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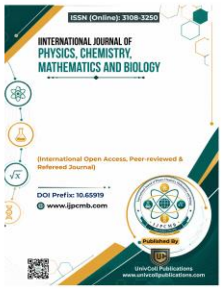

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Comprehensive Evaluation of Water Hardness and Contamination in Indian Hydro-Geological Systems: Analytical Quantification and Sustainable Remediation Strategies

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Abstract

Water hardness—driven primarily by dissolved divalent metal cations (Ca^{2+} and Mg^{2+})—presents significant technical, environmental, and socio-economic challenges across rural and urban India. This paper synthesizes empirical data from regional field assessments (e.g., Nagaur, Rajasthan), national infrastructure reports from the National Sample Survey Office (NSSO Report No. 584), and water quality monitoring programs under the Central Ground Water Board (CGWB). It evaluates analytical detection mechanisms via Ethylenediaminetetraacetic acid (EDTA) complex metric titration and investigates chemical, physical, and eco-friendly remediation techniques. Experimental evaluations reveal that traditional boiling reduces temporary hardness caused by HCO_3^-, whereas chemical precipitation using washing soda (Na_2CO_3) achieves up to an 80% total hardness removal efficiency. Additionally, recent advances in eco-friendly water treatment highlight natural bio-coagulants (e.g., Vigna mungo, Moringa oleifera, and Plantago ovata) capable of achieving over 90–98% turbidity reduction and significant alkalinity suppression. Integrating eco-friendly bio-coagulants with advanced membrane separation (Reverse Osmosis) and chemical softening provides a viable roadmap for decentralizing water treatment across vulnerable regions.

Keywords: Water Hardness, EDTA Titration, Natural Coagulants, NSSO Report No. 584, CGWB, Chemical Precipitation, Reverse Osmosis.

Key Points

- Hydro-Chemical Dynamics: Water hardness stems from rock-water interactions (limestone, dolomite, gypsum), resulting in high Ca^{2+} and Mg^{2+} concentrations that exceed the Bureau of Indian Standards (BIS IS 10500:2012) acceptable limit of 200 mg/L (as $CaCO_3$) across major arid and semi-arid Indian aquifers.
- National Exposure & NSSO Findings: NSSO 76th Round data shows that while over 50% of rural and 70% of urban households rely on groundwater abstractions (hand pumps, tube wells), a significant portion of wastewater is discharged untreated (48.1% in rural areas), exacerbating local salinity and mineral leaching into shallow aquifers.
- Analytical Measurement: Complexometric EDTA titration using Eriochrome Black T (EBT) at pH 10 delivers precise quantification of total calcium and magnesium hardness.
- Remediation Efficiency: Chemical precipitation via Na_2CO_3 (washing soda) yields ~80% hardness removal; Reverse Osmosis (RO) provides maximum ion removal, though constrained by high energy usage and reject brine production; Bio-coagulation using natural extracts (Moringa oleifera, Vigna mungo, Plantago ovata) achieves 82–98% turbidity and significant alkalinity removal, presenting a low-cost, eco-friendly alternative to conventional alum-based methods.

1. Introduction

Water is an indispensable resource for domestic consumption, agriculture, and industrial production. However, raw water quality is increasingly compromised by natural weathering processes and anthropogenic pollution. Among the critical parameters governing water suitability, water hardness and alkalinity present prominent operational and public health concerns.

Water hardness is defined as the concentration of polyvalent metallic cations dissolved in water—predominantly calcium (Ca^{2+}) and magnesium (Mg^{2+}), along with minor traces of iron (Fe^{2+}), strontium (Sr^{2+}), and manganese (Mn^{2+}). Hardness is broadly categorized into:

- 1. Temporary Hardness: Caused by dissolved calcium and magnesium bicarbonates [$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$], which can be precipitated out by thermal boiling.
- 2. Permanent Hardness: Caused by dissolved nitrates, chlorides, and sulfates of calcium and magnesium ($CaCl_2$, $MgSO_4$, etc.), requiring chemical precipitation or ion-exchange mechanisms for removal.

Classification of Water Hardness (BIS / Srinivas et al.):

- Soft: 0 – 60 mg/L as $CaCO_3$
- Moderately Hard: 61 – 120 mg/L as $CaCO_3$
- Hard: 121 – 180 mg/L as $CaCO_3$
- Very Hard: > 180 mg/L as $CaCO_3$

In domestic applications, hard water leads to excessive soap consumption due to the formation of insoluble curds (scum), skin irritation, and premature degradation of plumbing infrastructure. Industrially, hard water causes severe mineral scaling inside heat exchangers, boilers, and cooling towers. Scale formation reduces thermal conductivity, drastically increases energy consumption, and risks catastrophic boiler tube failures due to localized overheating.

1.1 Research Gap

Water hardness is a common groundwater quality problem in many parts of India, particularly in arid and semi-arid regions. Existing studies have examined different aspects of hard water, including its chemical composition, measurement by EDTA titration, and treatment through boiling, chemical softening, ion exchange, and reverse osmosis. Separate studies have also explored the use of plant-based coagulants for improving water quality.

However, these areas are often discussed independently rather than within a single analytical framework. There is still limited integrated assessment that connects the hydro-geological causes of water hardness with its analytical determination, regional occurrence, conventional treatment methods, and sustainable remediation options in the Indian context. In addition, many available studies focus on local samples or individual treatment techniques, making direct comparison of their efficiency, cost, environmental impact, and practical suitability difficult.

The present study addresses this gap by bringing together hydro-chemical evidence, standard hardness determination methods, reported treatment performance, and eco-friendly remediation approaches. It also examines the potential of combining conventional softening methods with natural bio-based treatment systems for decentralized water management in vulnerable rural and semi-arid regions of India.

1.2 Objectives of the Study

The present study has the following objectives:

1. To examine the major causes and regional occurrence of water hardness in India with reference to hydro-geological conditions and available NSSO and CGWB water-quality information.
2. To describe the determination of total water hardness through EDTA complexometric titration, with particular reference to calcium and magnesium ions.
3. To compare the effectiveness and limitations of boiling, washing soda treatment, ion-exchange resins, and reverse osmosis for the removal or reduction of water hardness.
4. To examine the reported performance of natural bio-coagulants, including *Moringa oleifera*, *Vigna mungo*, and *Plantago ovata*, in reducing turbidity, alkalinity, and suspended impurities from water.
5. To assess the scope of combining conventional water-softening methods with eco-friendly bio-coagulation for sustainable and decentralized water treatment in rural and semi-arid regions of India.

2. Literature Review

Water hardness has been widely recognized as an important water-quality concern because it affects domestic use, industrial operations, and the overall suitability of groundwater. In the Indian context, the problem is closely associated with the natural dissolution of calcium- and magnesium-bearing minerals from geological formations. The Bureau of Indian Standards (BIS) provides drinking-water quality specifications that serve as an important reference for evaluating hardness and related chemical parameters in water. These standards are particularly relevant in areas where groundwater contains elevated concentrations of dissolved minerals.

National-level information also shows that groundwater remains an important source of water for a large section of the Indian population. The National Sample Survey Office (NSSO), through its 76th Round report on drinking water, sanitation, hygiene, and housing conditions, provides useful information on household water sources and wastewater disposal practices. Such information is important because the quality of shallow groundwater may be influenced not only by natural mineral dissolution but also by local wastewater disposal and inadequate treatment infrastructure.

The Central Ground Water Board (CGWB) has documented considerable regional variation in groundwater quality across India. Groundwater in arid and semi-arid areas, particularly in parts of Rajasthan, Gujarat, and Andhra Pradesh, has been reported to show high electrical conductivity, total dissolved solids, hardness, fluoride, and nitrate. These observations indicate that groundwater hardness cannot be considered an isolated chemical problem; rather, it forms part of a wider hydro-chemical condition controlled by geology, climate, evaporation, groundwater movement, and local environmental factors.

Soni et al. (2025) investigated the determination and removal of hardness in water samples from Nagaur, Rajasthan. Their work is relevant to the present study because Nagaur represents a region where groundwater mineralization and hardness are important concerns. The study demonstrates the usefulness of analytical determination of hardness and examines practical treatment approaches for reducing dissolved calcium and magnesium salts. Such regional studies provide an important basis for comparing simple treatment methods with more advanced water-softening technologies.

Conventional treatment methods differ considerably in their mechanism and effectiveness. Boiling is mainly useful for temporary hardness associated with bicarbonates, whereas chemical treatment with sodium carbonate can precipitate calcium and magnesium salts and reduce permanent hardness. Ion-exchange systems provide a more efficient means of removing hardness-producing ions, while reverse osmosis can substantially reduce dissolved ionic constituents. However, these methods also differ in energy requirement, operating cost, maintenance needs, and waste generation. Therefore, selection of a suitable treatment method depends not only on removal efficiency but also on local economic and operational conditions.

Recent studies have also examined natural materials as alternatives to conventional chemical coagulants. Singh and Kishor (2026) reviewed the use of different natural coagulants for the removal of turbidity and alkalinity from wastewater. Plant-derived materials such as *Moringa oleifera*, *Vigna mungo*, and *Plantago ovata* have shown considerable potential for improving water quality through coagulation, adsorption, and flocculation processes. Their major advantage lies in their low cost, natural availability, and reduced dependence on synthetic chemical coagulants.

However, the role of natural coagulants should be distinguished from direct hardness removal. Their reported effectiveness is mainly associated with the reduction of turbidity, suspended particles, color, and, in some cases, alkalinity. They therefore may function more effectively as complementary treatment options rather than complete substitutes for ion exchange, chemical softening, or reverse osmosis when the primary objective is removal of dissolved calcium and magnesium ions.

Overall, the existing literature provides useful information on groundwater hardness, analytical determination, regional water-quality conditions, conventional softening methods, and natural treatment materials. Nevertheless, these aspects are often examined separately. The present study therefore brings together national and regional water-quality information, EDTA-based hardness determination, conventional softening techniques, and environmentally sustainable treatment approaches in order to provide an integrated understanding of water hardness management in the Indian context.

2. National Context & NSSO / CGWB Water Quality Overview

Groundwater represents the primary source of drinking water in India. According to the National Sample Survey Office (NSSO Report No. 584, 76th Round), approximately 51.4% of rural households and 72.0% of urban households rely on improved primary drinking water sources located within their premises. However, a substantial fraction of the rural population relies on deep groundwater accessed via tube wells and hand pumps.

Key Socio-Environmental Insights from NSSO & CGWB Data:

- Disposal Practices: Approximately 48.1% of rural households dispose of household wastewater without treatment into open low-lying areas or streets, while 71.1% of urban households discharge untreated wastewater directly into municipal drainage systems. This lack of centralized treatment facilitates urban-rural runoff and localized aquifer contamination.
- Regional Hardness Hotspots: CGWB groundwater assessments highlight that states with hyper-arid and semi-arid hydrogeological settings—particularly Rajasthan (e.g., Nagaur, Barmer, Churu, Jodhpur),

Gujarat, and parts of Andhra Pradesh—exhibit elevated Electrical Conductivity (EC > 3000 µS/cm), high Total Dissolved Solids (TDS), extreme hardness (> 500 mg/L), and high fluoride/nitrate leaching.

3. Experimental Methodology

3.1 Quantification via Complexometric EDTA Titration

The Ethylenediaminetetraacetic acid (EDTA) titration technique relies on chelation chemistry. EDTA (Y^{4-}) acts as a hexadentate chelating agent that forms stable, soluble 1:1 coordination complexes with dissolved divalent metal cations (Ca^{2+} and Mg^{2+}).

Complexation Reactions: $Ca^{2+} + H_2Y^{2-} \longrightarrow [CaY]^{2-} + 2H^+$
$Mg^{2+} + H_2Y^{2-} \longrightarrow [MgY]^{2-} + 2H^+$

Procedure Outline:

1. Buffer Setup: Add an ammonium chloride-ammonium hydroxide (NH_4Cl - NH_4OH) buffer solution to maintain a stable pH of 10.0 ± 0.1, preventing metal hydroxide precipitation while maximizing EDTA-metal stability constants.

2. Indicator Interaction: Add Eriochrome Black T (EBT). In the presence of free Ca^{2+} and Mg^{2+}, EBT forms a weak, wine-red complex:
Mg^{2+} + EBT $\longrightarrow$ [Mg-EBT] (Wine-Red)

3. Titration: Titrate against standardized 0.01 M EDTA solution. EDTA displaces the indicator due to higher complex stability constants, causing a sharp color shift from wine-red to distinct sky blue at the endpoint.

Formula: *Hardness (mg/L as $CaCO_3$) = (V_EDTA × N_EDTA × 50,000) / V_sample*

4. Experimental Findings and Treatment Comparative Analysis

Experimental evaluations conducted on high-hardness groundwater samples from Nagaur, Rajasthan demonstrate the comparative efficacy of thermal, chemical, and physical softening treatments.

4.1 Thermal Treatment (Boiling)

Boiling heat-drives the decomposition of soluble calcium and magnesium bicarbonates into insoluble carbonates, liberating carbon dioxide gas:

Thermal Decomposition: $Ca(HCO_3)_2 \xrightarrow{(\Delta)} CaCO_3 \downarrow + H_2O + CO_2 \uparrow$
$Mg(HCO_3)_2 \xrightarrow{(\Delta)} MgCO_3 \downarrow + H_2O + CO_2 \uparrow$

Result: While boiling effectively removes temporary bicarbonate hardness, it has no impact on permanent sulfate and chloride mineral hardness.

4.2 Chemical Treatment (Washing Soda Method)

Sodium carbonate (Na_2CO_3) reacts with soluble permanent hardness salts ($CaCl_2$, $MgSO_4$), driving precipitation reactions:

Precipitation Reactions: $Ca^{2+} + Na_2CO_3 \longrightarrow CaCO_3 \downarrow + 2Na^+$
$Mg^{2+} + Na_2CO_3 \longrightarrow MgCO_3 \downarrow + 2Na^+$

Result: Precipitation via washing soda yields approximately an 80% total hardness reduction in ground samples, reducing total hardness from initial values exceeding 300 mg/L down to lower, manageable concentrations.

4.3 Comparative Softening Performance Data

Softening Method	Target Hardness Type	Hardness Removal Efficacy	Electrical Conductivity (µS/cm)	Operational Cost / Complexity	Key Technical Limitations
Boiling	Temporary (HCO_3^-)	Partial (~25–35%)	Minor Decrease	High Thermal Energy Demand	Ineffective for permanent hardness (SO_4^{2-}, Cl^-).
Washing Soda (Na_2CO_3)	Permanent & Temporary	~80% Efficiency	14.82 µS/cm (treated)	Low Cost / Very Simple	Increases residual sodium (Na^+) ion concentration.
Ion Exchange Resins	Total Hardness (Ca^{2+}, Mg^{2+})	> 90–95%	Moderate	Moderate / Standard Regeneration	Requires periodic NaCl brine regeneration.
Reverse Osmosis (RO)	Total Dissolved Ions	> 98% Efficiency	Significant Drop	High Energy & Capital Cost	High reject water ratio (brine generation).

5. Sustainable Mitigation: Application of Natural Bio-Coagulants

To overcome the financial and environmental limitations of chemical precipitants and membrane systems, recent research emphasizes eco-friendly, seed- and plant-derived bio-coagulants. These organic bio-polymers contain active cationic proteins that neutralize negatively charged colloidal particles and induce charge-neutralization, bridging, and micro-flocculation.

Process Flow: *Raw Turbid / Alkaline / Hard Water*

↓

[Natural Bio-Coagulant] ⟶ *(Moringa oleifera / Vigna mungo / Plantago ovata)*

↓

[Polymer Bridging & Charge Neutralization]

↓

[Settled Precipitate / Sludge] ⟶ *High Efficiency (>85–98% Removal)*

Performance Metrics of Selected Natural Coagulants:

- Vigna mungo (Black Gram): Demonstrates up to 90% turbidity removal.
- Moringa oleifera Seed Powder: Achieves > 90% efficiency in removing turbidity, suspended solids, and color. Cationic polyelectrolytes in the seeds effectively bind with suspended particles.

- Plantago ovata (Isabgol): Yields up to 95.6% turbidity reduction across varied concentrations (50–300 NTU) at pH 6–8.
- Phyllanthus indica & Albizia saman Bark Extract: Provides 50% to 89.78% alkalinity reduction through natural adsorption and organic binding complexations.
- Combinatorial Bio-Extracts (Lupin Beans + Rice Straw / Oat + Onion): Yield up to 98.7% – 99% turbidity removal, presenting sustainable alternatives to traditional chemical coagulants such as alum.

6. Conclusion

Water hardness and secondary hydro-chemical contamination remain critical environmental engineering problems across India. Quantitative titration via the EDTA method provides accurate detection of Ca^{2+} and Mg^{2+} levels. While Reverse Osmosis delivers complete dissolved ion removal, chemical softening with washing soda (Na_2CO_3) offers a low-cost, highly effective (~80% removal) option for hard groundwater treatment in resource-constrained regions. Concurrently, integrating natural bio-coagulants (Moringa oleifera, Plantago ovata, Vigna mungo) provides an eco-friendly approach to removing alkalinity and suspended particulates without generating hazardous sludge. Broad deployment of hybrid bio-coagulation and decentralized softening infrastructure offers a sustainable path toward improving water quality in vulnerable rural and semi-arid communities.

Author's Declaration & Publication Consent

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