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TERI Advanced Oxidation Technology (TADOX®) to treat industrial wastewater with integration at pre- and post-biological stage: case studies from India

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ABSTRACT

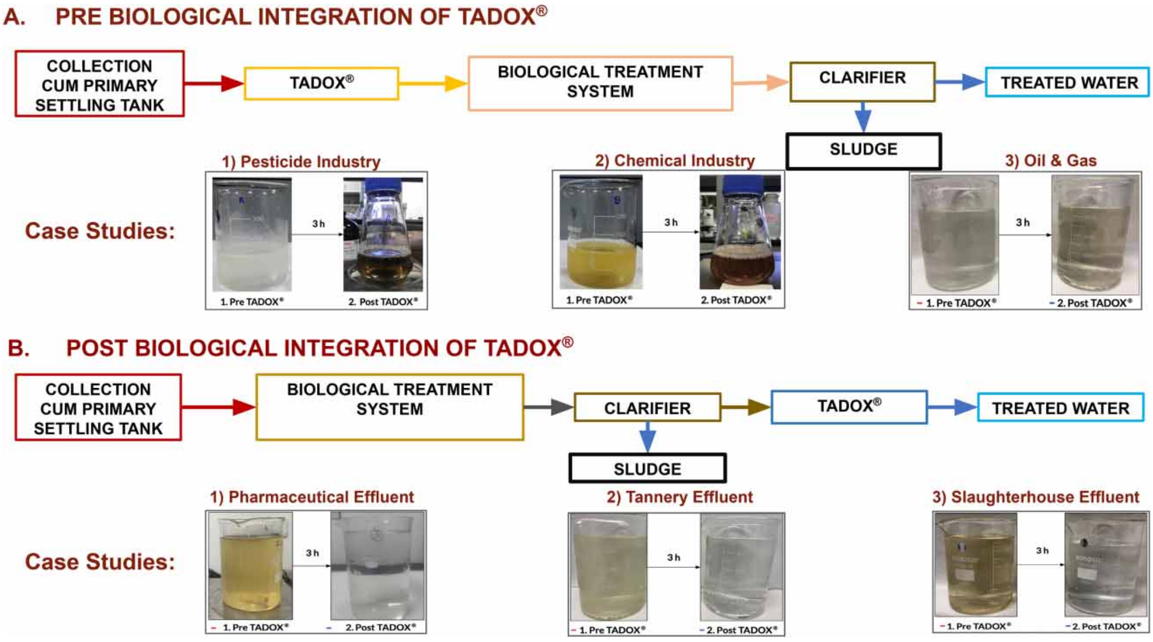
The current problem with industrial wastewater treatment is that we rely heavily on biological treatment systems without realising that these have severe limitations in terms of shock load-bearing capacities, ineffectiveness against removal of toxicity and recalcitrant and dissolved organics. However, biological systems have their own benefits as well. Therefore, it is essential to support them with integration of advanced oxidation nanotechnology (AON) interventions, which are expected to address these challenges. In this pursuit, The Energy and Resources Institute (TERI) has developed an AON-based wastewater treatment technology called TERI Advanced Oxidation Technology (TADOX®). This paper presents two sections of three case studies each, to showcase how TADOX® technology intervention at pre-biological and post-biological treatment helps in achieving adequate treatment. In the first section, TADOX® has been implemented at pre-biological stage for three highly polluting streams from (i) phenolic wastewater from a 2,4-dichlorophenoxyacetic acid (2,4 D) plant from a Gujarat pesticide manufacturing company, (ii) phenolic wastewater from an anisole plant of a Gujarat chemical industry, and (iii) hydrocarbon-rich effluent from the Jharkand oil and gas sector. Pre-biological integration is expected to support biological treatment by reduction in COD, toxicity, microbial growth hindering compounds and increase in biodegradability (BOD to COD ratio). The second section in the paper explores the implementation potential of TADOX® to treat biologically treated streams from (i) Uttarakhand pharmaceutical, (ii) Uttar Pradesh tannery and (iii) Uttar Pradesh slaughterhouse. The post-biological integration is expected to remove residual COD, colour, BOD and odour leading to treated water meeting norms for safe surface discharge and water reuse. Presented studies from India may be useful and relevant to other developing countries as a possible approach to sustainably manage water resources, together meeting the challenges of economic growth, industrial development, and regulatory and environmental compliance.

Key words: chemical & pesticide industry wastewater, industrial wastewater treatment, oil and gas produced water, slaughterhouse effluent, TADOX®, tannery effluent

HIGHLIGHTS

- Showcasing how TADOX® technology intervention at Pre-biological and post-biological treatment helps in achieving adequate treatment.
- Case studies of pre-biological integration of TADOX® for treating (i) phenolic wastewater, (ii) phenolic wastewater, (iii) oil and gas wastewater.
- Case studies of post-biological integration of TADOX® for treating (i) pharmaceutical, (ii) tannery and (iii) slaughterhouse streams.

GRAPHICAL ABSTRACT



INTRODUCTION

Industrial wastewater treatment is still a major challenge in developing countries such as India where waste streams are not adequately treated and free from dissolved organics and recalcitrant compounds, which prevents reuse and recycling of treated water. To improve the current state of treated water reuse, the Central Pollution Control Board (CPCB) under the Ministry of Environment, Forests and Climate Change (MOEF&CC), Government of India (GoI) in 2015 came out with regulation of complying with 'Zero Liquid Discharge' (ZLD) for grossly polluting industries such as tanneries, slaughterhouses, chemical industries, pharmaceutical manufacturers, pulp and paper, textile and dyeing etc. (CPCB (Ministry of Environment and Forests 2015). So far, the guidelines of ZLD have been opposed by various national, regional, and local industrial associations because the way ZLD is achieved is highly resource and energy intensive, unaffordable and unsustainable. This is mainly because the current technology providers, regulators and end-users are accustomed to a conventional type of biological degradation-based treatment and the same treatment is given to all streams alike without understanding their matrix, composition and treatment requirements. Due to this generic approach, the performance of various treatment systems is greatly reduced, leading to low=quality treated water, which when reaches for subsequent tertiary treatment, involving RO and MEE etc., puts up an additional load, thus making ZLD compliance unachievable.

In this context, The Energy and Resources Institute (TERI), New Delhi has developed advanced oxidation nanotechnology (AON) - based wastewater treatment technology called TERI Advanced Oxidation Technology (TADOX®), which has proved to be beneficial enough to be integrated in current systems to fill the gaps. Complete details of the technology and the process flow have been published and discussed in earlier reports (Bahadur & Bhargava 2019; Bahadur *et al.* 2020; Das *et al.* 2020). Some of the advantages of the advanced oxidation process (AOP)/AON approach are the minimal addition of chemicals, recovery and reuse of used nanomaterials and simultaneous destruction of recalcitrant organics and bio-pollutants including pathogens such as viruses and bacteria (Oturan & Aaron 2014).

Wastewater from chemical manufacturing units, pesticide manufacturers/formulation units, oil production wells and other organic chemical processing units generate highly toxic and non-biodegradable wastewater from their operations such as solvent recovery, plant washings, vessel washings etc. This biodegradability is indicated by BOD/COD ratio (Zhang *et al.* 2020; Saravanathamizhan & Perarasu 2021; Tooker *et al.* 2021); thus it is expected that AOP implementation at the pre-biological stage could break down complex organics and enhance biodegradability (Jamil *et al.* 2011; Oller *et al.* 2011; Vilar *et al.* 2012). Several AOP-based treatments have been reported at t pre-biological stage for streams such as chemical wastewater (Ribeiro *et al.* 2015; Ramteke & Gogate

2016; Oliveira Guimarães *et al.* 2019), phenolic wastewater (Ahmed *et al.* 2011; de Sá *et al.* 2018; Jay *et al.* 2019; Oliveira Guimarães *et al.* 2019) and oil drilling effluent (Yu *et al.* 2017; Jiménez *et al.* 2019). Hence for such effluent streams, TADOX® is planned to be integrated at a pre-biological stage, as shown in Figure 1.

Figure 1 | Schematic showing TADOX® Implementation at Pre-Biological Stage.

Now comes the issue, where the biologically treated water is unable to meet the criteria for reuse because of the residual recalcitrant organics present in the stream. These coloured and recalcitrant organics affect reverse osmosis (RO) membrane performance, multiple effect evaporator (MEE) performance, operation costs and condensate quality. Moreover, low boiling point organics such as solvents, alcohols etc., which are not efficiently degraded by biological systems or membrane processes, make their way eventually to MEE condensate, thus leading to lack of reusability of this stream. This is common in industries such as tanneries, slaughterhouses and pharmaceuticals. Figure 2 shows a schematic wherein it is proposed that TADOX® intervention at post-biological stage could result in better treatment of the residual organics and reduce load on downstream tertiary treatment system consisting of RO, MEE, MVR etc.

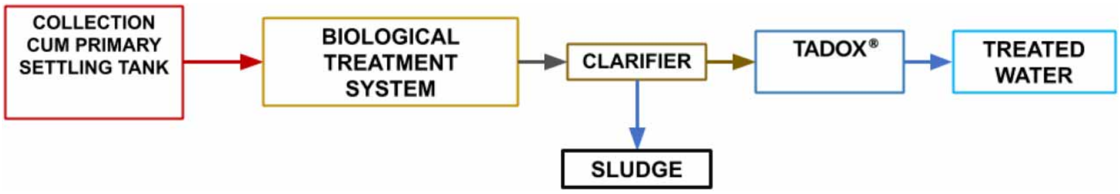


Figure 2 | Schematic showing TADOX® Implementation at post biological stage.

This integrated approach may also result in enhancement of quality of RO permeate, reduce number of RO cycles and reduce overall load on MEE. Earlier studies on polishing of tannery effluent (Panizza & Cerisola 2004; Hasegawa *et al.* 2014; Sivagami *et al.* 2018; Zhao & Chen 2019), pharmaceutical effluent (Janssens *et al.* 2017; Talwar *et al.* 2018; Fanourakis *et al.* 2020)and slaughterhouse effluent (Bustillo-Lecompte & Mehrvar 2016; Bukhari *et al.* 2018; Ozturk & Yilmaz 2019; Vidal *et al.* 2019) have shown promising results, which means that TADOX® implementation in a similar way can improve the scenario for these grossly and highly polluting industries.

This paper presents a total of six case studies showing versatility in integration and implementation of TADOX® at the pre-biological stage and post-biological stage, as per the nature of the effluent under analysis. To the best of our knowledge, there is no other publication that has given such an in-depth and versatile integration approach for any AOP-based technology. Case studies of integration of TADOX® at the pre-biological stage include three case studies of chemical effluents from 2,4 D pesticide manufacturing plants, speciality chemical anisole plant and hydrocarbon-rich stream from oil drilling waste pits with an aim to improve the performance of downstream biological treatment with improving biodegradability of the effluent (increased BOD/COD ratio) and reduction in toxicity of the effluent. Three case studies of integration at the post-biological stage includes, bio-treated pharmaceutical effluent, tannery effluent and slaughterhouse effluent. Further, this opens tremendous opportunities in implementation at the polishing stage, which is expected to improve legal compliance and enable high-end reuse of treated water, thereby improving water reuse efficiency in the plant.

MATERIALS & METHODS

Operation of the TADOX® plant

TADOX® involves coagulation and flocculation in primary treatment, followed by UV-TiO_2 photocatalysis coupled with nanomaterial recovery as secondary treatment step followed by tertiary treatment on point-of-use application basis. Complete design, and detailed methodology of working of the pilot plant has been reported in recent publications from the group. (Bahadur & Bhargava 2019; Bahadur *et al.* 2020; Das *et al.* 2020; Bahadur 2021). A representation of the overall system installed is shown in Figure 3.

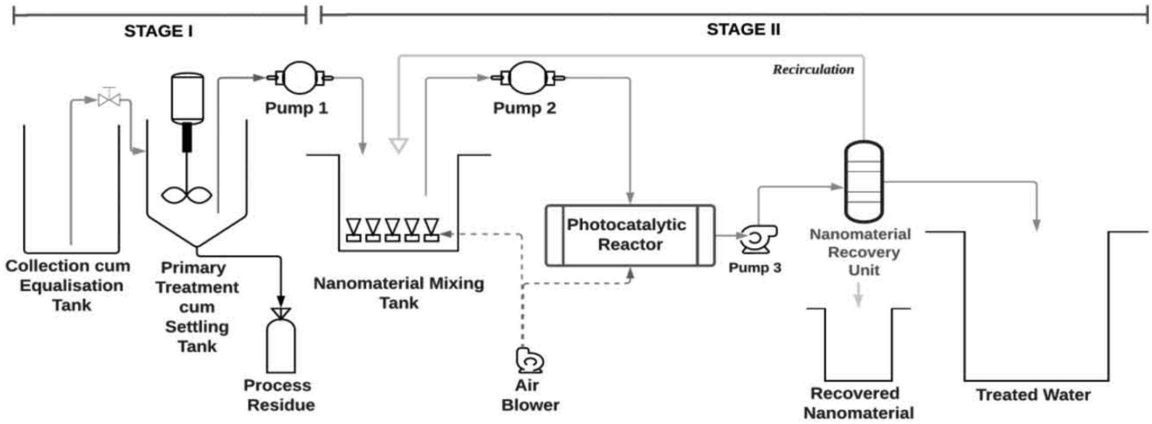


Figure 3 | Schematic representation of the TADOX® pilot-scale treatment (Bahadur & Bhargava 2019).

As shown in Figure 3 For primary treatment or Stage 1, to a 10–100 L/hr continuous flow wastewater sample, previously optimized dose of an alkali earth metal oxide and saturated solution of polyelectrolyte was added (proprietary formulation) under fast stirring for 5 min and later slow stirring for 15 min. Thereafter, the formed flocs could settle for about one hour or until a clear supernatant is obtained. Thereafter, a supernatant was aerated for mixing of n-TiO_2 powdered nanomaterial to be added subsequently. The obtained suspension was vigorously stirred and fine bubble aeration continued for 30 min. Thereafter, the suspension was left undisturbed for 30 min to attain adsorption-desorption equilibrium in the contact tank.

In the Stage II of the treatment, the suspension was re-aerated and well mixed for 10 mins before being pumped to a photocatalytic reactor (PCR) (patented design having optimised geometry and suitable UV light radiation source) and treated under recirculation mode for 120–180 min (as per requirement). Thereafter, the treated water was passed through an in-house designed and developed assembly utilising suitable filtration to separate used nanomaterial. Finally, treated water was obtained and spent nano-catalyst was recovered (Bahadur & Bhargava 2019; Bahadur *et al.* 2020; Das *et al.* 2020; Bahadur 2021).

Analysis of water samples and calculation of removal rate

pH, electrical conductivity, and total dissolved solids (TDS) were analysed by Pocket Pro Plus multi tester by HACH, USA. UV–vis spectra were recorded on UV–vis spectrophotometer model DR6000 by HACH, USA. Analysis of other wastewater quality parameters were carried out at National Accreditation Board for Testing and Calibration Laboratories, India (NABL) accredited laboratory as per ISO/ IEC 17025:2015. Micropollutants and pathogens were analysed as per standard methods given in APHA 23 edition 2017 at an accredited laboratory (Rice *et al.* 2017).

Computation of figures of merit

Electrical energy per order of magnitude of removal (E_{EO}) is used in the photocatalytic method used in TADOX® for comparing energy efficiency. E_{EO} was introduced as a Figure of merit by IUPAC and is defined as the electrical energy units in kilowatt hours (kW-hr) essential for breaking down any pollutant C by an order of magnitude in a unit volume (1 m^3) (Bircher *et al.* 2001). As per Equation (1), E_{EO} has been computed with respect to order removal of COD. This parameter is critical in estimation of the overall cost of treatment and an important parameter for upscaling photocatalytic processes such as TADOX® for field applications (Bahadur *et al.* 2020; Ghaffarian Khorram & Fallah 2020).

$$E_{EO} = \frac{Pt1000}{Vlog(C_i/C_f)} \tag{1}$$

where, P is the electrical power consumption (in kW), t denotes the time of treatment in hours and V is the volume of wastewater treated in m^3. C_i and C_f denote the initial and final COD values in mg/L of the water sample. Energy required to treat the unit volume of wastewater denoted as EE_{Volume} (in kWh m^{-3}) has been also calculated as per Equation (2) (Bahadur *et al.* 2020; Ghaffarian Khorram & Fallah 2020).

$$EE_{Volume} = \frac{Pt1000}{V} \quad (2)$$

The estimation of EE_{Volume} is significant to calculate the overall cost of treatment of wastewater (Bahadur *et al.* 2020).

Estimation of the overall cost of treatment

For estimation of cost of treatment, three of the most important parameters are considered, (i) chemical consumption, (ii) power consumption and (iii) cost of replacement of electromechanical units.

Firstly, to compute the cost of chemicals used in the treatment, the stagewise consumption in g/m^3 of coagulants, flocculants and Nanomaterials used in treatment have been estimated. Thereafter, the unit rates in INR/kg of each of the coagulants, flocculants and commercial nanomaterials have been used to compute stage wise cost of treatment for one cubic meter wastewater.

Secondly, the computation of the power consumption of the treatment has been done by considering the drawn current, rated voltage, and the operational hours for each of the electro-mechanical units such as agitator, air blower, pumps, UV lamps and nanomaterial recovery unit. The overall energy consumption is then computed in kWh per cubic meter of effluent treated and cost of treatment is then calculated in Indian rupees (INR) per cubic meter considering the INR 8 per kWh rates prevalent at the time of treatment in Haryana, India. Conversion from US dollars (USD) to INR has been done as per 1 USD equivalent to 75 INR.

Thirdly, the cost towards maintenance of the plant and machinery and cost towards the replacement of UV lamps and other electromechanical items have been estimated as per typical life of 12 months of continuous operation. Thus, computation of the total cost includes all expenses as elaborated above for the end-to-end treatment.

RESULTS AND DISCUSSION

Pre-biological implementation

Case study 1: treatment of pesticide wastewater from a 2,4-dichlorophenoxyacetic acid (2,4 D) plant, Gujarat, India

A wastewater sample was obtained from a 2,4 D manufacturing facility; obtained wastewater was slightly coloured with some turbidity and had a strong smell, indicating high phenolic content. The sample was subjected to TADOX® treatment to improve the biodegradability of the sample, making it fit for downstream anaerobic-aerobic biological treatment. Figure 4 shows the pre- and post-treated sample images and the change in water quality parameters is shown in Table 1.

As evident from Figure 4 and Table 1, there is substantial difference in the aesthetics and water quality after TADOX® treatment. Overall 5 h end-to-end treatment led to treated water having 62% reduction in BOD and 91% reduction in COD. The BOD/COD ratio, indicative of biodegradability, improved by almost four times

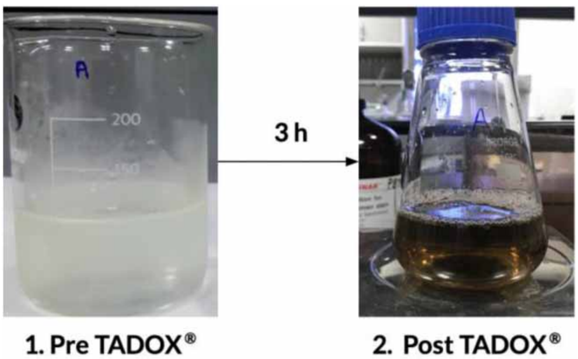


Figure 4 | Pre- and post-TADOX® treated sample images of the effluent from 2,4 D plant.

Table 1 | Wastewater quality parameters of pre-TADOX®, post Stage I (Pre-AOP) and post-TADOX® treated sample from 2,4 D plant

S.No.	Parameter, *Unit*	Pre-TADOX®	Post-Stage I	Post-TADOX®	% Change
1	pH	1.3	7.4	8.1	–
2	Turbidity, *NTU*	154	310	366	–
3	Total organic carbon, *mg/L*	8,467	6,755	504	94
4	Dissolved organic carbon, *mg/L*	7,486	5,644	476	93
5	BOD, *mg/L*	330	294	125	62
6	COD, *mg/L*	40,000	38,000	3,600	91
7	TSS, *mg/L*	729	432	379	48
8	Total phenols, *mg/L*	1,000	902	400	60

from 0.008 to 0.035 as the result of TADOX® treatment. Moreover, toxicity of samples is also expected to be reduced greatly because of 60% removal in total phenolic content from the treated water. Although there is a scope of further improvement in biological degradability of the stream with a better BOD to COD ratio (around 0.3) thus higher retention time of treatment could greatly benefit the results and can be planned in future. Such a toxicity reduction is essential to maintain the biological activity of the system in subsequent stage (Vollertsen & Hvitved-Jacobsen 2002; Vilar *et al.* 2012; Holkar *et al.* 2016; Zhang *et al.* 2020). From the picture it can be clearly seen that the sample became dark coloured, which is attributed to the oxidative degradation of the phenolic compounds and have resulted in the significant COD reduction. Odour of phenols from the sample was also reduced significantly. When treated with TADOX®, treated samples converted into dark brown colour which is indicative of oxidation of phenols and four times improved biodegradability with COD reduction of 90% and BOD reduction of 50–60% (without biological treatment). Thus, this study indicates that when TADOX® is integrated at a pre-biological stage it will help in downstream biological treatment and is also expected to reduce the load on subsequent tertiary treatment, thus elaborating the benefits.

E_{EO} for this stream has been estimated to be 15.5 kWh/order-COD·m^3, which is lower than literature reported data of application of photocatalytic process in similar streams, thus this makes TADOX® a promising approach for commercialisation. Energy requirements per unit treatment volume for this stream has been estimated to be 16.2 kWh/m^3. The overall treatment cost for this stream is calculated to be 3.3 USD/m^3 at laboratory scale in batch mode operation, which is expected to be reduced to 1.66 USD/m^3 at a commercial scale in continuous mode operation of TADOX® plant. The derived cost of treatment is 58% lower than the existing cost incurred by the industry for treatment of this difficult wastewater.

Case study 2: treatment of chemical wastewater from an anisole plant, Gujarat, India

Wastewater sample was obtained from an anisole manufacturing plant, which is required to be pre-treated before it is mixed with other wastewater or undertaken for downstream biological treatment. The obtained wastewater had strong colour and some turbidity and had a strong smell indicating high phenolic content. Figure 5 shows the pre- and post-TADOX® treated sample images and the change in water quality parameters is shown in Table 1.

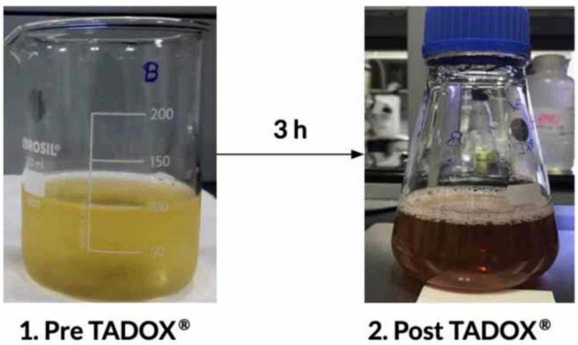


Figure 5 | Pre and Post TADOX® Treated images along with treatment results of treatment of effluent from Anisole plant.

As clearly shown in Figure 5 and data reported in Table 2, there is substantial change in the aesthetics of the sample and there is significant reduction in BOD (52%), COD (90%) and total phenolic content (49%). Residual parameters of the TADOX® treated sample shows that this water is suitable for downstream biological treatment with BOD/COD ratio increased from 0.093 to 0.45, i.e. five times higher biodegradability within 5 hours of end-to-end treatment (Holkar *et al.* 2016). E_{EO} for the treatment of this stream has been estimated to be 24.4 kWh/order COD·m^3, which is also lower than the previous estimations for energy consumption for photocatalytic treatment of industrial wastewater in the range of 50–200 kWh/m^3 (Miklos *et al.* 2018). The overall cost of treatment of this stream at lab scale implementation has been estimated at 5.35 USD/m^3, which is expected to be 3.46 USD/m^3 at commercial scale continuous mode plant operation. The derived cost of treatment is 43% lower than the existing cost incurred by the industry for treatment of this difficult wastewater. Thus, such a pre-treatment has resulted in removal of toxicity and improved biodegradability, which has led to an increase in overall efficiency of treatment together making the treatment cost effective and energy efficient.

Table 2 | Wastewater quality parameters of pre-TADOX®, post-Stage I (pre AOP) an final post-TADOX® Treated phenolic effluent from anisole plant

Sno.	Parameter, *Unit*	Pre-TADOX®	Post-Stage I	Post-TADOX®	% Change
1	pH	2.1	8.6	7.3	–
2	Turbidity, *NTU*	302	301	283	6
3	Total organic carbon, *mg/L*	31,665	29,324	4,097	87
4	Dissolved organic carbon, *mg/L*	27,654	28,543	3,994	85
5	BOD, *mg/L*	14,850	14,130	7,200	52
6	COD, *mg/L*	160,000	135,000	16,000	90
7	TSS, *mg/L*	2,666	2,202	972	64
8	Total phenols, *mg/L*	4,350	4,100	2,240	49

Case study 3: treatment of injection water from oil production well, Jharkhand, India

Figure 6 shows treatment of oil and drilling waste pit fluid obtained from the production well in Jharkhand, India. The sample contained a lot of hydrocarbons, evident from strong colour and pungent odour. There was visible oil content in the untreated effluent and the TADOX® treatment was given to this stream for making the stream biologically degradable and have less oils/hydrocarbon content.

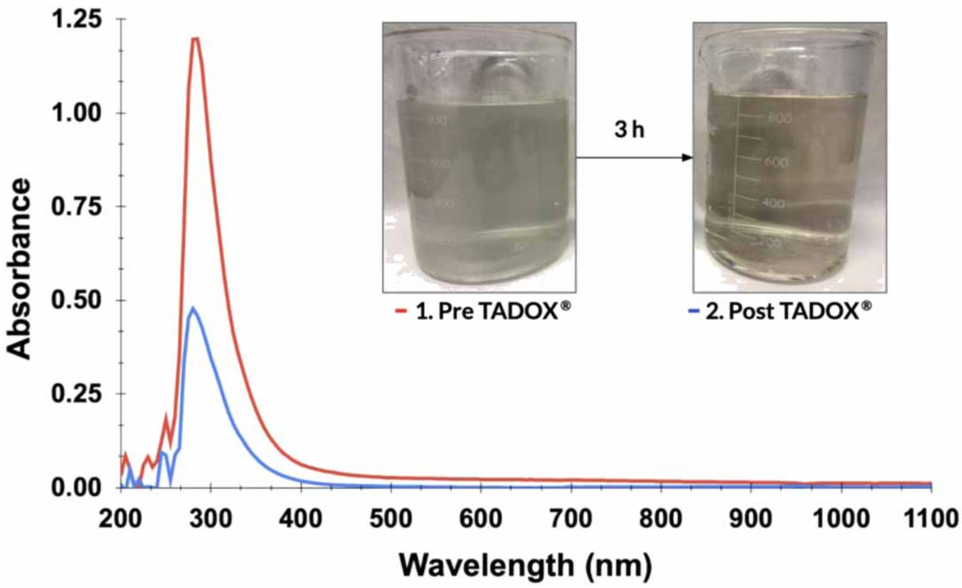


Figure 6 | UV-Vis spectra and photos (inset) of pre-TADOX® and post-TADOX® treated sample from oil and drilling waste pit fluid.

It is clear from above Figure 6 that TADOX® treatment led to improvement in colour, transparency, and turbidity of the sample. UV-visible spectra also show substantial changes, which indicate the reduction of colour, COD and dissolved organic content. Detailed water quality analysis of the pre- and post-treated samples is shown in the Table 3.

Table 3 | Comparative wastewater quality parameters of pre-TADOX®, post-Stage I (pre-AOP) and Post-TADOX® treated samples from oil and drilling wastewater

S.no	Parameter, *Unit*	Pre TADOX®	Post-Stage I	Post-TADOX®	% Change
1	pH	8.2	8.1	8.9	–
2	Turbidity, *NTU*	110	78	18	83
3	Total organic carbon, *mg/L*	80	73	26	67
4	Dissolved organic carbon, *mg/L*	72	70	20	72
5	Zinc, *mg/L*	0.2	0.2	0.05	75
6	BOD, *mg/L*	21	13	42	–
7	COD, *mg/L*	232	247	112	52
8	TDS, *mg/L*	7,041	6,878	3,357	52
9	Sodium, *mg/L*	2,112	1,898	1,057	50
10	Dissolved oil and grease, *mg/L*	588	401	312	47
11	Lead, *mg/L*	0.4	0.3	ND	99.9
12	Nickel, *mg/L*	3.2	3.0	1.4	55
13	Total suspended solids, *mg/L*	102.3	40.1	10.2	90

Table 3 shows significant reduction in heavy metal content such as Zn (75%), Pb (99.9%) and Ni (55%) with high 52% reduction in COD with 100% increase in BOD concentration. This reduction of COD and increase in residual BOD concentration is because the treatment led to degradation of long chain hydrocarbons, which are highly non-biodegradable, into smaller and biodegradable compounds, which resulted in higher BOD values. This means that biodegradability (BOD/COD) increased more than four times from 0.09 to 0.37, so TADOX® treated water can be efficiently degraded through downstream conventional biological treatment plants (Holkar *et al.* 2016). End-to-end TADOX® treatment of this effluent stream took 3 hours, which is much lower than conventional technologies and the E_{EO} was estimated to be 19 kWh/order COD·m^3 with overall cost of treatment at continuous scale to be 0.9 USD/m^3, which is about 80% lower than the current cost incurred by the industry for pre-treating this stream. Thus, such an intervention could result in substantial improvement in the current treatment regime.

Post-biological implementation

Case study 1: treatment of biologically treated wastewater from a pharmaceutical unit, Uttarakhand, India

A biologically treated (anaerobic followed by aerobic) wastewater sample was obtained from an ETP of a pharmaceutical and chemical manufacturing unit in Uttarakhand, India. From the picture of the pre-TADOX® effluent depicted in Figure 7, the high colour indicates the presence of residual organics, and the treated water cannot be discharged into the common drain that leads to a surface water body. It was thus subjected to TADOX® treatment for 3 h leading to complete decolourisation as evident by the UV-Vis spectra in the inset containing images of pre- and post-TADOX® treated samples.

As shown in Table 4, TADOX® treatment led to 96% removal of BOD, 93% in COD, 90% in total nitrogen and 98% in phosphorus content. TADOX® treatment result in treated water quality suitable for reuse in applications cooling tower makeup, boiler makeup etc. Overall cost of the treatment is expected to be 1.3 USD/m^3 at batch scale and may reduce to 0.86 USD/m^3 at continuous scale plants and the E_{EO} for the treatment has been evaluated to be 6.9 kWh/Order COD·m^3 with EE_{volume} of 8.1 KWh/m^3. Existing unit incurs about 1.4 USD/m^3, which translates to about 38% direct OPEX reduction through TADOX intervention in this treatment trail.

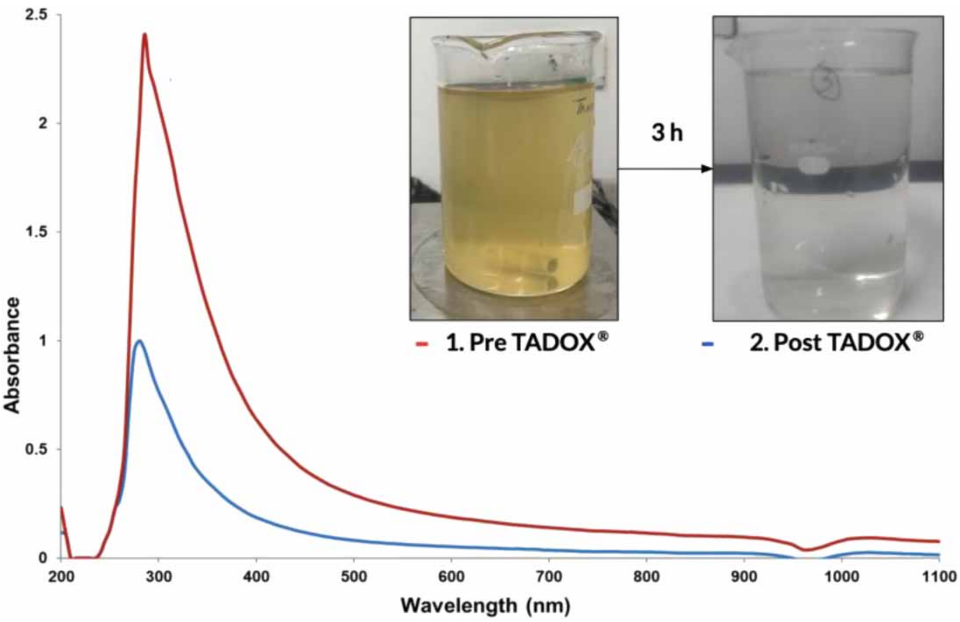


Figure 7 | UV-Vis spectra and photos (inset) of pre-TADOX® effluent, i.e., biologically treated pharmaceutical effluent and post-TADOX®.

Table 4 | Wastewater quality parameters of pre-TADOX®, post-Stage I (pre-AOP) and post-TADOX® samples from biologically treated pharmaceutical effluent

S.no	Parameter, *Unit*	Pre TADOX®	Post Stage I	Post TADOX®	% Removal
1	pH Value	6.2	7.8	8.1	–
2	Turbidity, *NTU*	130	10.2	<1	99
3	Total organic carbon, *mg/L*	300	288	15	95
4	Dissolved organic carbon, *mg/L*	290	282	24	92
5	BOD, *mg/L*	255.1	210.5	11.3	96
6	COD, *mg/L*	1,200	950	80	93
7	TSS, *mg/L*	40.8	30.4	25.6	37
8	Total nitrogen, *mg/L*	10.1	9.7	1.0	90
9	Total ammonia, *mg/L*	ND	ND	3.4	–
10	Total phosphorus, *mg/L*	5.5	1.2	0.1	98

Thus, when compared with application at pre-biological stage, the TADOX® integration at post-biological appears to be more energy efficient and cost competitive.

Case study 2: treatment of biologically treated tannery effluent

Tanneries are an important industry in a major part of Uttar Pradesh (UP) State in India and the process of leather manufacturing requires a lot of freshwaters in the process and leads to effluent with high dissolved organic matter, colour, TDS etc. Due to strict enforcement and prohibition of discharge of any treated/untreated wastewater from the process units, almost all medium-to-large-scale units have installed chrome recovery units for their high chromium wastewater; evaporator for their soaking water, which has very high salt content, while the other process water from liming, dehairing etc, processes are sent to conventional ETP systems. These conventional ETP systems cannot efficiently degrade the chemicals, organics and other complex constituents using biological treatment alone; however, due to the nature of the effluent to contain high amounts of biologically degradable contaminants it could be degraded within the norms of the regulator for horticulture development. However, it is not desirable to use this water for gardening purposes; instead, fresh water needs to be purchased from the utility for horticulture/gardening, so TADOX® is expected to polish this treated effluent and make it reusable with minimal cost investment and energy consumption. A typical TADOX® treatment for 3 hours end-to-end was carried out on the sample and the treatment results are shown in Figure 8 depicting UV-Vis spectra of the samples and the inset showing images of the pre- and post-TADOX® treated samples.

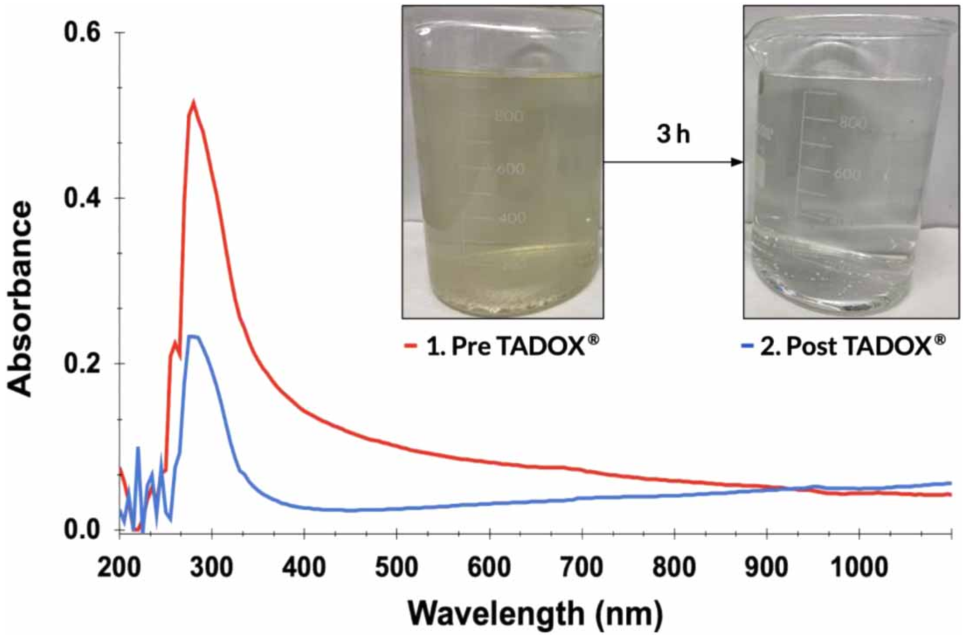


Figure 8 | UV-VIS spectra and photographs of pre- and post-TADOX® treated sample from biologically treated tannery effluent.

As shown in Figure 8, the biologically treated tannery effluent had residual colour, odour and dissolved organics, whereas after TADOX® treatment, the treated water is free from any colour and organics have been removed, which is also clearly evident from the UV-Vis spectra. Detailed water quality analysis has been carried out and tabulated in Table 5.

Table 5 | Comparative wastewater quality parameters of pre-TADOX®, post-stage I (pre-AOP) and post-TADOX® treated samples from biologically treated tannery effluent

Sno	Parameter	Pre TADOX®	Post Stage I	Post TADOX®	% Change
1	pH	8.2	8.2	8.2	NA
2	Turbidity, *NTU*	140	90	4	97
3	Total organic carbon, *mg/L*	90	85	20	78
4	Dissolved organic carbon, *mg/L*	80	80	20	75
5	Total suspended solids, *mg/L*	120	75	10	91
6	BOD, *mg/L*	7.8	7.6	24.6	–
7	COD, *mg/L*	128	110	80	37.5
8	Total dissolved solids, *mg/L*	1,040	918	767	26
9	Hexavalent chromium (Cr^{6+}), *mg/L*	1.2	1.12	0.06	95

From the data in Table 5, it could be seen that there is reduction in COD values and increase in BOD value indicating that the residual dissolved organics are biologically degradable, and the complex organics have been converted into simpler contaminants which are naturally degradable. Treated water quality obtained to have COD less than 100 mg/L and BOD less than 30 mg/L clearly meets the Inland Surface discharge norms as per GSR 422 (E) Environment Protection Rules, 1986 (Amended 2018) by MoEF&CC, Govt. of India (Central Pollution Control Board (Ministry of Environment and Forests 2018). Moreover, this quality meets the criteria for water reuse. The overall cost of treatment is expected to be 1.3 USD/m^3 with the overall energy requirement of

6 kWh/m^3 for the treatment, which is an affordable way to obtain such high-quality treated water. Existing unit incurs a cost of 2.1 USD/m3 for polishing of this water prior to its discharge into the industrial cluster drain, hence TADOX® implementation has potential to reduce cost of polishing by 38%.

Case study 3: treatment of biologically treated slaughterhouse effluent

Slaughterhouse industry, is a highly polluting processing industry, which produces meat and other animal-derived products such as fats and oils etc., which are used in several chemical and pharmaceutical industries. This industry houses a large portion of the workforce in UP, India. Regulators are pushing this industry to achieve high water quality standards for its treated water and reuse wastewater as much as possible; however, due to lack of technological options there has been a delay in the implementation of ZLD in this industry. The main problem of this effluent is the recalcitrant and residual organic content in the treated effluent, which cannot be degraded biologically and through conventional processes. TADOX® integration at the post-tertiary stage of treatment or polishing, so to say is expected to remove the residual organics, smell and colour from the sample making it reusable into processes such as washing, scrubbing and dust suppression within the plant premises. 3-hour end-to-end TADOX® treatment was carried out for this stream and the treatment performance has been shown in Figure 8 and wastewater quality parameters for the two samples is tabulated in Table 6.

Table 6 | Comparative wastewater quality parameters of pre-TADOX®, post-Stage I (pre-AOP) and post-TADOX® treated samples from biologically treated slaughterhouse effluent

Sno	Parameter, *Unit*	pre-TADOX®	Post-Stage I	Post-TADOX®	% Change
1	pH Value	7.4	7.1	7.8	NA
2	Turbidity, *NTU*	114	88	6	95
3	Total organic carbon, *mg/L*	10	8	4	60
4	Dissolved organic carbon, *mg/L*	8	6	<2	99
5	Total suspended solids, *mg/L*	285	192	20	93
6	Conductivity, μ*mho/cm*	6,902	5,952	5,290	23
7	Total dissolved solids, *mg/L*	3,434	3,010	2,646	23
8	Phosphate, mg/*L*	8.3	2.1	1.7	80
9	Sulphate, mg/*L*	1,244	921	822	34
10	Nitrate nitrogen, mg/*L*	66	61	60	8
11	COD, mg/*L*	32	30	6	81
12	BOD, mg/*L*	4	4	<1	100

It is evident from Figure 9 that treated wastewater from the slaughterhouse had a lot of residual colour and organics whereas the TADOX® treated wastewater had no residual colour and had impressive aesthetics. Detailed water quality characterization before and after TADOX® implementation is shown in Table 6.

Data from Table 6 clearly indicates that the TADOX® treated water was almost free from organics and had COD less than 10 mg/L and undetectable levels of BOD, indicating that water may be efficiently reused back in the process without any associated health risks. Overall treatment took 3 hours, and the energy requirements were 8.3 kWh/order COD·m^3 and the cost of operation has been estimated at 1.3 USD/m^3 for batch-scale smaller installations and 0.86 USD/m^3 for large-scale continuous flow systems. Thus, TADOX® intervention at tertiary stage is expected to be reduce OPEX by 50% in comparison to the current chemical-based treatment used by the industry.

CONCLUSIONS

Based on the discussed case studies, it maybe concluded that integration of TADOX® in existing systems is expected to improve quality of treated water, at the same time reduce operating expenses (OPEX). Implementation of TADOX® at large-scale installations such as common effluent treatment plants (CETP) can aid in handling shock loads of pollutants, due to non-selectivity of pollutants from mixed wastewater; TADOX® at CETPs may also be used at the pre-biological treatment stage to remove toxicity, reduce COD, and improve

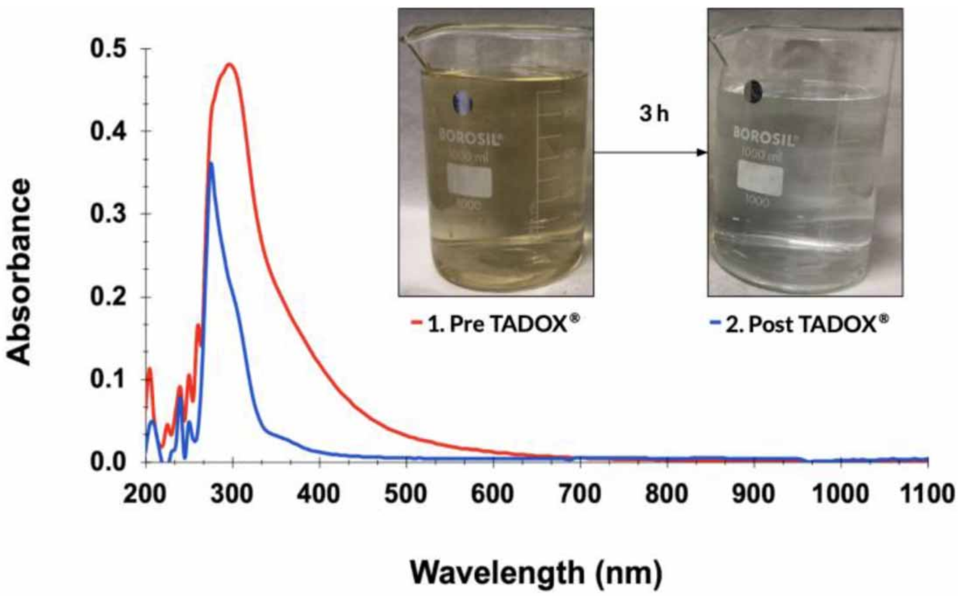


Figure 9 | Pre- and post-TADOX® sample image along with comparative wastewater parameters for treatment of biologically treated slaughterhouse effluent.

biodegradability. When used at the end of treatment i.e., at polishing stage, it improves reusability of treated water to comply with regulatory norms. TERI Advanced Oxidation Technology (TADOX®) might prove superior to existing technologies in the following ways:

(i) clean, green, and highly efficient technology utilising intrinsic property of nanomaterials and strong oxidising power of hydroxyl radicals as compared to other oxidising species involved in other AOPs,
(ii) complete degradation and mineralisation of suspended as well as dissolved organics,
(iii) highly cost effective as these have limited use of externally added chemicals,
(iv) generating negligible sludge, hence mitigate associated secondary pollution issues,
(v) integrated approach with existing systems for compliance with ZLD norms for recycle and reuse.

E_{EO} analysis for various difficult wastewater streams has been done in this study and it clearly shows that TADOX resulted in lesser electrical energy consumption promising as compared to those reported earlier by (de Sá *et al.* 2018; Miklos *et al.* 2018; Bahadur *et al.* 2020; Ghaffarian Khorram & Fallah 2020) who worked on similar difficult wastewaters. Thus, TADOX® proves to be highly efficient and economical as compared to other AOPs and similar technologies in this domain given that AOPs having E_{EO} below 50 kWh/m^3 maybe commercialised at large scale (Miklos *et al.* 2018; Loeb *et al.* 2019).

Further to the guidelines of ZLD in various polluting industries published by CPCB, GoI in 2015 wherein advanced technologies, newer and cleaner approaches for stream-specific treatment has been mentioned and introduced; TADOX® could be a useful integration approach in wastewater treatment for such highly polluting industries. Hence, TADOX® may be an important technology to bring in the much-needed revolution in wastewater treatment industry and promote enhanced water reuse.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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