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Integration of TADOX® technology to improve water reuse efficiency of constructed wetland-treated water

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ABSTRACT

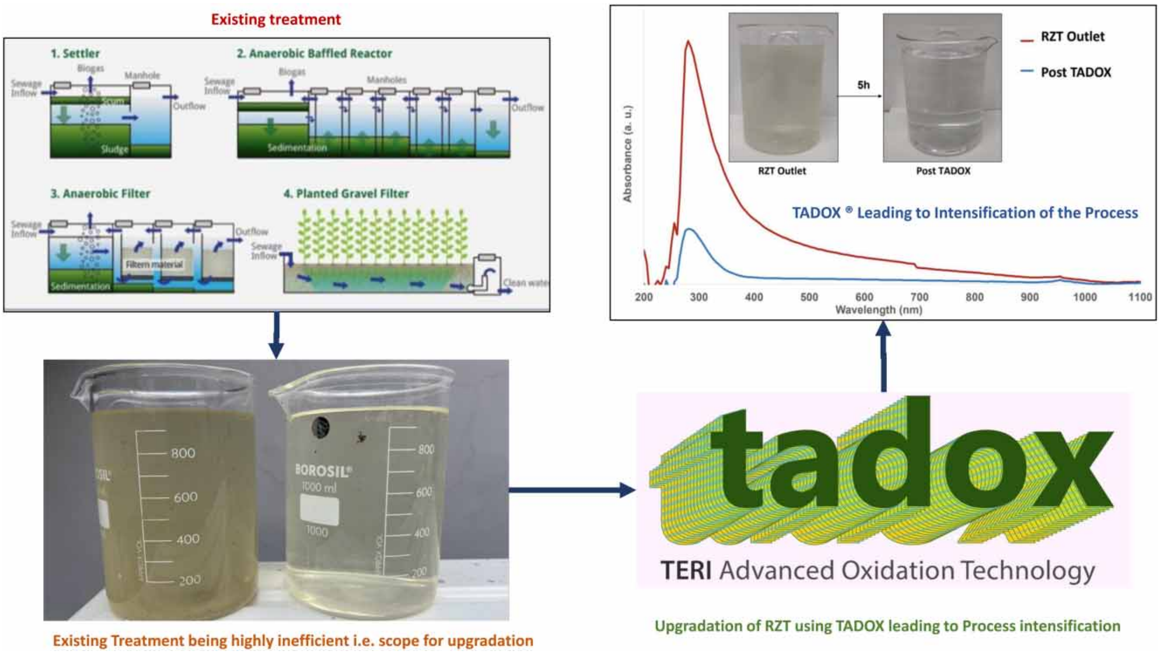
Constructed wetland (CW) is an effective and economical decentralized wastewater treatment (DWWT) method implemented in various developing nations. Such CW-treated water may be good for meeting discharge norms but when it comes to high-end reuse, it requires polishing and integration with advanced oxidation process (AOP)-based treatment. In this pursuit, TERI (The Energy and Resources Institute) Advanced Oxidation Technology (TADOX®) may be able to polish such streams and make the CW-treated water reusable. TADOX utilizes UV-TiO_2 Photocatalysis (PC) as a secondary treatment followed by nanomaterial recovery. This study aims at evaluating TADOX treatment to polish treated water from a root zone treatment (RZT) plant. Performance evaluation of the treatments is evaluated based on key parameters for treated sewage water such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids, color, pathogens (total and thermotolerant coliforms), and persistent organic pollutants (POPs) such as caffeine, acetaminophen, ibuprofen, and diclofenac.

Key words: micropollutants, municipal wastewater, root zone treatment, sewage treatment, TADOX®, treated water reuse

HIGHLIGHTS

- Root zone treatment (RZT) technology removed 75% COD, 13% BOD, and 67% phosphates.
- TADOX® treatment of RZT-treated water led to BOD, COD, NO_3-N, and PO_4-P % removal as 94, 50, 66, and 100.
- TADOX® was effective to remove micropollutants in the range of 79–88%.

GRAPHICAL ABSTRACT



INTRODUCTION

Increasing water demand and contaminated freshwater sources due to the dumping of untreated or partially treated wastewater onto the surface are among the major causes of water scarcity worldwide. In this regard, the reusability potential of domestic wastewater can contribute significantly, where effective reuse of adequately treated domestic wastewater is well known for applications such as groundwater recharge, horticulture, vehicle washing, firefighting, flushing, floor washing, dust suppression etc. Root zone technology (RZT) and constructed wetlands (CWs) have currently emerged as efficient treatment processes as these are relatively low-cost and energy options for wastewater treatment with ease in operation and maintenance, proficient in degrading a wide range of organic pollutants including emerging pollutants like pharmaceuticals and personal care products (PPCPs) and pathogens (Stefanakis & Tsihrintzis 2009, 2012; Stefanakis *et al.* 2011, 2016; Rana *et al.* 2016; Tondera *et al.* 2019; Tondera *et al.* 2021; Anigrou *et al.* 2022). Despite its significant performance in terms of wastewater treatment as depicted in many studies, CW is also associated with several practical, operational, and maintenance challenges (CPCB ENVIS Letter 2000; CPCB 2005; Stefanakis & Tsihrintzis 2009, 2012; Tare & Bose 2009; Hasan *et al.* 2019). Most importantly, in terms of treatment efficiency, it provides water quality that can be reused for low-end purposes only, such as for irrigation, washing, flushing (Rohilla 2014). Also, in some studies, CW was found inefficient in removing pathogens from sewage water which could be hazardous for many reuse applications (Talekar *et al.* 2018; Talekar & Mutnuri 2021).

Thus, the requirement of integrating CW/RZT with some advanced treatment processes has been identified in order to improve the reusability potential of the treated water. Advanced oxidation processes (AOPs) are widely suggested as the ultimate solution for improving the overall efficiency of the treatment process for wastewater treatment; these are more effective for the removal of micropollutants and pathogens. Nano-TiO_2-mediated UV photocatalysis (PC) is a widely explored AOP for the removal of recalcitrant pollutants and pathogens for various wastewater treatments. Various studies have shown that integration of AOPs with CW leads to significant improvement in physicochemical and microbiological characteristics in terms of COD, BOD, TOC, *Escherichia coli*, and total coliform (Horn *et al.* 2014; Machado *et al.* 2016; Rana *et al.* 2016; Talekar *et al.* 2018; Talekar & Mutnuri 2021).

TERI's Advanced Oxidation Technology (TADOX®) could be used to improve the quality of the treated water from a RZT Plant. TADOX® uses UV-TiO_2 PC to break down pollutants in water, making it reusable. Technical reports on the implementation and effectiveness of TADOX® for treating various polluting wastewater streams and integration with moving bed biofilm reactor-based sewage treatment plants has been published earlier

(Bahadur & Bhargava 2019, 2022; Bahadur *et al.* 2020, 2023a, 2023b; Bahadur 2021). This study evaluated the effectiveness of TADOX treatment on key parameters for the treated sewage water, including COD, BOD, suspended solids, color, pathogens, and persistent organic pollutants (POPs). In this study, the effectiveness of TADOX® has been evaluated for improving the quality of the treated water from RZT plants operating in TERI's campus. The objective of the integration of TADOX® treatment with the RZT unit is to improve water quality characteristics meet discharge norms and assess the suitability of this water for reuse by nearby industries for their process requirements.

METHODS

TERI's horizontal flow – CW-based technology known as RZT is installed at a hotel cum convention center with a total treatment capacity of 5,000 liters per day. Figure 1 shows photos of the wastewater treatment facility.

For this study, the treated water from RZT was collected in a jar and its polishing treatment was explored using TADOX® treatment. A simplified process flow diagram of the TERI advanced oxidation technology (TADOX®) is shown in Figure 2 which illustrates the n-TiO_2/UV PC integrated with Nano-material Recovery Unit (NMRU) for effective AOP treatment.

Figure 1 | Photos of TERI's CW-based treatment known as the RZT Plant.

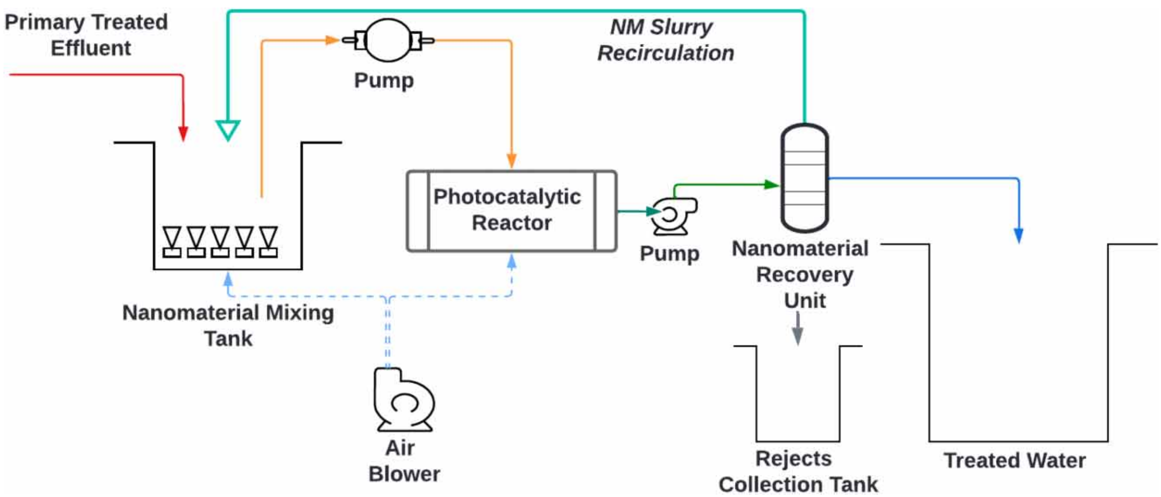


Figure 2 | Process flow diagram of the heterogenous photocatalysis system based on TERI Advanced Oxidation Technology (TADOX®) (Bahadur & Bhargava 2019; Bahadur *et al.* 2023b).

Detailed descriptions of the optimization studies and related works have been previously reported by the authors, a summary of the plant operation and sample treatment is as follows. In reference to the schematic shown in Figure 2, the primary treatment supernatant was aerated with coarse bubbling for efficient mixing and mechanical agitation of powdered nano-TiO_2; the slurry was continuously mixed for 30 min. Next, the suspension was left to rest undisturbed for 30 min to achieve adsorption–desorption equilibrium. The suspension was re-aerated and well combined for 10 min before being pumped to a photocatalytic reactor (PCR) and treated under recirculation mode for 120 min (patented design with optimized geometry and sufficient UV light radiation source). The treated water was then transferred via a built-and-developed mechanism with suitable filtration to remove spent nanomaterial, after which clean water was generated and the used nano-catalyst recovered.

RESULTS AND DISCUSSION

Figure 3 shows the TADOX® treatment was successful in completely removing the residual color from the wetland-treated municipal water, as only partial reduction in color took place after wetland treatment. The wetland-treated water also had a significant level of residual dissolved organic content which was significantly reduced by the TADOX® treatment, as can be seen in the given spectra.

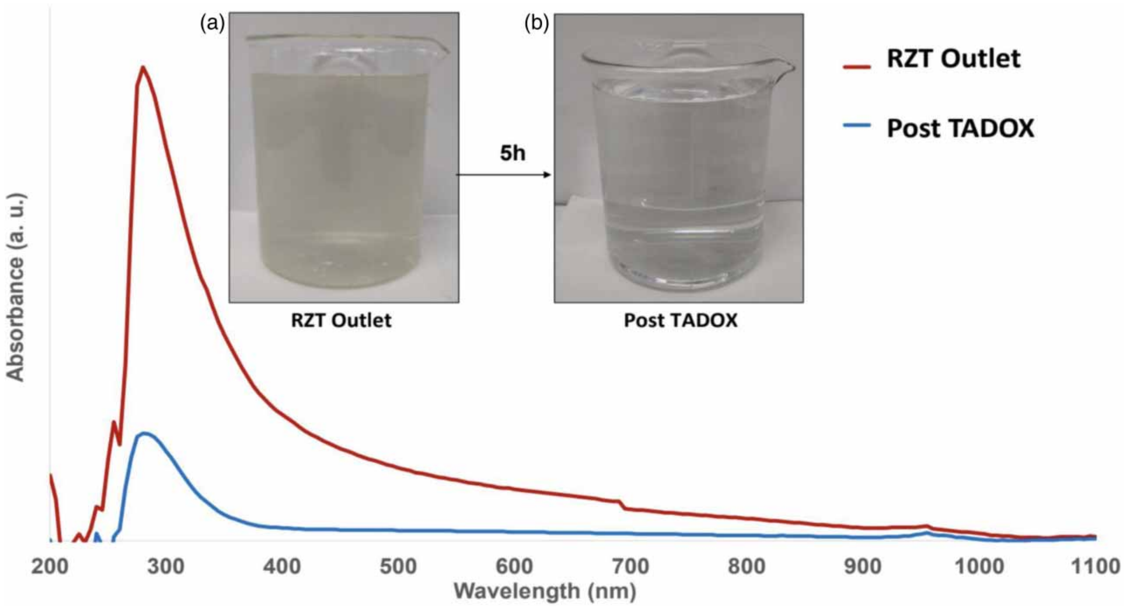


Figure 3 | UV–Vis spectra of the RZT outlet (a) and post TADOX® (b).

Photocatalytic treatment of the wetland-treated water also improved its physicochemical features, as represented in Table 1. Where, the COD of the wetland treated water was further reduced by 50% after TADOX® treatment, with a final value lower than the regulatory norms of COD, BOD of 250 and 30 mg/l, respectively (Ministry of Environment & Forests 1986). This removal in the physicochemical process agrees with the previously published report and its findings on TADOX® implementation in sewage treatment and other studies on improving treated water reuse efficiency (Bahadur & Bhargava 2022; Bahadur *et al.* 2023a, 2023b). Degradation of conductivity, TDS, and TSS may be attributed to the primary treatment system where novel alkali earth metal oxide formulations are used for coagulation flocculation and result in high removal of the solids (dissolved and suspended). Moreover, this same primary treatment simultaneously is responsible for the complete degradation of phosphates and nitrogen. Secondary treatment which involves UV titania resulting in *in situ* generated hydroxyl radicals degraded the organic pollutants represented by BOD and COD. The hydroxyl radicals oxidatively cleaved the organic compounds resulting in photooxidative degradation of carbon compounds into complete mineralization products such as CO_2, carbonates, and nitrates, and this is supported by previous work by the authors.

Table 1 | Water quality characteristics of the RZT outlet and post TADOX®

Parameter	Current treatment process RZT inlet (A)	RZT outlet (B)	% Change	Polishing treatment of RZT outlet with TADOX® (C)	% Change
pH value	6.57	6.97		9.81	–
Conductivity, μmho/cm	1,068	1,318	–	255.6	80.6
Total dissolved solids, mg/l	533.8	659	–	127.8	80.6
Total suspended solids, mg/l	91.1	90.2	0.9	4.5	95
COD, mg/l	163	40	75.5	20	50
BOD, mg/l	38	33	13.2	2	93.9
Nitrate nitrogen, mg/l	11.9	88.9	–	30	66.2
Nitrite nitrogen, mg/l	0.6	64.3	–	15.2	76.4
Total Kjeldahl nitrogen, mg/l	12.1	11.0	9.09	2.1	82.6
Phosphate, mg/l	6.71	2.19	67.4	ND	100
Pathogens					
E. coli, MPN/100 ml	126×10^5	92×10^5	26.9	2	5 log reduction
Total coliform bacteria, MPN/100 ml	200×10^6	185×10^6	7.5	30	6 log reduction
Total count, CFU $\times 10^5$/100 ml	7.05	6.75	4.2	0.01	5 log reduction
Micropollutants					
Caffeine (CFF), μg/l	0.191	0.187	2	0.030	83.9
Acetaminophen (ACT), μg/l	2.780	2.570	8	ND	100
Ibuprofen (IBU), μg/l	0.394	0.374	5	0.094	74.8
Naproxen (NPX), μg/l	0.462	0.381	18	0.210	44.9
Sulfamethoxazole (SMZ), μg/l	pND	ND	ND	ND	ND
Diclofenac (DCF), μg/l	0.647	0.614	5	0.129	79
Bisphenol-A (BPA), μg/l	0.331	0.161	51	0.120	25.5

The overall COD reduction efficiency of the combined process (wetland and PC) was 87.7%. A similar observation was reported by Talekar *et al.* (2018), where, an integrated treatment process comprised of full-scale wetland, followed by electrochemical oxidation was explored for the treatment of septage water from a septic tank, collecting single household or community toilet flushing at Birla Institute of Technology & Science (BITS) Pilani, Goa campus. The combined process, i.e., full-scale wetland and nearly 6 h of electrochemical oxidation resulted in around 89% of COD reduction. Also, this electrochemical oxidation treatment caused effective disinfection of pathogens under acidic conditions and chlorination in the anode chamber, where the generation of chlorine-based oxidants was reported (Talekar *et al.* 2018). Though the COD reduction efficiency is comparable in both the AOP-based studies, i.e., PC-based TADOX® and electrochemical oxidation, but the formation of chlorine by-products in the latter during disinfection can be a serious limitation. While in TADOX® there is no involvement of chlorine or other toxic chemicals. Moreover, TADOX® treatment needs 5 h for an end-to-end treatment while on the other hand electrochemical oxidation requires 6 h of treatment.

Another study reported integration of UV/H_2O_2 with a CW treatment to improve the overall treatment raw water treatment efficiency of the system, the study showed overnight coagulation and H_2O_2/UV process led to 93% of reduction in overall COD (Rana *et al.* 2016). Although the COD removal efficiency of H_2O_2/UV photo-oxidation is almost comparable or slightly higher with TADOX®, but TADOX® seems to be better in terms of treatment duration and treated water quality. On the other hand, this process of integrating photolysis of peroxide required 12 h of treatment while TADOX® requires much lesser treatment time. Moreover, the treated water generated by the H_2O_2/UV treatment was recommended for low-end use only, whereas the treated water quality provided by TADOX® can be considered for high-end use as well, as it was also found efficient in terms of pathogen and micropollutant removal.

Similarly, BOD removal in wetland-treated water was also significantly improved by TADOX® treatment. Where, the BOD reduction in sewage water after wetland treatment was found to be quite low with only 13.2% of reduction, while further treatment with TADOX® dramatically increased the BOD reduction to 93.9%. On the contrary, Rana *et al.* (2016), reported 81.7% of BOD reduction in wetland-treated synthetic grey water with 2 h of H_2O_2/UV process, which was preceded by 12 h of coagulation, whereas TADOX® is reporting 93.9% of BOD reduction within only 5 h (Rana *et al.* 2016).

Based on Table 1, RZT showed only marginal removal of micropollutants namely caffeine, acetaminophen, ibuprofen, naproxen, sulfamethoxazole and diclofenac, with reduction varying from 2 to 17.5%, except for Bisphenol-A which was reduced by 51.3%. TADOX® treatment of the RZT-treated water led to a significant reduction of these micropollutants with an efficiency ranging from 75 to 100%. Among them, Acetaminophen was completely removed from the treated water and was followed by an 83.9% reduction in caffeine. To the best of our knowledge, there is no other study that could be found in the literature which explored the efficiency of constructed wetlands with AOPs to remove such Contaminants of Emerging Concern (CEC)/POPs from sewage wastewater.

Therefore, TADOX® integration with such horizontal CW plants can significantly improve the quality of treated water from conventional technologies and make it suitable for industrial use. It is a faster and more efficient treatment process than conventional methods. The treated water can be used for boiler feedwater, cooling tower make up, etc. This can help to reduce the abstraction of groundwater and improve the availability of freshwater for domestic use.

CONCLUSIONS

TERI (The Energy and Resources Institute) Advanced Oxidation Technology (TADOX®) could polish treated water of a CW based on RZT processing domestic sewage effluent-treated water complying with norms of regulator. Performance evaluation of the treatments was evaluated based on key parameters for the treated sewage for CW-treated water and for TADOX-polished water. The RZT treatment led to removal of 75% COD, 13% BOD, 67% phosphates, and negligible removal in TSS; while TADOX Treatment of RZT-treated water led to BOD, COD, NO_3-N, and PO_4-P percentage removal as 94, 50, 66, and 100 along with simultaneous disinfection leading to insignificant residual total coliform (MPN/100 ml) and *E. coli* (in MPN/100 ml) levels. TADOX treatment achieved the removal of priority micropollutants suchas caffeine, acetaminophen, ibuprofen, naproxen, diclofenac, and bisphenol (A) by 83.9, 100, 74.8, 44.9, 79, and 25.5%.

It is evident that TADOX® could remove a wide range of pollutants from the treated water, including BOD, COD, NO3-N, PO4-P, and micropollutants. It can treat wastewater in a few hours, as opposed to the 24 h required by conventional plants like CW and RZT. Moreover, TADOX® is a much more robust, flexible, and reliable system that can handle varied characteristics of effluent and bear shock loads of load and pollutants. The treated water obtained after TADOX® was found to be highly reusable for a variety of applications like cooling tower makeup, boiler feedwater treatment, horticulture development, and dust suppression.

Hence, TADOX® has the potential to significantly impact the environment by reducing groundwater abstraction, increasing freshwater availability, and improving river water management. Further studies could be made on integrating TADOX® with Vertical CW plants to explore possibilities of enhancement of their treated water. All these results open up tremendous scope for the integration of AOP-based treatment to polish RZT/CW water and make treated water available for high-end reuse.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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