Research Article

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Recovery of Groundwater Contaminated by Tannery Effluents Using Nanomaterials

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ABSTRACT

Urbanization, driven largely by economic factors, also leads to significant environmental issues, including groundwater contamination. This focuses on the Pallavaram area in Chennai, India, where groundwater is affected by rapid urbanization, industrial effluents, sewage seepage, and improper solid-waste disposal. This situation poses a serious health hazard, as the area relies entirely on groundwater. The levels of BOD, COD, nitrates, chlorides, total dissolved solids (TDS), hardness, heavy metals, and pathogenic bacteria are substantially elevated, resulting in chemical and microbiological contamination. This study examines the causes, extent, and nature of groundwater contamination in Pallavaram by assessing key water-quality parameters and comparing them with the drinking-water standards (IS 10500:2012). It also evaluates sustainable treatment technologies, such as permeable reactive barriers (PRBs) incorporating multi-layered biochar, potassium permanganate, limestone, wood chips, zero-valent iron (ZVI), coarse aggregate, sand, and multi-walled carbon nanotubes (MWCNTs), as well as chlorination. The study highlights the importance of restoring water quality to protect public health and concludes that low-cost, eco-friendly remedial measures, such as PRBs combined with oxidative processes, can be applied to treat groundwater in Pallavaram.

Keywords: Groundwater contamination; Permeable Reactive Barriers (PRBs): Multi-Walled Carbon Nanotube (MWCNTs).

1. INTRODUCTION

Groundwater contamination is a significant environmental concern in industrial and suburban areas, where elevated levels of color, turbidity, hardness, sulfates, dissolved solids, heavy metals, and organic pollutants degrade water quality (AlAqad *et al.* 2025). This is one of the major problems faced by the residents of Pallavaram, Chennai, India, due to tanneries and the leather industries (Arora and Attri, 2020). Groundwater was found to be completely non-potable without filtration, and residents do not use it. Therefore, this study aims to provide an in-house solution with a simple setup, enabling cost-effective implementation (Budania and Dangayach, 2023). Adopting traditional remedial systems alone would not be sufficient to remove inorganic contaminants. Therefore, developing a multi-layered permeable reactive barrier (PRB) incorporating CNTs can help ensure safe groundwater for community use (Chandrakanthamma and Prasanna, 2026).

Groundwater in tannery-contaminated regions tends to have high concentrations of chromium, sulfate, total dissolved solids, and dyes, requiring complex multi-step treatment processes (Jothilakshmi *et al.* 2019). Conventional domestic filters are not capable of removing both inorganic and organic contaminants, including heavy metals and industrial chemicals that are resistant to degradation. PRBs have emerged as a green and *in-situ* remediation technology because they are passive, efficient over time, and can treat complex mixtures of contaminants (Krishnan *et al.* 2026).

PRBs are a promising and efficient remedial technology for treating groundwater contamination; they use reactive materials that enable the simultaneous adsorption, reduction, precipitation, ion exchange, and biodegradation of contaminants as they pass through the barrier (Gholami *et al.* 2019). PRB materials comprised a combination of limestone powder, biochar, wood chips, zero-valent iron (ZVI), sand, and gravel, which were intended to target a broad spectrum of contaminants (Hidalgo *et al.* 2022). The addition of diluted potassium permanganate ($KMnO_4$) directly to the biochar is the innovative aspect, which gradually diffuses into the PRB. MWCNTs act as a secondary polishing step, carefully entrapping organics, dyes, and dissolved contaminants that manage to escape the PRB (Liu *et al.* 2019). A final nano-filtration membrane is employed to filter out CNT residues, colloidal particles, and microbial contaminants, thereby producing high-purity water (Ma *et al.* 2025).

While several studies have examined PRB systems or CNT-based adsorption separately, there is limited research on their combined use in a decentralized, in-house treatment setup specifically for tannery-impacted residential groundwater (Rajeshkumar *et al.* 2023). Additionally, the combined effects of $KMnO_4$-enhanced biochar in a multi-layer PRB with MWCNT adsorption and nanomembrane filtration have not been

thoroughly assessed for small-scale domestic applications. This study fills the gap by proposing and testing an innovative multi-barrier treatment method that is cost-effective for residential use in regions affected by industrial pollution.

The integrated $KMnO_4$-enhanced PRB-MWCNT adsorption-nanomembrane filtration system provides a multi-barrier treatment to remove all contaminants and enhance groundwater quality (Prabha and Selvaraj, 2026).

The scientific importance of this study lies in its examination of how contaminated water in residential areas affects public health. Contaminated water causes serious health issues such as diarrhea, food poisoning, and intestinal disorders. Because residential areas are located near industrial zones, the provision of drinking water for workers and residents becomes more costly (Rad and Fazlali, 2020). A cost-effective in-house solution has been proposed to enable the use of groundwater rather than relying on an external water supply (Sajid *et al.* 2022). The solution proposed in this study is recommended as a cost-effective approach for providing drinking water to the residents of Pallavaram (Selvaraj and Velvizhi, 2022).

2. MATERIALS AND METHODS

The methodology adopted in this study was designed to systematically evaluate groundwater contamination and to develop a reproducible multi-barrier remedial system. The overall methodological framework comprised site identification, systematic sampling, laboratory characterization, PRB media preparation, column experimentation, polishing treatment, and performance evaluation.

2.1 Groundwater Analysis

The most affected area for groundwater contamination was identified in the nearby locality of Pallavaram, Chennai, India, which is surrounded by tanneries. The level of contamination was assessed at various depths using boreholes and wells. Most of the samples taken from the bores and wells were not potable. The color and odor were unpleasant, with TDS of 1150–2400 Mg/L, BOD of 115–125 Mg/l, and COD of 300–340 Mg/L. 125 groundwater samples ranging from 20 ft to 400 ft were collected. Subsequently, the samples were analyzed in the laboratory for 26 parameters, and the contaminants were identified. Based on the contaminant levels, a solution was derived using a PRB with MWCNTs and a nanofiltration membrane.

Groundwater samples were collected in pre-cleaned 1 L HDPE bottles to ensure reproducibility. Before sampling, borewells were purged for 5–10 min to obtain representative aquifer samples. BOD samples were collected in airtight BOD bottles to avoid air entrapment. All samples were kept at 4 °C and transported to the lab within 6 h. Physicochemical parameters, including pH, TDS, and turbidity, were measured using calibrated digital instruments. BOD (Fig. 1) (5-day incubation at 20 °C) and COD (closed reflux method) were analyzed following standard procedures. Heavy metals were assessed using atomic absorption spectroscopy (AAS). Triplicate measurements were taken to ensure accuracy and consistency.



Fig. 1: BOD analysis

2.2 Permeable Reactive Barrier (PRB)

PRB is a multilayered material in which each layer has distinct physicochemical and biological properties (Chandrakanthamma and Prasanna, 2024).

To test the PRB, a laboratory-scale vertical column with controlled flow rates was designed. Each reactive layer was packed one after the other to a uniform thickness and compacted gently to avoid preferential flow. A constant flow rate was maintained to simulate the groundwater velocity under saturated conditions. Hydraulic retention time (HRT) was monitored to assess treatment efficiency.

2.2.1 Limestone Powder ($CaCO_3$)

Limestone powder ($CaCO_3$) is an alkaline material that neutralizes groundwater passing through this layer and partially dissolves $CaCO_3$, releasing Ca^{2+} and carbonate ions, which raise the alkalinity and pH values to a neutral to slightly alkaline range (pH = 7–7.5). The increase in pH promotes the precipitation of metal ions such as Fe^{2+}, Mn^{2+}, and Cr^{3+}, which form insoluble hydroxides at higher pH values.

2.2.2 Biochar

Biochar produced by pyrolysis of organic biomass and infused with $KMnO_4$ was treated using a combination of adsorption and advanced oxidation. Its

microporous structure and extensive surface area enable the adsorption of compounds, including dissolved organic matter and odor-causing volatile organic compounds (VOCs). $KMnO_4$ modifies biochar and initiates a powerful oxidation–reduction reaction. Then, the molecules form as carboxylic acids. This process reduces the BOD and COD levels and also provides microbial disinfection.

The biochar was produced through controlled pyrolysis at 450–550 °C in oxygen-limited conditions. $KMnO_4$ impregnation was performed using a dilute aqueous solution, then dried at ambient temperature before being packed into the PRB column (Fig. 2).

2.2.3 Wood Chips

Wood chips release carbon substrates, promoting sustained microbial growth and establishing a biologically active zone. The wood chips support the growth of sulfate-reducing bacteria, which facilitate the precipitation of metal ions. This process helps to reduce the sulfate concentrations. BOD and COD are also reduced as they pass through this wood-chip layer.



Fig. 2: PRB with layers

The wood chips were pre-washed and air-dried before use to remove fines and impurities. Biological activity was allowed to stabilize during an acclimatization period before performance monitoring.

2.2.4 Zero-valent Iron (ZVI)

ZVI reduces several contaminants, such as chromium. Due to the electrons produced, nitrite chromium undergoes reductive dichlorination, resulting in its precipitation. It enhances the reduction in biochemical sources. It produces flocs that facilitate the precipitation and adsorption of metals and phosphates.

Commercial-grade granular ZVI was sieved to achieve a uniform particle-size distribution prior to packing, ensuring consistent permeability.

2.2.5 Sand and Gravel

Sand and gravel layers ensure uniform water flow and prevent clogging. Coarse gravel improves permeability, and fine sand improves filtration by capturing suspended solids and silt. These two media facilitate the deposition of MnO_2 and $Fe(OH)_3$. It also reduces turbidity and removes the color. This layer facilitates adsorption, ion exchange, precipitation, and physical filtration.

Both sand and gravel were carefully washed and then oven-dried to eliminate fines, ensuring consistent hydraulic performance.

2.3 Polishing Stage Using MWCNTs

MWCNTs facilitate advanced adsorption to remove the residual contaminants remaining after PRB treatment. MWCNTs are characterized by their graphite walls, which enable strong adsorption of compounds and heavy metals. Their structural imperfections provide binding sites for pollutants and enhance hydrogen bonding. Due to residual COD and BOD levels following PRB treatment, the nanotube surface rapidly adsorbs and reduces their concentrations. CNTs trap extremely fine particles and reduce turbidity and color, making the water visibly clear and chemically stable.

The MWCNT adsorption unit operated in a fixed-bed setup with controlled flow rates. Contact time was optimized to achieve peak adsorption efficiency before membrane filtration.

2.4 Nanofiltration Membrane

The nanofiltration membrane has a very small mesh and pore size, enabling the filtration of nanoparticles released from MWCNTs. The treated water is passed through this membrane to ensure the complete removal of CNT particles. The final polishing of dissolved organics and color is carried out to achieve Indian drinking water standards. It also provides a safety barrier by removing nanomaterials and completing the treatment process.

The membrane system operated under steady pressure conditions, with permeate flux periodically monitored to assess fouling behavior and treatment stability.

2.5 Chlorination

Chlorination is a final step involved in disinfection. The treatment stages, PRB, MWCNT, nanofiltration, and chlorination, ensure microbial safety and remove unpleasant odor. It is cost-effective, more reliable, and kills all waterborne bacteria (Selvaraj and Velvizhi, 2023). The chlorine tablets were added at the calculated dose of 1–2 mg/L. The minimum contact time for chlorination to achieve rapid microbial inactivation is 30 min.

Residual chlorine levels were measured after the contact period to ensure adherence to drinking water standards and prevent overdosing.

2.6 Innovation

In this remedial system, the innovation included a PRB with a layer of potassium permanganate infused with biochar. Subsequently, the MWCNT was passed through a nanofilter to remove nanoparticles that might be harmful upon consumption.

The integrated configuration was assessed as a decentralized, in-house treatment approach, confirming its technical feasibility, ease of operation, and reproducibility under controlled laboratory settings.

3. RESULTS AND DISCUSSION

3.1 Outcome of Permeable Reactive Barrier (PRB)

The PRB system, incorporating limestone powder, biochar infused with potassium permanganate, wood chips, ZVI, sand, and gravel, significantly improves groundwater quality. Initially, the raw water parameters indicate high contamination, with COD (315 mg/L), BOD (120 mg/L), color (118 Pt–Co units), turbidity (16 NTU), sulfates (61 mg/L), iron (1.09 mg/L), and chromium (0.19 mg/L). After PRB treatment, a significant reduction is observed due to the combined actions of the PRB.

The treatment effectiveness is evident from measurable decreases in key physicochemical parameters, highlighting the efficiency of the multi-layer PRB system.

Limestone powder raised the pH from 6.5 to 7.2, thereby improving metal precipitation and reaction reduction. Chromium contents were reduced from 0.19 to 0.02 mg/L, along with the decreased iron value. Biochar coated with $KMnO_4$ improved oxidative degradation. COD reduced from 315 to 72 mg/L and BOD from 120 to 25 mg/L. Biochar is also responsible for the color and odor. Wood chips release carbon source and promote sulfate-reducing bacteria. The sulfate concentration decreased from 61 to 28 mg/L. Sand and gravel improved clarity from 16 NTU to 4 NTU by removing suspended solids.

Contaminant removal in the PRB involves several mechanisms: (i) heavy metals precipitate at higher pH due to $CaCO_3$ dissolution, (ii) chromium is reduced by ZVI, (iii) organic pollutants undergo advanced oxidation via $KMnO_4$-modified biochar, (iv) microbial sulfate reduction in the wood chip layer produces insoluble metal sulfides, and (v) physical filtration and adsorption occur in sand and gravel layers. Together, these physicochemical and biological processes work synergistically to improve overall removal efficiency.

Compared to Indian drinking water standards (BIS 10500), the post-PRB turbidity (4 NTU) was nearly within acceptable limits, chromium (0.02 mg/L) was within permissible levels, and sulfates (28 mg/L) remained well below the maximum allowed concentration. However, further treatment was needed for COD and BOD, indicating the necessity for additional polishing stages.

3.2 Efficacy of MWCNT Polishing Stage

MWCNTs enhance water quality by providing a high surface area and strong adsorption capacity for residual pollutants. They reduce COD, BOD, color, and turbidity to levels that meet Indian water quality standards. It enhances the water quality by polishing, and it also reduces the iron and chromium to negligible levels (Selvaraj and Velvizhi, 2021; Krishnan *et al.* 2026).

The polishing stage greatly enhances treatment effectiveness by lowering residual organic materials to safe drinking water levels. The high surface area and π–π interactions of MWCNTs facilitate the adsorption of dissolved organic compounds and trace metals that bypass PRB treatment. This step is vital for meeting drinking water standards, especially for reducing COD, BOD, and color.

3.3 Nanofiltration for CNT Retention and Clarification

MWCNTs produce numerous nanoparticles that may be harmful upon ingestion. Therefore, nanofiltration removes and retains all nanoparticles, making the water safe to drink. The nanofiltration also reduces manganese and removes fluoride (Song *et al.* 2021).

The nanofiltration membrane functions as a barrier that filters based on size and charge, blocking nanoparticle passage and fully retaining CNT residues. It also partially rejects divalent ions such as Mn^{2+} and F^- due to its selectivity, thereby enhancing water quality and helping to meet drinking water standards.

3.4 Final Disinfection

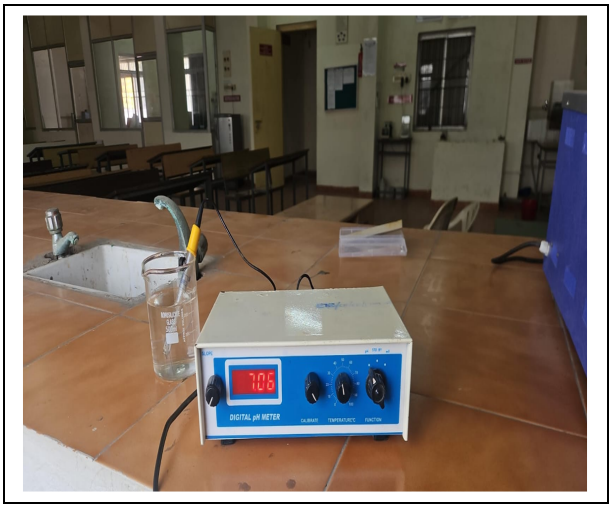


Fig. 3: Testing after treatment

Chlorination is the final step in water disinfection to ensure microbial safety. The minimal dosage was maintained for 30 min of contact time to ensure complete bacterial removal (Fig. 3).

Residual chlorine levels were kept within recommended limits to ensure effective microbial inactivation without overdosing. The final treated water met all microbiological standards for drinking water.

Overall, the combined system reduces all the major contaminants. All processes were integrated into a multi-barrier treatment system for contaminated groundwater.

The measured improvements in all parameters verify that the combined PRB–MWCNT–nanofiltration–chlorination system provides a thorough multi-barrier treatment solution.

4. MACHINE LEARNING

Based on the study, a predictive model was developed using Java and Python scripts to classify water quality as potable or non-potable. The predictive model was developed using four parameters: pH, TDS, BOD, and COD. 125 samples were collected and tested, with approximately 50 used for machine learning training. Once the values for these parameters are uploaded, either manually or via a file, subsequently, the water quality will be classified, and treatment recommendations, including recommended filtration sequences and expected final parameters, will be presented. This machine learning approach will be used for classification (Fig. 4), estimation of expected contamination levels before treatment, and prediction of treatment outcomes. This system helps in real-time potability analysis. The inputs can be in various document formats, including MS Word and MS Excel. During execution, the model compares pre- and post-parameters and classifies the water's potability (Yin *et al.* 2020).

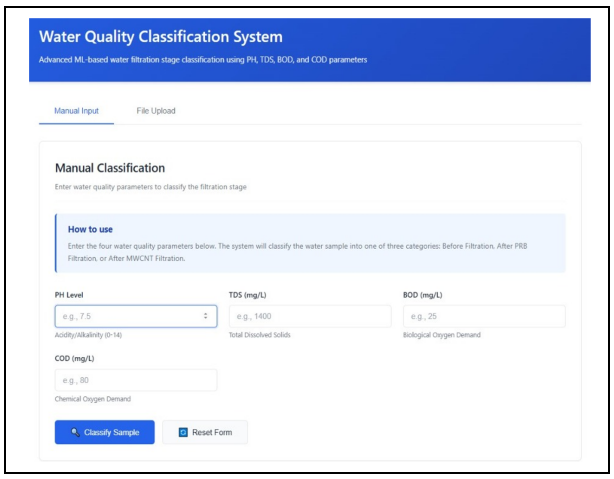


Fig. 4: Water quality classification system

Adding machine learning enhances the study by combining predictive analytics with environmental remediation, making it an innovative and engaging development.

It will provide a predictive remedial measure for groundwater treatment, thereby reducing remediation time. The ML test results were manually verified and correlated with 30 samples. 80% of the results matched the ML predictions.

For validation, the dataset included 125 samples, 50 for training, and the rest for testing and validation are shown in Fig. 5. The model's performance was assessed by comparing its predictions to laboratory-confirmed results. An 80% accuracy demonstrates decent predictive ability, but increasing the dataset size and applying cross-validation would improve the model's robustness and generalizability.

The results show in the Fig. 6 are the combined filtration process reduces contamination levels. Finally, chlorination was performed after multi-stage treatment. The system achieved high performance, delivered good results, and operated with simplicity, making it suitable for remediation.

Overall, the treatment performance shows significant improvement, with COD reduced from 315 to 7 mg/L, BOD from 120 to 3 mg/L, and turbidity from 10 to 0.1 NTU after PRB–MWCNT treatment. Sulfates decreased from 684 to 230 mg/L, while chromium and iron were reduced from 0.73 to 0.01 mg/L and 2.2 to 0.05 mg/L, respectively, meeting BIS limits. Although TDS (1430 mg/L), hardness (310 mg/L), alkalinity (540 mg/L), and chloride (890 mg/L) remain above desirable limits, they fall within permissible limits. The above values are indicated in the table 1.

Table 1. Water quality parameters at different treatment stages and comparison with BIS standards

Parameter	Unit	Before PRB	After PRB	After MWCNT	BIS Acceptable Limit	BIS Permissible Limit
Color	Hazen	117.4	18	8	5	15
Odor	–	Non-agreeable	Agreeable	Agreeable	Agreeable	Agreeable
pH	–	8	7.9	7.2	6.5	8.5
Turbidity	NTU	10	1.2	0.1	1	5
TDS	mg/L	2200	1450	1430	500	2000
Electrical Conductivity	µS/cm	4231	2850	2000	–	–
Total Hardness	mg/L	630	410	310	200	600
Sulfates	mg/L	684	310	230	200	400
Iron	mg/L	2.2	0.12	0.05	0.3	No relaxation
Fluoride	mg/L	0.79	0.6	0.5	1	1.5
Chromium	mg/L	0.73	0.01	0.01	0.05	No relaxation
Total Suspended Matter	mg/L	715	35	20	–	–
Total Alkalinity	mg/L	700	650	540	200	600
Phenolphthalein Alkalinity	–	Colour changed	Colour unchanged		–	–
Calcium Hardness	mg/L	320	300	260	–	–
Magnesium Hardness	mg/L	256	180	110	–	–
Magnesium	mg/L	62.5	40	40	30	100
Calcium	mg/L	154	165	165	75	200
Chloride	mg/L	1125	1080	890	250	1000
Residual Free Chlorine	mg/L	0	0	0	0.2	1
Total Solids	mg/L	1150	520	300	–	–
Carbonate Hardness	mg/L	320	310	300	–	–
Non-carbonate Hardness	mg/L	321	180	175	–	–
Acidity	mg/L	5	3		–	–
BOD	mg/L	120	12	3	≤ 2 (drinking)	–
COD	mg/L	315	40	7	≤ 10 (drinking)	–



Fig. 5: Recommended filtration sequence

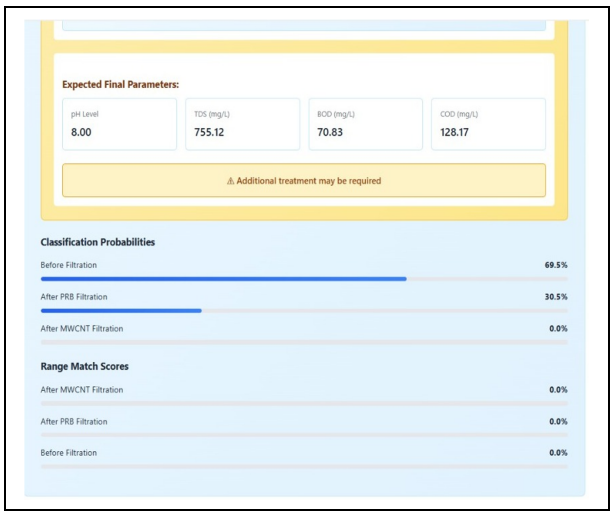


Fig. 6: Expected final parameters

5. CONCLUSION

This study demonstrated an integrated, multi-layered system comprising a Permeable Reactive Barrier (PRB), a multi-walled carbon nanotube (MWCNT) polishing column, nanofiltration, and chlorination for effective remediation of contaminated groundwater.

This study confirms that a hybrid system offers a sustainable and feasible approach for treating contaminated groundwater, particularly in regions such as Pallavaram, Chennai, India, where urbanization and industrial activities have increased contamination. The study incorporates low-cost reactive media and advanced nanotechnologies.

The conclusions align with the experimental results, showing substantial reductions in COD, BOD, turbidity, sulfates, iron, and chromium, thereby meeting drinking water standards. The multi-barrier setup confirmed that integrating physicochemical, biological, and nanotechnological methods within one treatment process is an effective framework.

The combined PRB–MWCNT–nanofiltration system offers a technically reliable, cost-effective, and scalable in-house solution for remediating contaminated groundwater.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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