

A REVIEW STUDY ON ORGANIC WASTE MANAGEMENT BY GREEN CHEMISTRY

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Abstract

Purpose: The review article discusses the title topic describing mostly authors' work on green chemical, photochemical and electrochemical methods for the treatment of organic wastes present in different matrices. Emphasis is mainly placed on the importance of the matrix, associated compounds and the method's selection.

Methodology: Different green methods of treatment for organic waste available are reviewed with an outline of scientific principles. Different case studies, from the authors, work, involving the treatment of organic waste present in different matrices are discussed. Available green chemical, photochemical, and electrochemical methods are reviewed, and results obtained are described and discussed. The rationale behind the choice of method was discussed in detail. Laboratory to plant adoption and the considerations therein are considered.

Main findings: The selection of treatment method depends on the nature of the organic waste and the matrix in which it is present. This has been brought out in the study. Advanced oxidation and electrochemical oxidation processes are practically useful methods for waste treatment and discussed with case studies. The optimization of the advanced oxidation process is still an empirical approach. It needs a sound scientific base.

Applications of the work: The case studies described in the paper enable the proper choice of treatment method among several available options. The study covers the essential green chemical techniques, viz., photochemical and electrochemical techniques.

The novelty of the work: Many of the organic substrates subjected to treatment study were rarely reported in the open literature. Laboratory to plant scale development and the factors involved therein have been brought in many places.

Keywords: Green Chemistry, Photochemical Oxidation, Electrochemical Oxidation, Advanced Oxidation Processes, Organic Waste, Organic Radioactive Waste, Incineration.

INTRODUCTION

There are more than nine million organic compounds known. Industries processing of organic compounds are numerous. Consequently, organic compounds as waste are ubiquitous in different matrices such as wastewater, air, or concentrated solid or liquid form.

Historically, the importance of wastewater treatment was realized because of its disease-causing potential, foul smell, and color. *Activated sludge process (ASP)* is a breakthrough in cost-effective sewage treatment and has been considered a milestone in the history of wastewater treatment ([Giusy& Jeanette,2010](#)).

As the complexity and diversity of the organic chemical industry have grown, the associated organic waste problem has also increased. Wastewaters containing non-biodegradable organic compounds such as phenols, pesticides, dyes, phthalates, pharmaceuticals have emerged. ASP alone could not degrade these refractory organic compounds as per regulations.

Simultaneously, the emergence of hazardous organic liquids/solvents and solids such as petroleum sludge, ion exchange resins, organic solvents, PCBs, pesticides, POPs, etc. has become a severe issue. Air emissions containing volatile organic compounds (VOC) such as acetone, ethanol, and acetic acid have also become a problem.

A distinct class of organic wastes arises from nuclear facilities. They are called organic radioactive wastes. Radioactive materials are present in this kind of organic wastes. The presence of radioactivity in the organic material changes treatment options many times. ([International Atomic Energy Agency, 2004](#)).

Organic Waste Management by 4R formula

'Reduce, recover, recycle, and reuse' strategy is the 4R formula and a general strategy for waste management, including organic waste. Green chemistry, by judicious process modification, attempts to implement 4R formula, especially 'Reduce.' 4R formula has become quite useful and essential. Efforts, such as the following, are being made:

- Research efforts are in progress to recover nutrients and other valuable compounds from sewage water for reuse.
- Zero liquid discharge has become mandatory for 'red category industries' such as the hazardous waste processing industry in India.
- Recovery and reuse of solvents by vacuum or atmospheric distillation are routinely followed in many industries. Tributyl phosphate in n-dodecane solvent (TBP solvent) waste generated in the nuclear industry, for example, is vacuum-distilled for recovery and reuse over several cycles.
- Recovery and reuse of organic ion exchange resins in the demineralization plant by acid/alkali regeneration process are well known in nuclear and other industries.
- Recovery and reuse of VOCs from air streams by condensation are followed if the VOC concentration is high and the process is economically viable.

Despite the best efforts, waste generation cannot be stopped totally, and the need for its treatment exists. *The focus of the review is organic waste treatment using green chemistry.*

Mineralization of Organic Waste

Thermodynamically, all organic compounds, without exception, are mineralizable to CO₂ and water. It is, mostly, the basis for the treatment of organic wastes in different media and forms. Kinetics varies from compound to compound.

Incineration has been the mainstay for the management of organic solid and liquid wastes for over a century. However, over the last few decades, it is losing its place in the scheme of things because of the evolution of stringent air pollution standards and the technical and economic issues associated with their compliance. Furan and dioxin, among others, are essential air pollutants from the incineration process ([Mukherjee et al., 2016](#)). The presence of radioactivity in the organic waste complicates the matter further making incineration impractical for even wastes such as tissue papers, which are made of hydrogen, oxygen, and carbon atoms.

GREEN CHEMISTRY IN ORGANIC WASTE TREATMENT

Organic waste treatment by green chemistry is, in most cases, mineralization of organic compounds using benign oxidants, listed below, under moderate experimental conditions:

- Oxygen
- Hydrogen peroxide
- Ozone
- Electron (directly or indirectly)

The following discussion, mostly authors' work as case studies using these green oxidants, has been presented briefly:

TNT-bearing wastewater treatment by Photo-Fenton reaction

Because of the toxic effect which explosive, TNT has been widely reported to have on the human and ecological environment, this waste stream cannot be discharged unless the concentration of TNT and other dissolved explosives in the water is less than 1 mg/L. In the study, the wastewater contained 50-100 ppm of TNT arising from TNT handling facilities with a maximum generation rate of about 6-8 m³/d.

Following advanced oxidation processes (AOP), listed below, can be considered for the treatment of this water: Many review articles have appeared discussing the principles of AOP ([Legrini et al., 1993](#); [Mehmet et al., 2014](#); [Miklos et al., 2018](#)).

- Fenton reaction
- Ozone/hydrogen peroxide or hydroxide
- Hydrogen peroxide/ultraviolet(U.V.)
- Photo-Fenton reaction
- Ozone/U.V.
- Photocatalytic oxidation using titanium dioxide

AOP is a process mediated by strongly oxidizing hydroxyl (OH) radicals with a standard potential of 2.8V(vs. SHE). These radicals are non-selective and kinetically fast, with rates controlled by diffusion ([Leon and Gerald, 1973](#)). OH, radicals initiate the oxidation process by hydrogen abstraction, double bond addition or electron transfer reactions.

H₂O₂/U.V. method

Among the AOP options, hydrogen peroxide/U.V. option is the cleanest. It involves U.V.(253.7 nm) irradiation of the mixture of wastewater and hydrogen peroxide. Hydrogen peroxide is converted into the water in the oxidation process. Low-pressure mercury lamps emitting this radiation monochromatically are available commercially. These lamps are used for disinfection

purposes as well. The authors used these lamps of 75W each in the full-scale facility for TNT treatment. Hydrogen peroxide decomposes to give OH radicals as follows:



The molar extinction coefficient (ϵ) for this absorption is low ($25 \text{ M}^{-1} \text{ cm}^{-1}$). Besides, TNT also absorbs this U.V. light (inner filter effect) with ϵ more than $10,000 \text{ M}^{-1} \text{ cm}^{-1}$ wastefully (Hughes et al., 2015). For these reasons, this method was not selected in our study. This method, however, shows promise if inner filter effects are absent and if the wastewater pH is 9-10 as the conjugate base of H_2O_2 , viz., HO_2^- absorbs 253.7 nm more strongly. ϵ of this base is $100\text{-}125 \text{ M}^{-1} \text{ cm}^{-1}$ (Legrini et al., 1993). Higher pH, however, tends to accelerate the decomposition of H_2O_2 wastefully.

Fenton reaction (Cheves, 1975)

Fenton reaction is a chemical reaction involving the reaction of Fe (II) ions with hydrogen peroxide



This reaction has a rate constant of about $70 \text{ M}^{-1} \text{ s}^{-1}$ at normal temperatures and a pH of 2-3. OH radicals can attack not only organics but also Fe (II), H_2O_2 at rates of the order of $10^7\text{-}10^{10} \text{ M}^{-1} \text{ s}^{-1}$ at normal temperatures (Leon and Gerald, 1973). Because of their non-selective rapid reactions with various reducing agents in the solution, their steady-state concentration is very low ($< \text{nanomolar}$) (Legrini et al., 1993). TNT mineralization reaction is coupled with a Fenton reaction. It means that OH and HO_2 radicals, H_2O_2 , oxygen, and ferric ion formed in Fenton reaction degrades TNT. It is challenging to write the stoichiometric reaction in this multi-oxidant reaction system. Ideally, the stoichiometric reaction of TNT with H_2O_2 can be expressed as follows:



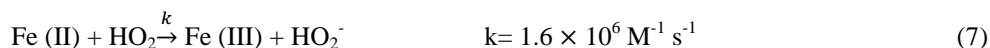
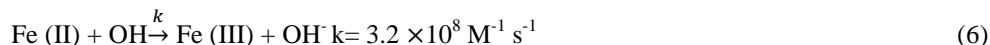
The above reaction does not take place directly without the presence of compounds such as ferrous salt in the reaction mixture to form OH radicals, which, in turn, form organic radicals. OH radicals also undergo single-electron reduction reactions such as the following:



Iron in the form of ferrous and ferric salts constitute the catalyst system for this reaction. Fe (III) can, slowly, reduce H_2O_2 by the following reaction with a rate constant value of $4.3 \times 10^{-3} \text{ s}^{-1}$ at 25°C (Eary, 1985): Activation energy of the reaction is 85.6 kJ/mol .



HO_2 radicals, mentioned above, form as intermediates in this reaction. They are less reactive than OH radicals as exemplified below:



No rational basis exists for selecting optimum reaction conditions for mineralization of a given organic compound in wastewater by AOP. Optimum conditions are determined based on experimentation. However, some commonalities, such as the following exist:

Since OH radicals are non-selective, their loss through unwanted reactions is a definite possibility. Therefore, their generation in a sustained manner is a requirement for rapid mineralization. Reaction (2) is a non-stoichiometric source of OH radicals. Thus, iron in the divalent state is to be maintained for high OH concentration in solution. Fe (III) in the reaction (2) can be reduced back to Fe (II) by H_2O_2 (reaction 5). The reaction rate is much slower. This limitation of Fenton reaction can be overcome by using *photo-Fenton reaction* as discussed below:

TNT mineralization reaction involves the formation of different carboxylic acids as intermediates. A detailed mineralization mechanism was discussed (Kaidar et al., 2010). This fact can be taken advantage of in photo-Fenton reaction. Fe (III) forms complexes with carboxylic acids, and upon irradiation with U.V. or visible radiation, these complexes photolyze with a high quantum yield to produce Fe (II) and CO_2 . This photolytic reaction contributes to CO_2 formation and TOC reduction directly. The best example is the oxalate complex of Fe(III), which decomposes with a quantum yield of nearly 1.0 upon irradiation in the UV-visible range. This principle is used in chemical actinometric measurements (Kuhn et al., 2004).

Because of these factors, the photo-Fenton reaction was chosen for the mineralization of TNT. The reaction was monitored using total organic carbon (TOC) as the global parameter. The experiments revealed that mineralization could be achieved using photo-Fenton reaction, and TNT concentration could be reduced to below one ppm.

Based on successful laboratory studies, a scaled-up facility of one cubic meter batch was installed with U.V. (253.7 nm) lamps of 75W each. The wastewater was brought to a pH of 2.5-3.0 using sulfuric acid to avoid hydrolysis of iron salts. Fe (II) concentration was initially maintained at 100 ppm. 30% hydrogen peroxide (250-300 mL of 30% strength) was introduced into the irradiated reaction mixture slowly in about an hour to avoid the accumulation of H₂O₂ in the reaction mixture, leading to its wasteful reaction with OH radicals as follows:



Air sparging was done to mix the contents. Moreover, oxygen also reacts with carbon centered-radical intermediates to promote oxidation ([Legrini et al., 1993](#)).

The pilot experiments showed that TNT could be quantitatively mineralized to less than one ppm with a light energy expenditure of about two kWh/m³ of wastewater ([Srinivas, 2005](#)). Photo-Fenton reaction is quite versatile to mineralize a wide variety of organic compounds. Our studies showed that besides TNT, RDX and tetraol could also be mineralized.

The authors have also developed methods to mineralize organic ion exchange resins used in demineralization applications using a photo-Fenton reaction. In this study, the solid resin was reactively solubilized using H₂O₂ under Fenton type reaction conditions to produce linear chains of the solubilized polymer ([Kubota 1983](#)). This was subjected to photo-Fenton reaction mineralization at room temperature quantitatively. The experiments were scaled to 20 liters ([Srinivas, 2003](#)).

Nuclear reactor decontamination aqueous formulations containing EDTA, ascorbic acid, and citric acid was also mineralized using photo-Fenton reaction in our studies. It is noteworthy that the carboxylic acids present in this mixture make photo-Fenton reaction an ideal choice for mineralization ([Srinivas, 2000](#)).

In conclusion, the photo-Fenton reaction is a versatile green option for the treatment of wastewaters. There is a scope for using solar light in photo-Fenton reaction because the absorption of carboxylate complexes of ferric ion extends to the visible region. This aspect is being pursued further.

AOP by photocatalytic oxidation using TiO₂ is handicapped by low quantum efficiency (<3%) for OH radical generation ([Legrini et al., 1993](#)). It is in the state of development to be used for commercial applications.

The application of ozone-based treatment will be discussed below in another case study.

Dibutyl phosphate-bearing wastewater treatment

Dibutyl phosphoric acid (DBP) or its salt form is a toxic substance used in the plastic industry as a plasticizer. In the nuclear industry, it is an unwanted byproduct in tributyl phosphate (TBP) solvent production and use. In this case study, the importance of the selection of a method for the treatment of a water-borne pollutant based on the composition of the medium will be discussed.

Wastewater bearing DBP is produced in Tributyl phosphate solvent production facilities during solvent purification with aqueous sodium carbonate. It was characterized by high COD of 30-40 g/L, predominantly contributed by DBP, high TDS of 25-30%, and pH was 9-10 ([Srinivas et al., 2004](#)). A simple approach to treat this water is to precipitate DBP by adding ferric chloride at a pH of 3-4. The results showed that the addition of 10-12 g/L of ferric chloride rendered the wastewater fit for reuse in the production plant with no discharge of water to the surroundings. It is interesting to note that a simple precipitation reaction has overcome the wastewater treatment problem and offered zero liquid discharge advantage. This scheme was adopted successfully at a plant scale with a positive environmental impact.

Dibutyl phosphate-bearing wastewater treatment in radioactive processing facilities ([Srinivas et al., 2010](#))

This radioactive wastewater was produced during the purification of radioactive TBP solvent using a sodium carbonate solution as before. In the wastewater, besides DBP, uranium and other radioactive elements will be present at a pH of 10-11. DBP in the wastewater renders this wastewater problematic and not amenable to standard treatment methods already available in radioactive waste management.

FeCl₃ dosing for precipitation of DBP cannot be done here since pH lowering to pH 3-4 will form a difficult to manage sticky Uranium-DBP precipitate contaminated with other radioactive elements in the wastewater. It is not a practical solution in the context of radioactive operations. It is of interest to note that the same compound, DBP, in different environments, needs different approaches for treatment.

Our study showed that *ozonation* of the wastewater eliminated the sticky precipitate formation problem created by DBP, and the ozone-treated wastewater was amenable to conventional radioactive waste treatment operations. Ozone can be produced on demand using an ozone generator working on the principle of corona discharge. Ozone generators from mg/hour to several kg/hour are available commercially. Ozone is a strong oxidant with a standard oxidation potential of 2.07V (vs. SHE). Ozone chemistry in AOP has been reviewed (Wei et al., 2017). It is a clean oxidant which can directly react with organic compounds or indirectly through OH radical participation under U.V. irradiation or H₂O₂ addition or if alkaline conditions are prevalent in the wastewater. It does not leave any residue after treatment. It is highly reactive towards aromatic compounds. A proper gas-liquid mixing reactor should be designed to prevent the escape of ozone through the water into the air. Ozone escape into the air should be minimized through proper design of the reactor. Gas induction reactors are ideal for this kind of application. They are commercially available. The ozonation process was adopted at the engineering scale to treat problematic radioactive waste successfully. Ozonated radioactive wastewater was amenable to traditional treatment without a problem.

Leachate wastewater treatment

Leachate wastewater (leachate) arises from the landfills of hazardous waste processing industries. This water arises because of the release of the water present in the immobilized waste product or rainwater ingress into the landfill. The leachate is toxic and characterized by high COD(10-15 g/L), high TDS (8%), intense foul smell and dark color. Black color and foul odor were attributed to humic acids and organo sulfurous compounds in leachate.

The wastewater conductivity was 45mS/cm contributed by chloride (2%) and other inorganic salts. The composition and conductivity of the leachate lead to the choice of mediated electrochemical oxidation for treatment. Electrochemical methods, such as the following, are emerging as green alternatives for different treatment wastewaters (Marco and Giacomo, 2009): These methods are inherently clean as the redox processes involve electron transfer in electrochemical cells instead of redox chemical dosing.

- Electro-coagulation
- Direct electrochemical oxidation
- Mediated electrochemical oxidation
- Electro-dialysis
- Saltwater splitting using bipolar membrane technology

Among these direct and mediated electrochemical oxidation methods (Marco and Giacomo, 2009; Carlos and Sergio, 2006) deal with the problem of organic waste mineralization in wastewater, which is the scope of the present review.

In the direct electrochemical oxidation process, the organic pollutant in the wastewater undergoes anodic oxidation directly by losing electron/s at the anode (Pt, Pd, etc.). Phenol oxidation, as shown below, is an example:



Water is the source of oxygen for this reaction. Protons liberated will be reduced at the cathode, as shown below:



Slow kinetics and electrode fouling are some of the problems in direct oxidation.

Boron doped diamond(BDD) anodes have been shown to have promise as an electrochemical AOP. The anodic process is shown below: Anodic oxidation of water with the formation of OH radicals as intermediates is the basis of the process.



Dissolved organics also co-adsorb on the anode. BDD's higher cost and lower stability are some of the limitations being addressed for the commercialization of the technique.

In the mediated electrochemical process, oxidants are produced at the anode in the electrolytic reaction. The oxidant mineralizes the organic compound in the wastewater. Mediated electrochemical oxidation methods are of two types:

- Non-metal mediated electrochemical oxidation(NMEO)
- Metal ion-mediated electrochemical oxidation (MEO)

Among the NMEOs, chlorine, ozone, hydrogen peroxide-mediated methods may be mentioned. Among these, chlorine-based NMEO discussed below, is widely used NMEO. Ship ballast water treatment for disinfection is conveniently done using this technique since seawater is rich in chloride content (Peter et al., 2015).

In our leachate treatment case study, the wastewater is ideal for chlorine-mediated NMEO because chloride is already present in the wastewater to the extent of 2%. Moreover, TDS is also very high(8%), which is essential for enhancing the wastewater's

electrical conductivity. If the wastewater conductivity is low, the deliberate addition of NaCl or inert electrolytes is necessary to reduce ohmic resistance offered by the wastewater. Therefore, this method was chosen in the experimental remediation study on actual wastewater.

Chloride is anodically oxidized, as shown below:



Chlorine and hypochlorite ion are responsible for the oxidation reaction. It is well known that chlorine is a bleaching agent (Gustaf, 1954) and a disinfectant and removes the color of different materials. Therefore, this process was studied in our laboratory. Using available platinum electrodes as anode and cathode, feasibility experiments were done in the laboratory on actual leachate water in the undivided electrolytic cell under constant current mode. Results were highly promising, as shown by the following photograph: Color and odor were removed by applying current *without the addition of any chemicals externally*. Electrochemical processes are rapidly emerging as green alternatives for many applications, including wastewater treatment and organic synthesis (Ming et al., 2017).



Figure 1: Leachate treatment for color and odor removal

Based on the promising laboratory results, the experiments were scaled to a 25-liter scale with graphite as anode and stainless steel as a cathode with a current density of 40-50 mA/cm² at a constant current of 200A. Graphite is cheaper with 1-2 years of service life. It was widely used in chlor-alkali electrolysis plants before the introduction of dimensionally stable anodes. It has higher oxygen overpotential(+ 0.95V). With the expenditure of 0.6 kWh of electrical energy, the foul odor has vanished in the leachate. With the expenditure of a total of 3.5-4 kWh of energy, the leachate's black color has also disappeared. There is a reduction of 30-40% in the COD of leachate also. In laboratory studies, it was observed that electrolysis over longer times resulted in a 75-80% reduction in COD. Therefore, chlorine-mediated electrolysis offered a green technique to treat leachate from a hazardous waste processing facility for odor and color removal and COD reduction simultaneously without the addition of reagents as the composition of the leachate allowed treating it.

Metal ion-mediated electrochemical oxidation (MEO) (Veerle&Andr'e, 1996; National Research Council, 1996; Nelson, 2002; Srinivasan et al., 2012)

Incineration has been a traditional method for managing solid and liquid organic wastes for over a century. However, many non-incinerable organic wastes arise in different operations. Tributyl phosphate solvent waste, ion exchange resin waste arising from nuclear facilities, for example, cannot be incinerated because of the complexity of radioactive off-gas treatment. Several organic wastes from defense and pesticide industries cannot be incinerated. Moreover, concern about the emission of dioxin and furan from incineration facilities has resulted in the decline of importance to Incineration. Green alternatives are evolving as an alternative to Incineration. MEO is one such green option (Zohar, 1995).

This process has been recommended as an alternative to Incineration by the United Nations' technical committee for the treatment of mixed hazardous organic wastes in developing countries because of the ease of transportation and assembly for on-site treatment options, among other factors (United Nations Environment Program, 2004).

In this method, strong oxidants such as Ag II, Ce IV, or Co III are generated at anode in-situ in an electrolytic cell with *divided configuration*, i.e., with the separate anode and cathode compartments. The authors have used H shaped glass electrolytic cells for the studies. The basic principle is described below with Ag (I)/Ag (II) couple:

Reactions at Anode (working electrode)([Paire et al., 1997](#))



Reactions at Cathode



Ag (II) produced in the anode is a potent oxidant ([Wojciech and Zoran, 2015](#)) and mineralizes a wide variety of organic compounds at *normal temperatures* (30-50°C) in anolyte consisting of AgNO₃ in nitric acid. Co (III) is as powerful as Ag (II) in mineralizing organic solid and liquid wastes. It is of interest to note that the same mineralization reaction in the incineration process occurs at 700-950°C. Many college and other laboratories generate small volumes of hazardous solvent and solid organic wastes regularly. There may not be hazardous waste treatment facilities nearby, especially in non-metro cities and towns. These wastes can, conveniently, be treated at the point of generation by MEO without the need for sophisticated equipment. If chlorine is present in the waste, Co (III) or Ce (IV)-mediated MEO can be adopted to avoid chloride precipitation. Ce (IV) mineralization reactions require 70-80°C for mineralization. The authors of this paper have studied the MEO of ion exchange resins and tributyl phosphate in an n-dodecane solvent using MEO using Ag (II) as a mediator catalyst and demonstrated the mineralization reaction at room temperature.

This method is not suitable for wastewaters as the reaction requires 4-8M nitric acid medium or sulfuric acid and silver, cobalt, or cerium salt catalyst for electrolytic mineralization. However, it is best suited for non-incinerable organic solid and solvent/liquid wastes arising from defense, nuclear and pesticide industries, etc. It is suitable for mixed waste treatment. The organic waste need not be a particular organic compound. It could be different compounds in the waste.

In conclusion, on electrochemical techniques, it can be said that they have a significant role to play as green alternatives for organic waste treatment in the future.

Wet Air Oxidation method (WAO)

This method is a promising option for the treatment of high COD-bearing wastewaters. It is a process in which oxidizable organic materials, either dissolved or suspended in an aqueous medium, are thermally mineralized by oxygen under pressure in an autoclave. The temperature varies between 200-300°C, and oxygen pressure ranges from 0.7 to 1.5 Mpa ([Mishra et al., 1995](#)). Copper sulfate is used as a catalyst to mineralize acetic acid and other refractory organic compounds in WAO.

In our studies, cation and anion exchange resin wastes arising from water demineralization plants were studied for mineralization using WAO. These resins are poly(styrene-divinylbenzene) backbone with strong sulfonic acid and quaternary ammonium hydroxide functional groups. In this process, before conducting WAO, the resins were subjected to reactive dissolution by Fenton type of reaction using copper sulfate as catalyst instead of ferrous sulfate since wet air oxidation is catalyzed by copper sulfate to bring the solid resins in an aqueous soluble form ([Kubota, 1983](#)). Copper sulfate, therefore, served the dual role of resin dissolution catalyst and wet air oxidation catalyst. WAO is conducted in an autoclave for conducting an oxidation reaction with oxygen at high pressures. At high pressures, the solubility of oxygen in the aqueous medium increases and enhances the reaction rate. Copper sulfate in millimolar concentration was used as a catalyst. Quantitative mineralization of resins in soluble form was achieved in these studies on cation and anion exchange resins in a 0.6-liter autoclave ([Gunale et al., 2009](#)) at 0.6-1.3 Mpa pressure and 200-300°C for the two resins.

In WAO, the oxidation conditions are sub-critical. Supercritical water oxidation is an advanced mineralization technique for the rapid mineralization of industrial wastes and sludges above supercritical water (374.17°C and 22.12 MPa). In SCWO, a wide range of organic wastes in water are rapidly mineralized. Under supercritical conditions, water behaves as a non-polar medium facilitating solvation of organic materials. Inorganic salts present in the wastewater precipitate out of the medium. It is an advantage as well as disadvantage. It will lead to a reduction of TDS in the wastewater. Simultaneously, it will lead to poor heat transfer in the reactor. Corrosion of reactor materials, high energy consumption, operating costs are some of the engineering issues in this process ([Bermejo and Cacero, 2006](#); [Zhang et al., 2017](#)).

CONCLUSIONS

- Several green chemical options are available for organic waste treatment.
- Several case studies describing the authors' work have been discussed in the study.
- Tributyl phosphate, dibutyl phosphate, hazardous waste leachate, ion exchange resin waste streams, and their treatment were discussed with principles. Organic solid, liquid, and wastewaters have been covered in the study.

- Advanced oxidation, electrochemical oxidation, and wet air oxidation processes were discussed.
- While selecting the treatment, the nature of the organic waste and the composition of the medium in which it is present should be carefully considered.
- The same pollutant in different media may change the treatment option.
- Several uncertainties exist in the optimization of AOP processes. These need attention and further work.

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LIMITATIONS AND STUDY FORWARD

Advanced oxidation studies and their optimization are mostly empirical. There is a need to rationalize the process of optimization. The use of solar energy in the photo-Fenton reaction is a definite possibility. This should be translated into commercial applications. Anion exchange resin reactive dissolution *in forms other than chloride* should be investigated by Fenton type reaction reported in this work. The authors could not succeed in this effort.

AUTHORS' CONTRIBUTION

Ms. Gitika Saheb Singh has contributed to the experimental work on leachate treatment, and Ag (II) mediated electrochemical oxidation of ion exchange resins and TBP solvents. Dr. C.Srinivas contributed to the conception, planning, execution of all experiments and preparation of the manuscript.

REFERENCES

1. Bermejo, M.D., and Cocero (2006). Supercritical water oxidation: A technical review. *AIChE Journal*, 52(11), 3933-3951. <https://doi.org/10.1002/aic.10993>
2. Carlos A.M and Sergio F. (2006). Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chemical Society Reviews*, 35, 1324-1340. <https://doi.org/10.1039/B517632H>
3. Cheves, W. (1975). Fenton's reagent revisited. *Accounts of Chemical Research*, 8 (4), 125-131. <https://doi.org/10.1021/ar50088a003>
4. Eary, L.E. (1985). Catalytic decomposition of hydrogen peroxide by ferric ion in dilute sulfuric acid solutions. *MTB* 16, 181-186. <https://doi.org/10.1007/BF02679709>
5. Gitika, S.S., Banerjee, D., and Srinivas C (2020). Ag(ii)-mediated Electrochemical Oxidation Technique for Organic Radioactive Waste Treatment and Analytical Applications. *Springer Nature Applied Sciences* J (communicated).
6. Giusy, L., Jeanette, B. (2010). Wastewater management through the ages: A history of mankind. *Science of the Total Environment*, 408, 5264-5264. <https://doi.org/10.1016/j.scitotenv.2010.07.062>
7. Gunale, T.L., Mahajani, V.V., Wattal, P.K., Srinivas, C. (2009). Studies on liquid phase mineralization of cation exchange resin by a hybrid process of Fenton dissolution followed by wet oxidation. *Chemical Engineering Journal* 148 (2009) 371-377. <https://doi.org/10.1016/j.cej.2008.09.018>
8. Gunale, T.L., Mahajani, V.V., Wattal, P.K., Srinivas, C. (2009). 'Liquid Phase Mineralisation of gel-type anion exchange resin by a hybrid process of Fenton dissolution followed by sonication and wet air oxidation,' *Asia-Pacific Journal of Chemical Engineering*, 4, 90-98. <https://doi.org/10.1002/apj.214>
9. Gustaf, H (1954), The chemistry of oxidizing and bleaching agents. *Chemical Reviews*, 54(1), 169-194. <https://doi.org/10.1021/cr60167a005>
10. Hughes, S., Samuel, D., Salma, B., Nya, W., Yu, H. (2015). Meisenheimer complex between 2,4,6-trinitrotoluene and 3-aminopropyltriethoxysilane and its use for a paper-based sensor. *Sensing and Bio-Sensing Research*, 5, 37-41. <https://www.sciencedirect.com/science/article/pii/S2214180415300015>
11. International Atomic Energy Agency (2004). Predisposal Management of Organic Radioactive Waste. Technical Reports Series No. 427, IAEA, Vienna. ISBN 92-0-103204-8.
12. Kaidar A., Eric D van H., Michel C., and Alain, B. (2010). Application of Advanced Oxidation Processes for TNT Removal: A Review. *Journal of Hazardous Materials*, 178(1-3), 10-28. <https://doi.org/10.1016/j.jhazmat.2010.02.042>
13. Kubota, M. (1983). Decomposition of Cation Exchange Resin by hydrogen peroxide. *Journal of Radioanalytical Chemistry*, 78(2), 295-305. <https://doi.org/10.1007/BF02530440>
14. Kuhn, H.J., Braslavsky, S.E., and Schmidt, R (2004). Chemical Actinometry. International Union of Pure and Applied Chemistry, IUPAC2004_Actin_March-23-04. <https://photochemistry.jp/acv/ENGLISH/Chemact.pdf>
15. Legrini, O., Oliveros, E. and Braun, A.M. (1993). Photochemical processes for water treatment. *Chemical Reviews*, 93 (2), 671-698. <http://doi.org/10.1021/cr00018a003>

16. Leon, M.D. and Gerald, E.A.(1973) Reactivity of the Hydroxyl radicals in Aqueous solutions' National Bureau of Standards Report NSRDS-NBS 46. <https://nvlpubs.nist.gov/nistpubs/Legacy/NSRDS/nbsnsrds46.pdf>
17. Marco Parizza and Giacomo Cerisola(2009) Direct and Mediated anodic oxidation of organic pollutants. Chem Rev. 109:6541-6569. <https://doi.org/10.1021/cr9001319>
18. Mehmet, A.O., Jean-Jacques, A.(2014). Advanced Oxidation Processes in Water/Wastewater Treatment: Principles and Applications. A Review. *Critical Reviews in Environmental Science and Technology*, 44, 2577–2641. <https://doi.org/10.1080/10643389.2013.829765>
19. Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., &Hübner, U. (2018). Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review. *Water Research*, 139, 118–131. <https://doi.org/10.1016/j.watres.2018.03.042>
20. Ming, Y., Yu, K., and Phil S.B.(2017).Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. *Chemical Reviews*, 117 (21), 13230-13319. <https://doi.org/10.1021/acs.chemrev.7b00397>
21. Mishra, N.S., Reddy, R., Kuila, A., Rani, A., Mukherjee, P., Nawaz, A., Pichiah, S.(2017). A Review on Advanced Oxidation Processes for Effective Water Treatment. *Current World Environment*, 12(3). <http://dx.doi.org/10.12944/CWE.12.3.02>
22. Mishra, V.S., Mahajani, V.V., and Joshi, J.B.(1995). Wet Air Oxidation. *Industrial Engineering Chemistry Research*, 34,2. <https://doi.org/10.1021/ie00040a001>
23. Mukherjee, A., Debnath, B., Ghosh, S.K.(2016). A Review on Technologies of Removal of Dioxins and Furans from Incinerator Flue Gas. *Procedia Environmental Sciences*, 35, 528-540. <https://doi.org/10.1016/j.proenv.2016.07.037>
24. National Research Council(1996). Review and Evaluation of Alternative Chemical Disposal Technologies. Chapter 5. Mediated Electrochemical Oxidation Silver II. The National Academies Press, Washington DC., <https://doi.org/10.17226/5274>
25. Nelson, N(2002). Electrochemical Destruction of Organic Hazardous Wastes. *Platinum Metals Reviews*, 46, 18-23. <https://www.technology.matthey.com/article/46/1/18-23/>
26. Paire, A., Espinoux, D., Masson, M., &Lecomte, M. (1997). Silver(II) Mediated Electrochemical Treatment of Selected Organics: Hydrocarbon Destruction Mechanism, *Radiochimica Acta*, 78(Supplement), 137-144. <https://doi.org/10.1524/ract.1997.78.special-issue.137>
27. Peter, P.S., Louis, P., Anita, G.J.B.(2015). A comparison of six different ballast water treatment systems based on U.V. radiation, electro chlorination, and chlorine dioxide. *Environmental Technology*, 36(16), 1-30. <https://doi.org/10.1080/09593330.2015.1021858>
28. Srinivas, C.(2000). Kinetic and Mechanistic Studies related to the treatment of Organic waste from the Nuclear Industry by wet oxidation. Ph.D. thesis, University of Mumbai, India.
29. Srinivas, C., Sugilal, G. and Wattal, P.K.(2003). Management of spent organic ion exchange resins by photochemical oxidation. Waste Management Symposium WM03, Tucson, Arizona (USA), Feb. 23-27, Session 51, Abstract No. 149. Paper presentation. https://digital.library.unt.edu/ark:/67531/metadc781687/m2/1/high_res_d/827468.pdf
30. Srinivas, C., Sugilal, G. and Wattal, P.K.(2004). TBP Plant effluent treatment process. BARC/2004/E/013. https://inis.iaea.org/collection/NCLCollectionStore/_Public/36/097/36097363.pdf
31. Srinivas, C. (2005). Photochemical process for the treatment of wastewater containing high energy particles. (Private communication in BARC, Mumbai).
32. Srinivas, C etal. (2010). Ozonation process for treatment of DBP-bearing aqueous Intermediate Level Radioactive Waste. BARC/I/2010/05.
33. Srinivasan, R., ChinnuSamy, A., Sudhagar, S., and Ravi, T.N(2012). Electro-oxidative process for the mineralization of solvent and recovery of plutonium from organic wastes. *Journal of Radioanalytical and Nuclear Chemistry*.291(3),681-684. <http://doi.org/10.1007/s10967-011-1462-7>
34. VeerleV.A. and Andr' e Rahier(1996). The electrochemical oxidation of organic waste and activated graphite by Ag 2+ in nitric acid: a literature study. SCK.CEN, Mol, Belgium. https://inis.iaea.org/collection/NCLCollectionStore/_Public/29/032/29032886.pdf
35. United Nations Environment Program (2004). Review of Emerging, Innovative Technologies for the Destruction and Decontamination of POPs and the Identification of Promising Technologies for use in Developing Countries, The Scientific and Technical Advisory Panel of the GEF United Nations Environment Programme, Final – GF/8000-02-02-2205, Section 2.3.3 &2.3.4. http://archive.basel.int/techmatters/review_pop_feb04.pdf
36. Wei, C., Zhang, F., Hu, Y., Feng, C., & Wu, H. (2017). Ozonation in water treatment: the generation, basic properties of ozone and its practical application, *Reviews in Chemical Engineering*, 33(1), 49-89. <https://doi.org/10.1515/revce-2016-0008>

37. Wojciech, G., and Zoran, M.(2015). Chemistry of silver(II): a cornucopia of peculiarities. *Philosophical Transactions of the Royal Society A*, 373, 20140179. <http://dx.doi.org/10.1098/rsta.2014.0179>
38. Zhang, S. etal. (2017). A Review of Challenges and Recent Progress in Supercritical Water Oxidation of astewater. *Chemical Engineering Communications*, 204(2), 265-282. <https://doi.org/10.1080/00986445.2016.1262359>
39. Zohar Chiba, Bruce Schumacher, Patricia Lewis, and Laura Murguia(1995). Mediated Electrochemical Oxidation as an Alternative to Incineration for Mixed Wastes. Lawrence Livermore Laboratory Report. UCRL-JC- 119133. <https://pdfs.Semanticscholar.org/e82d/bfaf88b206f90a2795e3d0bf9d892a42c2cc.pdf>

FURTHER READINGS

1. Srinivas, C., Ramaswamy, M., and Theyyunni, T.K.(1994). WET OXIDATIVE DESTRUCTION OF SPENT ION-EXCHANGE RESINS USING HYDROGEN PEROXIDE. Bhabha Atomic Research Centre Report. BARC/1994/E/041. <https://inis.iaea.org/collection/NCLCollectionStore/Public/26/074/26074278.pdf?r=1>
2. Olga, C.(2015). REMEDIATION OF TNT-CONTAMINATED WATER BY USING INDUSTRIAL LOW-COST RESIDUE PINE BARK. Ph. D. thesis, Mälardalen University Press Dissertations, Sweden. <https://www.diva-portal.org/smash/get/diva2:851197/FULLTEXT03.pdf>
3. Braun, A.M., Maurette, M.T., and E. Oliveros, E.(1991). Photochemical Technology, Wiley, New York. <https://doi.org/10.1002/ange.19921041147>