



Original Research Paper

Seasonal Water Quality Assessment of the Ayad River and Remediation Potential of Sunlight-Driven TiO₂ Photocatalysis: A Comparative Pre- and Post-Treatment Study

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Abstract

Urban and peri-urban rivers in semi-arid regions are increasingly endangered by continuous anthropogenic discharge and seasonal hydrological extremes. The Ayad River in Udaipur, Rajasthan, follows this pattern of progressive water quality decline. This study compares variation of seasons in the physicochemical quality of Ayad River water and investigated sunlight-driven TiO₂ photocatalysis as a supplementary treatment measure.

A pronounced seasonal increase in organic and nutrient pollution was depicted during summer, alongside a consistent upstream-to-downstream spatial gradient of anthropogenic impact. Photocatalytic treatment reduced BOD by approximately 35-61% and produced proportionally greater reductions in COD (33-60%), indicating oxidation of both biodegradable and recalcitrant organic fractions. Nitrate attenuation was most pronounced at high-load sites (up to 88% at Sukha Nala), while dissolved oxygen improved at every site (6-67% increase). Treatment efficiency scaled positively with initial pollutant concentration, whereas major inorganic ions and hardness constituents remained largely unchanged. Seasonal hydrology and cumulative urban discharge are the principal determinants of pollutant dynamics in the Ayad River. Although photocatalysis alone cannot ensure compliance with potable water standards, it represents a viable, low-energy, complementary intervention within an integrated river management strategy for semi-arid urban catchments.

Keywords: Ayad River; water quality; TiO₂ photocatalysis; advanced oxidation process; BOD/COD reduction; semi-arid urban rivers; seasonal pollution; solar remediation

1. Introduction

Freshwater systems are under pressure from urbanisation, population growth, and land-use change, on rivers as the principal source of agricultural, domestic, and industrial water demand (Pareta et al., 2024). In basins where wastewater is untreated or only partially treated, chronic exceedance of physicochemical thresholds and the entry of emerging contaminants are increasingly reported, with pronounced impacts in low- and middle-income regions where infrastructure development lags behind demographic change (Bharadwaj et al., 2025). Concurrently, evidence for visible-light-driven advanced oxidation processes (AOPs)-most notably TiO₂-based photocatalysis-continues to accumulate, depicting that refractory organic pollutants may be degraded via solar-assisted reactions (Malato et al., 2009; Chong et al., 2010). In Rajasthan, the semi-arid basins collection of low base flow and heavy reliance on surface water intensifies this seasonal sensitivity (Pareta, 2024).

Many investigations have recorded several gradients of nitrate, salinity, and fluoride across the basin, elevated organic loads downstream of industrial discharge points, and cumulative degradation in the linked urban lake network (Pareta et al., 2024; Bharadwaj et al., 2025). Conventional treatment trains-screening, coagulation-flocculation, sedimentation, and chlorination-remain the dominant management response, yet these processes are poorly suited to dissolved organics, trace contaminants, and chemically recalcitrant compounds, and chlorination itself carries the risk of disinfection by-product formation. Fujishima & Honda, 1972; Chong et al., 2010 concluded that TiO₂ generates electron-hole pairs which produces hydroxyl radicals and other reactive oxygen species capable of oxidising a broad spectrum of organic pollutants, including those resistant to biological degradation. Most photocatalytic studies till date have been done on synthetic or single-contaminant materials under in presence of artificial irradiation, leaving a gap in the evidence base for real, seasonally variable river water treated under natural sunlight.

This study addresses that gap by (i) characterising seasonal and spatial variation in the physicochemical quality of the Ayad River across four representative sites, and (ii) quantifying pre- and post-treatment differences to evaluate treatment efficiency and its dependence on initial pollutant load. The observations informs the evidence-based, seasonally aware remediation planning for the Ayad basin and comparable semi-arid urban river systems.

2. Materials and Methods

2.1 Study Area

The study was conducted on the Ayad River system in Udaipur district, Rajasthan, India-a semi-arid, urbanising catchment subject to residential, industrial, and peri-urban agricultural pressure, ultimately discharging into the Udaisagar Lake system. Regional rainfall is dominated by the southwest monsoon,

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producing marked seasonal contrast in river discharge and, consequently, in water quality. The Ayad basin was selected because it typifies the pollution dynamics of semi-arid urban river systems in India and because prior groundwater and surface-water investigations have documented progressive quality decline warranting focused remedial assessment (Pareta et al., 2024).

2.2 Sampling Strategy and Design

Four sites spanning the upstream-to-downstream continuum were sampled to observe a gradient of various influence: Thur-Madar (upstream reference), Ayad (urban corridor), Kanpur Mahadev/Kaldwas (industrial zone), and Sukha Nala/Udaisagar (downstream cumulative receptor). Sampling was carried out during two contrasting hydrological periods-summer (May 2025) and pre-monsoon (July 2025)-to capture both low-flow and transitional conditions. A comparative, before-after experimental design was used: at each site and season, water was collected in pre-cleaned polyethylene containers, with pH and temperature recorded in situ, transported under cooled conditions, and analysed promptly using standardised methods.

2.3 Physicochemical Analysis

Thirteen parameters were analysed for each sample: pH, electrical conductivity, total dissolved solids (TDS), chloride, sulphate, nitrate, total hardness, calcium, magnesium, fluoride, biochemical oxygen demand (BOD₅, 27°C), chemical oxygen demand (COD), and dissolved oxygen (DO). Instrument calibration and duplicate analyses were performed routinely to ensure analytical reliability.

2.4 Photocatalytic Treatment Procedure

Photocatalytic treatment was performed in a batch reactor using titanium dioxide (TiO₂) as photocatalyst under natural sunlight exposure. All samples received an identical catalyst dosage and were irradiated for an equivalent duration under comparable solar conditions, with continuous stirring to maintain catalyst suspension and maximise contact between the photocatalyst and dissolved pollutants. Following irradiation, the catalyst was removed by filtration and the treated samples were re-analysed using the identical analytical protocol applied at baseline. This sunlight-driven configuration was adopted to reflect field-realistic, low-energy treatment conditions appropriate to the high-insolation climate of the study region (Malato et al., 2009).

Removal efficiency was calculated using the standard expression:

$$\text{Removal efficiency (\%)} = [(C_{\text{pre}} - C_{\text{post}}) / C_{\text{pre}}] \times 100$$

where C_{pre} and C_{post} denote the pre- and post-treatment concentrations, respectively. This metric was applied primarily to BOD, COD, and nitrate, and expressed as a percentage increase for dissolved oxygen.

3. Results

3.1 Sampling Sites

Table 1 summarises the four sampling sites and their position along the river continuum, ranging from the relatively unimpacted upstream site (Thur-Madar) to the downstream cumulative receptor (Sukha Nala).

Table 1. Description of Sampling Sites along the Ayad River Continuum

Site code	Sampling location	Position along river continuum	Predominant anthropogenic influence
TM	Thur-Madar	Upstream reference site	Minimal direct urban discharge; predominantly rural/peri-urban runoff
AY	Ayad	Mid-stream, urban corridor	Domestic sewage and small-scale industrial effluent
KM	Kanpur Mahadev (Kaldwas)	Mid-to-downstream, industrial zone	Industrial and domestic effluent discharge points
SN	Sukha Nala (Udaisagar)	Downstream, cumulative receptor	Convergence of upstream urban and peri-urban drainage

3.2 Baseline and Post-Treatment Water Quality - Pre-Monsoon Season (July 2025)

Table 2 presents the complete pre- and post-treatment physicochemical dataset for the pre-monsoon sampling campaign across all four sites.

Table 2. Physicochemical Water Quality Parameters Before (Pre) and After (Post) Photocatalytic Treatment, Pre-Monsoon Season (July 2025)

Parameter	Unit	TM		AY		KM		SN	
		Pre	Post	Pre	Post	Pre	Post	Pre	Post
pH	-	7.03	8.18	7.3	7.95	7.02	8.2	6.8	7.94
Electrical conductivity	µS/cm	840	850	1460	1470	1350	1360	1090	1100
Chloride (Cl ⁻)	mg/L	113.3	108.4	172.46	177.39	170.39	170.39	142.89	157.68
Sulphate (SO ₄ ²⁻)	mg/L	27.64	27.71	141.5	147.4	102.2	123.9	90.98	94.91
Nitrate (NO ₃ ⁻)	mg/L	1.51	0.7	2.27	1.86	2.15	1.73	1.46	1.3

Parameter	Unit	TM		AY		KM		SN	
		Pre	Post	Pre	Post	Pre	Post	Pre	Post
Total dissolved solids	mg/L	532	544	936	944	864	872	696	708
Total hardness (as CaCO ₃)	mg/L	256	256	324	336	320	360	256	272
Calcium (Ca ²⁺)	mg/L	44.8	46.4	65.6	70.4	75.2	81.6	59.2	67.2
Magnesium (Mg ²⁺)	mg/L	34.56	33.6	38.4	38.4	31.68	37.44	25.92	24.96
Fluoride (F ⁻)	mg/L	0.8	0.5	0.6	0.3	0.7	0.4	1.5	1.1
BOD (3-day, 27°C)	mg/L	9.8	5	11.5	4.6	12	7.8	14	7.8
COD	mg/L	31.36	15.68	39.2	15.68	39.2	23.52	47.04	31.36
Dissolved oxygen	mg/L	5	5.5	5.8	6.2	3.6	6	4.8	8

3.3 Baseline and Post-Treatment Water Quality - Summer Season (May 2025)

Table 3 presents the corresponding dataset for the summer campaign, which represents the low-flow, high-temperature period of maximum hydrological stress.

Table 3. Physicochemical Water Quality Parameters Before (Pre) and After (Post) Photocatalytic Treatment, Summer Season (May 2025)

Parameter	Unit	TM		AY		KM		SN	
		Pre	Post	Pre	Post	Pre	Post	Pre	Post
pH	-	8.25	8.2	8.47	8.4	8.25	8.38	8.15	8.25
Electrical conductivity	μS/cm	1170	1230	2100	2200	1980	2000	1530	2000
Chloride (Cl ⁻)	mg/L	167.53	171.47	366.6	352.21	305.5	279.62	413.91	368.58
Sulphate (SO ₄ ²⁻)	mg/L	62.45	61.96	110.5	112.7	108.9	102.6	121.2	119.5
Nitrate (NO ₃ ⁻)	mg/L	1.97	1.91	39.19	20.54	46.02	41.17	43.75	5.29
Total dissolved solids	mg/L	770	790	1380	1450	1300	1320	1010	1310
Total hardness (as CaCO ₃)	mg/L	284	320	520	512	512	504	544	536
Calcium (Ca ²⁺)	mg/L	32	40	81.6	97.6	120	116.8	108.8	118.4
Magnesium (Mg ²⁺)	mg/L	48.96	52.8	75.84	64.32	50.88	50.88	65.28	97.6
Fluoride (F ⁻)	mg/L	0.1	<0.1	0.2	<0.1	1	0.1	0.6	0.3
BOD (3-day, 27°C)	mg/L	9.6	5.6	22.8	11.4	36.4	15.8	22.8	12.2
COD	mg/L	40.8	24.48	106.08	48.96	115.04	65.28	97.92	48.96
Dissolved oxygen	mg/L	4.6	5.2	7.4	8	4.6	5.2	5	6.2

Baseline comparison between seasons shows that organic and nutrient indicators were consistently higher in summer than in the pre-monsoon period at all sites. BOD at Kanpur Mahadev rose from 12.0 mg/L (pre-monsoon) to 36.4 mg/L (summer), and nitrate at the same site increased from 2.15 mg/L to 46.02 mg/L. This pattern is consistent with hydrological concentration of pollutants under reduced dilution and extended residence time during low-flow conditions. A stable spatial gradient was also evident, with pollutant concentrations increasing from the upstream Thur-Madar site through Ayad and Kanpur Mahadev to the downstream Sukha Nala site, reflecting the cumulative influence of urban and peri-urban discharge.

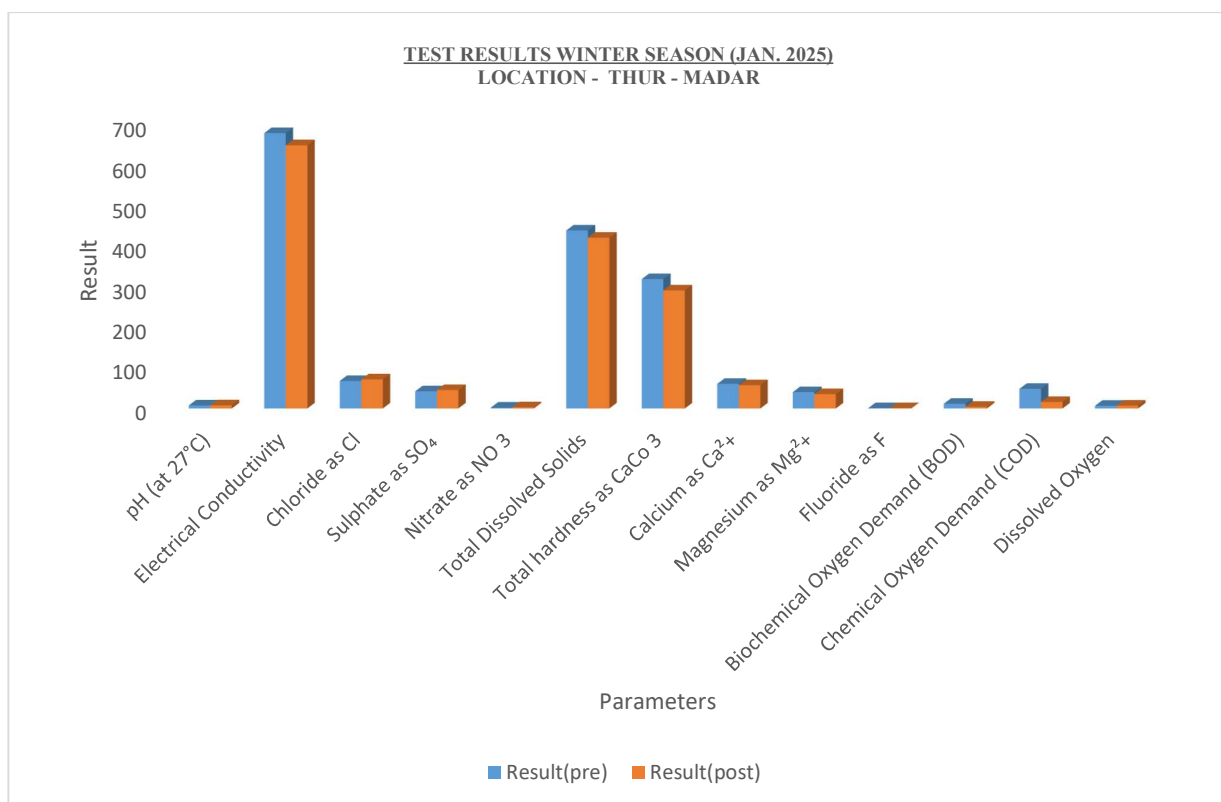
3.4. Discussion

The following tables and graphs present the results of the analysed physiochemical parameters.

TEST RESULTS WINTER SEASON (JAN. 2025)

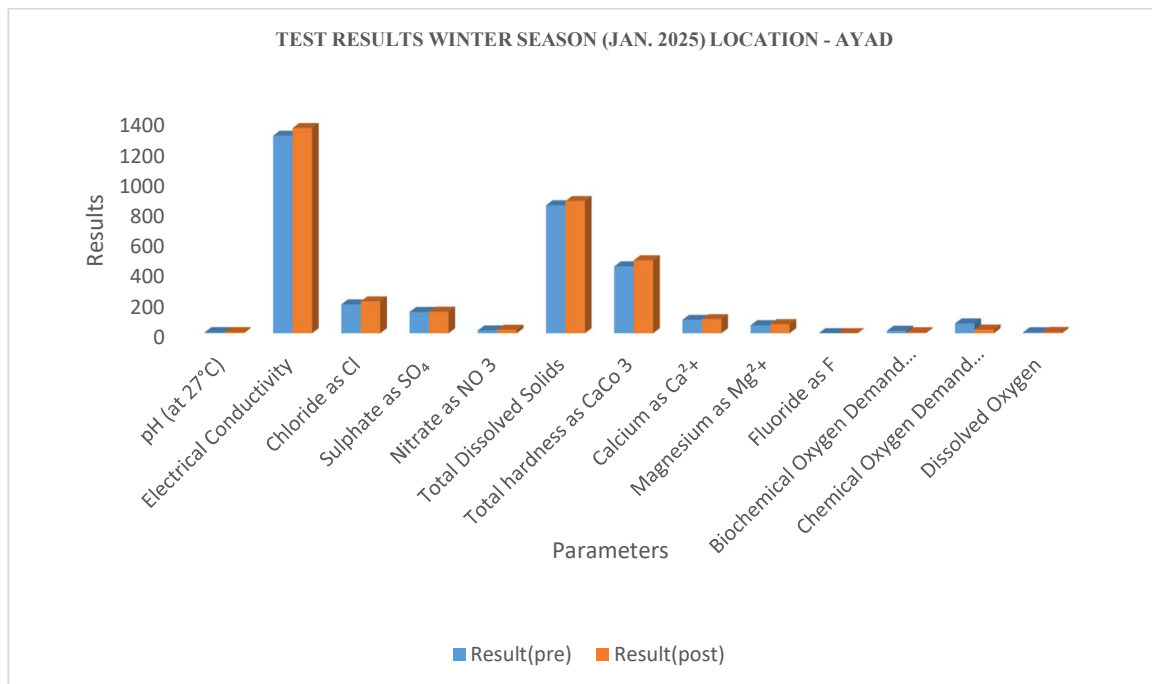
LOCATION - THUR - MADAR

S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.4	7.75
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	680	650
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	67.97	71.97
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	42.45	45.46
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	1.97	2.78
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	440	422
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	320	292
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	60.8	57.6
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	40.32	35.52
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.8	0.5
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	11.6	4.2
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	48.38	16.08
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	6.5	7.1



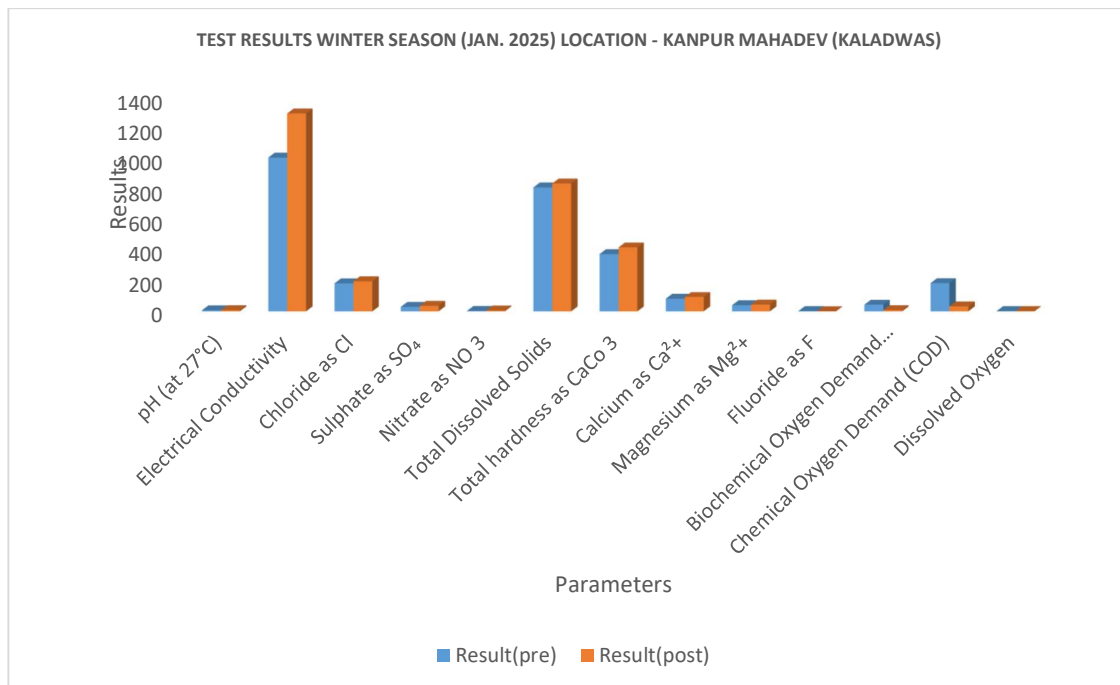
TEST RESULTS WINTER SEASON (JAN. 2025) LOCATION
- AYAD

S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.20	7.80
2.	Electrical Conductivity	IS 3025 (Part 14):2013	µS/cm	1300	1350
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	189.9	209.9
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	140.1	142
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	18.44	23.25
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	842	870
7.	Total hardness as CaCo ₃	IS 3025 (Part 21):2009	mg/L	440	480
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	88	92.8
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	52.8	59.52
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.6	0.4
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	16.2	6.2
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	64.51	24.19
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	6.8	8.1



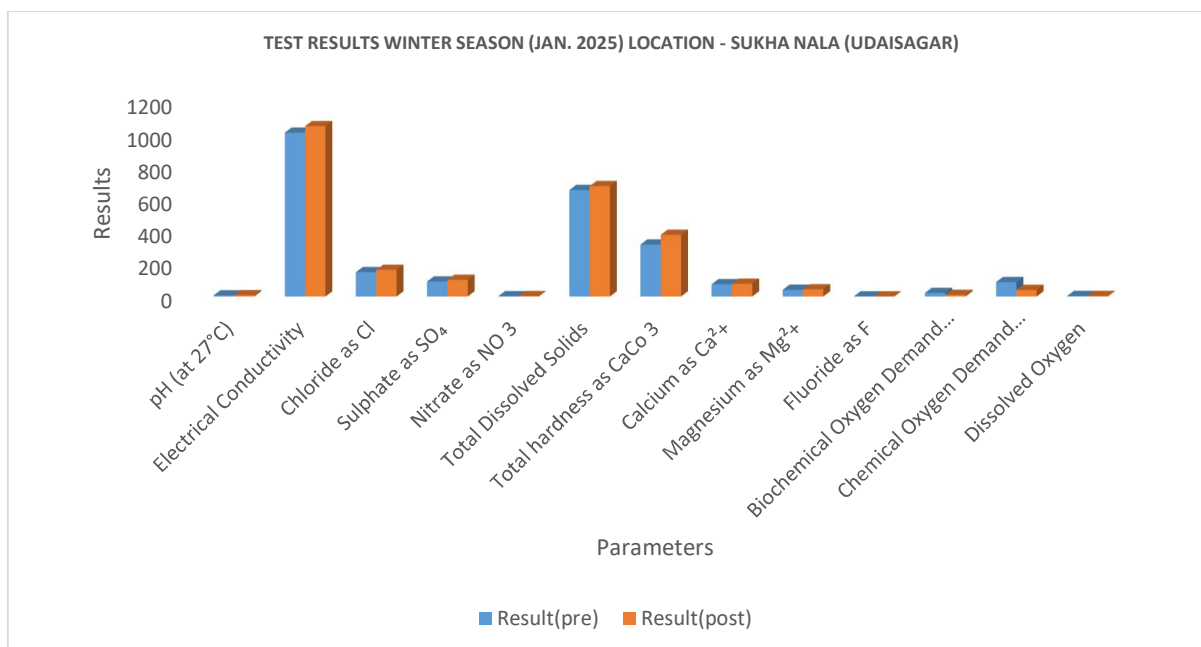
**TEST RESULTS WINTER SEASON (JAN. 2025) LOCATION -
KANPUR MAHADEV (KALADWAS)**

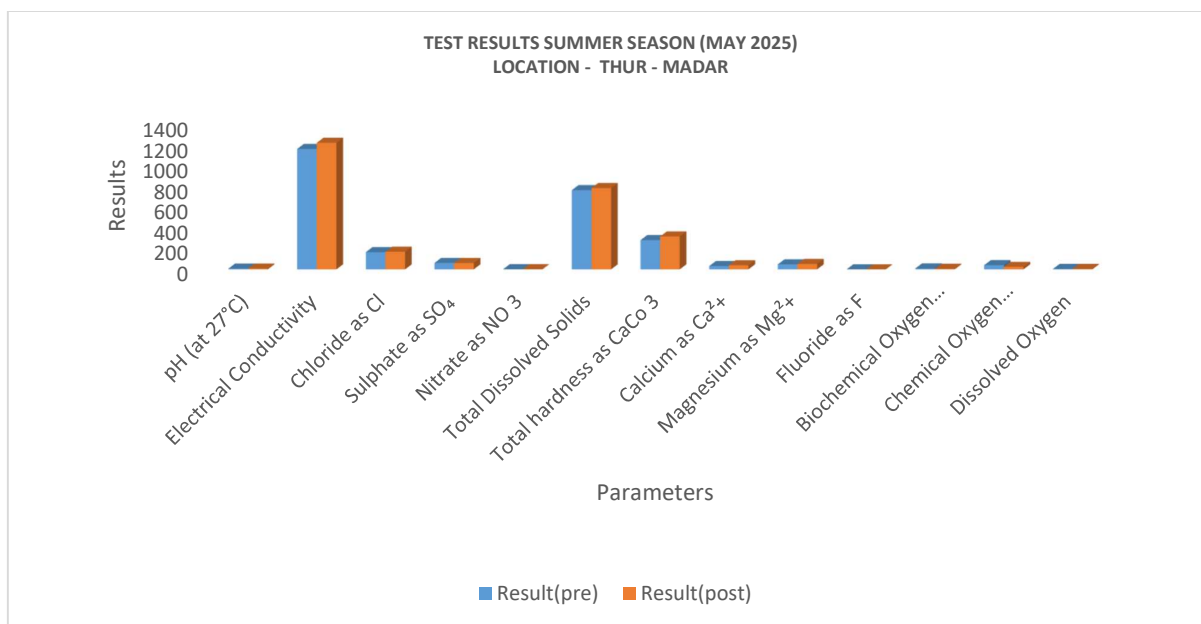
S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.15	7.88
2.	Electrical Conductivity	IS 3025 (Part 14):2013	µS/cm	1010	1300
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	183.9	197.9
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	29.3	36.4
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	3.17	5.8
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	814	840
7.	Total hardness as CaCo ₃	IS 3025 (Part 21):2009	mg/L	376	420
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	83.2	94.4
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	40.32	44.16
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	1.6	0.7
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	44	8.1
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	185.4	32.25
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	1.8	1.9



**TEST RESULTS WINTER SEASON (JAN.
2025) LOCATION - SUKHA NALA
(UDAISAGAR)**

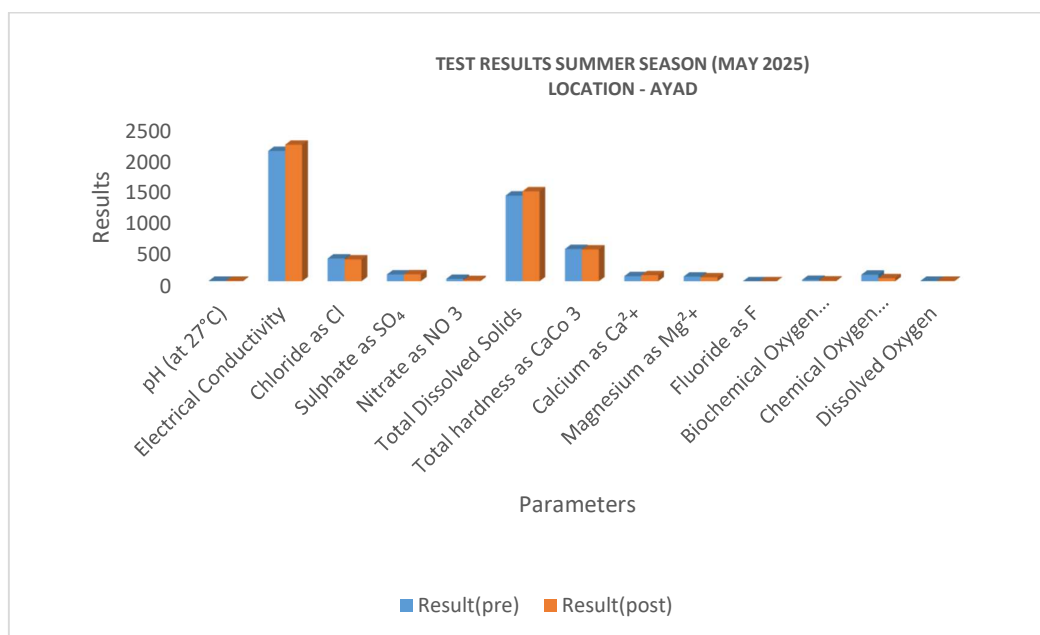
S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.05	7.8
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	1010	1050
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	149.95	163.94
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	92.3	102.4
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	1.29	1.92
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	656	680
7.	Total hardness as CaCo ₃	IS 3025 (Part 21):2009	mg/L	320	380
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	75.2	78.4
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	41.28	44.16
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.7	0.5
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	22	9.8
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	88.70	40.32
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	3.4	3.5



TEST RESULTS SUMMER SEASON (MAY 2025)**LOCATION - THUR – MADAR**

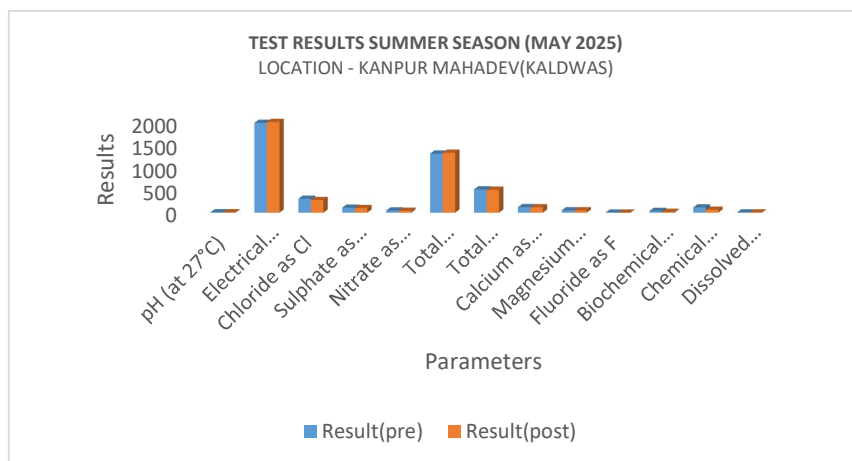
S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	8.25	8.20
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	1170	1230
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	167.53	171.47
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	62.45	61.96
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	1.97	1.91
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	770	790
7.	Total hardness as CaCo ₃	IS 3025 (Part 21):2009	mg/L	284	320
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	32	40
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	48.96	52.8
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.1	<0.1

11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	9.6	5.6
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	40.8	24.48
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	4.6	5.2

TEST RESULTS SUMMER SEASON (MAY 2025)**LOCATION - AYAD**

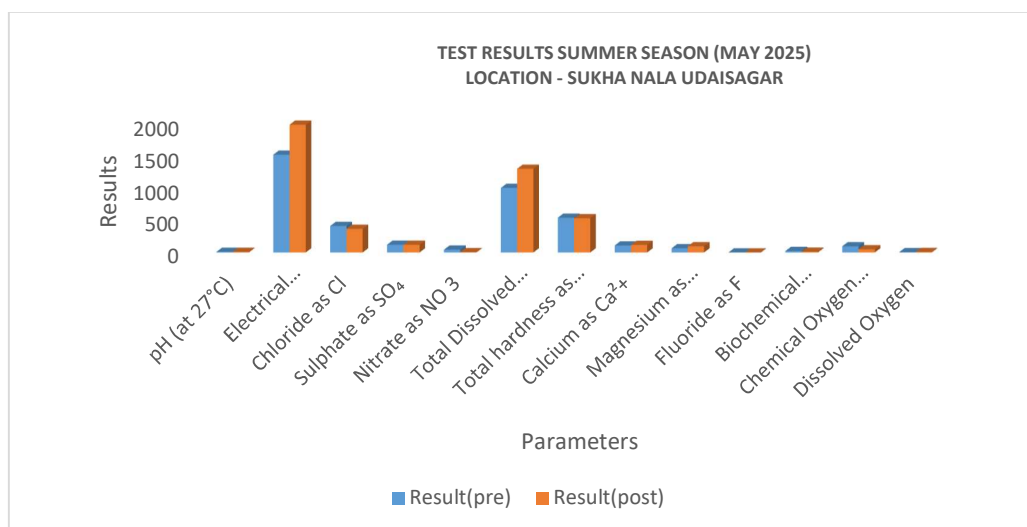
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1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	8.47	8.40
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	2100	2200
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	366.60	352.21
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	110.5	112.7
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	39.19	20.54
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	1380	1450
7.	Total hardness as CaCo ₃	IS 3025 (Part 21):2009	mg/L	520	512
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	81.6	97.6
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	75.84	64.32
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.2	<0.1

11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	22.8	11.4
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	106.08	48.96
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	7.4	8.0

TEST RESULTS SUMMER SEASON (MAY 2025)**LOCATION - KANPUR MAHADEV(KALDWAS)**

S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	8.25	8.38
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	1980	2000
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	305.50	279.62
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	108.9	102.6
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	46.02	41.17
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	1300	1320
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	512	504
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	120	116.8
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	50.88	50.88
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	1.0	0.1

11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	36.4	15.8
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	115.04	65.28
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	4.6	5.2

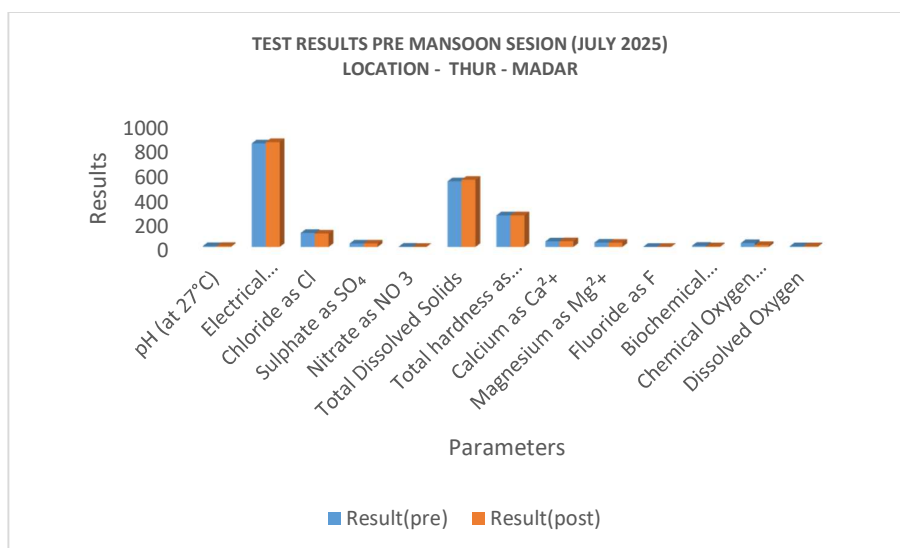
TEST RESULTS SUMMER SEASON (MAY 2025)**LOCATION - SUKHA NALA UDAISAGAR**

S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	8.15	8.25
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	1530	2000
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	413.91	368.58
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	121.2	119.5
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	43.75	5.29
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	1010	1310
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	544	536
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	108.8	118.4

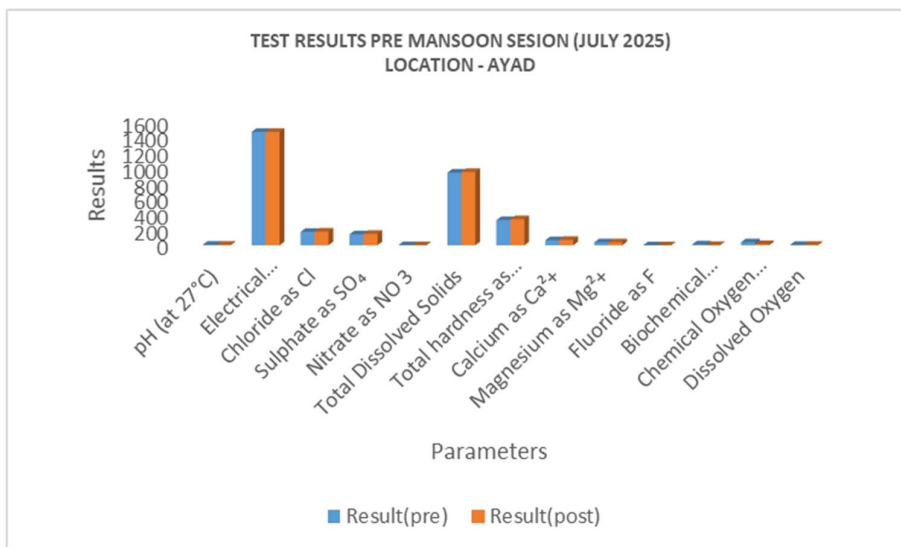
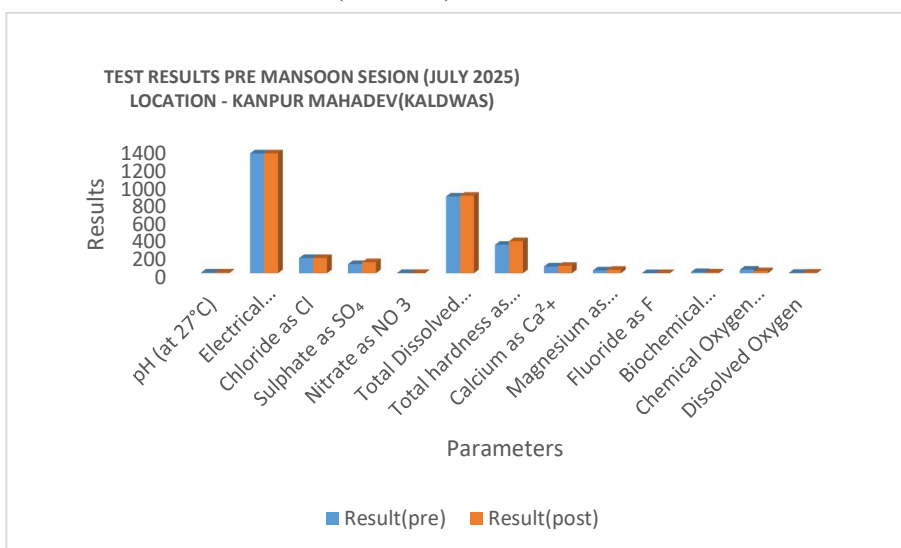
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	65.28	97.6
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.6	0.3
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	22.8	12.2
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	97.92	48.96
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	5.0	6.2

TEST RESULTS PRE MANSOON SEASON (JULY 2025)**LOCATION - THUR - MADAR**

S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.03	8.18
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	840	850
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	113.3	108.40
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	27.64	27.71
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	1.51	0.70
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	532	544
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	256	256
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	44.8	46.4
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	34.56	33.6
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.8	0.5
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	9.8	5.0
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	31.36	15.68
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	5.0	5.5

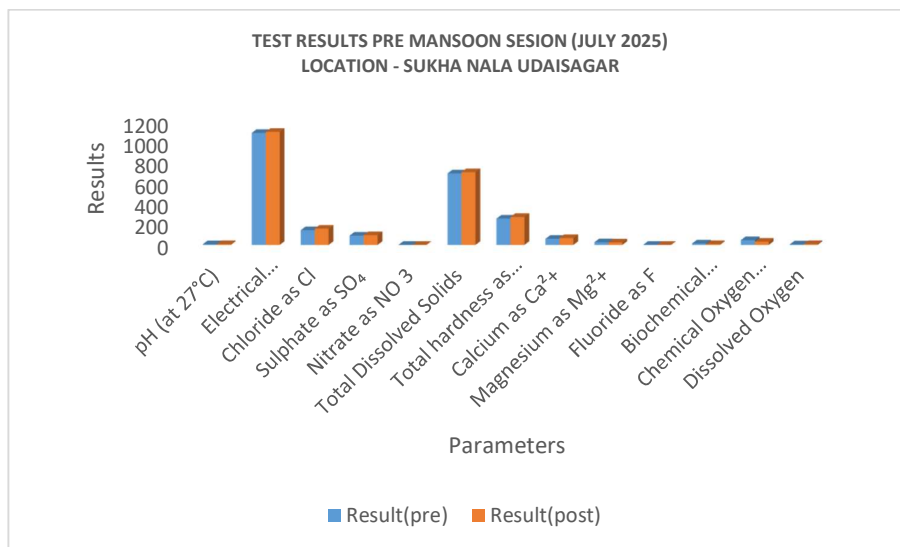
**TEST RESULTS PRE MANSOON SEASON (JULY 2025)****LOCATION - AYAD**

S	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.30	7.95
2.	Electrical Conductivity	IS 3025 (Part 14):2013	µS/cm	1460	1460
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	172.46	177.39
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	141.5	147.40
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	2.27	1.86
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	936	944
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	324	336
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	65.6	70.4
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	38.40	38.4
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.6	0.3
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	11.5	4.6
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	39.20	15.68
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	5.8	6.2

**TEST RESULTS PRE MANSOON SEASON (JULY 2025)****LOCATION - KANPUR MAHADEV(KALDWAS)**

S	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.02	8.20
2.	Electrical Conductivity	IS 3025 (Part 14):2013	µS/cm	1350	1350
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	170.39	170.39
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	102.2	123.90
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	2.15	1.73
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	864	872
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	320	360

8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	75.2	81.6
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	31.68	37.44
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.7	0.4
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	12	7.8
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	39.20	23.52
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	3.6	6.0

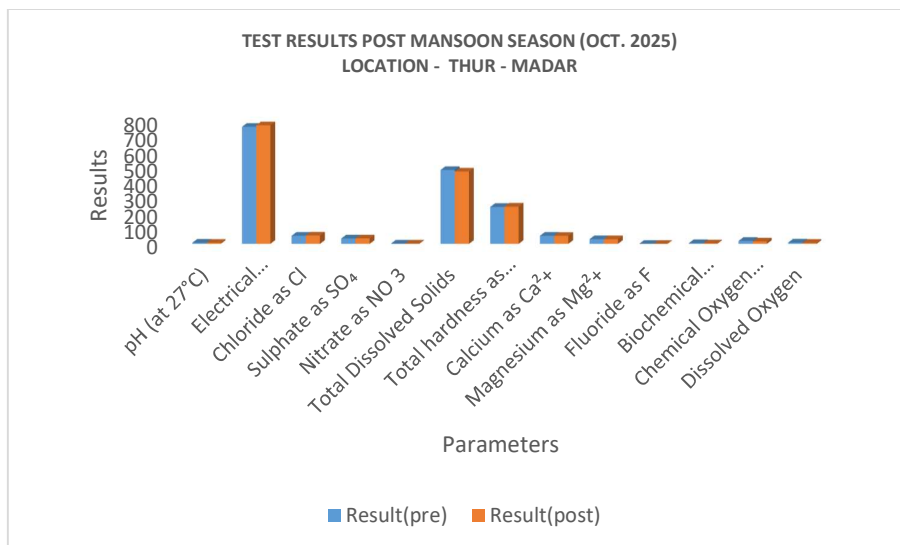
TEST RESULTS PRE MANSOON SEASON (JULY 2025)**LOCATION - SUKHA NALA UDAISAGAR**

S	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	6.80	7.94
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	1090	1100
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	142.89	157.68
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	90.98	94.91
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	1.46	1.30
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	696	708
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	256	272
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	59.2	67.2
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	25.92	24.96

10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	1.5	1.1
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	14	7.8
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	47.04	31.36
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	4.8	8.0

TEST RESULTS POST MANSOON SEASON (OCT. 2025)**LOCATION - THUR - MADAR**

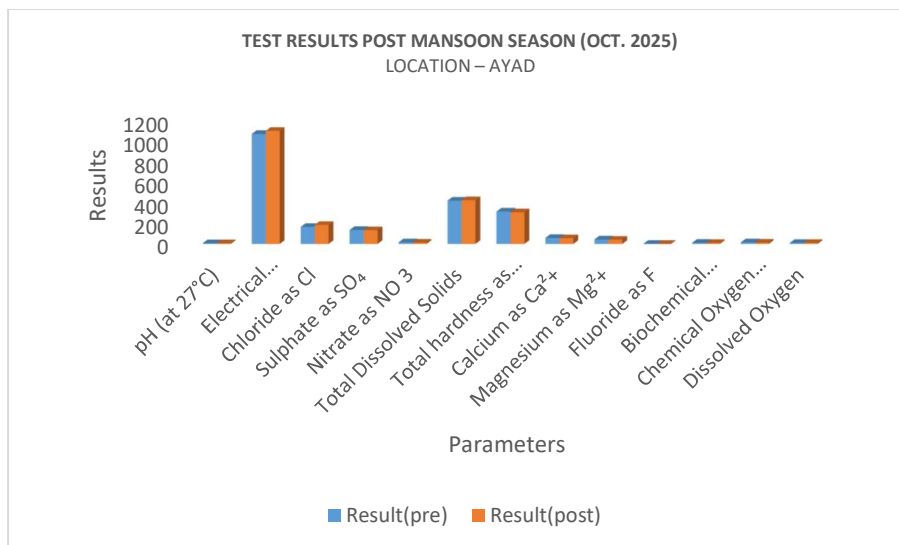
S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.35	7.05
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	760	770
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	52.67	54.32
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	35.04	35.45
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	1.78	1.76
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	480	470
7.	Total hardness as CaCo ₃	IS 3025 (Part 21):2009	mg/L	240	242
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	52.44	52.24
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	30.54	30.12
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.4	0.2
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	5	3
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	19.15	15.84
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	8.5	6.5



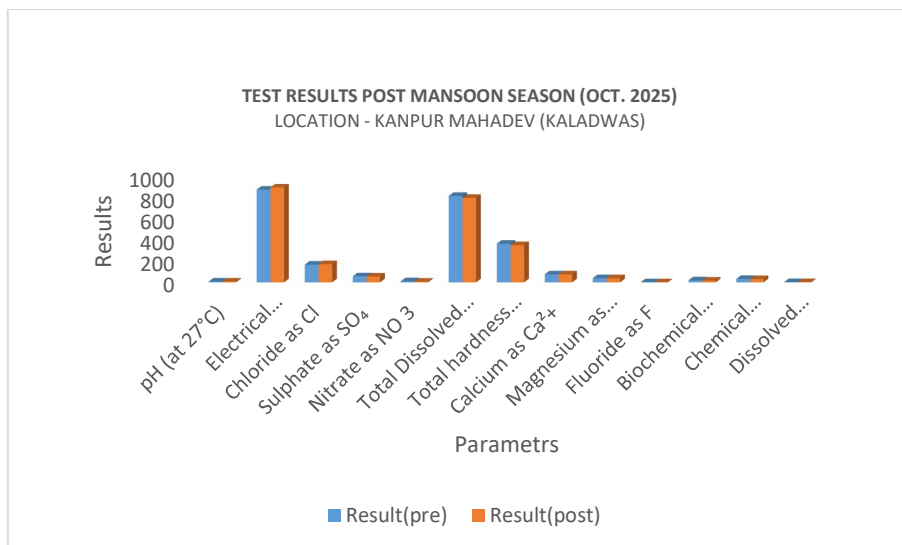
TEST RESULTS POST MANSOON SEASON (OCT. 2025)

LOCATION – AYAD

S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.18	7.08
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	1070	1100
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	165	184.8
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	135.6	133.42
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	15.31	13.07
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	421	425
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	315	308
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	58.6	55.4
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	42.7	40.5
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.4	0.1
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	10.5	9.01
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	15.60	12.20
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	9.01	9.9

**TEST RESULTS POST MANSOON SEASON (OCT. 2025)****LOCATION - KANPUR MAHADEV (KALADWAS)**

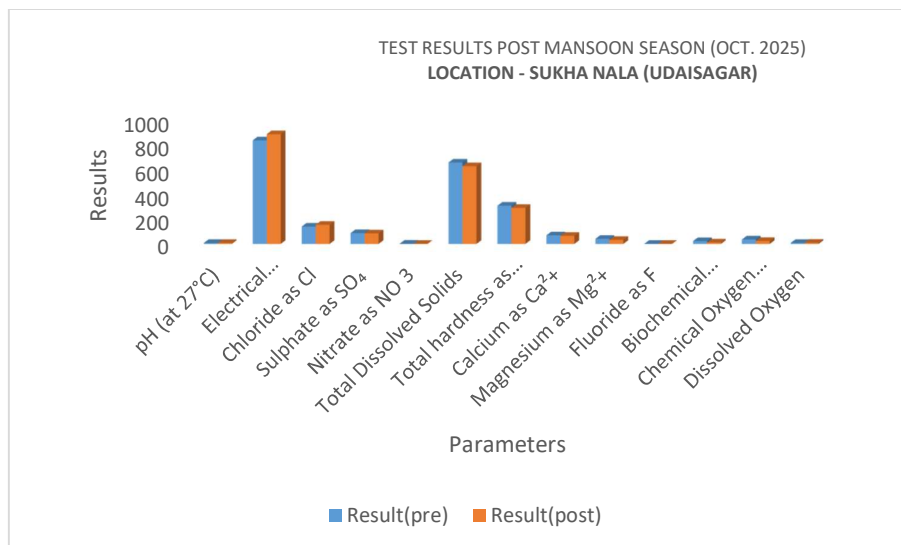
S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.2	7.5
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	870	890
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	165.4	169.9
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	56.4	54.2
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	9.5	6.1
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	810	792
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	362	349
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	75.09	74.12
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	38.3	38.3
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.5	0.4
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	18.4	16.2
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	32.20	30.04
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	1.2	1.7



TEST RESULTS POST MANSOON SEASON (OCT. 2025)

LOCATION - SUKHA NALA (UDASAGAR)

S N	Parameters	Test Method Reference	Unit	Result(pre)	Result(post)
1.	pH (at 27°C)	IS 3025 (Part 11):2022	-	7.4	7.9
2.	Electrical Conductivity	IS 3025 (Part 14):2013	μS/cm	840	890
3.	Chloride as Cl	IS 3025 (Part 32):1988	mg/L	140.6	154.8
4.	Sulphate as SO ₄	IS 3025 (Part 24):1986	mg/L	88.06	85.4
5.	Nitrate as NO ₃	IS 3025 (Part 34):1988	mg/L	1.3	1.02
6.	Total Dissolved Solids	IS 3025 (Part 16):1984	mg/L	660	630
7.	Total hardness as CaCO ₃	IS 3025 (Part 21):2009	mg/L	310	292
8.	Calcium as Ca ²⁺	IS 3025 (Part 40):1991	mg/L	69.4	65.3
9.	Magnesium as Mg ²⁺	IS 3025 (Part 46):1994	mg/L	40.9	32.5
10.	Fluoride as F	IS 3025 (Part 60):2008	mg/L	0.6	0.3
11.	Biochemical Oxygen Demand (BOD) At 27°C for 3 Days	IS 3025 (Part 44):1993	mg/L	23	11.2
12.	Chemical Oxygen Demand (COD)	IS 3025 (Part 58):2006	mg/L	35.8	24.4
13.	Dissolved Oxygen	IS 3025 (Part 38)	mg/L	8.2	9.7



3.5 Response of Hardness Constituents and Major Ions

In contact to the organic and nutrient parameters, hardness constituents (total hardness, calcium, magnesium) and major inorganic ions (chloride, sulphate) gives slow and inconsistent change following treatment across all seasons and sites. This selectivity shows that the photocatalytic process acts predominantly on oxidisable nitrogenous and organic species than on chemically stable dissolved mineral ions.

4. Discussion

4.1 Seasonal and Spatial Drivers of Pollutant Concentration

The consistent summer elevation of BOD, COD, and nitrate across all four sites is most plausibly attributed to hydrological concentration rather than an abrupt increase in pollutant discharge. Reduced river flow and elevated evaporation during summer diminish the dilution capacity of the channel and extend contaminant residence time, while higher ambient temperature accelerates microbial metabolism and organic decomposition, compounding oxygen demand. Bharadwaj et al., 2025 demonstrated that this interpretation is consistent with comparable findings from other South Asian river systems, where dry-season concentration effects-rather than source intensification alone-have been identified as the principal control on seasonal water quality variability. The parallel spatial gradient, in which pollutant concentrations increased progressively from the upstream Thur-Madar site to the downstream Sukha Nala site, reflects the cumulative influence of domestic, industrial, and peri-urban discharge along the river corridor-consistent with prior basin-scale assessments identifying an eastward intensification of contamination in the Ayad system (Pareta et al., 2024).

4.2 Mechanistic Basis of Photocatalytic Organic and Nutrient Removal

The substantial BOD reductions (35-61%) observed across all sites and seasons indicate effective oxidation of biodegradable organic substrates under sunlight-driven TiO₂ photocatalysis. Chong et al., 2010 observed that TiO₂ generates electron-hole pairs upon irradiation which react with dissolved oxygen and water for the formation of hydroxyl radicals and other reactive oxygen species. The generally larger proportional reduction in COD relative to BOD suggests that the photocatalytic process also degraded chemically recalcitrant, non-biodegradable organic fractions that conventional biological treatment would not readily remove-an outcome consistent with recent applications of TiO₂ nanoparticles to real river-water matrices, including polluted stretches of the Ganga, where comparable COD and BOD reductions have been reported (Singh, 2025).

Nitrate reduction was markedly concentration-dependent, with the largest relative decline (87.9%) occurring at Sukha Nala, the site with the highest pre-treatment nitrate load. This pattern points to a reaction mechanism in which the availability of dissolved nitrogen species governs the extent of photocatalytic or adsorptive interaction with the catalyst surface, broadly analogous to the concentration-dependent kinetics reported for photocatalytic degradation of organic pollutants (Malato et al., 2009). The consistent post-treatment increase in dissolved oxygen at every site-most pronounced where baseline organic loading, and hence oxygen demand, was highest-is best interpreted as an indirect consequence of reduced microbial respiration following organic-matter oxidation, rather than direct oxygen generation by the photocatalytic reaction itself.

5. Conclusion

This study depicts that the seasonal hydrology studies the physicochemical dynamics of the Ayad River, giving a consistent summer elevation of organic and nutrient pollutants and a stable upstream-to-downstream gradient of contamination. Treatment efficiency climbs positively with initial pollutant concentration, depicting that photocatalysis is best targeted at urban and peri-urban pollution hotspots better than applied uniformly across the river system.

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