper (Cu), cadmium (Cd), zinc (Zn), and lead (Pb) (2, 3). The ecosystem and the living things that inhabit it may suffer as a result of these metals (2). As a result, it's critical to keep an eye on the different contaminants that could be found in surface waters.

The Water Quality Index (WQI) (4), which shows the state of a water source, is used to evaluate the quality of water. Water quality is deemed good if the WQI is between 91 and 100; acceptable if it is between 71 and 90; regular if it is between 51 and 70; bad if it is between 26 and 50; and lowest if it is between 0 and 25. The country's location and water consumption have an impact on this index (5).

The Heavy Metal Pollution Index (HPI), which displays the cumulative impact of metals in surface waters (6), and the Heavy Metal Evaluation Index (HEI), which depicts the condition of the water body, are the two indices used to assess the quality of water with relation to heavy metals. Numerous pollution sources, including as mining, agriculture, volcanoes, forest fires, and urbanization, can have an impact on the condition of the water body.

The toxicity of heavy metals is an important factor to take into account because they endanger both human health and the natural equilibrium (7). Long-term exposure to heavy metals has been linked to a number of illnesses, including osteoporosis, neurological problems, Alzheimer's, and even mortality (2). This work attempts to do a comprehensive evaluation of various heavy metal removal techniques for these and numerous other reasons. We will concentrate on techniques like coagulation/flocculation and phytoremediation that are both economical and use plants or plant extracts to decontaminate surface waters. These techniques are very advantageous since they allow pollutants to be removed naturally without the need for chemicals.

Duckweed and tape grass have been used to remove manganese from water (9), while Guasimo (*Guazuma ulmifolia*), prickly pear cactus (*Opuntia ficus-indica*), dragon fruit (*Hylocereus triangularis*), water lettuce (*Pistia stratiotes*) (10, 11) for water retention, and *B. papyrifera* and *K. paniculata* have been used to remove manganese from soil (8). They are an environmentally friendly substitute, as these studies show.

It uses a variety of hyperaccumulating plants called macrophytes to remove contaminants. These plants are useful in removing metals from water through processes like phytoextraction, rhizofiltration, phytovolatilization, and phytostabilization (13). Plants retain heavy metals through a process called chelation (14).

There are benefits and drawbacks to phytoremediation. The challenge of getting rid of biomass that has toxins adsorbed onto it is one of its drawbacks. Nonetheless, there are other methods of disposal, including pyrolysis, gasification, microbiological extraction, and incinerator treatments (13, 15). The aquatic plant *Hydrilla Verticillata* is a member of the *Hydrocharitaceae* family. It is regarded as an invasive and aggressive species that has been utilized in research to remove phosphates from home wastewater (18) and red dye 120 from simulated wastewater (16, 17). The abundance of this plant in our aquatic environments, the fact that traditional treatments do not remove contaminants from it, and its potential application in eliminating iron and manganese (Fe and Mn), which give the water a brown hue and an unclean look, are the main reasons for research into this plant.

2. Sources of heavy metals and their toxicity:

2.1 Heavy metals:

At low concentrations, heavy metals are harmful and are defined as those with a density more than 4 g/cm^3 (19, 20). These include, but are not limited to, (Hg), (Zn), (Cu), (Cd), (Pb), (As), (Fe), (Mn), (Cr), (Ni), and (Co) (3, 20).

- At room temperature, mercury (Hg), a silver-coloured metal, is liquid and exists in the oxidation states (+4, +2, +1). It builds up in the majority of living things, is highly poisonous, and can lead to a variety of illnesses, including neurological, ophthalmological, dermatitis, rhinitis, hypersensitivity, and digestive disorders (nausea, foul breath, vomiting, diarrhea, etc.) (21).

- With oxidation states of -2, 0, +1, and +2, zinc (Zn) is an element that appears as a silver-grey solid. Despite being necessary for human health, consuming too much of it can lead to immunological dysfunction, increased testosterone, high cholesterol, and the risk of prostate cancer (22).
- Aquatic biota may be stressed by copper (Cu), a reddish solid with oxidation states of +1 and +2 (23). Furthermore, acute toxicity, physiological changes, and toxic effects can result from exposure to Cu in high concentrations (24, 25).
- The oxidation states of +1 and +2 and a bluish-white solid appearance are characteristics of the metal cadmium (Cd). The four most hazardous characteristics of a toxic contaminant-bioaccumulation, ease of transportation by air and water, toxicity to humans, and persistence in the environment are all present in this metal. It is a contributing factor to diseases of the kidneys, bones, and lungs because of its bioaccumulative nature (26).
- The central nervous system is harmed by lead (Pb), a dark-grey element with oxidation states (+2, +4) that also affects balance and the extent and direction of muscular activity (27).
- Because of its three allotropic states, arsenic (As), a metal having oxidation states (+3, +5), can be found in grey, yellow, and black hues. It is highly poisonous and can lead to poisonings and a higher risk of bladder, skin, and lung cancer (28).
- The grey-silver metal iron (Fe) has oxidation states of +2, +3. Its build-up in the liver can result in poisoning and the production of free radicals, which can induce oxidative stress. The central nervous, gastrointestinal, cardiovascular, and metabolic systems are all impacted by iron intoxication (29).
- In addition to being carcinogenic, chromium (Cr), which has a bright whitish-grey colour and oxidation states (+2, +3, +4, +6), can harm the skin and eyes. Consuming it can cause gastrointestinal harm, pneumonia, hemorrhages, and kidney failure (30).
- The most prevalent oxidation states of manganese (Mn), a whitish-grey transition metal, are (+2, +3, +4, +6, +7). In addition to causing respiratory issues and blocking the neurotransmitter system, it also produces manganism, an illness in which the patient displays symptoms like those of Parkinson's disease (31).
- Nickel (Ni) is a white solid element that is somewhat amber in colour and has oxidation states of +3, +2, and 0. Long-term exposure or consumption may result in pulmonary emboli, respiratory failure, seizures, chronic bronquitis, cutaneous eruptions, and pulmonary cancer, among other symptoms (32).
- Cobalto (Co) is a white-azulad metal with oxidation states of +5, +4, +3, +2, +1, and -1. Their consumption may result in changes to the buccal mucosal epitelios (33), ocular changes, hypothyroidism, cardiopathy, and skin eruptions (34).

2.2 Heavy metals sources

Waters whose composition has changed to the point where they no longer maintain ideal conditions for human consumption are considered polluted, according to the World Health Organization (WHO). A wide range of natural and man-made activities, including as mining, forest fires, agroindustry, urbanization, and volcanoes, contribute to the contamination of surface water sources (2). Considerable quantities of heavy metals are released into the environment as a result of each of these occurrences, endangering ecosystems and human health (Figure 1). Surface waterways can become contaminated with various heavy metals mostly as a result of human activities, such as mining, pesticides, and insecticides. In particular, when excessive levels of heavy metals are present in human drinking water, the organisms that are exposed to it may experience problems. The heavy metals, their origins, and the illnesses they can cause, and the highest levels that can be found in water are listed in Table 1.

Figure 1: ***Sources of Heavy Metas and Water pollution***

Table 1. ***Major heavy metals present in surface waters and their anthropogenic sources.***

Metals	**Sources**	**Suffering**	**Maximum allowed in drinking water (WHO)**	**Ref.**
Cr	Corrosion	Kidney failure, bronchitis, bleeding, and gastrointestinal damage	0.05 mg/l	[3, 30, 35–37], [WHO]
Pb	Mining, corrosion, agriculture, and cattle farming	Loss of sense of balance and direction and range of muscle movement	0,01 mg/l	[3, 27, 35–38]
Zn	Mining, corrosion, agriculture, and cattle farming	Prostate cancer, increased cholesterol, testosterone, and immune dysfunction	3 mg/l	[3, 22, 35–37]

Ni	Mining, corrosion	Pulmonary embolism, respiratory failure, dizziness, bronchitis, skin rashes, and lung cancer	0,02 mg/l	[3, 32, 35–37]
Cu	Mining, corrosion, agriculture, and cattle farming	Physiological alterations and acute toxicity	2 mg/l	[3, 24, 25, 35–37]
Cd	Mining, corrosion	Conditions in the lungs, bones, and kidneys.	0,003 mg/l	[3, 26, 35–37]
As	Mining, agriculture, and cattle farming	Poisoning, carcinogenic prevalence in lungs, skin, and bladder	0.01 mg/l	[3, 28, 35–38].
Fe	Corrosion	Effects on the central nervous system, gastrointestinal, cardiovascular	NGL**	[3, 29, 35, 37, 39]
Co	Corrosion	Alterations in epithelia of the oral mucosa, visual, hypothyroidism, cardiomyopathy, skin rashes	NM	[3, 33–35, 37, 39]
Mn	Agriculture and cattle farming	Respiratory problems, blockage of the neurotransmitter system, and manganism syndrome	0,5 mg/l	[3, 31, 35, 37]
Hg	Mining	Nausea, vomiting, diarrhea, neurological syndromes, ophthalmological syndrome, dermatitis, rhinitis, and hypersensitivity	0,001 mg/l	[21, 36, 38]

2.3 Toxicity of heavy metals

The International Agency for Research on Cancer (IARC) has identified aluminum production, iron and steel foundries, and heavy metals like chromium (VI), beryllium, arsenic, nickel, and cadmium as human carcinogens (38).

Certain divalent metal cations, such as Co^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, and Mn^{2+}, share structural similarities. They could probably compete with one another, which could cause issues with the cell's physiological processes (40). Ca, which is present in membranes and can be replaced by other metals to result in functional issues, is one example of this (41).

Many diseases, including cancer, neurological syndromes, ophthalmological syndromes, dermatitis, rhinitis, hypersensitivity (21), visual impairments, hypothyroidism, cardiomyopathy, skin rashes (34), elevated cholesterol, increased testosterone, and immune dysfunction (22), conditions in the kidneys, lungs, and bones (26), kidney failure, gastrointestinal damage (30), a syndrome known as manganism (31), poisonings, and more, can result from ingesting heavy metals and/or prolonged exposure to them. This highlights how crucial it is to investigate and develop different techniques for eliminating pollutants from waterways meant for human consumption (Figure 2).

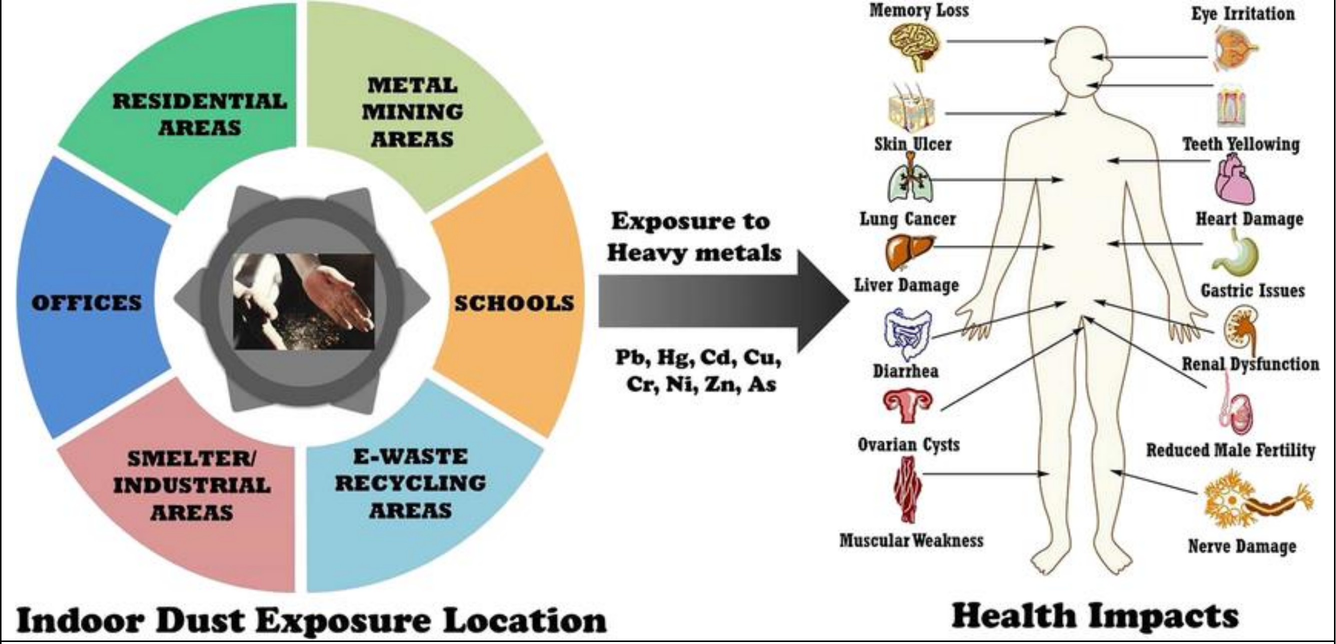

Figure 2. ***Alterations and toxicity in humans caused by ingestion of heavy metals.***

3. Techniques for removal of heavy metals

Surface waters can be treated using a variety of techniques, such as chemical, physicochemical, and biological approaches. Utilizing plants for water decontamination (phytoremediation) (7) (coagulation/flocculation) is one of the biological and physicochemical approaches. These two techniques are important because they can be used in rural locations that do not have the vast infrastructure needed to clean surface waters for human consumption.

3.1 flocculation / Coagulation

The technique makes use of plants or plant extracts that have the capacity to absorb pollutants, after which a coagulation/flocculation process makes it simple to separate the contaminants. However, a secondary pollutant is produced by this process (42).

3.2 Phytoremediation

Although it takes a long time and requires a lot of land, the method that uses plants to remove toxins from water is environmentally benign (43).

3.3 Photocatalytic process

Although photocatalysis has the ability to break down heavy metal complexes, has a high oxidative power, breaks down organic complexes, and doesn't produce any pollutants, its drawback is the high cost of the equipment required to operate (44).

3.4 Chemical precipitation method

Although it has several drawbacks, including the need for chemicals, the production of sludge, and handling costs, it is a simple and affordable technique that effectively eliminates a sizable proportion of heavy metals from water (45).

3.5 Electrochemical method

The approach that recycles heavy metals efficiently while using the fewest chemicals possible. This method's drawbacks are its high cost and lack of sensitivity, stability, and efficiency (46).

3.6 Reverse osmosis

The technique is easy to use, doesn't require any chemicals, and may be used with other techniques. Among the drawbacks are decreased water permeability, the potential for membrane contamination, the need for a lot of energy, and the high equipment and operating expenses (47).

3.7 Flotation

Purchasing equipment for a water treatment method where physical phenomena predominate can be inexpensive, but there are certain drawbacks, such as maintenance and operating expenses (48).

3.8 AOPs

This process doesn't produce sludge and uses very few chemicals. However, this method's inapplicability on a wide scale is one of its main drawbacks (49).

3.9 Ion-exchange process

The technique that makes use of a resin that is both economical and retains strong regeneration. Its adsorption of organic materials and handling challenges are its main drawbacks (50).

3.10 Membrane filtration

Under low pressure, this technique offers effective separation with good selectivity. Its costly operation and challenging post-use handling are its drawbacks (51).

3.11 Adsortion

An effective separation technique that is inexpensive, simple to apply, and suitable for a broad pH range. The requirement to replenish the adsorbent is the method's drawback (52).
As can be seen, each of the aforementioned techniques has certain drawbacks. But we wish to draw attention to the utilization of plants or plant extracts (phytoremediation) in this article. In remote locations with low resources for surface water treatment, this approach may be replicable.

4. Methodology and Experimental section

Three phases were taken into consideration in order to complete this work, and glass experimental units with a 10 L capacity were employed for each factor that was analyzed . *Hydrilla verticillata* (L.f.) Royle plants, cactus (*Opuntia ficus-indica*) extracts, and dragon fruit (*Hylocereus triangularis*) extracts were used to evaluate the removal effectiveness of Fe and Mn in natural water.

4.1 Step 1

It was decided how much *Hydrilla verticillata* (L.f.) Royle plant material would be employed in the work's latter stages. Four concentrations of the plant-20,000, 80,000, 120,000, and 160,000 mg per 10 L of water were taken into consideration. With all of its roots and new foliar system, the plant was taken out of a natural pond, weighed right away on a Pioneer, TM Ohaus scale, and then placed in the experimental unit.

Using a Thermoelectronatomic absorption system model S4AA System (Thermofisher Scientific, MA, USA), AAS first assessed the amounts of Fe and Mn in the raw water.

Each experimental unit received 200 mL of metals at a 2 ppm concentration. Water samples (1 L) were taken from each experimental unit at a depth of 0.5 cm from the surface every two hours after the process began (9 am, 11 am, 1 pm, and 3 pm) in order to measure the amounts of Fe and Mn. This makes it possible to comprehend how mass affects removal and identify the window of time when solar radiation has the biggest effect.

4.2 Step 2

200 mL of metal at concentrations of 1.5, 2.0, 3.0, and 4.0 mg/L were added to four experimental units, each with a 10 L capacity. Rapid mixing at 100 rpm for one minute and gentle mixing at 30 rpm for sixty minutes were used to homogenize the mixes.

For eighteen days, the chosen mass was dispersed throughout the experimental units. The amounts of total Fe and Mn, together with other physicochemical parameters, were measured at the start, middle, and end of the trial. Three samples were taken at 3 pm every six days. This was done in order to determine the maximum quantity of plant absorption and the impact of time.

4.3 Step 3

Pitahaya (*Hylocereus triangularis*) and cactus (*Opuntia ficus-indica*) extracts weighing 500 g (wet weight) were obtained. Using surgical gauze, they were manually grated and filtered three times while being compressed. For the cactus and dragon fruit, respectively, 10% and 20% (w/v) solutions were made due to the concentrated extracts' viscosity and instability. After that, these solutions were kept at 4°C (12). A jar test (Standard Practice for Coagulation-Flocculation Jar Test of Water) was performed to ascertain the proper dosage for each extract.

In order to determine and choose the right dosage of the extracts, 0.008, 0.01, 0.012, 0.015, and 0.020 L of the solutions made with the extracts under investigation were added to each 1 L container of raw water. It was mixed quickly for one minute at 100 rpm then slowly for sixty minutes at 30 rpm. For sixty minutes, the mixture was let to settle.

5. Statistical analysis

Each mass of the plant material was determined using a fully randomized design (CRD), and the mass with the highest performance was chosen using the Tukey HDS multiple range test. The Shapiro-Wilk and Cochran tests were used to examine the hypotheses of normality and homogeneity of variance of errors in the suggested designs, respectively. The Kruskal-Wallis test, which is non-parametric, was employed when they could not be guaranteed. Excel 2016 and the statistical software Statgraphics Centurion 16 were used for all tests.

After digestion with sulfuric-nitric acid for Fe and Mn, the direct flame atomic absorption method was employed for metal measurements. Table 2 below displays the procedure validation parameters.

Table 2: ***Method validation parameters.***

	Fe	**Mn**
Linear range	0.050–4000 mg/L	0.050–4000 mg/L

LDM	0.018 (+/−0.003) mg/L	0.021(+/−0.002) mg/L
LCM	0.050 (+/−0.004) mg/L	0.050 (+/−0.004) mg/L
Precision	1.11%	2.98%
Accuracy	99.69%	97.15%
Uncertainty	1.500(+/−0.119) mg/L	1.600(+/−0.088) mg/L

6. Results and discussion

See Table 3.

With the best results obtained for the mass of 160,000 mg in both cases, at different times of the day, and an average of 78.84% for Fe and 66.56% for Mn, respectively, the results show that the mass of plant material affects the removal of these metals.

For both metals at all masses, the morning hours were shown to have the lowest removal. This is because the material was only exposed to the metals dissolved in natural water for a brief period of time.

On the other hand, a greater percentage of metal removal is evident at all masses for water that has been exposed to the plant for longer periods of time, as demonstrated at midday (4 h) and in the afternoon (6 h). But in both situations, there are no appreciable variations in removal during daytime hours (Table 3).

Experimental unit 1 displays a 100% elimination of both metals after six days of the experiment. Furthermore, the concentration of metals that the plant can withstand is noted.

Since these experiments were carried out in situ, where the plants were extracted, the plants in experimental units 2, 3, and 4 exhibit signs of deterioration, and some of them died. This could be because of the surrounding climate (temperature, sunlight) and environmental conditions (pH, nutrients, and sodium chloride) (13).

Artisanal roofs were used to house the experimental units. For the reasons outlined above, the experiment could not be conducted on days 12 and 18.

After six days, a turbidity removal of 92.42% and 90.35%, respectively, was noted in experimental units 1 and 2, demonstrating the value of Hydrilla in the natural removal of turbidity. In rural areas, it can be used for this purpose to prevent the usage of chemicals and the dangers that come with them.

According to research by Lans et al. [12], natural extracts of *Guazuma ulmifolia*, *Hylocereus triangularis,* and *Opuntia ficus-indica* showed turbidity reduction percentages of 95% and 98.97%, respectively.

Table 3. ***Percentage removal of Fe and Mn (Hydrilla verticillata) as a function of solar radiation and mass.***

% removal Fe	**20,000 mg**	**80,000 mg**	**120,000 mg**	**160,000 mg**
Morning (2 h)	54.92 (±0.5)	59.58 (±0.3)	69.16 (±0.3)	75.19 (±0.4)
Half day (4 h)	65.32 (±0.7)	69.98 (±0.1)	73.54 (±0.4)	79.29 (±0.6)

Afternoon (6 h)	73.27 (±0.4)	75.46 (±0.7)	78.47 (±0.5)	82.04 (±0.6)
% removal Mn				
Morning (2 h)	59.81 (±0.1)	60.46 (±0.2)	61.93 (±0.5)	65.52 (±0.3)
Half day (4 h)	60.79 (±0.2)	62.26 (±0.4)	63.24 (±0.7)	66.67 (±0.2)
Afternoon (6 h)	62.26 (±0.2)	64.05 (±0.5)	65.85 (±0.9)	67.48 (±0.1)

The water's appearance before and after the plant material treatment is seen in Figures 3 and 4. It is evident that both the turbidity and the levels of Mn and Fe have drastically decreased. Because it is sensitive to high temperatures, hydrilla needs to be kept under control, and 323 K is the ideal temperature (17). As a result, exposure to extreme temperatures and direct sunshine alters its look. This enabled us to proceed with the experiment without exposing the plant to direct radiation (Figure 3).

Untreated raw water.

Water condition after six days of contact with 160 g of Hydrilla mass.

Change in the appearance of the plant after 1 day with direct sunlight and temperatures exceeding 32°C.

a b c

Figure 3. *Change in the appearance*

The removal efficiency of BOD, COD, and phosphates in freshwater and household wastewater has also been evaluated using Hydrilla verticillata, with removal efficiencies of up to 84% for BOD, up to 63% for COD, and up to 87% for phosphates (18).

According to Table 3, *Opuntia* and *Hydrilla* effectively reduced their Fe levels by 98.04% and 86.6%, respectively, and their Mn levels by 95.12% and 85.37%. The reduction of these elements in the Pitahaya extract was extremely inadequate. Opuntia has a greater degree of recovery than Hydrilla, although it is important to keep in mind that Opuntia needs an extract, which involves earlier labour.

Because Hydrilla is only exposed to the water that is being treated, it has an advantage. It is important to note that because there is a waiting period for removal, this procedure is slower. However, if Fe and Mn levels are too high, Hydrilla plants run the risk of dying before finishing their task.

In particular, it was noted that Hydrilla's turbidity and colour removal processes are slower than those of Opuntia extract, which yields nearly instantaneous results. Consequently, when the process began, the plant material was left for a longer amount of time (24 hours). It's possible that the endothermic adsorption of Fe and Mn is what caused their elimination (17).

7. Conclusions

Opuntia ficus indica and *Hydrilla verticillata* (l.f.) Royle were found to be effective in eliminating colour, turbidity, Mn, and Fe from natural waterways. It was discovered that *Hylocereus triangularis* extracts were ineffective at removing the metals under study from natural waters. *Hydrilla* is beneficial for rural populations because, like *Opuntia* and *Hylocereus*, it may be utilized to remove turbidity from natural waters.

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