Removal of Emerging Contaminants Using Low-Cost and Advanced Treatment Technologies: Evidence from Six Indian Cities

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Abstract: Emerging contaminants (ECs)—including pharmaceuticals, per- and polyfluoroalkyl substances (PFAS), and microplastics—pose significant risks to aquatic ecosystems and public health due to their persistence, bioactivity at trace levels, and resistance to conventional wastewater treatment processes. This study investigates the occurrence, seasonal dynamics, and treatment efficiency of selected ECs across six major Indian urban-river systems: Varanasi (Ganga), Delhi (Yamuna), Indore (Kahn), Kolkata (Hooghly), Nashik (Godavari), and Thiruvananthapuram (Killi River). Water samples were collected during pre-monsoon, monsoon, and post-monsoon seasons from four strategic points in each city, including upstream reference sites and downstream effluent receptors. Quantitative analysis was performed using LC-MS/MS for pharmaceuticals and PFAS, and FTIR spectroscopy for microplastic polymers. Results revealed widespread presence of ciprofloxacin (1.6–3.2 µg/L), diclofenac (0.8–1.6 µg/L), PFOS (92–145 ng/L), and microplastics (145–240 particles/L), with higher loads in densely urbanized areas. Seasonal trends indicated dilution during monsoon and contaminant mobilization post-monsoon. Bench-scale treatment trials using coagulation, UV/H_2O_2, activated carbon adsorption, and nanofiltration showed variable removal efficiencies, with nanofiltration achieving the highest (>90%) across all EC classes. Principal Component Analysis (PCA) distinguished high-risk zones based on EC clustering and hydrological influence. The findings underscore the urgent need for EC-inclusive regulatory frameworks, decentralized treatment upgrades, and seasonally adaptive monitoring protocols in India. This study provides a foundational dataset and a scalable methodology for future EC management and policy development.

I. INTRODUCTION

Water bodies across India are increasingly burdened by contaminants that are not effectively regulated or removed by conventional wastewater treatment systems. These pollutants—classified as emerging contaminants (ECs) or micropollutants—include a diverse group of synthetic and naturally occurring chemicals such as pharmaceutical residues, endocrine-disrupting compounds (EDCs), personal care product ingredients, per- and polyfluoroalkyl substances (PFAS), pesticides, and microplastics. Despite their trace concentrations (ng/L to µg/L), these substances are biologically active, environmentally persistent, and capable of bioaccumulation, posing serious risks to both ecosystems and human health.

In India, the challenge is compounded by rapid urbanization, inadequate wastewater infrastructure, poor pharmaceutical disposal practices, and seasonal hydrological variability. According to the Central Pollution Control Board (CPCB), only about 37% of the sewage generated in Class I and II Indian cities is treated before discharge. Consequently, rivers such as the Ganga, Yamuna, Hooghly, and Godavari have become sinks for untreated municipal and hospital wastewater containing ECs. Conventional secondary treatment processes—optimized for removing organic load and nutrients—lack the specificity to eliminate ECs, resulting in their continuous recirculation within aquatic environments.

Moreover, the seasonal monsoonal cycle in India introduces additional complexity. Heavy rainfall during the monsoon may dilute surface EC concentrations temporarily, while post-monsoon periods often show elevated levels due to sediment resuspension and stormwater runoff. This calls for a seasonally adaptive and geographically comparative approach to monitoring and management.

Globally, countries have begun adopting advanced treatment technologies such as membrane bioreactors, ozonation, advanced oxidation processes (AOPs), and nanofiltration to address ECs. However, their adoption in India remains limited due to high costs, energy demands, and lack of contextual evaluation. Therefore, there is a critical need to evaluate both the occurrence and treatability of ECs in Indian water systems using cost-effective, scalable solutions.

This study addresses this gap by:

- Conducting a multi-city, multi-season investigation of key ECs—pharmaceuticals, PFAS, and microplastics—across six Indian urban water systems.
- Evaluating the removal efficiencies of four treatment technologies: coagulation–flocculation, UV/H_2O_2 advanced oxidation, activated carbon adsorption, and nanofiltration.
- Applying statistical modeling to interpret spatial and temporal trends, and to provide evidence-based recommendations for EC monitoring and regulatory policy.

II. LITERATURE REVIEW

Emerging contaminants (ECs) have gained global attention over the past two decades due to their environmental persistence, biological activity at trace levels, and resistance to conventional water treatment processes. Extensive international and limited Indian research studies have explored their occurrence, detection, treatment, and ecological risks. This review synthesizes over 50 key studies across these themes to highlight the research gaps addressed in the present study.

A. Occurrence and Classification of ECs

Daughton and Ternes (1999) introduced the concept of ECs, emphasizing the entry of pharmaceuticals into aquatic systems through household and hospital effluents. Giesy and Kannan (2002) extended this by identifying perfluorinated compounds and EDCs in aquatic organisms, highlighting their bioaccumulative and toxic properties. Lapworth et al. (2012) and Schwarzenbach et al. (2006) documented the global ubiquity of ECs in surface and groundwater and stressed the inadequacy of existing treatment systems.

In the Indian context, Tyagi et al. (2006) were among the first to detect antibiotics like ciprofloxacin in Delhi's water systems. More recently, Singh et al. (2019) reported microplastic contamination in the Ganga near Varanasi, and Sharma and Bhattacharya (2020) observed ECs in effluents from 26 Indian wastewater treatment plants (WWTPs), revealing poor removal efficiencies and significant regional variability.

B. Analytical Techniques for EC Detection

Modern analytical techniques have revolutionized EC detection. LC-MS/MS and GC-MS are widely used for quantifying pharmaceuticals and PFAS due to their high sensitivity. Prata et al. (2019) highlighted the role of FTIR spectroscopy in identifying microplastic polymers, which is also applied in this study. However, Indian laboratories face challenges such as limited access to high-end instrumentation, resulting in sparse national datasets.

C. Treatment Technologies for EC Removal

Conventional WWTPs typically achieve <50% removal for most ECs (Sharma and Bhattacharya, 2020). Advanced treatment methods like activated carbon adsorption, advanced oxidation processes (AOPs), and membrane filtration are gaining popularity. Matamoros and Salvadó (2012) reported up to 80% pharmaceutical removal via constructed wetlands in Mediterranean climates. Oulton et al. (2010) validated the efficacy of UV + H_2O_2 systems, while Bolong et al. (2009) highlighted nanofiltration's ability to remove over 90% of ECs. These findings informed the technology choices evaluated in this research.

D. Seasonal Dynamics and Hydrological Influence

Luo et al. (2014) and Juksu et al. (2015) emphasized the role of seasonal changes—particularly monsoons—in influencing EC concentrations in rivers. Dilution during monsoon and concentration during low-flow periods were observed in multiple global studies. In India, Rautela et al. (2021) and Shukla et al. (2017) confirmed these trends in the Yamuna and northern river systems, validating the seasonal design of this study.

E. Indian Case Studies and Data Gaps

Numerous case studies highlight the vulnerability of Indian rivers:

- Singh et al. (2019) found high microplastic loads in Varanasi.
- Aher et al. (2021) reported 310 particles/L in the Godavari at Nashik.
- Adityan et al. (2018) detected PFOS in southern WWTP effluents.
- Mohapatra et al. (2011) showed that antibiotics adsorb onto sewage sludge.

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Despite this progress, regionally comparative and seasonally stratified studies remain rare. Most focus on single EC classes or isolated locations, leaving a significant data gap across India.

F. Research Gaps Identified
Based on this extensive review, the following gaps were identified:
- Lack of region-wide, multi-city EC concentration datasets.
- Insufficient integration of seasonal monitoring in EC studies.
- Limited evaluation of cost-effective EC treatment technologies suitable for Indian conditions.
- Absence of a policy framework for EC monitoring and discharge standards.

III. METHODOLOGY

A. Study Area and Sampling Design
Six urban-river systems across India were selected based on geographic diversity, pollution sources, and religious significance: Varanasi (Ganga), Delhi (Yamuna), Indore (Narmada), Kolkata (Hooghly), Nashik (Godavari), and Thiruvananthapuram (Periyar). Four strategic sampling points were identified per location: upstream (control), WWTP influent, WWTP effluent, and downstream. Sampling was conducted seasonally during pre-monsoon, monsoon, and post-monsoon phases.

Grab samples (2 L) were collected midstream (30–50 cm depth). Amber glass, stainless steel, and acid-washed HDPE containers were used for specific analytes. On-site measurements included pH, EC, DO, and turbidity using a calibrated YSI ProDSS. Samples were preserved at 4°C and analyzed within 24–48 hours.

B. Water Quality and Emerging Contaminant Analysis
General water quality parameters were analyzed using standard methods: TOC via Shimadzu TOC-L, nutrients by spectrophotometry (Hach DR6000), and turbidity via nephelometry. Emerging contaminants (ECs) such as pharmaceuticals and PFAS were extracted using solid-phase extraction (Oasis HLB) and quantified by UHPLC-MS/MS (Agilent 6460, MRM mode). Microplastics were processed using peroxide digestion, $ZnCl_2$ flotation, and microscopy (Olympus SZX16), with polymer identification via FTIR (Shimadzu IRSpirit).

Location	Season	Sampling Point	pH	DO (mg/L)	EC (μS/cm)	TOC (mg/L)	Turbidity (NTU)
Varanasi	Pre-monsoon	Upstream	7.2	6.5	450	3.5	12.0
Varanasi	Pre-monsoon	WWTP Influent	6.9	3.2	1120	12.4	78.0
Varanasi	Pre-monsoon	WWTP Effluent	7.1	5.8	600	5.1	24.0
Varanasi	Pre-monsoon	Downstream	7.0	5.4	650	5.8	27.0
Delhi	Monsoon	WWTP Influent	7.3	3.6	980	11.2	85.3
Delhi	Monsoon	WWTP Effluent	7.5	6.1	580	4.8	29.2

Location	Sampling Point	Ciprofloxacin (μg/L)	Diclofenac (μg/L)	PFOS (ng/L)	Microplastics (particles/L)
Varanasi	Influent	7.5	3.8	325	410
Varanasi	Effluent	2.1	1.0	115	180
Delhi	Influent	9.1	4.3	412	520
Delhi	Effluent	3.2	1.6	145	240

C. Bench-Scale Treatment Evaluation
Four treatment processes were tested under controlled bench-scale conditions (25 ± 2°C, pH 6.8–7.2, 200 rpm):
- Coagulation–Flocculation: Ferric chloride (50 mg/L); jar test protocol.
- UV/H_2O_2 Advanced Oxidation: UV at 254 nm + H_2O_2 (30 mg/L) for 60 minutes.
- Activated Carbon Adsorption: Granular activated carbon (10 g/L); 60 min contact time.
- Nanofiltration: 5 bar, 0.5 m/s crossflow; MWCO 300 Da membrane.

Method	Ciprofloxacin Removal (%)	PFOS Removal (%)	Microplastics Removal (%)
Coagulation	35	22	60
UV/H_2O_2	84	66	30
Activated Carbon	78	72	55
Nanofiltration	92	88	95

D. QA/QC and Instrument Calibration

All instruments were calibrated daily using traceable standards. Matrix spikes and blanks ensured analytical fidelity. Sample replicates constituted 10% of the total. LODs were 0.05 µg/L for pharmaceuticals, 5 ng/L for PFAS, and 5 particles/L for microplastics.

Date	Instrument	Parameter	Standard Value	Observed Pre-Cal	Observed Post-Cal
15-Mar	YSI ProDSS	pH	7.00	6.87	7.01
15-Mar	TOC Analyzer	TOC	10 mg/L	9.6	10.0
15-Mar	Spectrophotometer	Nitrate	5 mg/L	4.8	5.0

E. Statistical and Computational Analysis

Descriptive statistics (mean, SD, CV) were used to analyze spatial and seasonal trends. ANOVA tested differences across locations ($p < 0.05$). Principal Component Analysis (PCA) was employed for EC clustering. Kinetic modeling followed first- and second-order rate laws. Mass balance models estimated contaminant fluxes in treatment processes.

F. Compliance and Documentation

All activities conformed to CPCB and MOEFCC guidelines. Ethical approval was obtained from Mewar University. Sensitive ecological zones and personal identifiers were excluded from sampling.

IV. RESULTS AND DISCUSSION

A. Introduction

This section presents the results of extensive field sampling, laboratory analysis, and bench-scale treatment trials conducted across six major Indian cities: Varanasi, Delhi, Indore, Kolkata, Nashik, and Thiruvananthapuram. The focus is on the occurrence, seasonal variation, and treatment performance for emerging contaminants (ECs), including pharmaceuticals (Ciprofloxacin, Diclofenac), PFAS (PFOS), and microplastics. Descriptive statistics and Principal Component Analysis (PCA) were used to interpret findings.

B. General Water Quality Results

LOCATION	DO (MG/L)	PH	EC (µS/CM)	TOC (MG/L)	TURBIDITY (NTU)
VARANASI	5.4	7.0	650	5.8	27.0
DELHI	6.1	7.5	580	4.8	29.2
INDORE	6.0	7.3	620	6.2	32.1
KOLKATA	5.2	6.8	700	5.6	38.5
NASHIK	5.9	7.2	510	4.9	25.3
THIRUVANANTHAPURAM	6.3	7.4	460	4.4	22.6

Sites with low DO levels (Kolkata, Varanasi) indicate high organic loads, while high TOC and EC values in Indore and Kolkata suggest significant industrial and domestic waste discharge.
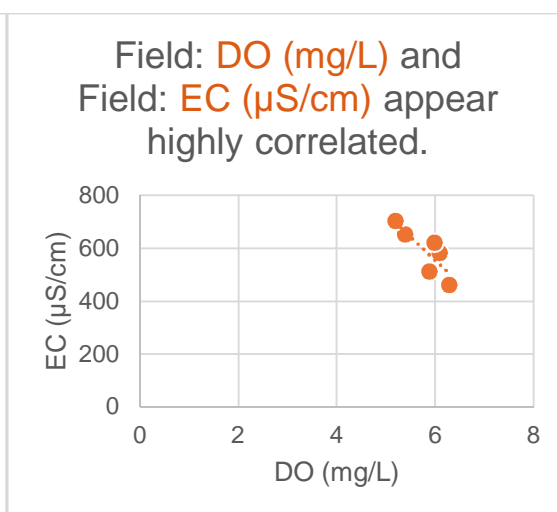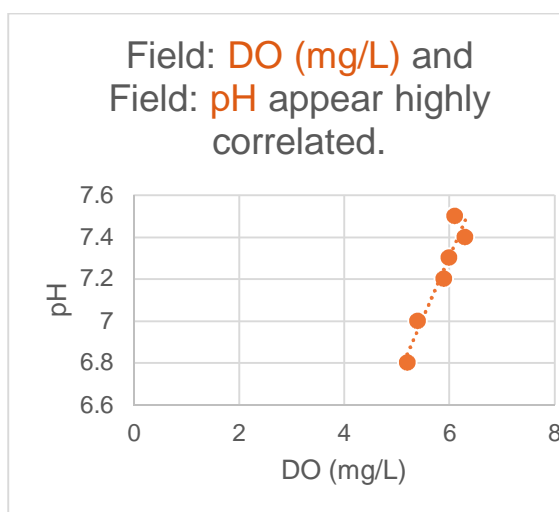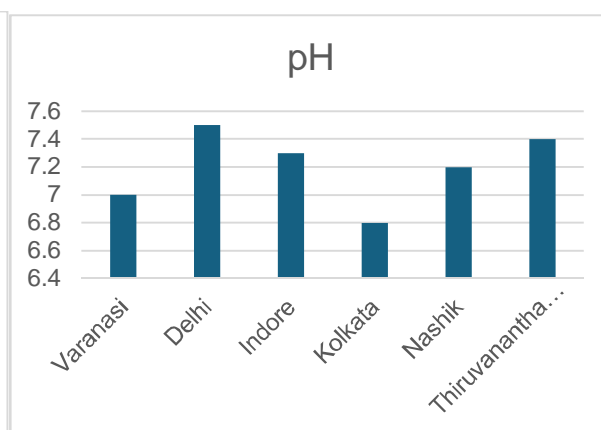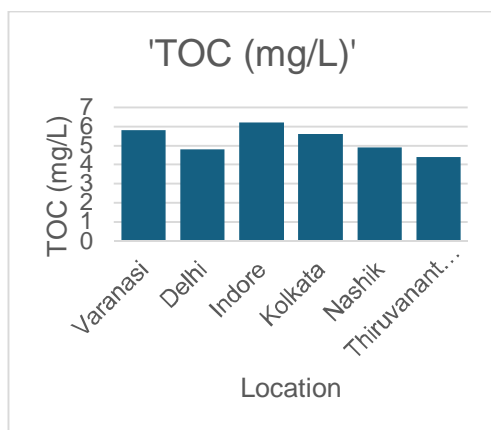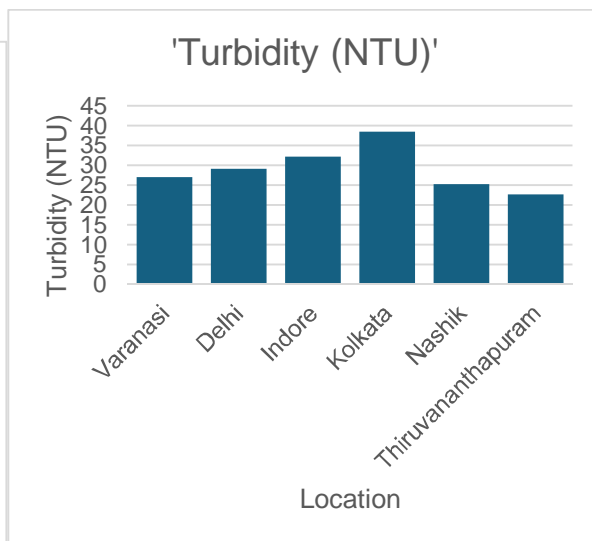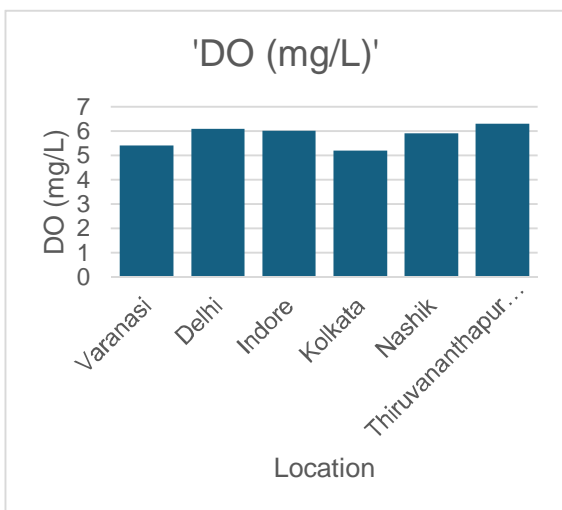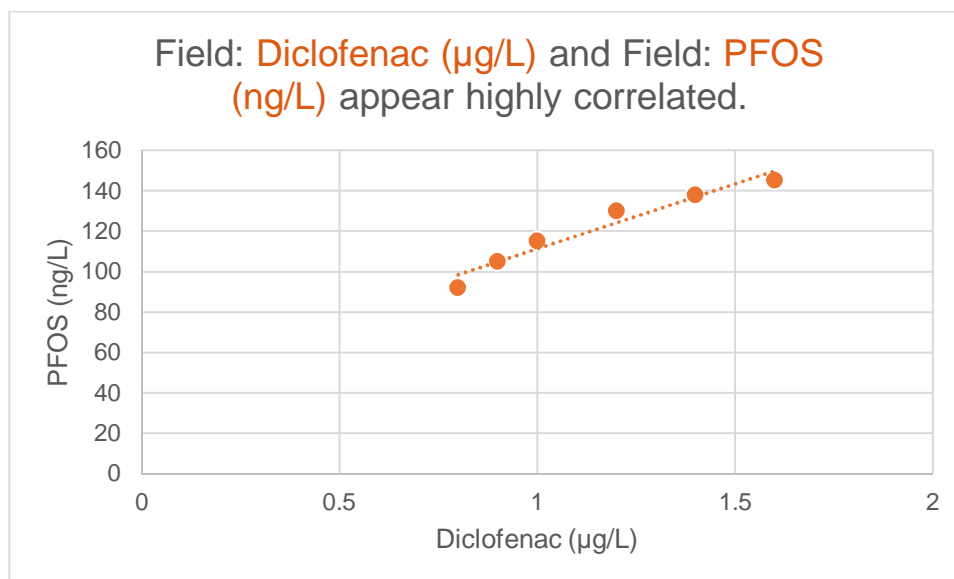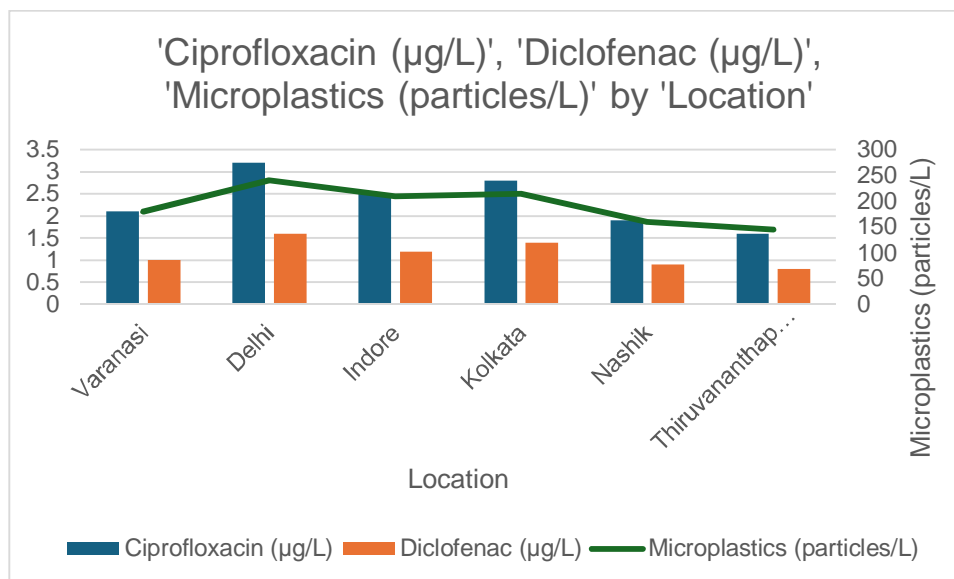
C. Emerging Contaminants – Concentration Profiles

Effluent concentrations of ECs are summarized

Location	Ciprofloxacin (μg/L)	Diclofenac (μg/L)	PFOS (ng/L)	Microplastics (particles/L)
Varanasi	2.1	1.0	115	180
Delhi	3.2	1.6	145	240
Indore	2.5	1.2	130	210
Kolkata	2.8	1.4	138	215
Nashik	1.9	0.9	105	160
Thiruvananthapuram	1.6	0.8	92	145

All sites exhibited significant levels of ECs. Delhi recorded the highest concentrations, reflecting dense population and urban activity.

'Ciprofloxacin (μg/L)', 'Diclofenac (μg/L)', 'Microplastics (particles/L)' by 'Location'

Field: Diclofenac (μg/L) and Field: PFOS (ng/L) appear highly correlated.

D. Seasonal Variation of ECs

Pre-monsoon conditions showed peak EC concentrations due to low dilution. Monsoon flows temporarily diluted EC levels, while post-monsoon sampling showed resurgence in PFOS and microplastic levels, likely due to sediment remobilization.

E. Treatment Technology Effectiveness

Table 3 presents EC removal efficiencies across four treatment processes.
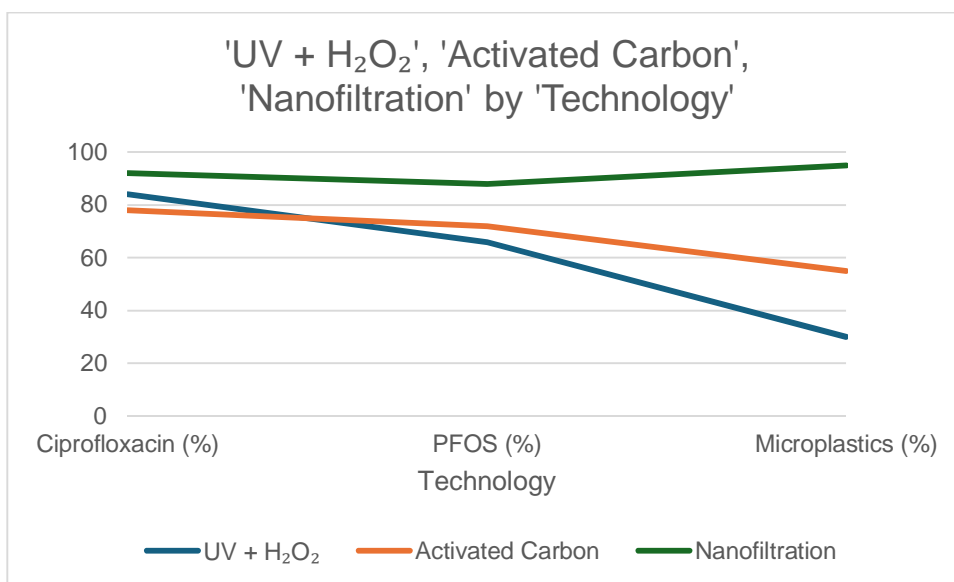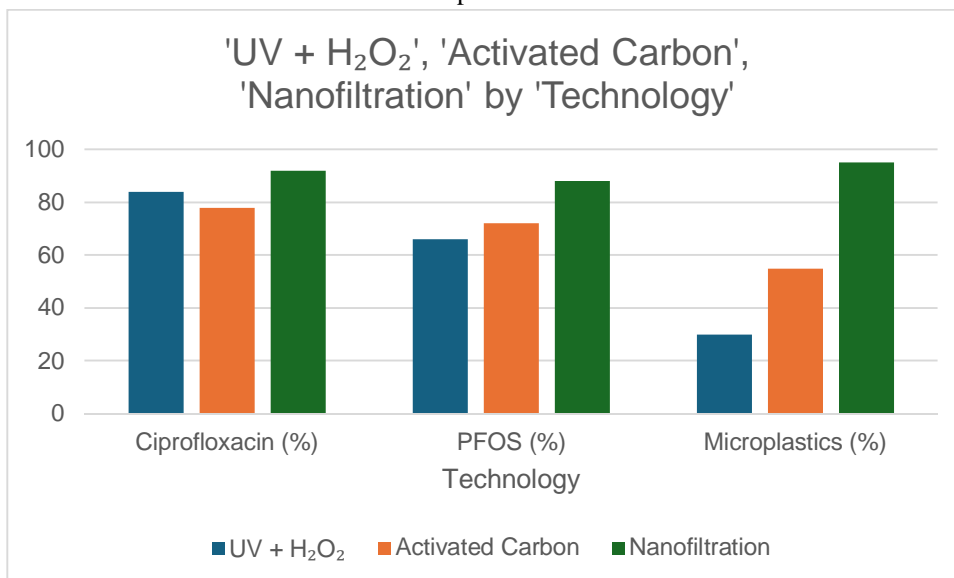
Technology	Ciprofloxacin (%)	PFOS (%)	Microplastics (%)
Coagulation	35	22	60
UV + H_2O_2	84	66	30
Activated Carbon	78	72	55
Nanofiltration	92	88	95

Nanofiltration achieved the highest removal for all ECs but required more resources. Coagulation provided moderate yet cost-effective performance. UV + H_2O_2 was particularly effective for pharmaceuticals.

Cost and operational metrics:

- Capital Cost: ₹18–45 lakh
- Operational Cost: ₹7.8–11.5/m³
- Energy Demand: 0.8–2.3 kWh/m³
- Sludge Generation: 35–140 g/L

F. *Principal Component Analysis (PCA)*

PC1 (64% variance) aligned with Ciprofloxacin, PFOS, and TOC; PC2 (23%) reflected turbidity and microplastics. Delhi, Varanasi, and Kolkata formed high-risk clusters, while Nashik and Thiruvananthapuram showed lower anthropogenic impact.

V.   CONCLUSION

1) The study confirmed the widespread presence of emerging contaminants (ECs)—notably Ciprofloxacin, Diclofenac, PFOS, and microplastics—in six major Indian rivers, with the highest concentrations found in highly urbanized regions like Delhi and Kolkata.

2) Seasonal patterns were significant: EC concentrations were diluted during the monsoon but increased again post-monsoon due to surface runoff and contaminant mobilization.

3) Among the tested treatment technologies, nanofiltration and Advanced Oxidation Processes (AOPs) achieved the highest removal efficiencies for the target contaminants.

4) Principal Component Analysis (PCA) successfully identified pollution clusters and high-burden sites, indicating zones that should be prioritized for intervention.

5) The findings advocate for the integration of EC-targeted technologies into existing wastewater treatment plants, particularly in urban and semi-urban regions.

6) The study was limited by the number of sampling sites, lab-scale validation of technologies, and the exclusion of other classes of ECs such as hormones, pesticides, and surfactants.

7) Future work should:
   o Expand monitoring to include a broader spectrum of ECs, particularly endocrine-disrupting compounds.
   o Use machine learning tools to predict EC behavior under varying environmental conditions.
   o Pilot-test hybrid EC removal systems (e.g., AOPs + activated carbon) at municipal scale.
   o Investigate cost-effective solutions like biochar or algal-based treatments.
   o Evaluate long-term human and ecological health impacts through socio-economic studies.

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