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Evaluation of efficiencies of radiolysis, photocatalysis and ozonolysis of modified simulated textile dye waste water

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The efficiencies of the advanced oxidation processes (AOPs) viz. electron beam radiolysis in presence of $K_2S_2O_8$, gamma radiolysis in presence of $K_2S_2O_8$, photocatalysis, photocatalysis in presence of $K_2S_2O_8$, photolysis of $K_2S_2O_8$, ozonolysis and ozonolysis in presence of $K_2S_2O_8$ were systematically investigated for the treatment of modified (pH adjusted with H_2SO_4) simulated textile dye waste water (MSTDWW)
10 containing Reactive Red 120. The efficiencies of these AOPs were investigated in terms of the oxygen-equivalent chemical oxidation capacity and the cost of energy and other ancillary inputs. The least amount of oxidant was required by electron beam radiolysis compared to other AOPs, studied here, to achieve the same extent of mineralization of MSTDWW. To the best of our knowledge, this study reports firstly an approach to calculate the equivalent cost of gamma radiolysis in comparison to other AOPs
15 consuming electrical energy. Among these AOPs, the effective cost involved in electron beam treatment of MSTDWW in the presence of $K_2S_2O_8$ was the lowest one.

1. Introduction

The textile effluents are hazardous to the ecosystem because of the implementation of intense colour to water from the bio-
20 resistant synthetic dye molecules even at very low concentrations. Moreover, the auxiliary chemicals (i.e., surfactants, sequestering agent, pH-adjusting acids, inorganic salts etc.) of the dye bath contribute to ~83% of the organic load of the effluent.[1,2] The heavy organic load of the textile effluent causes a negative impact
25 to the aquatic lives owing to the decrease in the dissolved oxygen (DO) concentration in the water stream.[3] The chemical oxygen demand (COD), which is a measure of the organic load of the effluent, varies in the ranges 2900 – 3000 ppm in the textile effluents. Since it is well above the permissible discharge limit
30 (COD ≤ 250ppm) set by the Central Pollution Control Board under the Ministry of Environment and Forest, Government of India, the development of an effective and efficient treatment process for textile effluents is necessitated.

The synthetic reactive azo dye is mostly used in the textile
35 industries, though it is hydrolyzed in the alkaline dye bath solution.[4] The physicochemical treatments, such as precipitation, coagulation, reverse osmosis, electrolysis and adsorption are being used in the conventional dye effluent treatment plants.[5] However, the large amount of sludge or secondary waste
40 generation as well as the resistance of the reactive dyes to photo- or bio- or chemical- degradation are the major disadvantages of physicochemical treatment processes.[6]

The heavy organic loads of the textile effluents come from the auxiliary organic components such as sodium
45 dodecylbenzenesulfonate (SDBS; detergent used for washing out the excess dye), ethylenediaminetetraacetic acid (EDTA; for

removing unwanted metal ions from the dye bath), acetic acid (CH_3COOH; for adjusting pH of the dye bath to 10) etc. used in the dye bath. On replacing organic acid (CH_3COOH) by
50 inorganic acid (H_2SO_4) in the pH adjustment step, we could be able to bring down the COD of the simulated textile dye waste water to 245 ppm by gamma radiolysis at 60 kGy in the presence of potassium persulphate ($K_2S_2O_8$).[7] A comparative study on the process efficiencies of three major advanced oxidation processes
55 (AOPs) viz. radiolysis (gamma and electron beam), photocatalysis, ozonolysis for the treatment of modified (pH adjusted with H_2SO_4) simulated textile dye waste water (MSTDWW) of Reactive Red-120 (RR-120) was investigated in this paper in terms of the oxygen-equivalent chemical oxidation
60 capacity (OCC) and the cost of energy and other ancillary inputs.

2. Experimental

2.1 Dye and chemicals

RR-120, sodium dodecylbenzenesulfonate (SDBS), ethylenediaminetetraacetic acid (EDTA), $K_2S_2O_8$, *tert*-butanol
65 were purchased from Sigma-Aldrich. The titanium dioxide (TiO_2) (Degussa (P25), particle size ~30 nm) was used as photocatalyst. All other chemicals used were of the highest purity and used without any pretreatment.

2.2 Preparation of MSTDWW

70 The dye bath composition was kept fixed, as reported by Paul et al, except the neutralizing acid.[7] The hydrolyzed dye effluent was prepared by refluxing the constituents with 1 M NaOH at 80-90 °C for 3 hours;[8,9] followed by the adjustment of pH to 10 by H_2SO_4. This solution will be henceforth called as MSTDWW.

2.3 Instruments and analytical procedures

Steady state radiolysis of MSTDWW solution was carried out using ^{60}Co gamma radiation in a gamma chamber GC-5000 with a dose rate of 1.3 kGy h^{-1} as determined using Fricke dosimetry [G(Fe^{3+}) = 15.6/100 eV^{-1}]. Electron beam irradiation was performed with a 10 MeV pulsed accelerator at a beam current of 1.2 mA and 10 kGy/pass dose. Dosimetry for EB was performed using a FWT60 radio-chromic film dosimeter calibrated with graphite calorimeter. The photocatalytic experiments were carried out using Rayonet Photochemical Reactor containing 16 mercury lamps of 8W power each. The lamps emitted photons near-UV region (mainly around 350 nm) with a flux of 5.0×10^{15} photons cm^{-2} s^{-1}. Ozone was generated from pure oxygen using ozone generator (Model UOS02). The rate of flow of ozone through the solution was determined as 6.7×10^{-3} mol dm^{-3} min^{-1} by iodometric method. The COD of the solutions were measured by using Spectroquant$^{®}$ Pharo 300 COD analyzer.

# 3. Results and Discussion

3.1. Radiolysis of MSTDWW in presence of $K_2S_2O_8$

Gamma radiolysis of water in the pH range 3-11 produces three main reactive species viz. hydrated electron (e$_{aq}^{-}$), $^{•}$OH radical and hydrogen atom (H$^{•}$). The G-values [species per 100 eV] of the intermediates are given below.[10]

$$G(e_{aq}^{-}) = 2.7; \ G(^{•}OH) = 2.7; G(H^{•}) = 0.6 \qquad (1)$$

During radiolysis of water in presence of $K_2S_2O_8$, the e$_{aq}^{-}$ and H$^{•}$ preferentially react with $S_2O_8^{2-}$ producing $SO_4^{•-}$ (Reduction potential=2.6 V) and it can subsequently react with different components of MSTDWW present in the system.

$$e_{aq}^{-} + S_2O_8^{2-} \ \rightarrow \ SO_4^{•-} + SO_4^{2-} \qquad (2)$$
$$S_2O_8^{2-} + H^{•} \ \rightarrow \ SO_4^{•-} + HSO_4^{-} \qquad (3)$$
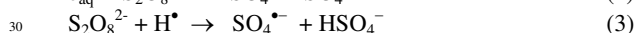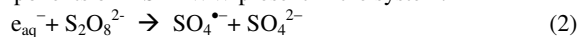
In addition, $^{•}$OH radical also can react independently with those components of MSTDWW. The gamma radiolysis in presence of $K_2S_2O_8$ is recently proven to be an efficient technique for the mineralization of the organic molecules.[7,11] The higher extent of mineralization of organic molecules during radiolysis in the presence of $K_2S_2O_8$ compared to the radiolysis in the absence of $K_2S_2O_8$ happens because of the preferential formation of benzyl type of radicals via the formation of benzene radical cation. Therefore, MSTDWW was irradiated for various doses at pH 10.0 in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$. The mineralization extent at different doses is shown in Fig. 1a. It shows 20% and 75% mineralizations at doses of 11 and 60 kGy, respectively. It could be noted that, at the same does, only 16% and 54% mineralizations were observed for the STDWW (pH adjusted with CH$_3$COOH).[7] Further, 80% mineralization was observed for the gamma radiolysis of MSTDWW at 80 kGy dose, while only 60% mineralization was observed for the gamma radiolysis of STDWW at 100 kGy.[7] Therefore, the nature of the pH adjusting acid influences the extent of mineralization of MSTDWW with that of the STDWW. It is important to mention that $K_2S_2O_8$ itself can produce $SO_4^{•-}$ by thermal decomposition at 38-40°C which is the usual temperature of the solution during gamma radiolysis.[12] Therefore, the extent of mineralization of MSTDWW in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$ was studied at 40°C under room condition (no irradiation) and no mineralization of MSTDWW was observed.

The MSTDWW solution was irradiated at different doses by EB at pH 10.0 in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$. The extent of mineralization of MSTDWW increased at each dose by ~20% (Fig. 1b). The high intensity electron beam rapidly deposits energy to the aqueous solution and it elevates the temperature of the aqueous solution from the ambient temperature.[13,14] Therefore it can be speculated that high yield of $^{•}$OH radical and $SO_4^{•-}$ (by the conjugated effects of radiolytic and thermal decompositions) enhanced the % mineralization of MSTDWW to ~34% and 96% at 11 kGy and 60 kGy doses, respectively. At 60 kGy, the COD of the final solution was brought down to below 100 ppm, which is below the recommended limit of discharge ($\leq$250 ppm).
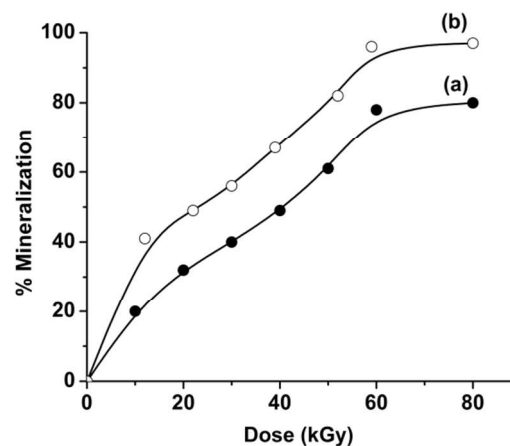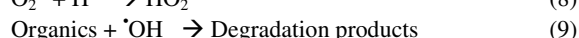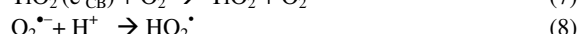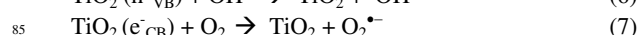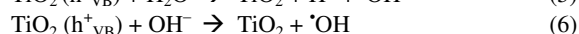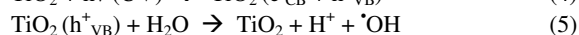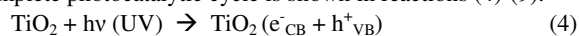

Fig.1 Mineralization of MSTDWW in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$ during (a) gamma radiolysis (b) Electron beam radiolysis.

3.2. Photocatalysis of MSTDWW

On illuminating the photocatalyst such as TiO$_2$ with UV light, the electrons from the valence bands (VB) are promoted to the conduction bands (CB) generating a hole in the valence band. The promoted electron in the conduction band reacts with the dissolved oxygen producing $O_2^{•-}$ and $HO_2^{•}$, whereas, the hole generated in the valence band can react with either with organic moiety or OH^{-}. The reaction of the hole with OH^{-} produces $^{•}$OH radical, which can also oxidize the organic moieties.[9] The complete photocatalytic cycle is shown in reactions (4)-(9):

$$TiO_2 + h\nu \ (UV) \ \rightarrow \ TiO_2 \ (e^{-}_{CB} + h^{+}_{VB}) \qquad (4)$$
$$TiO_2 \ (h^{+}_{VB}) + H_2O \ \rightarrow \ TiO_2 + H^{+} + {}^{•}OH \qquad (5)$$
$$TiO_2 \ (h^{+}_{VB}) + OH^{-} \ \rightarrow \ TiO_2 + {}^{•}OH \qquad (6)$$
$$TiO_2 \ (e^{-}_{CB}) + O_2 \ \rightarrow \ TiO_2 + O_2^{•-} \qquad (7)$$
$$O_2^{•-} + H^{+} \ \rightarrow HO_2^{•} \qquad (8)$$
$$Organics + {}^{•}OH \ \rightarrow Degradation \ products \qquad (9)$$

Where, hν is the photon energy required to excite the semiconductor electron from the VB to CB.

Photocatalysis of MSTDWW was carried out for different time intervals. However, only 30% mineralization of MSTDWW was observed after 10 hours of photocatalytic treatment (Fig. 2a) and no appreciable change in the extent of mineralization was observed at longer times. It could be noted that only 24% mineralization of STDWW was observed under the same photocatalytic condition.[7] It is important to mention that the TiO$_2$ particles made very stable suspensions with the aqueous solution of the individual components of MSTDWW. However, it settled

down rapidly in MSTDWW. We speculated that the presence of high salts concentration (~2 × 10^4 ppm of NaCl) in the MSTDWW might be responsible for changing the surface properties of TiO$_2$ particles and it finally led to the easy

5 settlement of the catalyst in MSTDWW. Since, we do not have the photoreactor with stirring facilities, we can only speculate, but could not confirm that the rapid settlement of catalyst in MSTDWW might be one of the reasons behind the poor efficiency of photocatalytic mineralization of MSTDWW. On the

10 other hand, the coulombic repulsion between the negatively charged surface of TiO$_2$ (pH$_{pzc}$ = 6.0 ± 0.2) and OH$^-$ (at pH 10.0) could also prevent the production of $^\bullet$OH resulting into the poor mineralization of MSTDWW.[7,9,15]

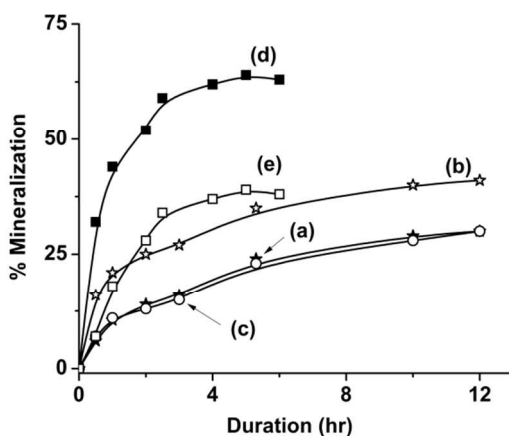15 **Fig. 2** Mineralization of MSTDWW at different durations in (a) photocatalysis (b) photocatalysis in presence of 4 × 10^{-2} mol dm^{-3} K$_2$S$_2$O$_8$, (c) photolysis of 4 × 10^{-2} mol dm^{-3} K$_2$S$_2$O$_8$, (d) ozonolysis and (e) ozonolysis in presence of 4 × 10^{-2} mol dm^{-3} K$_2$S$_2$O$_8$.

Instead of molecular oxygen, S$_2$O$_8$$^{2-}$ can also take the

20 conduction band electron from TiO$_2$ nanoparticles producing SO$_4$$^{\bullet-}$ radical (reaction 10):[16]
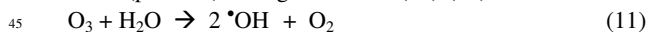
$$S_2O_8^{2-} + e^-_{CB} \rightarrow 2SO_4^{\bullet-} \qquad (10)$$

Therefore, the effect of K$_2$S$_2$O$_8$ on the photocatalytic degradation of MSTDWW was also investigated in presence of

25 4×10^{-2} mol dm^{-3} K$_2$S$_2$O$_8$. The extent of mineralization increased by ~10-12% during the photocatalysis of MSTDWW in the presence of K$_2$S$_2$O$_8$ (Fig. 2b). The increase in the %mineralization of MSTDWW during the photocatalysis in presence of K$_2$S$_2$O$_8$ is attributed to (i) the decrease in the

30 probability of recombination of the photogenerated electrons and holes and (ii) forming SO$_4$$^{\bullet-}$ having higher mineralization efficiency.[7,16] However, the application of this process is limited by the coulombic repulsion between the negatively charged surface of TiO$_2$ (pH$_{pzc}$ = 6.0 ± 0.2) and S$_2$O$_8$$^{2-}$ (at pH 10.0) and

35 rapid settlement of catalyst in MSTDWW.

The photolysis (photochemical decomposition of K$_2$S$_2$O$_8$ in absence of TiO$_2$) did not impart any enhancement in the extent of mineralization (Fig. 2c). This is speculated by the lower yield of SO$_4$$^{\bullet-}$ radical from photolysis of S$_2$O$_8$$^{2-}$ with ~350 nm UV light.[16]
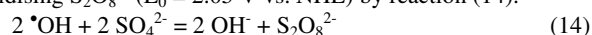
40 *3.3. Ozonolysis of MSTDWW*

Ozone, which itself is a strong oxidant (Reduction potential=2.07 V vs. NHE), can produce more powerful oxidant

i.e. $^\bullet$OH (Reduction potential=2.8 V vs. NHE) under alkaline condition (pH 10.0) through reactions (11)-(13).[17,18]

45
$$O_3 + H_2O \rightarrow 2\,^\bullet OH + O_2 \qquad (11)$$
$$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^\bullet \qquad (12)$$
$$O_3 + HO_2^\bullet \rightarrow 2O_2 + {}^\bullet OH \qquad (13)$$

Therefore, $^\bullet$OH is assumed to be predominant reactive species available under experimental conditions.[19,20] The extent of

50 mineralization of MSTDWW was studied at different durations of ozonolysis at pH 10.0. About 30% and 60% extent of mineralization of MSTDWW were achieved after 0.5 and 4 hours of ozonolysis, respectively. However after 4 hours no significant increase in mineralization extent was observed (Fig. 2d). It could

55 be noted that only 13% and 25% mineralization of STDWW was observed under the same photocatalytic conditions.[7] The effect of K$_2$S$_2$O$_8$ on the ozonolysis of MSTDWW was investigated in presence of 4×10^{-2} mol dm^{-3} K$_2$S$_2$O$_8$ (Fig. 2e). The extent of mineralization was decreased drastically in case of ozonolysis in

60 presence of K$_2$S$_2$O$_8$. The K$_2$S$_2$O$_8$ does not produce SO$_4$$^{\bullet-}$ during ozonolysis (in absence of any radiation or thermal activation), instead, being the counter ions of the neutralizing acid (H$_2$SO$_4$), a plenty of SO$_4$$^{2-}$ ions remains in the solution. Therefore, $^\bullet$OH (Reduction potential = 2.8 V vs. NHE) radical produces less

65 oxidising S$_2$O$_8$$^{2-}$ (E$_0$ = 2.05 V vs. NHE) by reaction (14).

$$2\,^\bullet OH + 2\,SO_4^{2-} = 2\,OH^- + S_2O_8^{2-} \qquad (14)$$

Therefore, the extent of %mineralization decreased during ozonolysis in presence of K$_2$S$_2$O$_8$.

3.4 Comparison of the process efficiencies of radiolysis,
70 *photocatalysis and ozonolysis for the mineralization of MSTDWW*

3.4.1. In terms of the OCC

The process efficiencies of different AOPs were compared in the terms of OCC, which is defined as the kg of O$_2$ that are

75 equivalent to the quantity of oxidant reagents used in an AOP to treat 1 m^3 of wastewater.[21] It gives an index of the chemical efficiency of the oxidants used in an AOP by quantifying the amount of the oxidants (kg$_{O2}$) added per m^3 of the wastewater. The OCC of radiolysis (gamma irradiation and electron

80 beam)(equation 15), photocatalysis/photolysis (equation 16) and ozonolysis (equation 17) are calculated by the following equations (15-17):[7]

$$1\ OCC_{Radio}(kg\ O_2\ m^{-3}) = D\ (J\ kg^{-1}) \times \rho(kg\ m^{-3}) \times G(kmol\ J^{-1}) \times \frac{1\ kmol\ O_2}{4\ kmol} \times \frac{32\ kg\ O_2}{1\ kmol\ O_2} \qquad (15)$$

85 where, D is the dose, ρ is the density of water, G (SO$_4$$^{\bullet-}$) = 3.4×10^{-10} kmol J^{-1} or 3.3/100 eV; G ($\bullet$OH) = 2.8×10^{-10} kmol J^{-1} or 2.7/100 eV.

$$1\ OCC_{Photo}(kg\ O_2\ m^{-3}) = \frac{[I_0(cm^{-2}s^{-1}) \times A\ (cm^2) \times t(s) \times 10^6\ (cm^3 m^{-3})]}{[6.023 \times 10^{26}(kmol^{-1}) \times V(cm^3)]} \times \frac{1\ kmol\ O_2}{4\ kmol} \times \frac{32\ kg\ O_2}{1\ kmol\ O_2} \qquad (16)$$

90 $$1\ OCC_{Ozo}(kg\ O_2\ m^{-3}) = O_3(kg\ O_3\ m^{-3}) \times \frac{1\ kmol\ O_3}{48\ kg\ O_3} \times \frac{6\ kmol\ e^-}{1\ kmol\ O_3} \times \frac{1\ kmol\ O_2}{4\ kmol\ e^-} \times \frac{32\ kg\ O_2}{1\ kmol\ O_2} \qquad (17)$$

Fig. 3 shows that the lowest degree of mineralization of MSTDWW (to the extent of 28%) was observed in photocatalysis and photolysis of K$_2$S$_2$O$_8$. Thus OCC values and the cost of

energy source and other ancillary inputs of different AOPs were compared only for 28% mineralization of MSTDWW. It could be noted that the OCCs of radiolysis, photocatalysis, ozonolysis and radiolysis (+$K_2S_2O_8$) of STDWW could be calculated only for 16% mineralization, which was the lowest observed degree of mineralization of STDWW.[7] The OCC values of photocatalysis, photocatalysis (+$K_2S_2O_8$), photolysis of $K_2S_2O_8$, ozonolysis, ozonolysis (+$K_2S_2O_8$), gamma (+$K_2S_2O_8$) and electron beam (+$K_2S_2O_8$) radiolysis for 28% mineralization were calculated to be 6.29, 2.46, 7.63, 9.29, 38.83, 0.08 and 0.04 kg equivalent O_2 m^{-3}, respectively. EB radiolysis in presence of $K_2S_2O_8$ showed maximum chemical efficiency (~96% mineralization) of the oxidants at 0.3 kg equivalent O_2 m^{-3} OCC. About 78% mineralization in gamma radiolysis and less than 10% mineralization were observed for others at 0.3 kg equivalent O_2 m^{-3} OCC. It could be noted that 0.3 kg equivalent O_2 m^{-3} OCC could mineralize only 54% of STDWW by gamma radiolysis in presence of $K_2S_2O_8$.[7] Therefore, it could be safely concluded that least amount of oxidant was required to achieve the same extent of mineralization of MSTDWW by EB radiolysis compared to other processes studied here. Therefore, The OCC for 28% mineralization of MSTDWW follows the order: electron beam (+$K_2S_2O_8$) radiolysis < gamma (+$K_2S_2O_8$) radiolysis < photocatalysis (+$K_2S_2O_8$) < photocatalysis ~ photolysis of $K_2S_2O_8$ < ozonolysis < ozonolysis (+$K_2S_2O_8$). The mechanism of enhancement in the extent of mineralization of MSTDWW (pH adjusted by acetic acid) and ibuprofen during radiolysis in presence of $K_2S_2O_8$ has been studied in details by the authors.[7,11] Since, only the nature of pH adjusting acid is changed, we speculate the mechanism of mineralization of the components of MSTDWW was quite similar to that of STDWW.[7,11]
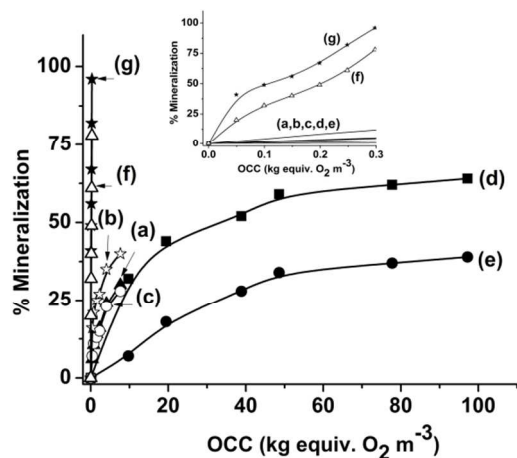

Fig. 3 Mineralization of MSTDWW with OCC for (a) photocatalysis, (b) photocatalysis in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$, (c) photolysis of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$, (d) ozonolysis, (e) ozonolysis in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$, (f) gamma radiolysis in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$ and (g) electron beam radiolysis in presence of 4×10^{-2} mol dm^{-3} $K_2S_2O_8$.

3.4.2. In terms of the cost of energy source and other ancillary inputs

The efficiencies of electron beam (+$K_2S_2O_8$) and gamma (+$K_2S_2O_8$) radiolysis, photocatalysis (+$K_2S_2O_8$) and ozonolysis were evaluated in terms of the cost of energy and other ancillary inputs. The cost of electrical energy required for electron beam (+$K_2S_2O_8$) radiolysis, photocatalysis (+$K_2S_2O_8$) and ozonolysis and can be calculated using equation (18).

$$EEC = P \times (t/60) \times (1000/v) \qquad (18)$$

Where EEC (in kWh/m^3) is the electric energy consumed (in kWh) to degrade a contaminant in unit volume (in m^3), P is the rated power (in kW) of the AOP system, t is the duration (in min) of treatment and v is the volume (in L) of SWDDT treated in time t.

The duration of treatment for 28% mineralization of MSTDWW by EB (+$K_2S_2O_8$) radiolysis, photocatalysis (+$K_2S_2O_8$), ozonolysis were observed to be 0.6, 180, 30 min, respectively. The cost of the electrical energy along with the ancillary chemicals (if any) for these AOPs are summarized in Table 1. Among these processes, the cost involved in EB (+$K_2S_2O_8$) treatment was the lowest one.

(Table 1 should be placed here)

In the gamma radiolysis of MSWDDT (which did not involve electrical energy) the cost of the energy source could be estimated by accounting 5 effective half lives of ^{60}Co source using following equation (19)

$$CTP = I \times R \times t/(t_{1/2} \times 5 \times 365 \times 24) \times (1000/v) \qquad (19)$$

Where, CTP (INR/m^3) is the average cost of treatment process in Indian rupee (INR), I is the initial activity in Curie (Ci) of ^{60}Co source, R is the price (in INR) of ^{60}Co source/Ci, t is the treatment time (in hours), $t_{1/2}$ is the half life (hour) of ^{60}Co and v is the maximum volume capacity (in L) of the gamma chamber that can be treated in time t. In our study, the initial activity of ^{60}Co was 10000 Ci involving a cost of INR 70/Ci and volume of the gamma chamber was 5 L. Therefore, the cost for 28% mineralization using gamma radiolysis was calculated as INR 7931/m^3. The total cost of gamma radiolysis (+$K_2S_2O_8$) for the treatment of MSTDWW was found to be INR 20906/m^3. This is the first approach to calculate the equivalent cost of gamma radiolysis in comparison to other AOPs consuming electrical energy.

The above results showed that the cost involved in EB (+$K_2S_2O_8$) treatment was the lowest one among the studied AOPs for the mineralization of MSTDWW. It is important to note that the AOPs are emerging technologies being commercialized worldwide. A few UV/H_2O_2 based AOPs have been internationally commercialized for treatment of drinking water and industrial water using the advantage of both chemical and energy inputs.[23,24] There are few companies such as AST clean water technologies, China; Trojan Technologies, Canada; Calgon Carbon Corporation and Xylem Global, USA have brought some of the AOPs to the international markets. In parallel, the radiation technology is internationally emerging out for the waste water treatments.[25-27] The radiation based pilot sludge treatment plants have been established in New Mexico, USA (Gamma); Weldel, Germany (EB); Verginia Key, USA (EB); Takasaki, Japan (EB); Sao Paulo, Brazil (EB); Tucuman, Argentina (Gamma); Daejeon, Korea (EB). [25-27] I addition, radiation based commercial sludge treatment plants were also established in Vadodara, India (Gamma) and Munich, Germany. [25-27] A pilot plant for treating 1,000 m^3/day of dyeing wastewater with EB has been constructed and operated since 1998 in Daegu, Korea together with the biological treatment facility.[28,29] Therefore, we understand that

the studies presented in this paper have lots of scopes to advance the radiation based technologies for the treatment of textile effluents. Further, the EB has the ability to simultaneously disinfect the water during the degradation process.[30] At this stage, the used EB (+$K_2S_2O_8$) treatment process does not produce water suitable for reuse or drink. Hence, a multi-step treatment system would be designed in near future.

Conclusions

This study explores a reliable, promising and cost effective way to use electron beam radiolysis in presence of $K_2S_2O_8$ for complete mineralization of recalcitrant organics in to CO_2 and H_2O. Least amount of oxidant was required for electron beam radiolysis in presence of $K_2S_2O_8$ to achieve the same extent of mineralization compared to gamma radiolysis in presence of $K_2S_2O_8$, photocatalysis, photocatalysis in presence of $K_2S_2O_8$, photolysis of $K_2S_2O_8$, ozonolysis and ozonolysis in presence of $K_2S_2O_8$. To the best of our knowledge, this study reports firstly an approach to calculate the equivalent cost of gamma radiolysis in comparison to other AOPs consuming electrical energy. Among these processes, the cost involved in electron beam treatment in presence of $K_2S_2O_8$ was the lowest one.

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Notes and references

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Table 1 Comparison of the cost of energy and ancillary chemicals for different AOPs.

	Ozonolysis	**Photocatalysis (+K$_2$S$_2$O$_8$)**	**Electron beam radiolysis**
Power employed in the process (kW)	0.08	0.128	1
Treatment time (min)	30	180	0.6
*Volume of STDWW treated (L)	0.04	0.26	1.9
EEC (kWh)/m^3 of STDWW	1000	1477	5.3
Electrical energy cost (INR)/m^3 of STDWW @INR 8.5/kWh	8500	12554	45
Cost of additional chemicals/gas (INR)/m^3 of STDWW	246000 (O$_2$ cylinder cost @ INR 164/m^3)	3000 (TiO$_2$ cost @ INR 3/g) + 12975 (K$_2$S$_2$O$_8$ cost @ INR 1.2/g)	12975 (K$_2$S$_2$O$_8$ cost @ INR 1.2/g)
Total cost/m^3 of STDWW	254500	28529	13020
* It is guided by the maximum volume capacity of the instrument to treat the STDWW under the same treatment condition.			