**BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI**
**PILANI CAMPUS, VIDYAVIHAR, PILANI, RAJASTHAN**

# Removal of Fluoride from Groundwater in Pilani

*A Hydro-Geochemical and Socio-Technical Assessment with a Proposed Solar-Electrochemical* ***Prosopis juliflora*** *Biochar Remediation Pathway*

## STUDY ORIENTED PROJECT REPORT

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# Abstract

Fluoride contamination of groundwater in the Shekhawati region of Rajasthan represents a chronic, multi-generational public health emergency. In the Jhunjhunu district, in which Pilani lies, geogenic enrichment of the deep hard-rock aquifer is compounded by alkaline pH conditions, agricultural intensification, and over-exploitation, producing a heterogeneous contamination profile ranging from 0.7 mg/L to over 7 mg/L. This report presents a comprehensive baseline investigation of the problem and a proposed remediation pathway.

The work is organised in two complementary parts. The first part establishes the theoretical, environmental, and historical context: the geochemistry and toxicology of the fluoride ion, the specific hydrogeology and contamination matrix of Pilani, and a critical review of past mitigation efforts ranging from the Nalgonda technique and Activated Alumina filters of the Rajasthan Integrated Fluoride Mitigation Programme to contemporary Distributed Reverse Osmosis models deployed by Piramal Sarvajal. A clear gap is identified for a remediation technology that is selective, water-efficient, low-energy, and capable of operating reliably in the demanding socio-technical environment of rural Rajasthan.

The second part proposes and prototypes an Integrated Solar-Electrochemical Prosopis juliflora Biochar Adsorption System. Initially conceived around imported pine char, the methodology was pivoted to Prosopis juliflora—an aggressively invasive species locally abundant in arid Rajasthan—thereby converting an ecological liability into a sustainable, near-zero-cost feedstock. The experimental programme covers feedstock pyrolysis in a custom anoxic aluminium retort, granulometric segregation across four sieve fractions (600–300–150–75 µm), chemical activation by calcium-chloride impregnation, and a gravity-fed fixed-bed column test using contaminated Pilani groundwater. Preliminary colorimetric assessment by the Zirconyl-Alizarin method proved inconclusive owing to matrix interference, and the protocol has accordingly been re-tooled around $^{19}$F Nuclear Magnetic Resonance spectroscopy for quantitative validation. The report concludes by outlining the next steps required to convert the laboratory prototype into a field-deployable point-of-use unit.

# 1. Introduction

## 1.1 The Silent Hydro-Toxicological Crisis

Water, the universal solvent and the fundamental substrate of biological existence, paradoxically serves as a vehicle for chronic toxicity for millions of inhabitants in the arid and semi-arid belts of the Indian subcontinent. The search for a viable, scalable, and chemically robust process to remediate fluoride from the groundwater of Pilani, Rajasthan, is not merely an academic engineering challenge—it is a critical intervention into a multi-generational public health disaster. This report constitutes the foundational Phase I analysis for the proposed research project, titled "Understanding the Problem and Context." It provides an exhaustive, granular examination of the hydro-geochemical realities of the Jhunjhunu district, dissecting the pathology of contamination, the specific environmental matrix of Pilani, and the historical trajectory of mitigation attempts ranging from state-sponsored schemes to grassroots technological innovations.

The crisis of fluoride in Rajasthan is distinct from other water quality challenges due to its insidious nature. Unlike bacteriological contamination, which manifests as acute illness, fluoride toxicity is cumulative and progressive. It is a "hidden hunger" of the bones, slowly calcifying the skeletal framework of a population that relies heavily on physical labour for survival. Rajasthan, possessing only 1.16 % of India's surface water resources yet sustaining over 5 % of its population and 11 % of its livestock, faces a stark hydrological reality. The over-reliance on deep aquifers—driven by the exhaustion of shallow, sweet-water sources—has brought the population into direct biological conflict with the geochemistry of the ancient Aravalli basement rocks.

## 1.2 Scope and Objectives of the Study

This report establishes the empirical baseline necessary for developing robust remediation technologies. It moves beyond generic definitions to analyse the specific hydrogeological and socio-economic variables of Pilani. By synthesising data from the Central Ground Water Board (CGWB), peer-reviewed literature from local institutions such as BITS Pilani, and operational reports from non-governmental organisations such as Piramal Sarvajal, the document aims to provide a "State of the Science" overview. It explores why technically sound solutions such as the Nalgonda technique failed in the field, why Reverse Osmosis (RO) presents an ethical dilemma in a desert, and how emerging research into electrocoagulation and bio-adsorbents offers a glimpse of a sustainable future.

The specific objectives of this Study Oriented Project are:

- To characterise the geochemical and toxicological behaviour of fluoride in the groundwater of the Jhunjhunu district.
- To quantify the magnitude of contamination in Pilani and its surrounding blocks against both WHO and BIS regulatory thresholds.
- To critically review historical and contemporary mitigation programmes and identify the operational and ethical gaps they leave behind.

- To propose, design, and laboratory-prototype an integrated Solar-Electrochemical Prosopis juliflora biochar adsorption system tailored to the matrix-resilient, water-efficient, low-energy constraints of rural Rajasthan.
- To validate the proposed methodology through fixed-bed column experiments and to define a quantitative analytical pathway via $^{19}$F NMR spectroscopy.

## 2. Theoretical Framework: Geochemistry and Toxicology of Fluoride

To design a removal process, one must first understand the adversary. Fluoride is not a passive contaminant; it is a highly reactive, geochemically mobile ion whose behaviour is governed by complex thermodynamic equilibria and physiological interactions.

### 2.1 The Chemical Nature of the Fluoride Ion

Fluorine (F), the most electronegative element in the periodic table, rarely exists in its elemental gaseous form in nature. In the hydrogeosphere it occurs almost exclusively as the fluoride ion ($F^-$). Its high electronegativity and small ionic radius (~1.33 Å) govern its chemical behaviour and associations. In groundwater, fluoride acts as a “hard” base and exhibits strong affinity for “hard” acids such as calcium ($Ca^{2+}$), magnesium ($Mg^{2+}$), and aluminium ($Al^{3+}$).

The widespread occurrence of fluoride in groundwater is largely controlled by the solubility products ($K_{sp}$) of fluoride-bearing minerals. The most important among these are fluorite ($CaF_2$), fluoroapatite [$Ca_5(PO_4)_3F$], cryolite ($Na_3AlF_6$), and hydroxy-silicate minerals such as biotite and muscovite mica. In regions such as Rajasthan, fluorite serves as the primary mineral source of fluoride. Its dissolution in groundwater is governed by the equilibrium:

$$CaF_2\,(s) \rightleftharpoons Ca^{2+} + 2F^-$$

This equilibrium highlights a key hydrochemical relationship: fluoride concentration is inversely proportional to calcium concentration. In waters rich in calcium, the common-ion effect suppresses fluorite dissolution, thereby maintaining low fluoride levels. However, groundwater in Rajasthan is typically alkaline and promotes the precipitation of calcium as calcite ($CaCO_3$), locally known as “kankar.” As calcium is removed from solution through calcite precipitation, the equilibrium shifts toward increased dissolution of fluorite to restore balance. This process, known as the “calcite-precipitation effect,” is a major factor responsible for elevated fluoride levels in calcium-deficient, alkaline aquifers.

Additionally, the similar ionic radii of fluoride ($F^- \approx 1.33$ Å) and hydroxyl ($OH^- \approx 1.40$ Å) ions enable isomorphous substitution in mineral structures. Under alkaline conditions (high pH), common in the arid regions of Jhunjhunu, the abundance of hydroxyl ions facilitates the displacement of fluoride ions from the crystal lattices of mica and clay minerals. This anion-exchange mechanism releases geogenic fluoride into the groundwater, leading to further enrichment as a direct consequence of elevated pH conditions.

### 2.2 Toxicology and Health Impacts: The Spectrum of Fluorosis

The physiological impact of fluoride is determined by the “Goldilocks principle”—too little leads to dental caries, while too much leads to toxicity. The therapeutic window is perilously narrow, particularly in hot climates where water intake is high.

### 2.2.1 Dental Fluorosis: The Visible Scar

Dental fluorosis is the earliest clinical sign of chronic fluoride toxicity, occurring when excess fluoride is ingested during the years of tooth development (amelogenesis), typically from birth to eight years of age. Fluoride interferes with the function of ameloblasts, the cells responsible for enamel formation, leading to hypomineralisation and increased porosity of the tooth surface.

In the early stages this manifests as Dean’s Index score 1 or 2—opaque, chalky-white striations or “snow-capping” on the teeth. As severity increases (scores 3–4), the porous enamel absorbs extrinsic stains from food and oxidation, turning yellow, brown, or black. In severe cases (score 5) the enamel becomes pitted and brittle, prone to chipping.

The prevalence of dental fluorosis in the Jhunjhunu district is alarmingly high. Recent studies of school children in the region report prevalence rates ranging from 69.84 % to 96.6 % in endemic villages. The psychological and social impact of this condition on children in rural Rajasthan cannot be overstated; the permanent discolouration is often a source of stigma and social anxiety.

### 2.2.2 Skeletal Fluorosis: The Crippling Burden

With prolonged exposure (typically over 10–20 years) to fluoride levels exceeding 3–6 mg/L, toxicity migrates to the skeleton. Fluoride ions replace the hydroxyl ions in the bone’s hydroxyapatite structure to form fluorapatite, $Ca_{10}(PO_4)_6F_2$. Although fluorapatite is chemically more stable and less soluble than hydroxyapatite, the resulting bone structure is disorganised, denser, yet paradoxically more brittle.

The clinical progression begins with sporadic pain and stiffness in the joints (often misdiagnosed as arthritis). It advances to the calcification of ligaments, tendons, and interosseous membranes. In the advanced stages the vertebral column fuses, leading to a permanent rigidity of the spine. This condition, known locally as “Bank Patti” (bent strip), forces the individual into a permanent stoop (kyphosis). In the agricultural communities of Pilani and Surajgarh, where manual labour is the primary livelihood, skeletal fluorosis is an economic catastrophe, rendering able-bodied adults incapable of working in the fields.

### 2.2.3 Non-Skeletal Effects: Systemic Toxicity

Contemporary research has expanded the understanding of fluoride toxicity beyond calcified tissues. Fluoride is a protoplasmic poison that inhibits enzymatic activity by binding to co-factors such as magnesium. High fluoride intake has been linked to gastrointestinal distress (non-ulcer dyspepsia), reproductive toxicity (decreased sperm motility), and neurological effects. Studies in high-fluoride belts of India have suggested a correlation between chronic fluoride exposure and reduced Intelligence Quotient (IQ) in school-age children, indicating that the neurotoxic effects may be significant.

## 2.3 Regulatory Standards: The Disconnect between Policy and Physiology

Navigating the regulatory landscape is essential for defining the target parameters of any remediation project. The definition of “safe” water is subject to debate and varies based on climatic conditions.

The World Health Organization (WHO) sets a Guideline Value of 1.5 mg/L for fluoride in drinking water. However, the WHO explicitly states that this limit should be adapted based on local conditions, specifically air temperature and water intake. In temperate climates an adult might consume 1.5–2 L of water per day. In the scorching heat of the Thar Desert, where summer temperatures in Pilani regularly exceed 45 °C, daily water intake for a working adult can easily reach 5–8 L. Consequently, the total daily dose of fluoride ingested at 1.5 mg/L is significantly higher in Rajasthan than in Europe or North America.

The Bureau of Indian Standards (BIS) reflects this complexity in IS 10500:2012:

- **Acceptable Limit:** 1.0 mg/L.
- **Permissible Limit:** 1.5 mg/L (in the absence of an alternate source).

Most of the groundwater supply in Jhunjhunu operates under the “permissible-limit” clause due to the lack of alternatives. However, considering the high ambient temperature and the cumulative total intake, a robust research objective for a Pilani-based remediation process should ideally target a concentration below 1.0 mg/L to provide a genuine safety margin.

## 3. The Pilani and Jhunjhunu Context: Magnitude of the Problem

To design a solution for Pilani, one must understand the specific environmental theatre in which it must operate. Pilani is not a generic location; it is a specific hydrogeological entity with unique constraints.

### 3.1 Geographical and Climatic Setting

Pilani is situated in the Surajgarh tehsil of the Jhunjhunu district, part of the semi-arid Shekhawati region of Rajasthan. The district covers an area of approximately 5,928 square kilometres and sustains a population of nearly two million. The topography is a rolling sandy plain, punctuated by stabilised sand dunes and isolated rocky outcrops of the Aravalli range.

The climate is extreme. Winters can see temperatures dip below freezing, while summers are intensely hot, with high evaporation rates. The average annual rainfall is a meagre 350 mm, most of which falls during the erratic monsoon season. This climatic profile defines the water balance: potential evapotranspiration far exceeds precipitation, leading to a negligible rate of natural groundwater recharge. This lack of fresh recharge water means there is little dilution of the geogenic contaminants accumulating in the aquifer.

### 3.2 Hydrogeology of the Study Area

The groundwater regime in Pilani is governed by the subsurface geology. The area is underlain by the Delhi Supergroup of rocks (Pre-Cambrian age), consisting primarily of quartzites, mica-schists, phyllites, and impure marbles. These metasedimentary rocks are intruded by post-Delhi granites, pegmatites, and amphibolites.

The aquifers are generally of two types:

1. **Alluvial Aquifers:** Occurring in the shallow overburden of wind-blown sand and kankar. These have largely dried up or are heavily contaminated with nitrates from surface activities.
2. **Hard-Rock Aquifers:** Located in the fractured zones of the underlying quartzite and granite. As shallow sources fail, borewells are drilled deeper (100–150 m) to tap these fractures. It is in these deep, long-residence-time waters that the interaction with fluoride-bearing minerals such as biotite and fluorite is most intense.

CGWB data classify the Surajgarh block (containing Pilani) as "Over-Exploited," meaning the rate of extraction exceeds the rate of recharge. This over-exploitation creates a cone of depression, potentially drawing in more saline and mineralised water from surrounding formations.

## 3.3 Quantitative Assessment of Contamination (2020–2024)

Recent data provide a granular view of the contamination landscape. While "fluoride" is the headline, the reality is a "cocktail" of contaminants.

### *3.3.1 Fluoride Concentrations*

The distribution of fluoride in Jhunjhunu is heterogeneous, varying significantly even between neighbouring wells due to the complex fracture patterns of the hard-rock aquifers.

- **Regional Overview.** The Pre-monsoon 2024 report by the CGWB indicates that fluoride contamination remains a "prime concern" in the district, with 33.04 % of groundwater samples across the state exceeding permissible limits.
- **Specific Village Data.** A focused study covering the Chirawa, Buhana, and Surajgarh blocks found fluoride levels ranging from 0.7 mg/L to 1.4 mg/L in the sampled wells. Specific locations such as the "Pilani water box" and "Chirawa CHC" were found to have levels around 0.7 mg/L, which is technically safe. However, this data point must be contextualised against broader studies (e.g., sample "Kakoda" at 1.4 mg/L) and historical data showing levels in the Shekhawati region spiking between 3.5 mg/L and 7.2 mg/L in isolated pockets.
- **Extreme Values.** In the nearby Nawa-Kuchaman zone, fluoride levels as high as 5.8 mg/L have been recorded in villages such as Piprali. This variability implies that a remediation process in Pilani must be robust enough to handle input loads that can fluctuate widely from 1.5 mg/L to >5.0 mg/L depending on the specific source well.

### *3.3.2 The Co-Contaminant Matrix*

A critical oversight in many lab-scale research projects is testing with distilled water spiked with fluoride. Real groundwater in Pilani is a complex matrix containing interfering ions that can drastically reduce the efficiency of removal processes.

- **Nitrate ($NO_3^-$).** This represents a major parallel concern. According to 2024 CGWB data, nearly 50 % of groundwater samples in Jhunjhunu exceed the permissible nitrate limit of 45 mg/L, with maximum concentrations reaching up to 95 mg/L. Nitrate interferes with fluoride removal by competing for active sites in ion-exchange resins and by influencing electrochemical conductivity in treatment processes.

- **Salinity (TDS).** Groundwater in the region is often brackish, with elevated levels of sulphate ($SO_4^{2-}$), chloride ($Cl^-$), and bicarbonate ($HCO_3^-$). Among these, bicarbonate is particularly problematic as it acts as a pH buffer and competes strongly for adsorption sites on metal-oxide-based adsorbents, thereby reducing treatment efficiency.
- **Uranium (U).** An emerging contaminant of concern in Rajasthan's groundwater, uranium has been detected in recent CGWB reports, with approximately 7.59 % of state samples showing its presence. Although less frequently monitored, its occurrence necessitates strict safety protocols for the handling and disposal of spent filtration media.

## 4. Etiology of Contamination: The "Why" and "How"

To solve the problem, one must understand its origins. The high fluoride levels in Pilani are the result of a synergistic interplay between natural geological processes and human intervention.

### 4.1 Geogenic Drivers (Natural Sources)

The primary source of fluoride in groundwater is the aquifer matrix itself.

- **Mineralogy.** The post-Delhi granites and pegmatites prevalent in the Pilani subsurface are rich in fluoride-bearing accessory minerals. The dissolution of fluorite ($CaF_2$) is the most direct and significant contributor to fluoride enrichment.
- **Weathering in Alkaline Conditions.** As established in the theoretical framework, the high alkalinity of groundwater ($pH > 8.0$) promotes the desorption of fluoride from clay and mica surfaces. The arid climate further intensifies this process by enhancing evapotranspiration, which removes pure water and leaves dissolved salts, including fluoride, concentrated in the remaining groundwater.
- **Residence Time.** The "over-exploited" status of the aquifer indicates that the extracted groundwater is relatively old. Prolonged residence time—spanning centuries or even millennia—allows extensive interaction between water and host rock, enabling dissolution reactions to approach equilibrium and resulting in elevated fluoride concentrations.

### 4.2 Anthropogenic Drivers (Human-Induced)

Human activity has accelerated and exacerbated these natural processes.

- **Agricultural Intensification.** The economic shift towards water-intensive cash crops has led to the widespread use of phosphatic fertilisers (DAP and Superphosphate). Phosphate rock naturally contains high levels of fluoride (1–4 %) as an impurity. When these fertilisers are applied to the sandy, permeable soils of Jhunjhunu, the fluoride leaches rapidly into the shallow groundwater. This "return flow" from irrigation is a significant source of anthropogenic fluoride.

- **Groundwater Mining.** The excessive extraction of groundwater for agriculture lowers the water table. This changes the hydraulic gradients, potentially inducing the upwelling of deeper, more mineralised water into the pumping zones of village tube-wells.
- **Industrial Influence (Khetri Copper Belt).** Although located some distance from Pilani, the Khetri Copper Complex has a regional footprint. Decades of copper mining and smelting have generated vast quantities of tailings. Weathering of these sulphide-rich wastes releases acid, which can dissolve fluoride-bearing minerals in the surrounding rock, mobilising them into the regional groundwater-flow system.

# 5. Literature Review: A History of Interventions

The history of fluoride mitigation in Rajasthan is a graveyard of well-intentioned but failed projects. Understanding these failures is crucial to ensuring that new research does not repeat old mistakes.

## 5.1 Government Interventions: The Rise and Fall of RIFMP

In the early 2000s, the Government of Rajasthan, supported by UNICEF, launched the Rajasthan Integrated Fluoride Mitigation Programme (RIFMP). It was envisioned as a decentralised solution to a decentralised problem.

### *5.1.1 The Technological Approach*

The programme relied heavily on two technologies:

3. **The Nalgonda Technique.** A process of chemical precipitation involving the addition of Alum (aluminium sulphate), Lime (CaO), and Bleaching Powder to the water. The aluminium salts hydrolyse to form heavy flocs of aluminium hydroxide, which adsorb fluoride and settle to the bottom.
4. **Activated Alumina Filters (DDUs).** Domestic Defluoridation Units distributed to households, containing a bed of activated alumina to adsorb fluoride.

### *5.1.2 The Failure Analysis*

Despite the chemical validity of these methods, the programme faced severe operational headwinds in the field:

- **Operational Complexity.** The Nalgonda technique requires precise dosing based on the specific fluoride level of the water, which fluctuates. Villagers often under-dosed (ineffective) or over-dosed (leaving residual aluminium, a neurotoxin, in the water).
- **Supply-Chain Collapse.** The logistics of supplying fresh chemicals and regenerating the activated alumina media (which requires acid and alkali wash) proved impossible to sustain in remote villages.

- **Sludge Toxicity.** The process generated large volumes of toxic sludge containing concentrated fluoride and aluminium. With no safe disposal mechanism, this sludge was often dumped locally, leading to soil contamination.
- **Social Rejection.** The treated water often had a metallic taste, and the daily drudgery of mixing chemicals led to high abandonment rates.

## 5.2 The Shift to Surface Water: Jal Jeevan Mission

Recognising the limitations of treating groundwater, state policy has shifted towards source substitution.

- **Kumbharam Lift Canal.** This massive infrastructure project aims to bring Himalayan water from the Indira Gandhi Canal to the thirsty districts of Sikar and Jhunjhunu.
- **Yamuna Water Pact (2024).** A historic MoU signed in February 2024 between Rajasthan and Haryana facilitates the transfer of Yamuna floodwaters to the Shekhawati region via underground pipelines.
- **Current Status.** While these projects are the ultimate solution, they are capital-intensive and face long gestation periods. Many villages in Jhunjhunu still rely on groundwater stand-posts and will continue to do so for years. Thus, point-of-use treatment remains a critical interim necessity.

## 5.3 NGO and Corporate Models: The RO Revolution

Where the government stepped back, private and non-profit entities stepped in—most notably Piramal Sarvajal, which has its roots in Bagar, Jhunjhunu.

- **The Sarvajal Model.** Moving away from the complexity of chemical dosing, Sarvajal adopted Distributed Reverse Osmosis (DRO).
- **Technology.** Small-scale, solar-powered RO plants were established in villages, coupled with Water ATMs—cloud-connected vending machines that dispense water for a fee (pay-per-use).
- **Impact.** This model solved the maintenance issue by using a franchise system in which a local entrepreneur is incentivised to keep the machine running. RO technology effectively removes fluoride, nitrate, and salinity, providing a “one-stop” solution to the matrix problem.
- **Sustainability Critique.** The primary drawback of RO is water wastage. In a typical village plant, for every litre of clean water produced, 1–2 L of “reject water” (brine) is discarded. In a water-scarce desert, this is an ethical and environmental challenge. However, regarding health safety, it remains the gold standard currently deployed in the region.

## 5.4 Academic Research: The Contribution of BITS Pilani

Situated at the epicentre of the crisis, BITS Pilani has a long history of research into appropriate technologies for fluoride removal. This local academic output is a goldmine for any new researcher.

### *5.4.1 Electrochemical Remediation*

Research led by faculty such as Dr. Somak Chatterjee has focused on Electrocoagulation (EC).

- **Mechanism.** Instead of adding chemical salts (as in Nalgonda), EC uses aluminium plates as sacrificial anodes. When a current is passed, $Al^{3+}$ ions are released into the water, forming active coagulant species in situ.
- **Advantages.** This method produces significantly less sludge than chemical coagulation and is easier to automate.
- **Findings.** Studies have demonstrated fluoride removal efficiencies of up to 85.2 % at neutral pH. Recent SERB-funded projects have advanced this by integrating co-axial electrospun nanofiber membranes for the simultaneous removal of arsenic, lead, and fluoride, pushing the frontier of material science.

### *5.4.2 Bio-Adsorbents and Green Chemistry*

Another significant stream of research focuses on “waste-to-wealth” approaches, utilising the abundant biomass of the invasive Prosopis juliflora (Vilayati Babool) tree.

- **Innovation.** Researchers have converted the bark and wood of P. juliflora into high-surface-area activated carbon.
- **Performance.** Lab-scale studies report removal efficiencies ranging from 93.45 % to 97.26 %, with the adsorption following Langmuir isotherms and pseudo-second-order kinetics.
- **Patent IN387689.** A notable output from BITS Pilani is the patent for a formulation using starch, ceramic powder, and clay. This points towards a low-cost, passive filtration technology that leverages locally available materials (clay) and biodegradable polymers (starch), addressing the “sludge toxicity” and “cost” barriers simultaneously.

## 6. Synthesis: Gap Analysis and Strategic Direction

The review of the problem context and existing literature reveals a clear dichotomy:

- **High-Tech (RO).** Effective but wasteful and energy-intensive.
- **Low-Tech (Nalgonda / Adsorption).** Water-efficient but chemically messy, labour-intensive, and prone to failure.

There is a glaring gap for a “middle-path” technology that is selective, passive or low-energy, and matrix-resilient. This necessitates the introduction of a new paradigm utilising engineered bio-adsorbents combined with clean energy for regeneration. The remainder of this report develops such a paradigm, beginning with the initially proposed Pine Char system (Section 7) and then documenting the strategic pivot to Prosopis juliflora biochar (Section 8) once the practical constraints of feedstock availability in Rajasthan were appreciated.

## 7. Initially Proposed Methodology: Integrated Solar-Electrochemical Pine-Char Adsorption System

Addressing the drawbacks of both conventional chemical dosing and wasteful RO technologies requires transitioning to a “circular-economy” model. The first iteration of the proposed system integrated high-efficiency bio-adsorption using pine char with solar-powered electrochemical regeneration, culminating in zero-waste resource recovery.

### 7.1 Selection and Synthesis of Conductive Pine Char

Standard agricultural waste is generally ineffective for electrochemical processes due to its lack of electrical conductivity. The method addresses this limitation by utilising pine wood and pine bark chars produced via fast pyrolysis in an auger reactor at high temperatures (typically ~500–700 °C).

- **Pore Dynamics and Swelling.** Although the dry BET surface area of these biochars is relatively low (~10–50 $m^2/g$) compared with commercial activated carbons (~800–1500 $m^2/g$), they exhibit remarkably high fluoride removal per unit surface area. This is attributed to their high oxygen-functional-group content (~10–20 wt %), which enables significant swelling when submerged in water. As a result, large internal pore volumes and additional adsorption sites become accessible—features that are not measurable under dry conditions.
- **Conductivity.** The high-temperature pyrolysis process ensures sufficient carbonisation of the char, imparting electrical conductivity. This allows the material to function effectively as a capacitive electrode during the regeneration phase of the electrochemical treatment process.

### 7.2 Adsorption Mechanics (Defluoridation)

In this phase, raw fluoride-contaminated water is passed through a fixed bed of pine biochar.

- **Optimal Conditions.** Maximum fluoride adsorption occurs under highly acidic conditions ($pH \approx 2.0$). At low pH, the elevated concentration of hydronium ions ($H_3O^+$) protonates the basic functional groups on the biochar surface, generating positively charged (cationic) sites that strongly attract and bind negatively charged fluoride ions ($F^-$).
- **Mechanisms.** Fluoride removal is governed by multiple mechanisms, including ion exchange, metal–fluoride precipitation, electrostatic attraction, and diffusion into the internal pore structure of the biochar. Adsorption isotherm analysis shows strong agreement with the Langmuir and Redlich–Peterson models, indicating predominantly uniform monolayer adsorption behaviour.

### 7.3 Solar-Powered Electrochemical Regeneration (Electro-Desorption)

The major limitation of traditional adsorption systems is the need for harsh chemicals (such as NaOH or HCl) to regenerate saturated media, which often results in the generation of toxic sludge. The proposed methodology overcomes this issue by employing electrochemical pH-swing and electro-desorption, powered entirely by solar photovoltaic (PV) panels.

- **The Process.** Once the biochar bed becomes saturated, a direct current is applied across the conductive pine char. The resulting electric field reverses the electrostatic forces at the active adsorption sites, causing the desorption of fluoride ions ($F^-$) from the carbon matrix.

- **Efficiency and Lifespan.** This capacitive deionisation and electro-desorption approach concentrates the released fluoride into a small volume of reject stream. Electrochemical regeneration can repeatedly restore the adsorbent to ~90–95 % of its original efficiency over multiple cycles, with minimal loss in adsorption capacity. The process operates at ambient temperature and eliminates the need for continuous chemical inputs, making it both sustainable and cost-effective.

## 8. Revised Methodology: Integrated Solar-Electrochemical Prosopis juliflora Biochar Adsorption System

During the course of the study, limitations in the regional availability of pine biomass—a commonly researched precursor—in Rajasthan necessitated the reconsideration of the adsorbent feedstock. Consequently, Prosopis juliflora, an aggressively invasive and abundantly available phreatophyte shrub in the arid regions of Rajasthan, was selected as the alternative precursor.

### 8.1 Strategic Shift in Feedstock

Utilising P. juliflora offers a synergistic "waste-to-value" approach. Harvesting this invasive biomass provides an essentially free, sustainable, and local feedstock, drastically improving the cost-effectiveness and scalability of the defluoridation unit. Furthermore, harvesting it contributes directly to ecological management by curbing the spread of a species that heavily depletes local groundwater and threatens native biodiversity.

To ensure electrical conductivity—a prerequisite for electrochemical regeneration—the P. juliflora lignocellulosic biomass is subjected to pyrolysis at controlled temperatures (typically ~500–700 °C). The inherent lignocellulosic structure of P. juliflora enables the formation of a highly porous biochar network enriched with active oxygen-containing functional groups. When compared with pine-derived biochar, several key differences emerge:

- **Porosity and Surface Area.** Pine biochar generally exhibits a low dry BET surface area (~10–50 $m^2/g$) and relies significantly on water-induced swelling to expose internal adsorption sites. In contrast, P. juliflora-derived biochar naturally develops a well-defined mesoporous structure with substantially higher specific surface areas (typically ~200–800 $m^2/g$, and in some cases exceeding 1000 $m^2/g$ depending on activation methods).
- **Surface Chemistry.** P. juliflora biochar contains abundant oxygenated functional groups (hydroxyl, carbonyl, and carboxyl) along with a distinct mineral ash composition. While the fundamental adsorption mechanisms remain similar, these surface characteristics, combined with higher intrinsic porosity, enhance reaction kinetics and enable faster fluoride uptake.
- **Regeneration Compatibility.** When optimally carbonised, P. juliflora biochar exhibits sufficient electrical conductivity, allowing it to function effectively under applied electric fields. This ensures reliable performance during electro-desorption and supports consistent regeneration across multiple operational cycles.

### 8.2 Adsorption Mechanics (Defluoridation)

In this phase, raw fluoride-contaminated water is passed through a fixed bed of the P. juliflora biochar. The biochar functions as a highly effective adsorbent for fluoride removal primarily through a combination of ion exchange, electrostatic attraction, and surface complexation. The rich distribution of surface functional groups—particularly hydroxyl and carboxyl groups—act as active binding sites for the electronegative fluoride ions. The adsorption kinetics for P. juliflora biochar typically follow a pseudo-second-order model, indicating that chemisorption plays a governing role in the binding process. At optimal pH levels, protonation of the biochar surface enhances the electrostatic pull on the target anions, facilitating rapid uptake and diffusion into the extensive porous network.

### 8.3 Solar-Powered Electrochemical Regeneration

The proposed methodology replaces chemical regeneration with electrochemical pH-swing and electro-desorption, powered entirely by solar photovoltaic (PV) panels.

- **The Process.** Once the P. juliflora biochar bed becomes saturated, a direct current is applied across it. The applied electric field reverses the electrostatic forces at the active sites, causing the desorption of fluoride ions ($F^-$) from the solid carbon matrix.
- **Efficiency and Lifespan.** This capacitive deionisation and electro-desorption approach concentrates the released fluoride into a very small volume of reject water. Electrochemical regeneration can consistently restore the adsorbent to high efficiency over multiple cycles without significant structural degradation, thereby eliminating the need for a continuous chemical supply chain.

### 8.4 Zero-Waste Mineralisation (Closing the Loop)

While electrochemical regeneration cleans the filter media, it leaves behind a highly concentrated fluoride reject stream. To ensure a 100 % zero-waste, environmentally benign process, this liquid must be stabilised.

- **Calcium Precipitation.** The concentrated reject water is treated with a low-cost and sustainable calcium source. Recent approaches advocate the use of Oyster-Shell Powder (OSP), which is rich in calcium carbonate ($CaCO_3$). Dosing OSP at ~5 g/L has been shown to achieve up to ~95–98 % fluoride removal from highly concentrated streams, while simultaneously neutralising the acidic pH.
- **Resource Recovery.** The dissolved calcium reacts with fluoride ions to form insoluble calcium fluoride ($CaF_2$), which precipitates out as solid crystals.
- **Circular Economy.** Instead of generating hazardous sludge, this process produces calcium fluoride ($CaF_2$), a valuable industrial mineral widely used in metallurgy, hydrofluoric-acid production, and semiconductor manufacturing. This converts a toxic waste stream into a marketable resource, helping offset operational costs and enabling a near zero-waste treatment cycle.

## 9. Detailed Experimental Methodology and Process Engineering

The transition from a conceptual framework to a functional, lab-scale remediation system required the development of a highly specific material-synthesis protocol. The following subsections detail the chronological workflow executed by the research team, moving from raw biomass harvesting to the final column filtration and advanced spectroscopic analysis.

## 9.1 Phase I: Feedstock Acquisition and Pre-Treatment

The foundation of any biochar-based filtration system is the precursor material.

### *9.1.1 Biomass Selection*

*Prosopis juliflora* was selected as the precursor: the heartwood and branches of the shrub were harvested locally. This selection is ecologically and practically justified. *Prosopis juliflora* is an aggressively invasive phreatophyte shrub abundant in the arid regions of Rajasthan. Utilising this specific biomass offers a synergistic "waste-to-value" approach, drastically improving the cost-effectiveness and scalability of the defluoridation unit. Furthermore, its inherent lignocellulosic structure enables the formation of a highly porous network when carbonised.

### *9.1.2 Desiccation (Drying) Process*

Upon harvesting, the wood was manually debarked to remove high-ash exterior layers and sectioned into manageable blocks. The raw wood was then subjected to a rigorous drying phase.

**Engineering Reasoning.** *Freshly harvested Prosopis* contains a significant percentage of intracellular moisture and sap. If raw, "green" wood is introduced directly into a high-temperature environment, the thermal energy is initially consumed by the latent heat of vaporisation to boil off the water, rather than breaking carbon bonds. Furthermore, trapped moisture converts to steam, which can rupture the internal micropores of the wood, compromising the structural integrity of the final char. Drying the wood ensures a uniform thermal gradient during pyrolysis and prevents the formation of excessive volatile tars that clog active adsorption sites.

## 9.2 Phase II: Custom Pyrolysis and Carbonisation

To convert the dried lignocellulosic biomass into a conductive, high-surface-area biochar, a custom, localised carbonisation setup was engineered.

### *9.2.1 The Aluminium Anoxic Chamber (Retort)*

A custom pyrolysis chamber was fabricated utilising an aluminium enclosure.

**Engineering Reasoning.** The fundamental principle of creating charcoal (carbonisation) requires the application of high heat in the strict absence of oxygen. If oxygen is present, the carbon undergoes complete combustion, converting into carbon dioxide ($CO_2$) and leaving behind only inorganic mineral ash. Aluminium was chosen for the chamber because it is highly thermally conductive—allowing external heat to penetrate the chamber rapidly—while providing an impermeable barrier to ambient atmospheric oxygen. This localised "retort" method effectively simulates industrial anaerobic pyrolysis.

### *9.2.2 Ignition and Pyrolytic Cascade using Acetone*

To achieve the rapid temperature spike necessary for optimal char formation, a controlled volume of acetone ($C_3H_6O$) was used as an accelerant to initiate the burn.

**Engineering Reasoning.** Acetone is a highly volatile, clean-burning solvent. In a makeshift or lab-scale retort, achieving the critical activation energy required to initiate the exothermic pyrolytic decomposition of wood can be challenging. By using acetone, an immediate, high-temperature thermal envelope was generated around the aluminium chamber. Unlike heavy hydrocarbon accelerants (such as diesel or kerosene), acetone combusts completely, leaving zero organic residue that could otherwise contaminate the biochar or artificially alter its surface chemistry. This rapid heat transfer allowed the internal temperature of the chamber to quickly reach the target range (~500–700 °C), ensuring optimal pore formation and electrical conductivity.

## 9.3 Phase III: Granulometric Analysis and Sizing

Once the carbonisation was complete and the chamber cooled, the raw *Prosopis* biochar was extracted and subjected to mechanical crushing.

### *9.3.1 Sieve Segregation (600 µm, 300 µm, 150 µm, and 75 µm)*

The crushed char was passed through a series of graded laboratory sieves to segregate the material into four specific particle-diameter ranges: 600 µm, 300 µm, 150 µm, and 75 µm.

**Engineering Reasoning.** In fixed-bed adsorption dynamics, particle size is the primary variable controlling both reaction kinetics and system hydraulics. This specific gradient was chosen to empirically determine the operational “sweet spot”:

- **Coarse Fraction (600 µm and 300 µm).** These larger granules ensure excellent hydraulic conductivity (water flows easily without clogging), but they possess a lower external surface area, potentially limiting fluoride uptake.
- **Fine Fraction (150 µm and 75 µm).** These micro-granules offer a massive external surface area, drastically reducing the intra-particle diffusion path and theoretically maximising fluoride adsorption. However, particles this fine act as a major hydraulic barrier, causing severe head loss and potential clogging in a gravity-fed column.

By isolating these four distinct sizes, a controlled variable was engineered to test exactly at what micrometre size the adsorption kinetics are maximised before the physical column fails hydraulically.

## 9.4 Phase IV: Chemical Activation (Doping)

Raw biochar relies primarily on physical adsorption (physisorption) governed by pore size, which is highly inefficient for capturing specific, small monovalent ions such as fluoride ($F^-$).

### *9.4.1 Calcium Chloride ($CaCl_2$) Impregnation*

To convert the passive char into an active chemical trap, the sieved samples were soaked in a solution of calcium chloride.

**Engineering Reasoning.** Fluoride acts as a “hard” base and exhibits a strong chemical affinity for “hard” acids such as calcium ($Ca^{2+}$). By submerging the char in $CaCl_2$, the calcium ions diffuse into the mesoporous network of the *Prosopis* char. When fluoride-laden water enters these pores, a localised precipitation reaction occurs:

$$\mathbf{Ca^{2+} + 2F^{-} \rightarrow CaF_2\,(s)}$$

This process, known as chemical doping, shifts the removal mechanism from weak physical trapping to strong, permanent chemisorption. Calcium was specifically chosen because the dissolution of fluorite ($CaF_2$) is governed by the common-ion effect; adding surplus calcium forces the equilibrium toward precipitation, effectively locking the fluoride into the carbon matrix.

### 9.5 Phase V: Column Hydrodynamics and Testing

The final physical stage involved the assembly of the point-of-use filtration prototype.

#### *9.5.1 Fixed-Bed Column Set-up*

Exactly 2.0 g of the $CaCl_2$-activated *Prosopis* char was loaded into a vertical filtration column. A measured volume of fluoride-contaminated groundwater (sourced from the Pilani area) was then allowed to percolate downward through the media via gravity.

**Engineering Reasoning.** A fixed-bed column closely simulates real-world domestic water filters. The choice of 2 g represents a deliberate “micro-scale” stress test. By using a small mass of adsorbent against a known volume of contaminated water, the “Breakthrough Curve” can be accurately plotted—the exact moment the active sites on the 2 g of char become fully saturated and allow untreated fluoride to pass through. Regulating the drip rate ensures adequate Hydraulic Retention Time (HRT), which is necessary for the $Ca^{2+}$ and $F^{-}$ ions to interact.

## 10. Analytical Results and Validation

### 10.1 Qualitative Assessment: The “Yellow” Indicator and Inconclusive Results

Initial effluent testing was conducted using the Alizarin Visual Method (Zirconyl–Alizarin reaction) to determine the post-filtration fluoride levels.

- **Observation.** Upon addition of the reagent to the filtered water, the sample yielded a bright yellow coloration.
- **Analysis.** In the Zirconyl–Alizarin assay, the dye-lake is reddish-pink in the absence of fluoride. As fluoride concentration increases, it dissociates the complex, progressively lightening the hue. A distinct yellow result visually indicates a high residual fluoride concentration, typically signalling levels at or above 1.8–2.0 mg/L.
- **Engineering Conclusion (Inconclusive Findings).** Because the initial untreated water was tested at 1.8 mg/L, the yellow result of the filtered water rendered the qualitative experiment ultimately inconclusive. The test could not definitively establish whether the concentration remained exactly

1.8 mg/L (indicating zero adsorption), if it dropped slightly but remained above the visual detection threshold of the dye, or if alkaline/organic interference from the Prosopis char caused a false-positive bleaching of the reagent. While it confirmed that complete remediation did not occur under these specific column parameters, it failed to provide actionable quantitative data.

### 10.2 The Quantitative Pivot: $^{19}$F NMR Spectroscopy

Because the colorimetric testing yielded an inconclusive "yellow" result, it became imperative to move beyond the limitations of visual approximation. To obtain scientifically rigorous, quantifiable data and validate the methodology, the protocol has transitioned to Nuclear Magnetic Resonance (NMR) Spectroscopy, specifically targeting the $^{19}$F isotope.

**Reasoning for NMR:**

5. **Elimination of Interferences.** Unlike the Alizarin method, $^{19}$F NMR is entirely unaffected by water turbidity, organic colour leaching from the biochar, or the presence of non-fluorine dissolved solids (such as nitrates or sulphates) that often trigger false readings in Pilani groundwater.
6. **Absolute Quantification.** NMR provides direct, absolute quantification of the molar concentration of fluoride remaining in the effluent. By integrating the signal peaks, the exact milligrams of fluoride adsorbed per gram of char (mg/g) can be calculated across the four chosen sieve diameters (600 µm down to 75 µm), enabling a rigorous comparison of adsorption capacity as a function of particle size.

## 11. Conclusion and Future Work

The problem of fluoride in the groundwater of Pilani is not a static chemical equation; it is a dynamic interaction between a hostile geology and a thirsty population. The "solution" cannot simply be a chemical process; it must be a socio-technical intervention. The failures of the past (RIFMP) teach us that logistics and ease of use are as important as adsorption capacity. The successes of the present (Sarvajal) teach us that users value reliability and are willing to pay for it.

The proposed Integrated Solar-Electrochemical Prosopis juliflora Biochar framework offers a highly promising pathway forward. It leverages the waste-to-wealth efficiency of a locally abundant invasive species, the off-grid reliability of solar electricity, and circular-economy mineralisation to eliminate secondary toxic waste. The pilot fixed-bed column experiments performed in this study established the feasibility of the synthesis workflow—from anoxic aluminium-retort pyrolysis through granulometric segregation, calcium-chloride doping, and gravity-fed column testing—while simultaneously exposing the limitations of qualitative analytical methods in a complex groundwater matrix.

The immediate future work is therefore three-fold. First, the protocol must complete the planned $^{19}$F NMR campaign across all four sieve fractions to quantitatively map adsorption capacity against particle size and to establish a defensible breakthrough curve. Second, the regeneration loop—solar-powered electro-desorption followed by oyster-shell-powder mineralisation—must be closed in a single integrated bench-scale rig to demonstrate true zero-waste operation. Third, a field-deployment study, ideally in partnership with a local NGO such as Piramal Sarvajal or the village panchayat of an endemic Shekhawati settlement, is essential to validate the laboratory results against the operational, social, and economic realities of rural Rajasthan. For a researcher embarking on this journey, the mandate is clear: the laboratory constraints must mimic field realities, ensuring the technology is robust enough to survive in the harsh, arid environment of the Thar Desert, serving the people who have waited decades for safe water.

# Appendix A: Consolidated Data Tables

## Table A.1 Regulatory Standards vs. Environmental Reality in Pilani

| Standard | Limit (mg/L) | Context and Implication for Pilani |
|---|---|---|
| **WHO Guideline** | 1.5 | Based on 2 L/day intake. Inadequate for Pilani, where summer intake of >4 L/day leads to toxic dosing. |
| **BIS (Acceptable)** | 1.0 | The research target. Ideal for long-term health safety. |
| **BIS (Permissible)** | 1.5 | The current “emergency standard” widely used due to lack of alternatives. |
| **US EPA (MCL)** | 4.0 (under review) | Often cited but largely irrelevant; the US EPA is considering lowering this to 1.5 mg/L due to new toxicity data. |

## Table A.2 Groundwater Quality Snapshot – Jhunjhunu District, 2024

| Parameter | Observed Range / Value | Notes |
|---|---|---|
| **Fluoride ($F^-$)** | 0.7 – 7.2 mg/L | Highly heterogeneous. Deep aquifers show higher concentrations. |
| **Nitrate ($NO_3^-$)** | 9.0 – 95.0 mg/L | 50 % of samples exceed the permissible limit. Indicates fertiliser and sewage contamination. |
| **Salinity (TDS)** | Variable; often brackish | High salinity often correlates with lower fluoride removal efficiency in adsorption-based processes. |
| **Uranium (U)** | Detected (>30 µg/L in pockets) | Emerging contaminant; requires monitoring in new research. |

## Table A.3 Comparative Analysis of Mitigation Technologies in the Rajasthan Context

| Technology | Removal Efficiency | Water Wastage | Operational Complexity | Suitability for Pilani |
|---|---|---|---|---|
| **Nalgonda (Alum)** | Moderate (pH-dependent) | Low | High (chemical dosing) | Low. Failed historically due to logistics and sludge. |
| **Reverse Osmosis (RO)** | Very High (>95 %) | High (50–60 % reject) | Medium (high energy) | Medium. Best for health, worst for conservation. |

| Technology | Removal Efficiency | Water Wastage | Operational Complexity | Suitability for Pilani |
|---|---|---|---|---|
| **Electrocoagulation** | High (80–90 %) | Low (<10 % sludge) | Moderate (electricity) | High. Solar-compatible; low sludge. |
| *P. juliflora* **Biochar + Electro-Regeneration** | High (90–98 %) | Very low (zero waste) | Low (solar-powered) | High. Solves sludge toxicity, limits water loss, uses local invasive biomass. |

### Table A.4  Feedstock Comparison – Pine Biochar vs. Prosopis juliflora Biochar

| Factor | Pine Biochar | Prosopis juliflora Biochar |
|---|---|---|
| **Availability (Rajasthan)** | Low | High (locally invasive) |
| **Cost** | High transport cost | Very low |
| **Sustainability** | Moderate | Uses invasive species (ecological benefit) |
| **Adsorption Capacity** | Good | Good (comparable, often higher) |
| **Field Applicability** | Limited | Strong |
| **Research Support** | Well established | Growing and locally relevant |

## Appendix B: Key Data Sources and References

The following primary sources informed the data, regulatory thresholds, and operational case studies cited in this report.

- **CGWB.** Pre-Monsoon Groundwater Quality Report, Jhunjhunu District, Rajasthan (2024). Central Ground Water Board, Ministry of Jal Shakti, Government of India.
- **BIS.** IS 10500:2012 – Drinking Water Specification (Second Revision). Bureau of Indian Standards, New Delhi.
- **WHO.** Guidelines for Drinking-Water Quality, 4th edition (2017). World Health Organization, Geneva.
- **UNICEF – Government of Rajasthan.** Rajasthan Integrated Fluoride Mitigation Programme (RIFMP) – Programme Evaluation Reports.
- **Piramal Sarvajal.** Annual Operating Reports, Water ATM and Distributed Reverse Osmosis Network, Shekhawati Region.
- **Chatterjee, S. et al.** Electrocoagulation for fluoride removal at neutral pH – SERB-funded projects, BITS Pilani, Department of Chemical Engineering.
- **Indian Patent IN387689.** Composite filter formulation using starch, ceramic powder, and clay for fluoride removal – BITS Pilani.
- **Various peer-reviewed studies** on Prosopis juliflora-derived activated carbon for fluoride removal (Langmuir isotherm, pseudo-second-order kinetics, 93.45–97.26 % efficiency).