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Optimization and Removal of Heavy Metals from Groundwater Using *Moringa* Extracts and Coconut Shell Carbon Powder

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Abstract: This study focuses on enhancing the efficacy and elimination of heavy metals from groundwater by employing bio-absorbents generated from *Moringa* extracts and Coconut shell carbon powder. The green synthesis technique was utilized to produce cost-effective absorbents, including powdered *Moringa* seeds, leaves and carbon from coconut shells. The study examines the effectiveness of synthetic bio-absorbents in removing heavy metals, including Copper (Cu), Cadmium (Cd), Iron (Fe), Lead (Pb), Chromium (Cr), and Zinc (Zn), from groundwater. Identifying functional groups such as Hydroxyl (OH), C-H of alkenes, C=C of alkenes, and C-O from carboxylic acids have been determined to be essential for removing metals in groundwater. The method of FT-IR spectroscopy was used to characterize these functional groups. The examination of the morphology of *Moringa* seeds indicated the presence of consistent spherical network sheets, but *Moringa* leaves had a hexagonal network structure like a flower. The coconut shell photos revealed the presence of irregular, small-sized flakes that were clustered together to create a sheet. In light of the escalating deterioration of groundwater quality in Vijayawada as a result of industrial expansion, urban development, and significant infrastructure initiatives, the primary objective of the study was to ascertain the primary contaminants present in the groundwater. Subsequently, adsorption methods utilizing natural bio-absorbents were employed. Water samples were gathered and exposed to bio-absorption utilizing powdered *Moringa olifera* leaves, powdered *Moringa olifera* seeds, and powdered carbon derived from coconut shells. The technique of Atomic Absorption Spectroscopy was utilized to examine the decrease in concentrations of heavy metals. The findings demonstrated that the bio-absorption of heavy metals was more prominent in *Moringa olifera* seed powder than in *Moringa olifera* leaf powder and coconut shell carbon powder. The highest levels of adsorption for copper, cadmium, and lead were achieved at 98.5%, 99.5% and 99.4%, respectively. This work offers useful insights into the potential of bio-absorbents manufactured using green methods for effectively eliminating heavy metals from groundwater. It addresses the crucial problem of water quality in metropolitan areas.

Introduction

Water is the most important essential component of life. A significant issue and developing global resource concern is heavy metal water contamination. Fu and Wang (2011) emphasized a persistent worldwide escalation in the contamination of ecosystems by heavy metals, particularly in emerging nations. Hence, it is imperative to devise a highly efficient and economical

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water purification technique capable of removing even trace amounts of metals. Diverse methods have been utilized to eliminate heavy metals from wastewater, such as chemical precipitation (Fu and Wang, 2011), ion exchange (Cho et al., 2005), ion flotation (Dabrowski et al., 2004; Peleka and Matis, 2008), adsorption (Wang and Wu, 2006; Alinnor, 2007), reverse osmosis (Qdaisand and Moussa, 2004; Chanand and Dudeney, 2008), and membrane filtering (Dabrowski et al., 2004; Peleka and Matis, 2008).

While treated wastewater is utilized in numerous places internationally, the safety and quality of wastewater reuse continue to face issues (Ternes, 1998). Adverse effects on the environment and people's health were caused by heavy metal poisoning of water bodies, which affected both aquatic and terrestrial ecosystems. India has millions of people who live in cities and the countryside and rely on groundwater for drinking water. Research findings show that groundwater pollution with trace elements is alarming in all of India's states. Good quality of drinking water is an essential criterion for sustainable life. The natural toxicity of heavy metals is dangerous as they pollute water bodies and concentrate in food chains. To treat water and wastewater, the chemical coagulant salts iron and Aluminium sulphates are used in the conventional method (Ali and Seng, 2018; Aziz et al., 2016), which has many drawbacks. In recent years, containing heavy metals can be dangerous and harmful because they can build up in the tissue of living things. The main sources of heavy metals in water, which may cause kidney damage, are the pigments, electroplating, plastic and metal finishing industries, damage hypertension, bone loss, renal disease, and red blood cell apoptosis (Amin et al., 2006). Heavy metals can be eliminated from aqueous solutions using various techniques, like ion exchange, chemical precipitation, membrane separation, adsorption, etc. Maina et al. (2016) reported heavy metal removal from waste water and borehole water processes using *Moringa* seed pods and nut shells.

However, some of these techniques have limitations, including low metal concentrations, ineffectiveness, and high costs (Araujo et al., 2013; Bansal et al., 2009). The exploration for another suitable solution is therefore of paramount importance. Recently, researchers have focused on the natural alternatives. The *Moringaceae* family, which consists of only one genus of bushes, includes *Moringa oleifera*. It was first imported from India and is now in all tropical nations. This tree grows in sand or dirt, can withstand extreme temperatures, is simple to plant and survives in less water (El Nemr et al., 2008). The majority of the parts of the multi-use *Moringa oleifera* tree can be used for a variety of purposes. Natural coagulants, flocculants, softeners, disinfectants, sludge conditioners in water treatment, and heavy metal removers in water and wastewater treatment have all been discovered to be properties of *Moringa oleifera* seeds and leaves (Fu and Wang, 2011). Vijayawada, a commercial city in a developing capital region situated on the banks of the Krishna River in Andhra Pradesh's NTR district, is surrounded by beautiful green agricultural land. Passing on the south, the Krishna River wets the entire city with three major irrigation canals: Bandar Canal, Eluru Canal and Ryves Canal. These three canal networks of Krishna River are the major sources of drinking water, industrial water, irrigation, and groundwater recharge. There are reports of contamination that these three canals receive huge effluents from industrial and agricultural sectors during the course of their journey. The southern regions of the central groundwater board in Vijayawada have found high contaminants and total dissolved solids in groundwater (Ghafar et al., 2017).

The present experimental area, Kanur in Vijayawada, is an emerging domestication area from agricultural lands. Literature reviews state that there are reports of groundwater contamination in Kanur panchayath due to industrial and agricultural sources. It is crucial to know how much water is safe for drinking to plan ways to obtain safe drinking water. In this regard, water samples were initially collected from 16 bore wells and tested to identify the contamination of groundwater bodies with heavy metals. Laboratory analysis reports are identified with heavy metals like Copper, Cadmium, Iron, Lead, Chromium and Zinc, which exceeded the ISI limits. All the sampling analyses were carried out as per FASSAI (Manual_Water_Analysis, 2017), the Govt. of India water quality manual (1999), and the Bureau of Indian Standards. Result reports were observed with higher levels of heavy metals than BIS limits.

Trace elements in water can be hazardous and need to be removed from water. Few studies reported the removal of some heavy metals from water by natural plant sources and carbon absorbents. This was an effort to identify the trace metals' absorption using *Moringa olifera* leaves, *Moringa olifera* seeds, and carbon powder prepared from coconut shells.

Objectives

- To identify low-cost, locally available, simple economical and eco-friendly sustainable house hold materials to remove metals from water.

- To identify the heavy metal removal efficiency of *Moringa olifera* leaves powder, *Moringa olifera* seeds powder and coconut shell carbon powder.

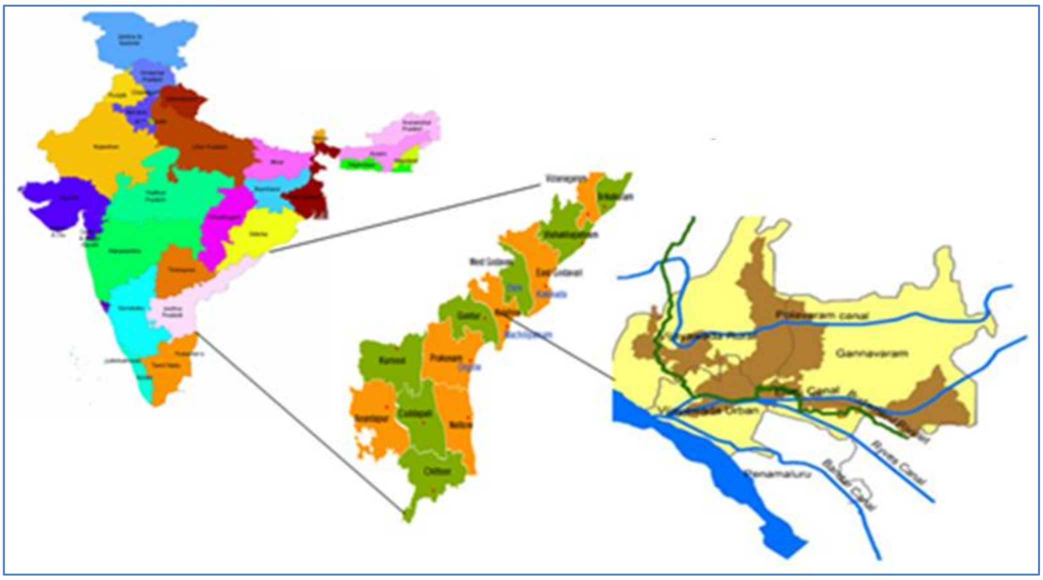

Figure 1. Location of the studied area.

Figure 2. a) *Moringa olifera* seeds powder b) *Moringa olifera* leaves powder c) Coconut shells carbon powder.

Materials and Methods

Preparation of *Moringaolifera* seeds powder

Moringa olifera pods were collected and dried under the shaded region for a week. The kernels were hand-shelled then sieved through a 600-micron stainless steel sieve after being processed in a home blender.

Preparation of *Moringa olifera* leaves powder

Fresh leaves of *Moringa olifera* were collected and dried under the shaded region for a week. Dried leaves were removed, mashed in a home blender, and sieved using a stainless steel sieve with a 600-micron mesh size.

Preparation of carbon powder from Coconut shells

Coconut shells were washed and cleaned to remove the husk and dried under sunlight for a week. The shells were grinded to 2mm to 3mm granules size and then

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carbonized at 450oc for 3 hours to produce carbon coconut shell charcoal. The charcoal samples were grinded and sieved through 600-micrometre stainless steel sieve. The finely grinded charcoal was washed with 4N nitric acid. It was heated for about 3 hours at 450C. To get rid of the acid and any other contaminants, it was then washed many times with distilled water. The sample was dried in air-oven at 120^{0}C for 6 hours. The dried material was stored in an air-tight container for experimental use.

Water Samples

Ground water samples were collected from kanur panchayath bore wells and tested to observe heavy metal concentrations. The water samples were observed with Copper, Cadmium, Iron, Lead, Chromium and Zinc with 0.5 mg/L to 8 mg/L concentrations. The observed values are listed in Table 1.

Table 1. Concentrations of Heavy metals in Groundwater samples.

Parameter	IS10500Max Limit mg/L	Observed values mg/L
Copper	0.05	0.13
Cadmium	0.01	0.16
Iron	0.3	2.42
Lead	0.1	1.47
Chromium	0.05	0.83
Zinc	5.0	8.10

Analysis Techniques employed in order to determine the presence of various chemical functional groups and vibration modes, FT-IR spectra of the synthesized samples are measured in the middle infrared region 4000-400 cm-1 at room temperature using a Fourier transform infra-red spectrophotometer (SHIMADZU-IR, affinity-1S FT-IR spectrophotometer). Scanning electron microscopy (SEM; TESCAN, VEGA3 LMU model) was used to study surface morphology at a 15 KV accelerating voltage carefully. A jar test was conducted to determine the effective coagulant treatment to reduce the heavy metals from the groundwater samples.

Optimization study is the discipline that involves modifying a process to obtain the optimal combination of factor levels for a given set of parameters in order to produce the maximum response while abiding by certain constraints. The primary objective of optimizations is to reduce or completely eliminate time and resource waste, needless costs, bottlenecks, and errors. The present research conducted an Optimization study on copper, cadmium and lead.

Results and Discussion

FT-IR Spectra:

Heavy metal ions interact with atoms on functional groups like oxygen on carboxyl and hydroxyl groups and nitrogen on amine groups because they are powerful and hard acids. In the case of adsorption, the presence of alkenes causes the concentration of electron density on

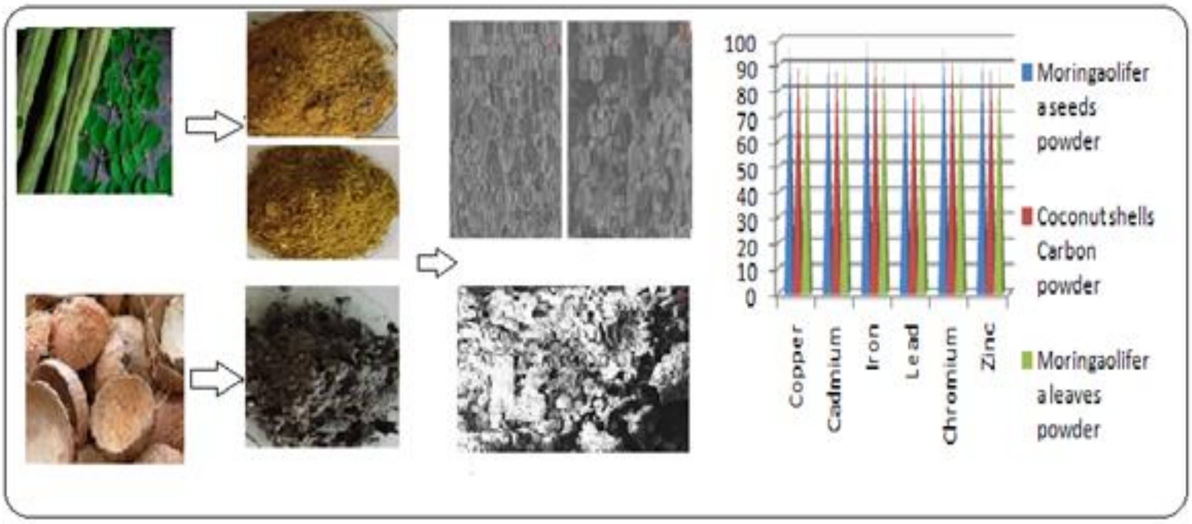

Figure 3. Various images of *Moringa olifer* leaves, seeds, Coconut shells and their powders, as well as their SEM images and optimization study.

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them to create dipole moments, with the negative dipole moment being concentrated on the centre of the double bond (Maina et al., 2016). Positively charged metal ions will then adhere to these regions of high electron density. The most prevalent organic acids are carboxylic acids, distinguished by having at least one carboxyl group. This would be the primary mechanism for efficiently removing metals. To observe the phenomena, FT-IR spectra of *Moringa olifera* seeds powder, *Moringa olifera* leaf powder, and coconut shell carbon powder were employed and shown in Figure 4.

The FTIR spectra shown in Figure 4 indicate broad bands around 3296-3387cm-1 attributed to the surface hydroxyl group. The bands at 2925 and 2851 cm-1 are due to the C-H group of the alkenes, at 1743cm-1 are the C=O from esters, at 1648 cm-1 are the C=C aromatics and C-O from carboxylic acids at 1457 to 1045 cm-1. The decrease in intensity and shift of the peaks mentioned above are shown in Figure 2. The metal adsorption capacity is influenced strongly by the surface structures of Carbon (Mohan and Pittman, 2007; Sadegh et al., 2017).

Surface Morphology

The surface morphology of prepared *Moringa* seeds, *Moringa* leaves, and coconut shells is shown in Figure 5**.** Morphological images of *Moringa* seeds show uniform spherical network sheets, and *Moringa* Leaves show flower-like hexagonal networks. Coconut shell images show non-uniform small-sized size, closely packed flakes forming a sheet with agglomeration.

The surface morphology of prepared *Moringa* seeds, *Moringa* leaves, and coconut shells is shown in Figure 3**.** Morphological images of *Moringa* seeds show uniform spherical network sheets, and *Moringa* Leaves show flower-like hexagonal networks. Coconut shell images show non-uniform small-sized size, closely packed flakes forming a sheet with agglomeration.

Adsorption Analysis

(Removal Efficiency of Heavy Metals in Groundwater by *Moringa* seeds, *Moringa* leaves and Carbon from coconut shell)

Experimental procedure of adsorption studies

A jar test was conducted to determine the effective coagulant treatment to reduce the heavy metals from the groundwater samples. Each jar is filled with 500 ml collected groundwater samples. Accurately weighed, 1 gram of *Moringa olifera* leaves powder was added to the first jar, 1 gram of *Moringa olifera* seeds powder was added to the second jar and 1 gram of coconut shell carbon powder was added to the third jar. A schematic representation of the JAR-Test is shown in Figure 6.

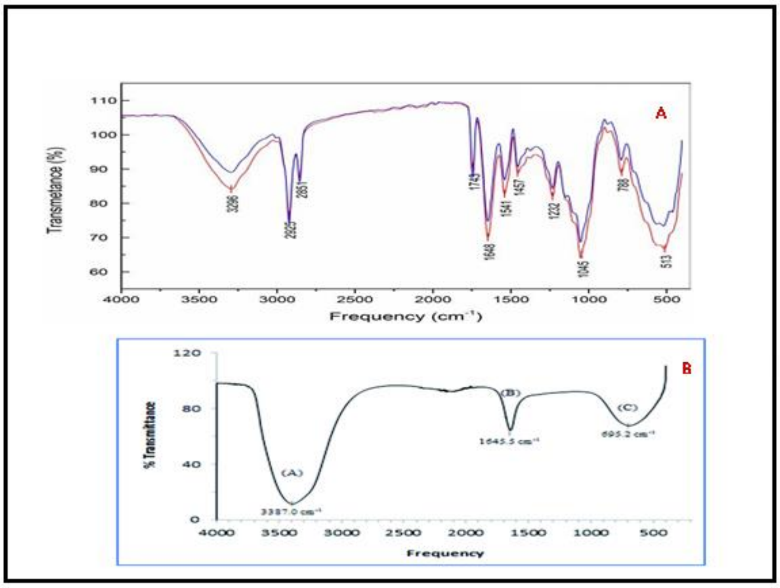

Figure 4. FT-IR spectra of A) *Moringa olifera* seeds powder (indicated in red coloured line), *Moringa olifera* leaf powder (indicated in blue coloured line) and B) Coconut shells carbon powder.

The standard protocol was adhered to, involving rapid agitation at a speed of 120 revolutions per minute for 10 minutes. Subsequently, the mixture was subjected to gentle agitation at a rate of 20 revolutions per minute for

The removal percentages of Fe, Cu, Cr, Cd, Zn and Pb were high in water treated with *Moringa olifera* seeds powder with 99.5%, 97.75%, 96.71%, 92.72%, 93.79% and 88.16%, respectively.

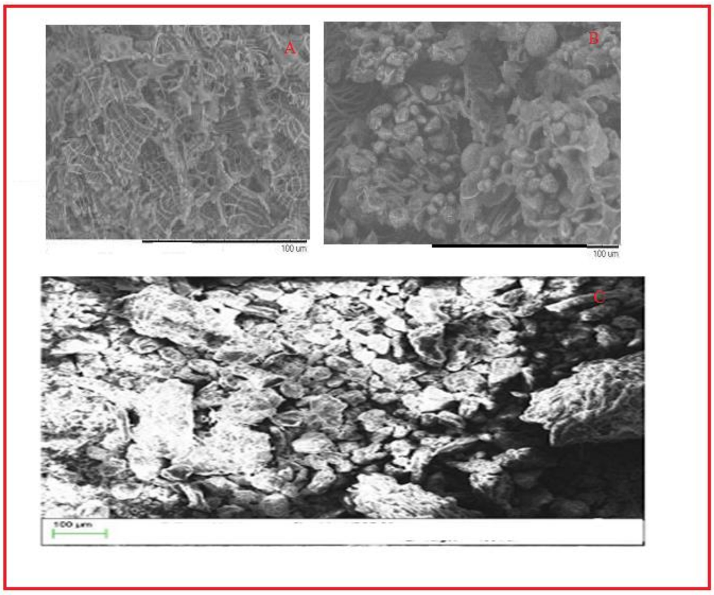

Figure 5. Morphological images of (A) *Moringa olifera* seeds powder (B) *Moringa olifera* leaf powder (C) Coconut shells carbon powder

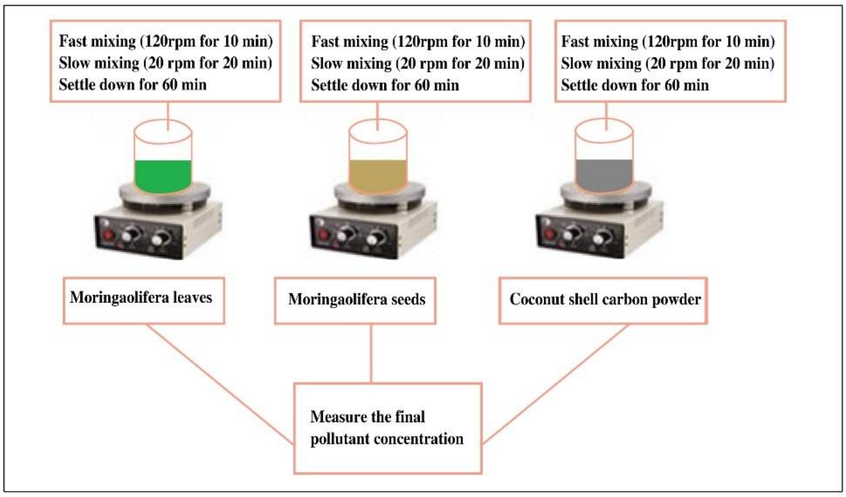

Figure 6. Schematic representation of JAR-Test.

20 minutes, followed by a settling period of 60 minutes. After one hour, the solutions underwent filtration using Whatman 42 filter paper. Subsequently, the concentration of heavy metals was determined using an Atomic Absorption Spectrometer, as documented in Table 2.

The percentage reduction of each metal was computed and observed as

Adsorption efficiency (%) = $\mathbf{C_0 - C_1 / C_0}$ × 100

Where, C_0= Initial concentration of sorbet solution in (mg/L) and C_1 is the final concentration of sorbet at equilibrium in (mg/L).

Water treated with *Moringa olifera* leaves powder and coconut shell carbon powders also showed a good percentage of adsorption. Fe, Cr, Zn and Pb removal efficiency is higher in coconut shell carbon powder than in *Moringa olifera* leaves powder. This may be due to the more porous nature of carbon powder. As the selected absorbent materials performed well in removing heavy metals, they can be adopted and widely used in industries to reduce the costs and improve the profitable benefits of commercial purposes for a sustainable environment.

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Table 2. Heavy metals removal by natural extracts

Parameter	Percentage Removal of Heavy Metals by		
	***Moringa olifera* leaves powder**	***Moringa olifera* seeds powder**	**Coconut shells carbon powder**
Copper	91.21±0.152	97.75±0.166	91.57±0.031
Cadmium	92.01±0.018	92.72±0.017	90.12±0.044
Iron	90.63±0.176	99.51±0.045	94.24±0.206
Lead	80.13±0.024	88.16±0.157	85.76±0.127
Chromium	91.11±0.015	96.71±0.098	93.66±0.106
Zinc	89.30±0.103	93.79±0.135	90.35±0.140

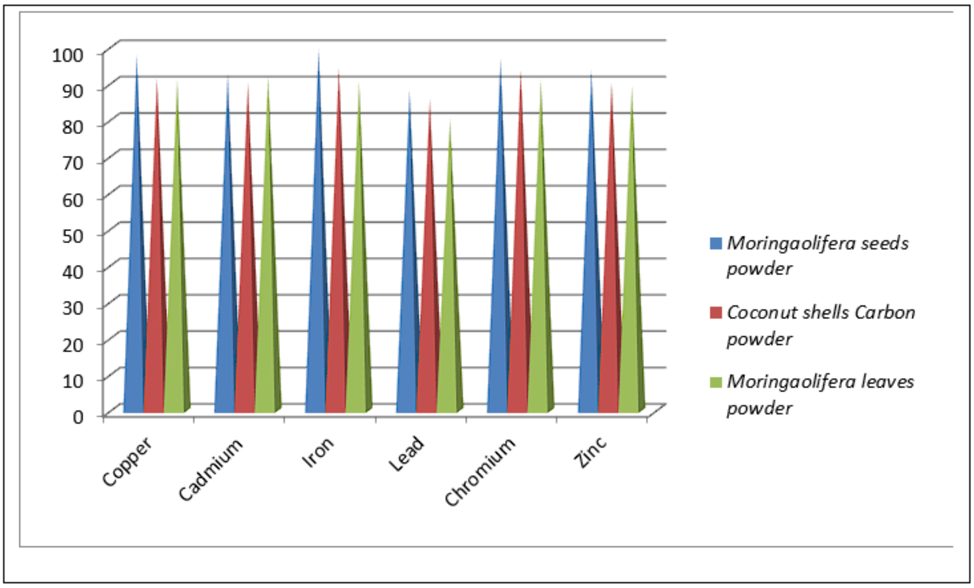

Figure 7. Graphical representation of removal percentage of Fe, Cu, Cr, Cd, Zn and Pb in groundwater

Model and Statistical Analysis for Adsorption Studies

Quadratic regression using the method of curve fitting

A quadratic model in the form of expression below was developed to study the adsorption of metals.

Suppose there are two functions, x and y. The unknown coefficients a, b, and c are determined by computing the least-squares fit of the data by minimizing the sum of the squares of the data's deviations from the model.

Equation for Quadratic Regression applied

$$y = ax^2 + bx + c$$

Where coefficients can be calculated as

$$a = \frac{[S(x^2y)\times S(xx)]-[S(xy)\times S(xx^2)]}{[(S(xx)\times S(x^2x^2)]-[S(xx^2)]^2}$$

$$b = \frac{[S(xy)\times S(x^2x^2)]-[S(x^2y)\times S(xx^2)]}{[S(xx)\times S(x^2x^2)]-[S(xx^2)]^2}$$

$$c = \left[\frac{(Syi)}{n}\right] - \left\{b \times \left[\frac{(Sxi)}{n}\right]\right\} - a \times \left[\frac{S(xi^2)}{n}\right]$$

The ideal conditions that the software (MATLAB) predicted lead to the maximum adsorption of the three metals are shown in Table 4.

The most crucial factor in the removal of ions observed was pH. Due to decreased hydrogen ions (H+), lead ion removal was encouraged at lower pH levels, while copper and cadmium removal was preferred at higher pH levels.

The availability of active sites during the initial stages contributed to the adsorption efficiency's initial increase with time and subsequent reduction. After some time, the rise in boundary layer thickness also contributes to reducing adsorption stages. Cadmium adsorption occurred at a high rate and for long retention times.

Due to increased active sites, all metals' adsorption efficiencies rise with the adsorbent dose.

By contrasting experimental results with the expected results, they were further validated by adjusting r^2.

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Table 3. Regression equations.

Parameters	Regression Equations
Copper	$Y = 4.83E^{-06}(x^2) - 0.01162\ (x) + 8.378905$
Cadmium	$Y = 1.63E^{-06}(x^2) - 0.00403\ (x) + 2.747512$
Lead	$Y = -3.07E^{-07}(x^2) + 7.82E^{-04}(x) - 0.49016$

Table 4. Optimum factors predicted by software

Parameter	Initial % (mg/L)			pH	Dosage (g)	Time (min)	Final % removal in			Desirability
	MLP	MSP	CSCP				MLP	MSP	CSCP	
Copper	0.13	0.12	0.13	8.0	1	8.3	96	98	98	97
Cadmium	0.17	0.16	0.16	8.0	1	12.5	95	96	96	98
Lead	2.59	2.48	2.42	7.8	1	10.0	94	98	99	97

Table 5. Validated result.

Solution No.	% removal of copper		% removal of cadmium		% removal of lead	
	Actual	Predicted	Actual	Predicted	Actual	Predicted
1	97.5	98.4	99.9	100	98.1	99.9
2	97.8	98.3	98.2	99.0	98.2	99.9
3	98.2	98.5	96.2	99.7	97.2	98.5
r^2	0.96		0.93		0.97	

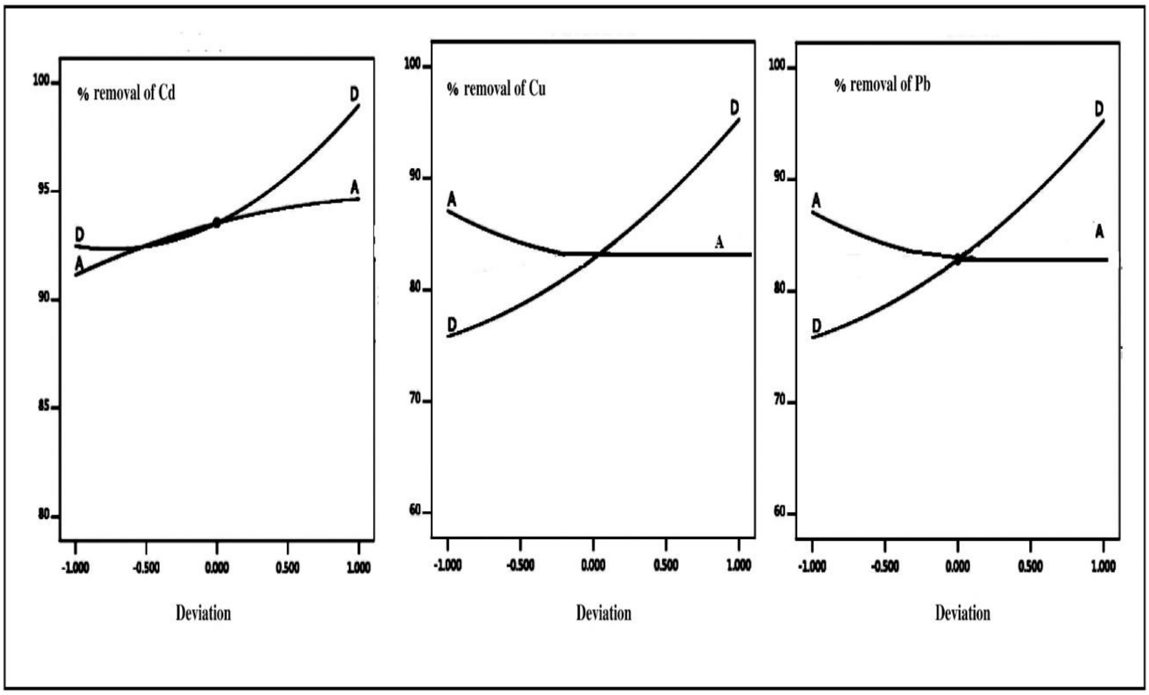

Figure 8. Adsorption percentages of cadmium, copper and lead.

Conclusion

This study uses the green synthesis method to prepare low-cost absorbents such as powdered *Moringa* seeds, *Moringa* leaves, and carbon from coconut shells. The removal efficiency of heavy metals like Copper, Cadmium, Iron, Lead, Chromium and Zinc from ground water was observed by using synthesized bio-absorbents. The *Moringa* seeds, leaves, and coconut shells are all considered lignocellulose adsorbents since they contain cellulose, hemicellulose, and lignin. These have functional groups that, through ion exchange, can absorb metal ions. The functional groups responsible for metal removal in ground water are hydroxyl (OH), C-H of the alkenes, C=C alkenes and C-O from the carboxylic acids using FT-IR spectroscopy technique. Morphological images of *Moringa* seeds show that uniform spherical network sheets and *Moringa* leaves show a flower-like hexagonal network connection. Coconut shell images show non-uniform small-size flakes forming a sheet with agglomeration. The present experimental study focused on the potential use of natural materials and showed a significant ability for heavy metal removal from water. If inexpensive adsorbents effectively remove heavy metals at a low cost, they can be widely used in industries to reduce costs, increase efficiency, and boost profitability. The current analysis reports that there are unquestionably many prospective commercial advantages to low-cost adsorbents. Optimization study conducted in copper, cadmium and lead predicted the maximum adsorption with pH factor that agrees typically with cation adsorption behaviour. Activation conditions for this investigation are restricted, and only a few metals with high concentrations in certain samples are used as a trial study. More in-depth study is required on improving active circumstances as well as other prevalent water toxins. However, the current study supports the use of *Moringa olifera* seeds powder, leaves powder and coconut shell carbon powders as natural absorbents to remove heavy metals from ground water. These products were simple, cheap, environmentally friendly bio absorbents. With less effort and money, the current statistical analysis will assist in managing and monitoring water quality. Other parameters may also be studied using this statistical analysis.

Declarations

There is no conflict of interest to disclose.

Ethics-approved: The research was conducted without using any species threat.

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