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Seasonal Assessment of Physico-Chemical Water Quality of the Kharun River and Constructed-Wetland Treatment of Gray Water in Chhattisgarh, India

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ABSTRACT: Sustainable approaches for the treatment of river water pollution and domestic wastewater should have efficient pollutant removal and low energy and operational requirements. The present study assesses the seasonal variation in the physico-chemical quality of the Kharun River and explores the possible complementary roles of natural biofilm formation and phytoremediation in improving water quality. In summer, rainy and winter seasons, six parameters namely temperature, turbidity, pH, BOD₅, COD and Fe were evaluated with 49 observations per season. Significant seasonal variations were observed for BOD₅, COD, pH, turbidity and temperature, but Fe did not show any significant seasonal variation. The BOD₅ mean concentrations were 17.41, 16.20 and 16.67 mg/L and the concentrations of COD were 18.55, 17.60 and 17.68 mg/L in summer, rainy and winter respectively. Turbidity showed marked seasonal variation with means of 38.67, 7.43 and 15.82 NTU. The results suggest that natural biofilms may have a direct role in organic matter degradation by microbial activity and that vegetation and associated rhizospheres serve complementary functions, including particle retention, sediment stabilization, nutrient uptake and pollutant immobilization. Moreover, the treatment potential was evaluated by a proposed constructed wetland for gray water treatment at Atora village, Durg district, Chhattisgarh. Each parameter was tested for ten inlet and outlet observations. The turbidity, BOD₅, COD and Fe decreased from 72.50 to 21.27 NTU (70.66 %), 44.00 to 13.24 mg/L (69.91 %), 105.94 to 41.59 mg/L (60.74 %) and 0.214 to 0.089 mg/L (58.41 %), respectively. Temperature was comparatively stable and pH showed a slight increase from 7.21 to 7.31. These results demonstrate the potential of constructed wetlands to enhance gray-water quality through integrated physical, microbial and plant-mediated processes. In general, biofilm formation and phytoremediation should be regarded as complementary mechanisms of treatment. But seasonal observations alone do not allow us to quantify the removal contribution of individual species; controlled or paired inlet–outlet experiments are necessary to assess mechanisms.

INTRODUCTION

Water pollution is one of the major environmental problems. It is caused by the discharge of untreated or incompletely treated wastewater into natural water bodies. It can affect the quality of the water, the aquatic ecosystems, human health and the aesthetic quality of the environment. The increasing generation of wastewater and the limitations of conventional treatment technologies have forced the development of treatment approaches that are effective, economically feasible, energy efficient and environmentally sustainable. The use of engineered treatment systems in combination with natural purification mechanisms

is a promising approach for improving water quality without the need for energy intensive treatment infrastructure. Constructed wetlands are a nature-based treatment technology that can combine physical, chemical and biological processes in a single treatment system. Pollutants are removed from such systems by processes such as screening, settling, sedimentation, filtration, adsorption and biological transformation. The treatment media provide ideal surfaces for the formation of naturally occurring microbial biofilms which can degrade or transform organic pollutants. Likewise, the wetland vegetation and its associated rhizosphere are also involved in the phytoremediation process via filtration, sediment stabilization, pollutant retention and plant root-microorganism interactions. Synergism between these processes allows the simultaneous removal and transformation of a number of pollutants under relatively low energy operating conditions. In this study, the potential of an integrated water-purification approach consisting of constructed wetlands, naturally developed microbial biofilms and phytoremediation to improve water quality was assessed. The treatment performance was evaluated using the main physico-chemical indicators, namely, temperature, turbidity, pH, 5-day biochemical oxygen demand (BOD₅), chemical oxygen demand (COD) and iron (Fe). The efficiency of constructed wetland was evaluated by comparing water quality parameters of inlet and outlet of treatment system. The results showed that BOD₅, COD, turbidity and Fe were significantly reduced while pH was relatively stable and temperature showed little variation. BOD₅, COD, turbidity and Fe has been decreased from 44.00 to 13.24 mg/L, 105.94 to 41.59 mg/L, 72.50 to 21.27 NTU and 0.214 to 0.089 mg/L respectively [1, 2]. These reductions are indicative of the ability of the integrated wetland system to improve water quality through the combined effects of filtration, microbial activity and plant associated treatment processes. The study also examined seasonal variations in the water quality of the Kharun River in an effort to characterize the temporal variability of the selected water-quality parameters and to investigate environmental conditions that may affect treatment processes. The seasonal variations of temperature, turbidity, pH, BOD₅, COD & Fe were studied. The seasonal variation was significant for BOD₅, COD, turbidity, pH and temperature and relatively lower for Fe [3, 4]. This temporal variability could be due to change in temperature, rainfall, dilution, surface runoff and pollutant loading which can affect both water quality characteristics and biological treatment process. Energy efficiency and operational self-sufficiency of the integrated treatment system were also studied, as these are important factors for long-term sustainability of nature-based water-treatment systems.

1. WATER QUALITY PARAMETERS SELECTED FOR ASSESSMENT

Six water quality parameters including temperature, turbidity, pH, BOD₅, COD and Fe were selected for evaluation based on their relevance to the physical, chemical and pollution characteristics of the Kharun River water. These parameters provide complementary information on the overall status of water quality and pollution status of the river. In Table 1, physico-chemical characteristics of Kharun River water have been measured in summer season. The observed temperature, turbidity, pH, BOD₅, COD and Fe values were used to characterize the baseline water quality and to evaluate the changes associated with the integrated treatment process.

Table 1. Physico-chemical parameters of Kharun River water during the summer season.

Sample No.	Temperature (°C)	Turbidity (NTU)	pH	BOD ₅ (mg/L)	COD (mg/L)	Fe (mg/L)
1	25.8	35.2	8.02	17.1	18.2	0.24
2	26.2	37.8	8.1	17.5	18.6	0.27
3	26.7	40.1	8.14	17.8	19	0.29
4	27.1	39.4	8.06	17.3	18.4	0.25
5	25.9	34.6	8.18	17	18.1	0.22
6	26.4	42.3	8.09	17.6	18.7	0.28
7	26.8	36.7	8.12	17.4	18.5	0.26
8	25.6	31.8	8	16.9	17.9	0.21
9	26.3	38.5	8.15	17.2	18.3	0.25
10	27	44.1	8.08	17.9	19.2	0.31

11	26.5	37.1	8.11	17.5	18.6	0.27
12	25.7	33.9	8.03	17	18	0.23
13	26.1	36.4	8.07	17.3	18.4	0.24
14	26.9	41.7	8.2	17.7	18.9	0.3
15	27.3	45.2	8.13	18	19.3	0.32
16	26	32.5	8.05	16.8	17.8	0.2
17	26.6	39.2	8.09	17.4	18.5	0.26
18	25.8	35.8	8.16	17.1	18.2	0.23
19	26.4	40.6	8.04	17.6	18.8	0.28
20	27.2	43.5	8.1	17.8	19	0.3
21	26.7	37.5	8.17	17.5	18.6	0.27
22	25.5	30.9	8.01	16.7	17.7	0.21
23	26.2	34.7	8.06	17	18.1	0.24
24	26.9	46.3	8.12	18.1	19.4	0.33
25	27	42.8	8.14	17.7	18.9	0.29
26	26.3	38.9	8.08	17.4	18.5	0.26
27	25.9	35.1	8.03	16.9	18	0.22
28	26.5	39.7	8.11	17.6	18.7	0.28
29	27.4	48.2	8.19	18.2	19.6	0.34
30	26.8	41.2	8.07	17.8	19	0.3
31	25.7	33.4	8.02	16.8	17.9	0.21
32	26.1	36.8	8.09	17.2	18.3	0.25
33	26.6	40.3	8.15	17.5	18.7	0.27
34	27.1	44.7	8.13	17.9	19.2	0.31
35	26.4	38.1	8.05	17.3	18.4	0.26
36	25.8	32.7	8	16.7	17.8	0.2
37	26.7	39.5	8.18	17.6	18.8	0.29
38	27.3	47.1	8.1	18	19.3	0.32
39	26	34.3	8.04	17	18.1	0.23
40	26.5	37.6	8.07	17.4	18.5	0.26
41	27	43.2	8.16	17.8	19	0.3
42	25.6	31.5	8.01	16.9	17.9	0.22
43	26.3	36.2	8.12	17.2	18.3	0.25
44	26.9	41.9	8.09	17.7	18.9	0.28

45	27.2	45.8	8.2	18.1	19.4	0.33
46	26.1	35.6	8.05	17.1	18.2	0.24
47	26.6	39	8.14	17.5	18.6	0.27
48	25.9	33.1	8.03	16.8	17.8	0.21
49	26.8	42.5	8.11	17.9	19.1	0.3

Table 2 shows the physico-chemical characteristics of Kharun River water during rainy season including temperature, turbidity, pH, BOD₅, COD and Fe.

Table 2. Physico-chemical parameters of Kharun river water in rainy season.

Sample No.	Temperature (°C)	Turbidity (NTU)	pH	BOD ₅ (mg/L)	COD (mg/L)	Fe (mg/L)
1	19.8	7.1	7.6	15.2	15.8	0.24
2	20.1	7.5	7.8	16	17.2	0.27
3	20.5	7.8	7.9	16.7	18.4	0.29
4	21	7.2	7.7	17.2	19.1	0.25
5	19.5	6.8	7.5	15.4	16	0.22
6	20.4	8	7.9	16.5	18	0.28
7	20.7	7.6	8	17	18.7	0.26
8	19.2	6.5	7.6	14.9	15.2	0.21
9	20	7.3	7.8	15.8	17	0.25
10	21.2	8.3	8.1	17.8	20.2	0.31
11	20.3	7.4	7.7	16.2	17.5	0.27
12	19.7	6.9	7.6	15.1	16.1	0.23
13	20.6	7.7	7.9	16.8	18.5	0.24
14	20.9	8.1	8	17.1	19	0.3
15	19.4	6.2	7.5	14.8	15	0.32
16	20.2	7	7.8	15.7	16.8	0.2
17	20.8	7.9	8	16.9	18.9	0.26
18	19.9	7.2	7.7	15.5	16.5	0.23
19	20.5	7.5	7.9	16.4	17.8	0.28
20	21.1	8.5	8.1	17.6	20	0.3
21	20	6.7	7.6	15	15.9	0.26
22	19.6	6.4	7.5	14.7	15.4	0.22
23	20.3	7.6	7.8	16.1	17.3	0.25
24	21.3	8.7	8.2	18	20.4	0.33

25	20.7	7.8	7.9	16.7	18.6	0.29
26	20.1	7.1	7.7	15.6	16.7	0.26
27	19.3	6.3	7.6	14.6	15.1	0.21
28	20.6	7.4	7.8	16.3	17.9	0.28
29	21	8.2	8	17.4	19.5	0.34
30	20.4	7.7	7.9	16.5	18.1	0.3
31	19.7	6.6	7.5	15	15.7	0.21
32	20.2	7.3	7.7	15.8	17.1	0.25
33	20.9	8	8	17	18.8	0.27
34	21.4	8.9	8.2	18.2	20.7	0.31
35	20.5	7.5	7.8	16.4	17.9	0.26
36	19.1	6.1	7.4	14.5	14.9	0.2
37	20.3	7.8	7.9	16.6	18.3	0.29
38	21.1	8.4	8.1	17.7	20.1	0.32
39	19.8	6.9	7.6	15.2	16	0.23
40	20.4	7.2	7.8	16	17.4	0.26
41	20.8	8.1	8	17.2	19.2	0.3
42	19.5	6.5	7.5	14.9	15.5	0.22
43	20	7.4	7.7	15.7	17	0.25
44	20.7	7.9	7.9	16.8	18.6	0.28
45	21.2	8.6	8.2	18.1	20.3	0.33
46	19.9	6.8	7.6	15.3	16.2	0.24
47	20.5	7.6	7.8	16.3	18	0.27
48	19.4	6.2	7.5	14.7	15.3	0.21
49	20.6	8	8	17.1	18.9	0.3

Table 3 depicts the physico-chemical characteristics of the Kharun River water in relation to the selected water quality parameters during the winter season.

Table 3. Physico-chemical characteristics of Kharun River water in winter season

Sample No.	Temperature (°C)	Turbidity (NTU)	pH	BOD ₅ (mg/L)	COD (mg/L)	Fe (mg/L)
1	15.2	14.1	7.2	14.8	15.1	0.24
2	16.1	15.4	7.5	16.2	17	0.27
3	17.3	16.8	7.8	17.4	18.5	0.29
4	18	17.2	8	18.5	20.1	0.31

5	15.8	13.9	7.4	15.5	16.2	0.22
6	16.5	15.7	7.7	17	17.8	0.26
7	17.1	16.2	7.9	18	19	0.28
8	14.9	13.5	7.1	13.9	14.8	0.21
9	16	15.1	7.6	16	16.8	0.25
10	18.2	18.4	8.1	19	20.8	0.32
11	16.7	15.8	7.7	17.2	17.7	0.27
12	15.5	14.4	7.3	14.9	15.8	0.23
13	17	16.5	7.8	17.6	18.7	0.29
14	17.8	17.6	8	18.3	19.8	0.3
15	14.7	13.2	7	13.8	14.5	0.2
16	16.3	15	7.6	16.1	16.9	0.25
17	17.5	16.9	7.9	18.1	19.2	0.28
18	15.9	14.7	7.5	15.8	16.5	0.24
19	16.8	15.9	7.7	17	17.9	0.26
20	18.4	19.1	8.2	19.5	21	0.33
21	15.4	13.8	7.2	14.5	15.2	0.22
22	14.8	12.9	7	13.7	14.3	0.19
23	16.2	15.3	7.6	16.5	17.2	0.25
24	18.6	20	8.3	20	21.5	0.35
25	17.2	17	7.9	17.8	18.8	0.29
26	16	14.8	7.5	15.9	16.7	0.24
27	14.6	13.1	7.1	13.5	14.7	0.2
28	16.6	15.6	7.7	16.9	17.8	0.27
29	17.9	18.2	8	18.7	20	0.31
30	16.9	16.4	7.8	17.3	18.4	0.28
31	15.3	13.7	7.2	14.6	15.3	0.21
32	16.4	15.2	7.6	16.3	17.1	0.25
33	17.6	17.3	7.9	18.2	19.4	0.3
34	18.7	20.5	8.3	20.2	21.8	0.34
35	16.8	15.9	7.7	17.1	18	0.27
36	14.5	12.7	7	13.4	14.1	0.19
37	17	16.7	7.8	17.5	18.6	0.29
38	18.1	18.8	8.1	19.1	20.5	0.32

39	15.7	14.3	7.3	15	15.9	0.23
40	16.5	15.5	7.6	16.4	17.5	0.26
41	17.7	17.8	8	18.6	19.7	0.3
42	15	13.4	7.1	14.2	15	0.21
43	16.1	14.9	7.5	15.7	16.6	0.24
44	17.4	16.6	7.8	17.7	18.9	0.28
45	18.3	19.4	8.2	19.6	21.2	0.34
46	15.6	13.9	7.3	15.1	16	0.22
47	16.9	16.1	7.7	17	18.1	0.27
48	14.9	13	7.1	13.9	14.8	0.2
49	17.1	17.1	7.9	18	19.1	0.29

Table 4 presents permissible limits for selected physico-chemical parameters of water quality as reported by UNEP/WHO (1996) and WHO (2004). The reference values can be used for comparison of the observed water-quality characteristics of the Kharun River and for assessment of its pollution status.

Table 4. Permissible limits for selected physico-chemical parameters of water quality (UNEP/WHO, 1996; WHO, 2004).

S. No.	Parameter	Unit	Reference value / guideline	Appropriate source
1	Temperature	°C	—	No universal WHO permissible limit
2	Turbidity	NTU	5	WHO drinking-water reference
3	pH	—	6.5–8.5	Common drinking-water standard/reference
4	BOD ₅	mg/L	—	No universal WHO guideline value
5	COD	mg/L	—	No universal WHO guideline value
6	Iron (Fe)	mg/L	0.3	WHO reference value

2. RESULTS AND DISCUSSION

2.1. Change of BOD₅ and Effect of Natural Biofilm and Phytoremediation in Kharun River
 Biochemical Oxygen Demand over 5 days (BOD₅) is an important indicator of biodegradable organic pollution and is the oxygen required by microorganisms in the oxidation of organic matter. The seasonal variation of BOD₅ concentrations in the Kharun River water was assessed in summer, rainy and winter seasons to evaluate the potential role of natural biological purification mechanisms. One-way ANOVA showed a significant difference in BOD₅ between seasons ($F = 16.15285$, $p = 2.10435 \times 10^{-9}$). The R^2 value of 0.20153 indicates that the seasonal variation can be explained by the BOD₅ variation of 20.15% while the remaining variation can be explained by river flow, rainfall, dilution, temperature, organic loading, microbial activity and wastewater inputs. The mean BOD₅ concentrations were 17.41 mg/L in summer, 16.20 mg/L in rainy season and 16.67 mg/L in winter. The highest concentration was found in summer, which might be due to lower river flow and higher concentration of biodegradable organic matter, while higher flow and dilution during rainy season might have led to lower BOD₅ concentration [5, 6]. Natural microbial biofilms on sediments, gravel, stones and plant roots can help the self-purification of rivers by degrading organic matter through activity of microorganisms. Root-associated microbial activity, filtration, sediment stabilization and nutrient uptake by aquatic and riparian vegetation can also improve treatment. These mechanisms are complementary and can work together to reduce BOD₅. The seasonal differences were statistically significant, but the present

analysis does not allow to quantify the individual contribution of biofilm or phytoremediation. The results indicated that the environmental conditions in different seasons influenced BOD₅ concentrations and may affect the efficiency of the natural biological purification processes in the Kharun River. The mean BOD₅ concentrations are shown in Figure 1 and the results of the corresponding one-way ANOVA are shown in Figure 2.

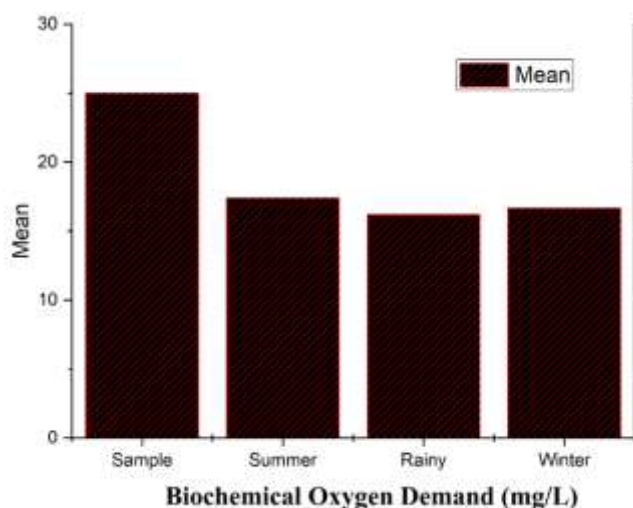


Figure 1. Seasonal variation of mean BOD₅ concentration in Kharun River water.

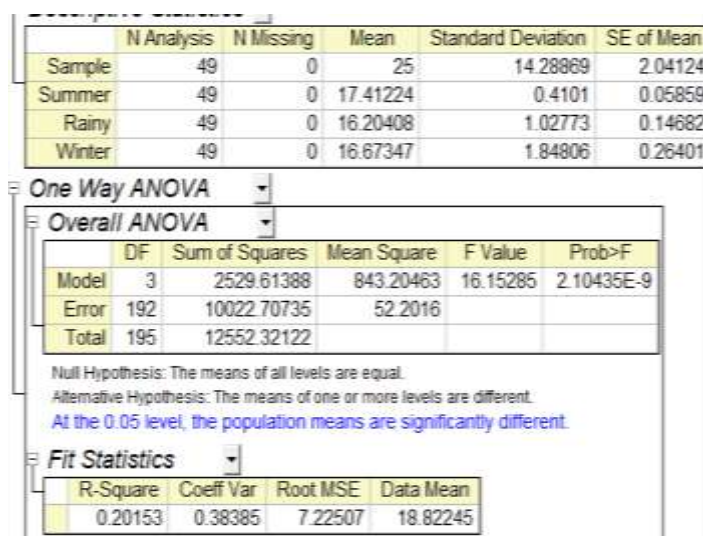


Figure 2 One-way ANOVA analysis of BOD₅ concentration in different seasons

2.2. Variation in COD and Role of Natural Biofilm and Phytoremediation in the Kharun River

The chemical oxygen demand (COD) is an important index for oxidizable organic pollution in river water. It is the oxygen that is employed in the chemical oxidation of organic and other oxidizable substances. In this study, the COD concentrations were measured in summer, rainy and winter seasons to study the seasonal variation and contribution of natural biological purification mechanisms. The average concentrations of COD were 18.55 mg/L, 17.60 mg/L and 17.68 mg/L in summer, rainy season and winter, respectively. Hence summer season had highest COD and rainy season had lowest COD. The higher concentration in summer may be due to lower river flow and higher concentration of wastewater and oxidizable organic matter. Higher flow and dilution of rainy season may result in reduced concentrations of COD. The value of winter was higher than the rainy season one. This can be explained by the seasonal variations of the river flow and the biological transformation processes. The one-way ANOVA analysis showed a statistically significant seasonal difference in COD ($F = 5.61$, $p = 0.0045$) except for the

inappropriate “Sample” group. Therefore, the null hypothesis was rejected for the mean concentrations of COD in the summer, rainy and winter seasons. The mean value of COD in rainy season was reduced about 5.13% than the summer value and winter mean is reduced about 4.70% than the summer value. These are seasonal variations and should not be considered as efficiencies of treatment removal. Natural microbial biofilms on stones, sediments, gravel and roots of plants can be involved in the degradation and transformation of the biodegradable part of the oxidizable organic matter. The efficiency of the system depends on temperature, dissolved oxygen, nutrient availability, amount of organic loading, hydraulic conditions and availability of surfaces for microbial attachment. Aquatic and riparian vegetation can improve root-zone filtration, sediment stabilization, nutrient uptake, and surfaces for microbial colonization, and thereby improve these processes. Thus, biofilm formation and phytoremediation could be additive mechanisms in the natural purification of the Kharun River [7–9]. However, the individual contribution of biofilm and phytoremediation for COD removal cannot be quantified by seasonal ANOVA. Treatment efficiency could be estimated by paired measurements of specific treatment zones before and after treatment. The results indicate a significant seasonal variation in COD, with the highest mean concentration occurring during the summer and the lowest during the rainy season. Natural microbial and plant-associated processes can influence the river self-purification capacity [10]. Figure 3 shows the mean concentrations of COD for the entire data set and for each season. The corresponding one way ANOVA results are shown in Figure 4.

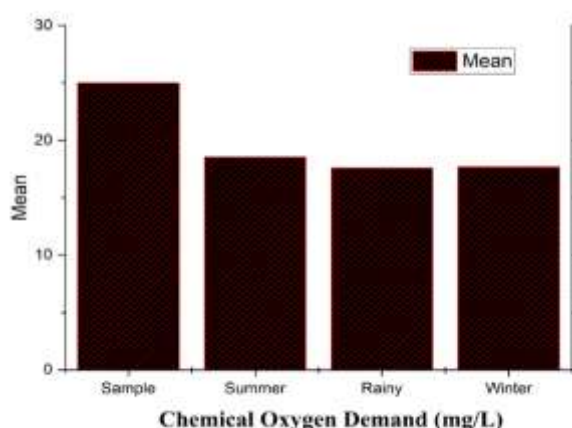


Figure 3 Seasonal variation of mean COD concentration in Kharun River water.

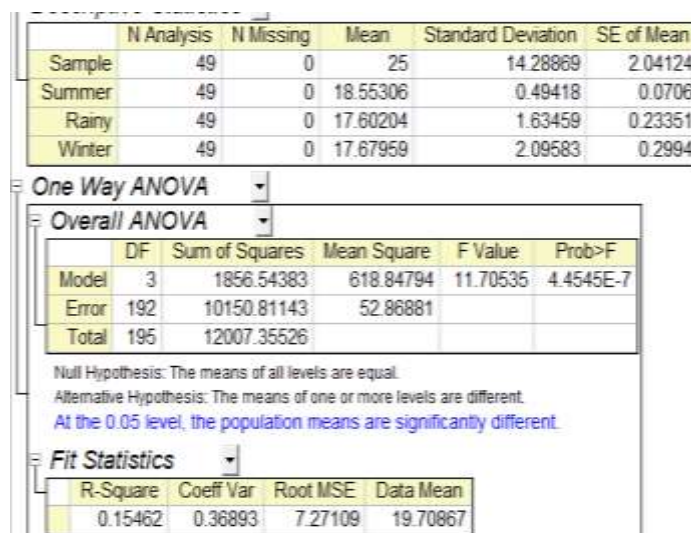


Figure 4 One-way ANOVA analysis of BOD₅ concentration in different seasons.

2.3. Natural Phytoremediation and Biofilm of Kharun River and Seasonal Variation of Iron (Fe)

Iron (Fe) is an important water-quality parameter because its concentration can reflect inputs from natural weathering, soil erosion, sediments and anthropogenic wastewater sources. In this study Fe concentrations were quantified in 49 water samples in summer, rainy and winter seasons to evaluate seasonal variation and possible role of natural purification mechanisms. The mean concentrations of Fe were 0.26429 mg/L in summer, 0.26429 mg/L in rainy season and 0.26347 mg/L in winter with the overall mean of about 0.26402 mg/L. The corresponding standard deviations were 0.03736, 0.03725, and 0.04221 mg/L respectively, indicating relatively low seasonal variability. The difference between the maximum and minimum seasonal means was 0.00082 mg/L (~0.31%) which indicate a high degree of stability in Fe concentration over the year. The original ANOVA included a fourth group called “Sample” which is sample identification and not an experimental season. Hence, this group was removed from the analysis. The corrected one-way ANOVA for the three seasons resulted in $F = 0.0072$ and $p = 0.993$ ($df = 2, 144$) and there was no statistically significant seasonal variation in Fe concentration. Thus, Fe concentrations are probably more controlled by persistent sources or background geochemical conditions than by seasonal changes in hydrological conditions. Natural microbial biofilms may play a role in Fe retention and transformation via adsorption, precipitation, oxidation-reduction reactions and incorporation into extracellular polymeric substances. Biofilms developing on sediments, stones and plant roots can thus play a role in the immobilization of Fe in the river system[11, 12]. Similarly, Fe may be influenced by aquatic and riparian vegetation through root-zone filtration, stabilization of sediments, adsorption to root surfaces and metal accumulation. In addition, plant roots are surfaces for microbial colonization, resulting in complementary biofilm-rhizosphere interactions[13, 14]. However, the current seasonal data do not allow quantification of the individual contribution of biofilm or phytoremediation to Fe removal. Such assessment would need paired inlet and outlet measurements for the respective treatment zones. Fe concentrations were relatively stable over seasons but natural biofilm and plant associated processes may contribute to its retention and immobilization. The mean Fe concentrations for the entire dataset and individual seasons are shown in Figure 5. The results of the corrected one-way ANOVA for the three seasonal groups are shown in Figure 6.

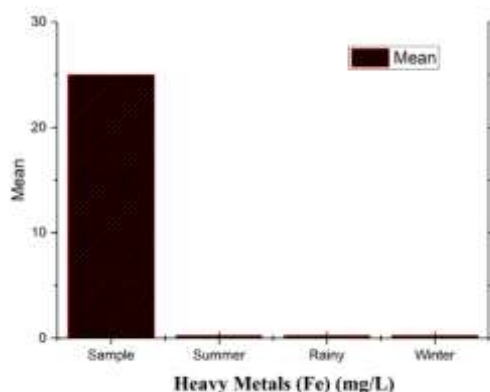


Figure 5 Seasonal variation of mean Fe concentrations in Kharun River water.

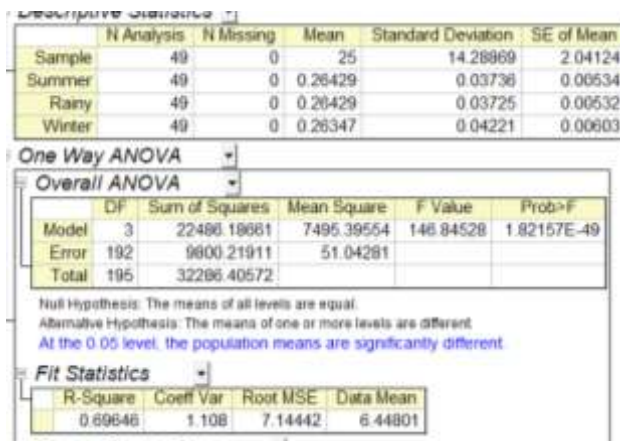


Figure 6 One-way ANOVA analysis of Fe concentrations in different seasons.

2.4. Seasonal variation of pH and role of natural biofilm and phytoremediation in Kharun River

pH is an important water quality parameter that influences chemical reactions, microbial activity, nutrient availability, metal mobility and processes in aquatic ecosystems. The pH of 49 samples of Kharun River water was measured in summer, rainy and winter seasons in the present study to study seasonal variation and to examine the possible role of natural biofilm and phytoremediation. The mean pH value was 8.09469 in summer, 7.80204 in rainy season and 7.63673 in winter with standard deviation was 0.05594, 0.21163 and 0.36497, respectively. The water was slightly alkaline with mean pH in summer highest and lowest in winter. The pH decrease may be associated with seasonal changes in photosynthetic activity, rainfall, dilution, temperature, respiration and microbial processes. Higher pH values in the summer months may be attributed to higher rates of photosynthesis and associated CO₂ uptake, while higher runoff and lower biological activity in the rainy and winter periods may explain lower values.

The original ANOVA had a fourth group called "Sample" which was sample ID instead of an experimental season. When this group was removed, the corrected one-way ANOVA for the three seasons showed $F = 43.65$, $p < 0.001$ ($df = 2, 144$), indicating a statistically significant variation of pH across the seasons. Average pH decreased from summer to rainy season by 3.61% and 5.65% from summer to winter. These are not efficiencies of treatment but differences between seasons. Natural biofilms can change the local pH by microbial photosynthesis, respiration and decomposition of organic matter. Aquatic and riparian vegetation can also influence pH through photosynthesis, respiration, nutrient uptake and interactions in the root zone. Plant roots also provide surfaces for microbial colonization linking phytoremediation to biofilm mediated processes. In combination, these mechanisms can help to buffer and regulate the pH of river water in a natural way. However, the available observational data are not sufficient to quantify the individual contribution of the biofilm or phytoremediation to the pH regulation. The results indicated that the pH of the Kharun River showed significant seasonal variation and the regulation and maintenance of suitable aquatic conditions may be related to natural microbial and plant-associated processes[15–17]. The mean pH values for the whole data set and for each season are shown in Figure 7. The results of the corrected one-way ANOVA can be seen in Figure 8.

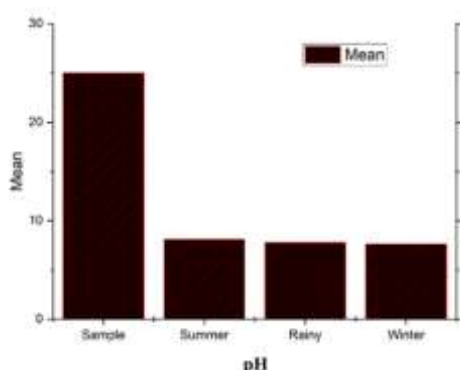


Figure 7 Seasonal variation of mean pH in Kharun River water.

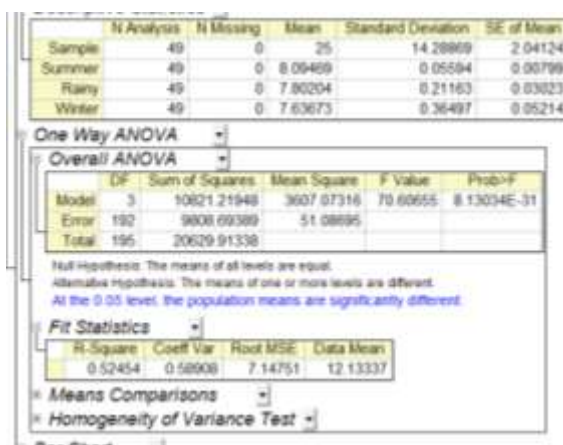


Figure 8 One-way ANOVA analysis of pH in different seasons.

2.5. Seasonal Variation of Turbidity and Effect of Natural Biofilm and Phytoremediation in Kharun River.

Turbidity is an important physical parameter for water quality and indicates the presence of suspended and colloidal substances such as silt, clay, organic matter and microorganisms. The present study was conducted to measure turbidity in 49 samples of Kharun river water during summer, rainy and winter seasons to determine seasonal variation and the possible contribution of natural biofilm and phytoremediation in water clarification. The mean of the turbidity values was 38.67 NTU in summer, 7.43 NTU during the rainy season and 15.82 NTU in winter with standard deviations of 4.42, 0.70 and 1.95 NTU, respectively. The turbidity was maximum in summer and minimum in rainy season. Greater turbidity in summer could be associated with lower flow, sediment deposition and resuspension, wastewater and organic particulate matter inputs. The much lower rainy season value may be a reflection of increased flow and dilution under the sampling conditions. However, rainfall induced runoff can also increase turbidity depending on local conditions. Winter turbidity was intermediate. The first ANOVA mistakenly included a fourth group “Sample”, which represented sample identification, not season. The corrected one-way ANOVA for the three seasons, excluding this group, yielded $F = 1611.09$, $p < 0.001$ ($df = 2, 144$) confirming the highly significant seasonal variation. The mean turbidity showed a decrease of 80.78% from summer to rainy season and 59.07% from summer to winter. These values reflect seasonal differences and should not be interpreted as treatment removal efficiencies. The corrected analysis suggested that the seasonal grouping accounted for about 95.7% of the observed turbidity variability. Natural biofilms on stones, sediments, gravel, submerged vegetation and plant roots may contribute to particle retention through their extracellular polymeric matrix which facilitates trapping, aggregation and stabilization of suspended material. Phytoremediation can contribute to this by increasing the flow velocity by vegetation, filtering the root zone, and stabilizing sediments and trapping suspended particles. Plant roots also provide additional surfaces for microbial biofilm development, resulting in an integrated plant-microbe treatment environment [18, 19].

The results demonstrate the considerable seasonal variation of turbidity; however, the present analysis does not allow for the quantification of the individual contribution of biofilm or phytoremediation. Such treatment efficiencies would require paired inlet and outlet turbidity measurements from particular treatment zones. Overall, the results demonstrate high seasonal variability of Kharun river turbidity with the least mean value in the rainy season. The natural biofilm and vegetation may be playing a role in the particle-retention and clarification processes of the river. Figure 9 shows mean turbidity values for the whole dataset and for each season. Figure 10 shows the corrected one-way ANOVA results.

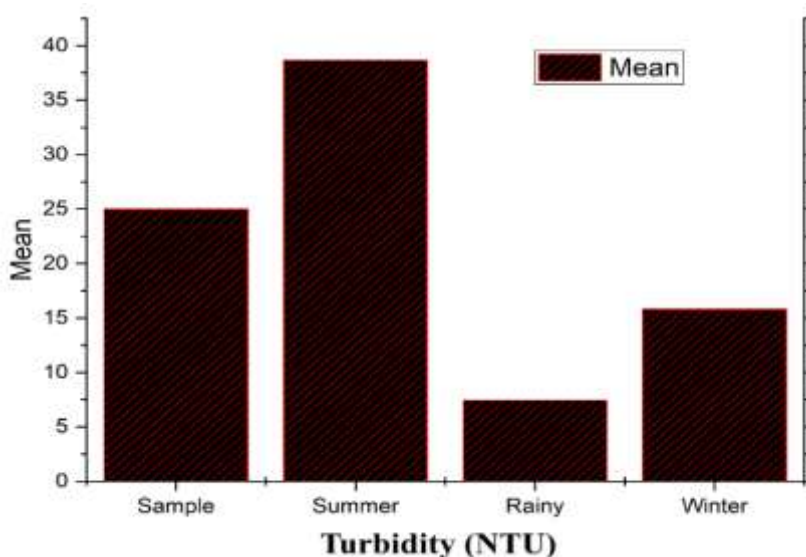


Figure 9 Seasonal variation of mean turbidity in Kharun River water.

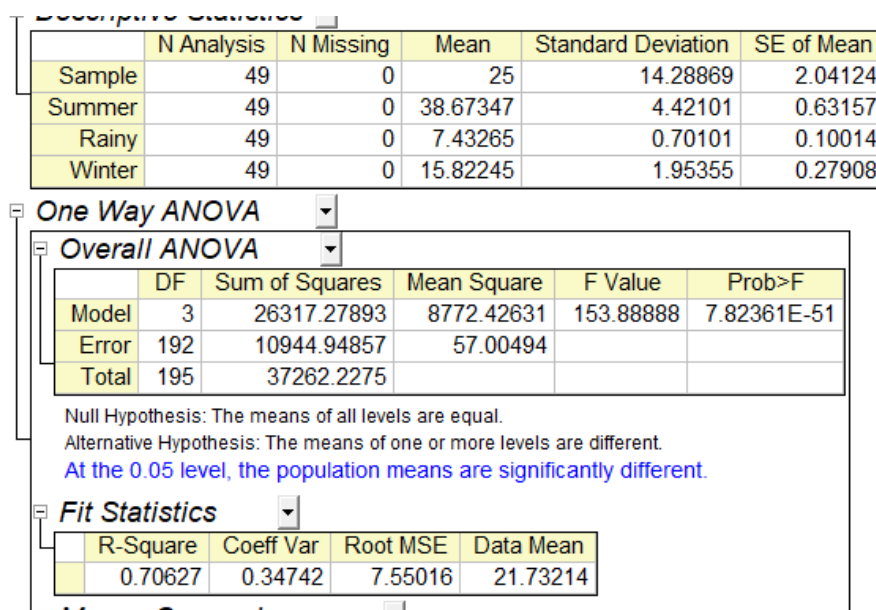


Figure 10 One-way ANOVA analysis of turbidity in different seasons.

2.6. Seasonal Variation of Temperature and Role of Natural Biofilm and Phytoremediation in Kharun River

Water temperature is an important factor in the river environment, affecting the chemical and biological characteristics of river water, including microbial metabolism, the amount of dissolved oxygen, the speed of biochemical reactions, and the growth of aquatic plants and algae. In the present study, seasonal variation and its implication on natural biofilm and phytoremediation processes were studied by measuring temperature in 49 water samples during summer, rainy and winter seasons. Summer mean water temperatures were 26.45°C (SD=0.52), rainy season mean water temperature 20.31°C (SD=0.60), and winter mean water temperature 16.56°C (SD=1.16). Summer temperatures were the highest and winter temperatures the lowest, in accordance with seasonal variation in solar radiation, ambient temperature, rainfall, cloud cover and river flow. The original ANOVA had a fourth group labeled “Sample” that represented sample identification rather than season. Excluding this group, the corrected one-way ANOVA of the three seasons gave $F = 1236.6$, $p < 0.001$ ($df = 2, 144$), showing a very significant seasonal variation. The mean temperature decreased by about 23.22% from summer to rainy season and 37.43% from summer to winter. These changes reflect environmental seasonality, and are not to be interpreted as efficiencies of treatment removal. Temperature is not a parameter for pollutant removal but it is an important factor controlling natural biological treatment. Temperature fluctuations affect microbial growth and metabolism in biofilms on stones, sediments, plant roots and other submerged surfaces. Warmer conditions can improve microbial degradation of biodegradable organic matter, while lower winter temperatures can reduce microbial activity. But very high temperatures can influence dissolved oxygen availability and microbial community composition.

Aquatic and riparian vegetation can indirectly influence temperature-related treatment processes by shading, evapotranspiration, and alteration of local flow conditions. In addition, plant roots also provide substrates for microbial colonization and biofilm growth. Thus, vegetation and biofilm processes may interact to create localized microenvironments that allow for the biological transformation of pollutants. The seasonal temperature pattern thus provides an important environmental context for interpreting variations in BOD₅, COD and other biologically influenced water quality parameters[20, 21]. Figure 11 shows the mean water temperatures for the whole data set and individual seasons. Figure 12 shows the corrected one-way ANOVA results.

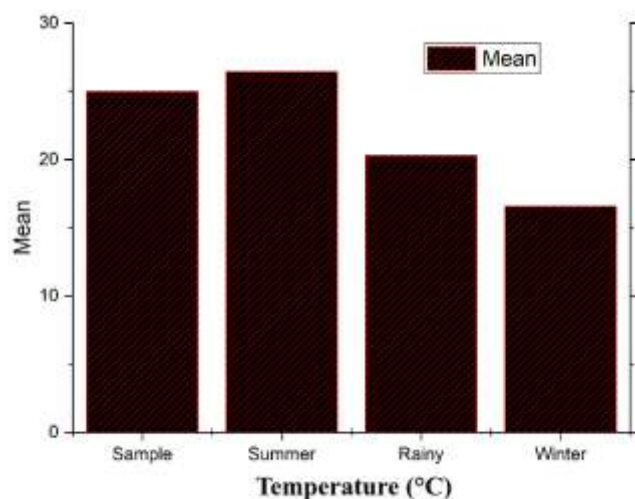


Figure 11 Seasonal variation of mean temperature in Kharun River water.

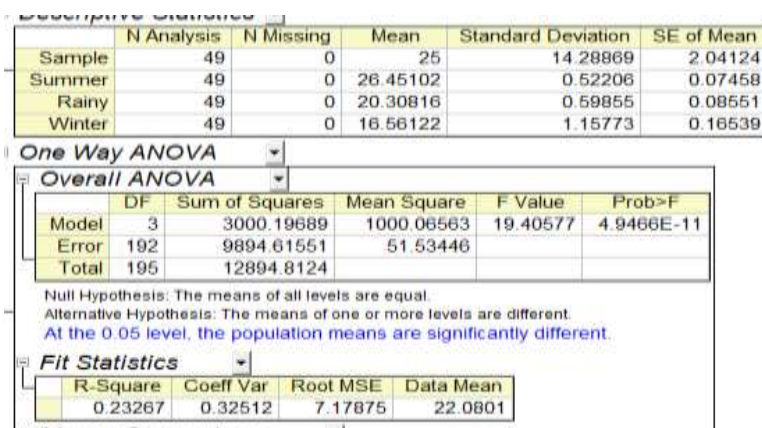


Figure 12 One-way ANOVA analysis of temperature in different seasons.

2.7. Biofilm formation-phytoremediation synergism on Kharun River physico-chemical parameters

Biofilm formation and phytoremediation may act as complementary biological processes affecting the physico-chemical quality of Kharun River water. Biofilms serve as microbial surfaces for biodegradation, transformation, adsorption and immobilization, and aquatic and riparian vegetation provide through root-zone filtration, sediment stabilization, nutrient uptake, pollutant immobilization, and provision of surfaces for microbial colonization. The seasonal average of BOD₅ was 17.41, 16.20 and 16.67 mg/L for summer, rainy and winter season, respectively and the average of COD was 18.55, 17.60 and 17.68 mg/L. Lower values in the rainy- and winter-season may be attributed to changes in organic loading and hydrological conditions. Biofilm associated microorganisms and plant-root rhizospheres may have supported organic matter degradation. The iron concentrations were almost constant (0.26429, 0.26429 and 0.26347 mg/L), with a limited seasonal variation. However, biofilms and plant roots may locally contribute to Fe adsorption, precipitation and immobilization.

Turbidity had the greatest seasonal variation with means of 38.67, 7.43 and 15.82 NTU respectively. Biofilms can trap suspended particles and vegetation may reduce flow velocity, encourage sedimentation and stabilize sediments. Mean pH decreased from 8.09 in summer to 7.80 and 7.64 in rainy and winter seasons, respectively, which may be due to seasonal variations in photosynthesis, respiration and microbial activity. The temperature decreased from 26.45 °C to 20.31 °C and 16.56 °C and was acting mainly as an environmental control on biological processes instead of a removable pollutant. To summarize, the results demonstrate complementary roles of biofilm and phytoremediation, especially for BOD₅, COD and turbidity. However, seasonal differences should not be interpreted as direct efficiencies of treatments. Paired inlet-outlet measurements or

controlled experiments are required to quantify the removal integrally[4] . Biofilm formation and phytoremediation synergistically affect water quality in different seasons . Seasonal variation of water quality at Kharun River showed lower BOD₅, COD and turbidity during rainy season and the mean values were 16.20 mg/L, 17.60 mg/L and 7.43 NTU respectively. The corresponding pH, Fe and temperature were 7.80, 0.264 mg/L and 20.31°C. In summer, BOD₅, COD, and turbidity were higher whereas minimum temperature and turbidity were moderately higher in winter than in the rainy season. These observations suggest that seasonal hydrological and environmental conditions influence water quality and could impact on biofilm and phytoremediation processes. Table 5 Seasonal comparison of selected physico-chemical parameters of water in Kharun River.

Table 1 Seasonal variation of water quality parameters of Kharun River.

Parameter	Summer	Rainy	Winter	Better season based on the observed value
Temperature (°C)	26.45	20.31	16.56	Winter*
Turbidity (NTU)	38.67	7.43	15.82	Rainy
pH	8.09	7.8	7.64	Rainy†
BOD ₅ (mg/L)	17.41	16.2	16.67	Rainy
COD (mg/L)	18.55	17.6	17.68	Rainy
Fe (mg/L)	0.2643	0.2643	0.2635	Winter, but difference is negligible

Temperature is an environmental factor, not a pollutant, so lower temperature does not necessarily mean better water quality. Also pH should be considered in terms of desirable range rather than the absolute value. The best conditions for turbidity and organic pollution were during the rainy season, with reductions of about 80.8% in turbidity, 6.9% in BOD₅ and 5.1% in COD compared to the summer. Biofilm formation may be more directly responsible for the reduction of BOD₅ and COD through microbial degradation of organic matter. Phytoremediation may provide complementary effects through root-zone filtration, sediment stabilization and Fe immobilization. Vegetation and associated roots may also provide surfaces for microbial colonization and particle retention . However, the seasonal data cannot identify which of the mechanisms is quantitatively more effective. The respective removal efficiencies of controlled biofilm only, plant only and combined systems would be needed to be determined[22, 23] .

2.8. Water Quality Status at Aтора Village after Constructed Wetland Treatment

The proposed constructed wetland (CW) at Aтора Village, Patan Block, Durg District, Chhattisgarh is based on filtration, sedimentation, microbial degradation, plant uptake and rhizosphere interactions for the improvement of the quality of wastewater. For each parameter, ten observations (N = 10) were recorded at the inlet and outlet. Temperature, turbidity and pH exhibited different inlet-outlet variations (Figure 13). One-way ANOVA revealed statistically significant difference between groups ($F = 533.89473$, $p = 5.07787 \times 10^{-52}$, $p < 0.05$; Figure 14). Figure 15 shows the average BOD₅, COD and Fe concentrations before and after treatment. BOD₅ and COD were reduced significantly and Fe concentrations were relatively low. ANOVA also indicated a significant difference between the inlet and outlet measurements ($F = 1430.91323$, $p = 2.48524 \times 10^{-65}$, $p < 0.05$; Figure 16), which shows significant changes in the measured water-quality parameters after constructed wetland treatment.

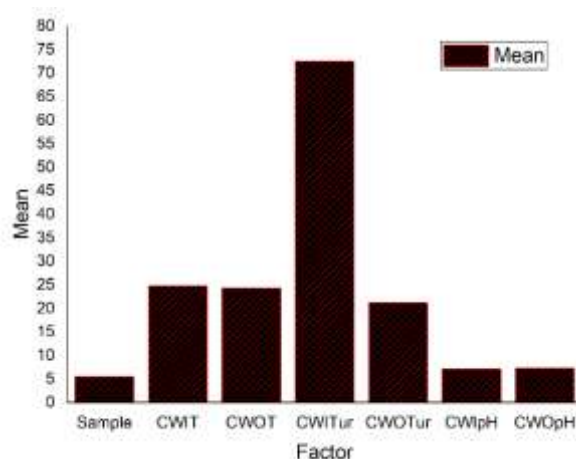


Figure 13 Mean of water quality parameters in inlet and outlet of constructed wetland.

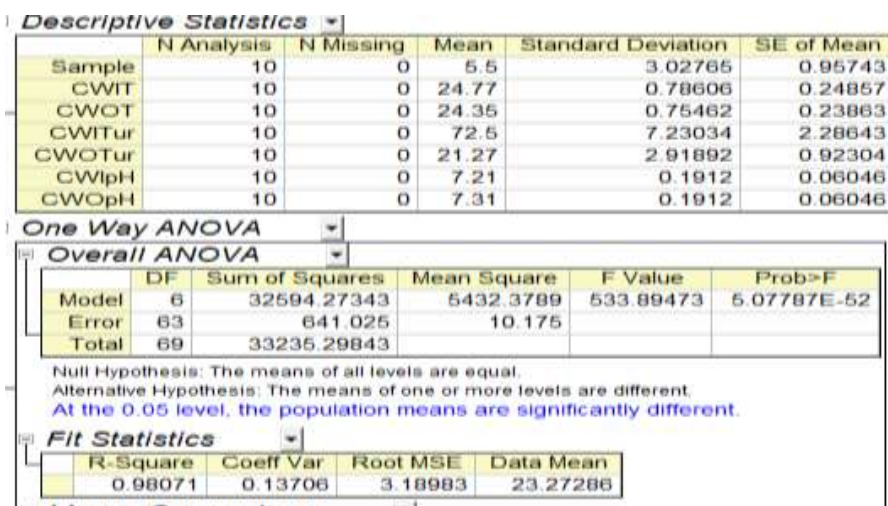


Figure 14 One-way ANOVA analysis of temperature, turbidity and pH at the inlet and outlet of constructed wetland.

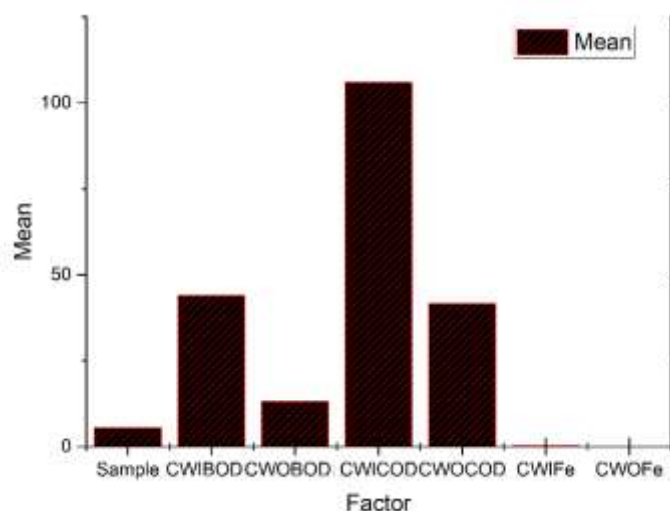


Figure 15 Average concentrations of BOD₅, COD and Fe in inlet and outlet of constructed wetland.

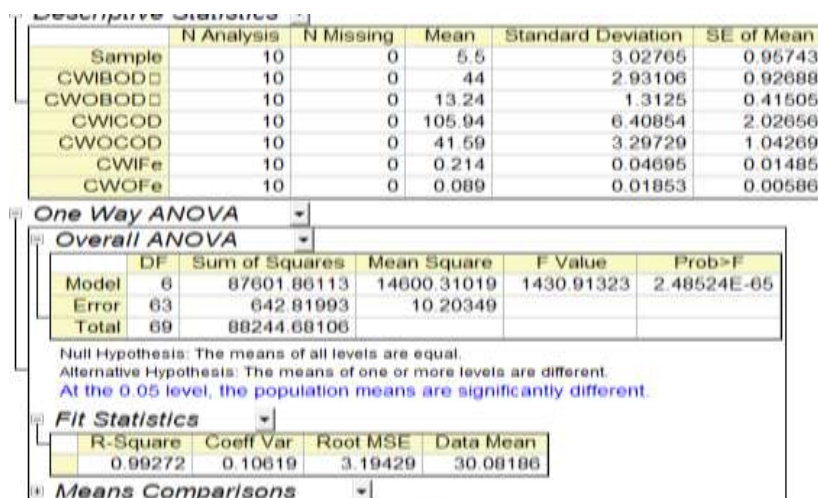


Figure 16. One-way ANOVA for changes in BOD₅, COD and Fe concentrations before and after treatment in the constructed wetland.

The physico-chemical characteristics of the gray water measured at the inlet and outlet of the constructed wetland are given in Table 6. They include temperature, turbidity, pH, BOD₅, COD and Fe. The values provide a comparative evaluation of water-quality conditions before and after wetland treatment.

Table 4.6 Water-quality parameters of gray water at inlet and outlet of the constructed wetland.

Sample	CWIT	CWOT	CWITur	CWOTur	CWIpH	CWOpH
1	24.1	23.8	68	19.5	7.1	7.2
2	24.8	24.4	72	21.2	7.2	7.3
3	25.2	24.9	75	22.8	7.3	7.4
4	25.7	25.3	81	24.6	7.4	7.5
5	23.9	23.5	65	18.1	7	7.1
6	24.6	24.1	70	20.3	7.2	7.3
7	25.4	24.8	78	23.4	7.4	7.5
8	23.7	23.3	62	16.9	6.9	7
9	24.3	23.9	69	19.8	7.1	7.2
10	26	25.5	85	26.1	7.5	7.6

Sample	CWIBOD ₅	CWOBOD ₅	CWICOD	CWOCOD	CWIFe	CWOFe
1	41.8	12.4	101.2	39.8	0.18	0.08
2	43.5	13.1	104.8	41.6	0.21	0.09
3	45.2	13.8	108.5	43.2	0.24	0.1
4	47.1	14.7	112.3	45.1	0.27	0.11
5	40.6	11.8	98.7	37.9	0.16	0.07
6	44	13	106.1	40.5	0.2	0.08

7	46.3	14.2	110.7	44	0.25	0.1
8	39.8	11.3	96.4	36.8	0.15	0.06
9	42.7	12.6	103.5	39.7	0.19	0.08
10	49	15.5	117.2	47.3	0.29	0.12

The average inlet temperature (CWIT) was 24.77 ± 0.79 °C as compared to 24.35 ± 0.75 °C at the outlet (CWOT), a small drop of 0.42 °C (1.70%). This change is a response to environmental effects such as shading by vegetation, evapotranspiration and heat exchange, not removal of pollutants. Turbidity showed the highest improvement from 72.50 ± 7.23 NTU at the inlet to 21.27 ± 2.92 NTU at the outlet, a reduction of 51.23 NTU (70.66%). This reduction may be ascribed to screening, sedimentation, filtration through the media bed, retention of particles in the root zone and reduced flow velocity. The roots also provide surfaces for the development of microbial biofilms. pH increased slightly from 7.21 ± 0.19 to 7.31 ± 0.19 indicating maintenance near neutral conditions possibly due to plant-microbe interactions, dissolved CO₂, photosynthesis and respiration. The overall ANOVA ($F = 533.895$, $p = 5.08 \times 10^{-52}$, $R^2 = 0.98071$) cannot be considered as primary evidence because different parameters and units were aggregated. Separate paired analyzes are preferred [24–26]. The treatment performance of the constructed wetland for gray-water treatment is shown in Table 7, by comparing the physico-chemical parameters at inlet and outlet. The comparison shows the variation of temperature, turbidity, pH, BOD₅, COD and Fe after wetland treatment and offers an in-depth evaluation of the improvement in water quality

Table 7 Performance of constructed wetlands in treating water based on inlet-outlet water quality parameters.

Parameter	Inlet mean	Outlet mean	Change	Interpretation
Temperature	24.77°C	24.35°C	↓ 0.42°C (1.70%)	Slight reduction
Turbidity	72.50 NTU	21.27 NTU	↓ 70.66%	Major improvement
pH	7.21	7.31	↑ 0.10 (1.39%)	Slight stabilization

The constructed wetland at Atora Village showed significant improvement of selected gray-water quality parameters. The reduction of turbidity was the highest among the physical parameters, from 72.50 to 21.27 NTU, equivalent to 70.66% removal. The improvement may be due to screening, sedimentation, gravel/media filtration, reduction of flow velocity, and particle retention in the plant root zone. The temperature was relatively stable decreasing from 24.77 to 24.35 °C and the pH increased slightly from 7.21 to 7.31, indicating slight modification of the environment rather than removal of pollutants. For organic pollutants, the BOD₅ was reduced from 44.00 ± 2.93 to 13.24 ± 1.31 mg/L, showing a reduction of 30.76 mg/L or 69.91%. The COD reduced from 105.94 ± 6.41 to 41.59 ± 3.30 mg/L, which is a reduction of 64.35 mg/L or 60.74 %. These reductions indicate that microbial degradation, filtration and retention in the wetland bed greatly attenuate biodegradable and chemically oxidizable organic matter. Biofilms developing on gravel, sediments, and roots of plants provide active surfaces for microbial transformation. The rhizosphere intensifies the contact between the microorganisms, wastewater and the roots of the plants. The iron concentration was reduced from 0.214 ± 0.047 to 0.089 ± 0.019 mg/L, which is a reduction of 0.125 mg/L or 58.41%. The reduction can be caused by adsorption, precipitation, retention in sediment, interactions with microbes and immobilization or uptake by plant roots. Thus, the activity of the biofilm and the phytoremediation are complementary parts of the constructed-wetland process of treatment rather than separate mechanisms. The generic treatment sequence is: screening → settling → media filtration → biofilm activity → plant-root/rhizosphere processes → treated-water outlet. The results showed significant reduction in turbidity, BOD₅, COD and Fe where temperature and pH were fairly stable. Table 8 summarizes the water quality characteristics of inlet and outlet and the treatment performance of the constructed wetland[18].

Table 4.8. Water quality parameters at inlet and outlet of constructed wetland to find out changes after treatment.

Parameter	Inlet Mean	Outlet Mean	Reduction	Removal Efficiency
BOD ₅ (mg/L)	44	13.24	30.76	69.91%
COD (mg/L)	105.94	41.59	64.35	60.74%
Fe (mg/L)	0.214	0.089	0.125	58.41%

The removal efficiency followed the order of BOD₅ (69.91%) > COD (60.74%) > Fe (58.41 %). The higher BOD₅ reduction shows that biodegradable organic matter is effectively attenuated while COD reduction indicates removal of chemically oxidizable substances and Fe reduction indicates retention or transformation within the wetland. The combined ANOVA indicated $F = 1430.913$ and $p = 2.49 \times 10^{-65}$, with $R^2 = 0.99272$. However, as BOD₅, COD and Fe are different parameters with different units, this overall ANOVA should not be interpreted as a direct test of treatment efficiency. The analysis of inlet–outlet about the parameters is more proper. In general, the constructed wetland was very effective in decreasing organic pollution and the concentration of Fe in Atora gray water.

3. CONCLUSION

The study reports significant seasonal variations in physico-chemical properties of Kharun River water indicating the possible complementary role of natural biofilms and phytoremediation in improving water quality. BOD₅, COD, pH, turbidity and temperature were significantly different between seasons. Fe was relatively stable. In the rainy season the BOD₅, COD and turbidity were significantly lower than summer. Temperature and pH should be interpreted as environmental parameters and not as direct indicators of pollutant removal. Natural biofilms are biologically active surfaces that can be used by microorganisms to degrade and transform organic matter. Aquatic and riparian vegetation contribute through root-zone filtration, sediment stabilization, immobilization of pollutants and the support of microbial communities. Cumulative impacts are especially relevant for BOD₅, COD and turbidity, but Fe attenuation and pH regulation are more strongly controlled by environmental and biological conditions. The proposed constructed wetland at Atora Village showed obvious treatment potential. The turbidity, BOD₅, COD and Fe decreased by 70.66%, 69.91%, 60.74%, and 58.41% respectively, whereas temperature and pH were stable and unchanged. Results showed that gray-water quality can be improved by combined operation of physical filtration, sedimentation, microbial biofilm activity and plant-root processes. Importantly, the seasonal differences noted in the Kharun River should not be viewed as direct removal efficiencies of biofilm or phytoremediation. Likewise, a combined ANOVA of parameters measured in different units is not a suitable primary test of treatment efficacy. Future work should incorporate parameter-specific paired inlet-outlet analyzes and controlled comparisons of biofilm-only, plant-only and combined systems. Such studies would provide quantitative evidence for the individual and synergistic contributions of microbial and plant-mediated processes and support optimization of constructed wetlands as sustainable wastewater-treatment systems.

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