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Application of dielectric dicharge based non-thermal plasma tool for treatment of wastewater

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Recently the pharmaceutical compounds also called as "emerging pollutants" are becoming a vital class of pollutants due to their non-biodegradable nature. They are introduced into the food chain through aquatic life and suffer biomagnification thereafter, as a result of which they are of important concern. The methods conventionally applied hitherto for the treatment of water fail when applied for removal of such bio-recalcitrant compounds. Herein comes the importance and relevance of Advanced Oxidation Processes (AOPs). So as to make sure that the fluid after treatment that is let flow into the stream is safe from the environment point of view, detailed study and chemical analysis of the water after treatmentis done. This paper presents a review of the type of water pollutants degradable and treatable efficiently by Non-thermal Plasma (NTP)and recent works where application of NTP is studied for removal of persistent organic and bio-recalcitrant pollutants. The analytical measures and parameters to compute the degradation efficiency of NTP tool based waste water treatment is also reviewed making a comparative study with the efficacy of the conventional methods of treatment.

Keywords: Advanced oxidation process, dielectric barrier discharge, non-thermal plasma, emerging contaminants.

Introduction

The gradual and increased prevalence of emerging contaminants (ECs), also called micro-pollutants or trace elements (contaminants) into the aquatic environment has become an issue of dire importance because of the harsh effects that they cause to marine organisms and humans alike. Emerging contaminants include hormones which are steroidal in nature, pharmaceutical compounds and personal care products, insecticides and other surfactants. Conventional plants for waste water treatment is not constructed in specific to eliminate ECs. Some of these pharmaceuticals like anti-epileptics and anti-hypertensives are persistent in nature. Therefore, AOPs are required to degrade these pollutants where *in situ* oxidizing species like hydroxyl radical, hydrogen peroxide, peroxy-nitrites, ozone are generated which interact with the bio-recalcitrant compounds and degenerate them[1]. The targeted pharmaceuticals attempted to be removed by NTP tool[2,3] may be classified under different therapeutic groups like analgesics, anxiolytics, lipid regulators, anti-convulsant, vasodilators, anti-hypertensives and anti-biotics. Non thermal plasma is one such advanced oxidation tool studied newly and applied for the removal of such difficult pharmaceuticals from waste water oxidatively. After treatment of waste water infested with such bio-recalcitrant compounds by the NTP technology they are partially mineralized and degenerated at a faster rate than the conventional approaches[4–8]. Table 1 enlists the commonly detected pharmaceuticals in wastewater. The paper is organized into five sections. The first section is the introduction which incorporates the different sources of emerging pollutants in water that are commonly found, with examples of each kind. The second section discusses the conventionally used Advanced Oxidation Processes (AOPs) that are used to eliminate bio-recalcitrant pollutants from wastewater. The third and fourth section include the role of dielectric discharge based non-thermal plasma tool for waste water treatment and their comparative analysis of degradation efficiencies. In the final section the conclusion of the review is provided which summarizes the limitations that have restricted scaling up of the pilot projects using NTP for waste water treatment.

Advanced oxidation processes

Advanced oxidation process has been defined in exact terms by Glaze *et al.* as "Water treatment processes carried

Table 1. Pharmaceuticals commonly detected in wastewater

Generic name	Therapeutic value	Examples
Antibiotics	Fight bacterial infections	Erythromycin, Ofloxacin
NSAIDs	Pain relievers	Aspirin, Diclofenac, Ibuprofen
Anti-hypertensives	Prevent high blood pressures	Metoprolol, Propranolol, Atenolol
Hormones	Excreted by humans	17-b Estradiol, Estriol, Estrone
Anti-convulsant	Fights epileptic seizures	Carbamazepine, Primidone, Dilantin
Anti-depressants	Fights anxiety disorders	Fluoxetine, Paroxetine, Diazepam
Lipid regulators	Reduces blood cholesterol level	Bezafibrate, Chlofibric acid, Gemfibrozil

out at room temperature and normal pressure and based on generation of oxidizing species in the site itself such as hydroxyl radical OH^-, at a sufficient concentration to effectively decontaminate water". Different types of AOPs are classified based on *in situ* creation of hydroxyl radicals through numerous chemical, photo-chemical, sono-chemical and/or electro-chemical reactions. The most primitive and predominantly used chemical AOP is the Fenton method, in which a mixture of a soluble iron(II) salt and H_2O_2, known as the Fenton's reagent is applied to degenerate and destroy persistent organic pollutants (POPs). Other AOPs include electrohydraulic cavitation and sonolysis where bubbles are formed by pulse powered plasma and thereafter detached in liquid, electron beam and γ-ray irradiation, wet air oxidation and supercritical water oxidation treatment which are used to treat highly concentrated contaminated water, photocatalysis and ozonation. Some of these AOPs have shown promising degradation efficiencies with organic compounds however the removal time with non-biodegradable pollutants has been large. Herein comes the importance of non-thermal plasma-based treatment of waste water which is elaborated in the subsequent section.

Non-thermal plasma for waste water treatment

A non-thermal plasma, cold plasma or non-equilibrium plasma is defined as plasma which is not in thermodynamic equilibrium because the electron temperature is much hotter than the temperature of heavy species (ions and neutrals). Water treatment by means of plasma discharge takes an interesting and promising place among the advanced oxidation techniques, as it can generate a wide spectrum of oxidative species like the hydroxyl radical OH^- which is often named as the most important oxidant, due to its high oxidation potential of 2.85 V and unselective nature while oxidation. Further, plasma in contact with liquid can generate significant amounts of O_3 and H_2O_2. There are different configurations of the NTP based waste water treatment depending on the electrode configurations and the interface between the plasma channel and water surface of which dielectric barrier discharge based NTP is reviewed in this paper. There are different methods to generate NTP of which the most prominent one is dielectric barrier-based (DBD) plasma reactors[9,10]. In DBD based plasma reactors the discharge interaction occurs in gaseous phase. Most frequently, glass material is used, specifically quartz-glass, while Al_2O_3 material ceramic type barriers is also used as mentioned in literature but with less frequency. The DBD based reactors in non-thermal plasma technology over surface of water usually have high the energy efficacy for degeneration of organic species the value of efficiency increases with increase in input power. In DBD based plasma generation there may be different classification on the basis of the electrode configuration as well as the nature of the interface between plasma and the pollutant to be removed. The different types of DBD based reactors are electrohydraulic discharge reactors (Fig. 1a), bubble discharge reactors (Fig. 1b), coaxial reactors with falling water film (Fig. 1c), low energy spray discharge reactors (Fig. 1d) and hybrid reactors (Fig. 1e).

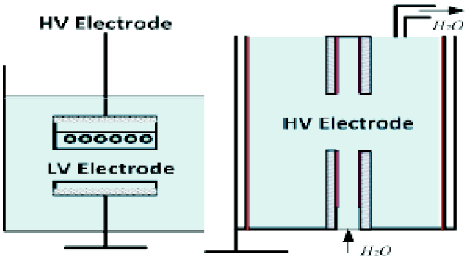

Fig. 1a. Electrohydraulic discharge reactor.

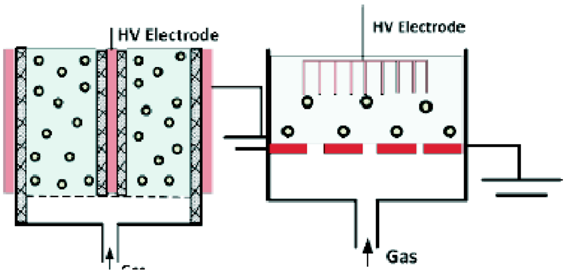

Fig. 1b. Bubble discharge reactor.

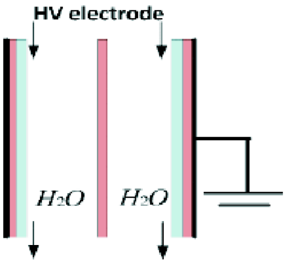

Fig. 1c. Coaxial reactor.

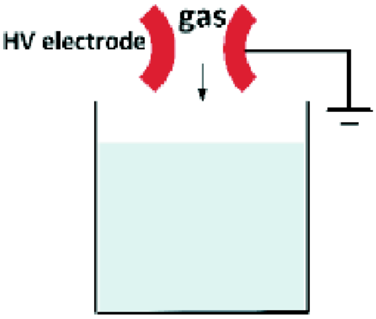

Fig. 1d. Spray discharge Reactor.

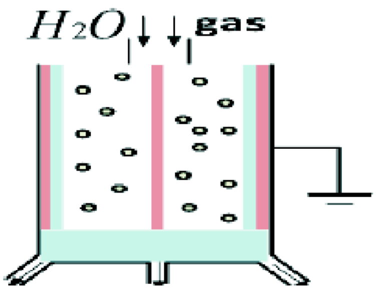

Fig. 1e. Hybrid reactor.

One of the most attractive ways of non-thermal plasma generation is by means of electro-hydraulic cavitation. Here the discharge starts by initiation of cavitation or holes which creates a high volume of non-thermal plasma and water interface. However, the energy efficiency goes down as energy is lost on the generation of cavitation. In order to increase the reduced efficiency of electro-hydraulic cavitation external bubbles are applied by using bubbling discharge reactors.

The process of initiation of discharges in the gaseous phase minimises erosion of electrode which increases the lifetime of the system. The intensity of the radical density is increased by bubbling. The feed gas also plays a crucial role in determining discharge efficacy. The direction of the gas flow, choices of nozzle material, dimensions and orientations determine the shape of the bubble during formation and position after the detachment which influence plasma characteristics. Another common type of reactor for electrical discharges is coaxial geometry in which water is let fall as a falling film actually wetting the wall of the reactor as opposed to DBD reactor where the barrier protects the reactor wall. It is seen that with smooth water flow and the water film completely covering the anode gives the maximum efficiency as the heavy water current does not wash away the ion-wind. There is an optimized wall radius for discharge, if the wall is too small the contact area is lessened and if the wall radius is too large the radical life is short-lived. When the treated solution is let flow as a spray instead of falling film its efficacy of degradation goes up manifold. Hybrid reactors as the name suggests is a combination of two or more of the discharge configurations. Sometimes bubble discharge reactor is combined with coaxial reactor with falling water film. In order to have an idea about the efficacy of NTP on the degradation of the contaminants into their mineralized states two important parameters are considered. The first one is removal rate given by eq. (1) and the second one is degradation efficiency given by the energy yield *Y* given by eq. (2). Ideally for total removal of the contaminants the value of removal rate should be as close as 100% as possible. The degradation efficiency is given by the energy yield defined as the amount of compound removed per unit of energy spent in the process.

Table 2. Reported results on compounds degradation by NTP

Compound	Discharge type	Discharge power (W)	Initial conc. (mg/L)	Treatment time (min)	Removal rate (%)	Energy (g/kWh)
Amoxicillin	DBD with falling liquid film	2	100	10	100	105
Sulfadiazine	Corona with falling liquid film	100	10	27	99	0.0022
Tetracycline	Point to plate corona with gas bubbles	36	50	24	61.9	0.54
Tetracycline	Point to plate corona with gas bubbles with TiO_2	36	50	24	85.1	0.7
Diclofenac	Corona above water	24	50	15	100	0.76
Ibuprofen	Wetted-wall	3	60	80	91.7	6.9

$$R = \left(1 - \frac{c}{c_0}\right) \times 100 \tag{1}$$

where c_0 and c are the initial and final concentrations of the pharmaceutical compound in solution, respectively.

$$Y = \left(\frac{c_0 VR}{Pt}\right) \times \frac{1}{100} \tag{2}$$

where c_0 is the initial concentration of the investigated pharmaceutical (in g/L), V is the solution volume (in L), R is the removal rate in (%), P is the power dissipated in the discharge (kW) and t is the treatment time (in h).

Ideally for complete degradation the removal rate must be 100% and energy yield should be as low as possible. Table 2 gives the summary of the different measures of degradation efficacy applied to some pharmaceuticals after their treatment with different non-thermal plasma treatment[11–15].

It is observed that the same compound tetracycline when treated with point to plate corona with gas bubbled through it shows removal rate of 61.9% with same initial concentration and treatment time the removal rate becomes 85.1% with addition of catalyst TiO_2. The energy yield value is very high for dielectric discharge-based treatment whereas it is low for wetted wall corona method. Ideally, after complete mineralization the products remaining should also be analyzed with methods like gas chromatography. This is to ensure safe discharge into the stream. This part is not included in the present review.

Comparison of non-thermal plasma technology with other AOPs

It is really a challenging task to compare non-thermal plasma-based oxidation technique with other conventional advanced oxidation methods on a same platform. Firstly, the parameters that are particularly defined for NTP methods to determine the degradation efficiencies do not apply for the conventional methods. Secondly it is rather difficult to keep conditions same for all methods with respect to volume and characteristics of the solution, additional substances added and initial pollutant concentration. Still effort was made for comparing the efficacy of different AOPs for treating diclofenac and the results were tabulated in Table 3[16–20]. It is seen that in ozonation full removal is not reached. Photocatalysis and sonolysis require huge treatment time even with small initial concentrations of diclofenac. Considering all the parameters non-thermal plasma shows optimal performance with respect to removal of diclofenac from the solution. The wastewater from the industries first go through primary treatment which involves filtration of suspended solids, grit and fat removal.

The water then goes for secondary treatment for biological treatment thereafter it goes for tertiary treatment for removal of dissolved compounds. Non-thermal plasma reactors are a part of this tertiary treatment unit. A typical labora-

Table 3. Comparison of results of degradation of diclofenac by different AOPs

AOP method	Initial conc. (mg/L)	Treatment time (min)	Removal rate (%)	Energy yield (g/kWh)
Ozonation	200	30	More than 99	0.76
TiO_2 photocatalysis	10	240	85	0.00826
Sonolysis	8.9	40	More than 90	0.0055
H_2O_2 and UV	296	90	More than 95	4.6
Photo-Fenton	50	60	100	–
Plasma (pulsed corona) above water	50	15	100	1

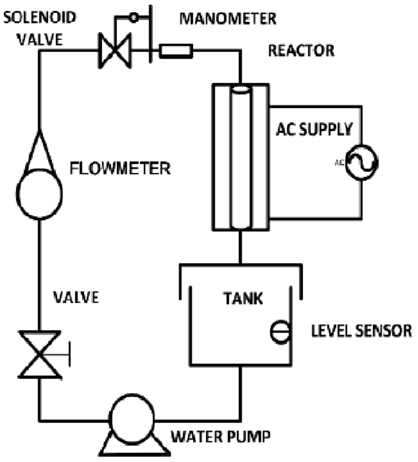

Fig. 2. NTP treatment for water purification-laboratory prototype.

Table 4. Parameters chosen for Laboratory prototype plasma reactor

Apparatus	Specifications
Reactor	Geometry coaxial with Cu electrodes outer hollow, inner solid bar. Length- 490 mm, Diameter-120 mm. Borosilicate glass of 2.4 mm thickness as DBD material.
Power supply	20 kV pk-pk
Nozzle	Flowrate-10 l/min, Pressure-50 psi.
Pipelines	PVC
Pump	1 ph, 1 hp
Tank	48 L, made of fiberglass
Others	Control system, Variable frequency drive, Solenoid valve

tory prototype reactor with DBD-based plasma generation[21] is given by Fig. 2 and the ratings of the different parts of the setup is tabulated in Table 4.

The impure water with all kind of impurities is first made free of its suspended impurities by filtration and other conventional water treatment methods like flocculation, sedimentation and others. The biodegradable wastes are then removed by methods applied conventionally. Non-thermal plasma-based water treatment is applied for removal of non-biodegradable wastes specifically and the main advantage extracted out of it is its fast removal time. The water is pumped into a tank equipped with level sensors and the high voltage reactor with power supply in the range of 20–30 kV where the water is treated by plasma with different reactor geometry. The valves control the flow of water discharged and the flow and pressure are measured with the help of flowmeter and manometer respectively. The water after treatment is analyzed with different chemical methods like chromatography for comparison of initial and final concentration of the impurities which is not under the purview of the present review.

Conclusion

In this review non-thermal plasma based advanced oxidation method has been covered with its advantages over other conventionally used oxidation processes for treatment of waste water infested with bio-recalcitrant compounds. Typical laboratory set up for NTP based water treatment has been also reviewed and a comparative analysis for treatment of waste water with different AOPs have also been studied.

Non-thermal plasma technology for the removal of waste water showed promising results for degeneration of the most commonly found bio-recalcitrant pharmaceutical compounds in waste although on a pilot scale. The main advantages that can be extracted out of the NTP methods is the small treatment time for complete mineralization and the observed biodegradability of the treated solution goes up with this method. The capital expenditure apart from the energy due to the electrical discharges like the price of feed gases and the pumping of the solution to be treated into the reactor chamber are the major concerns. In order to extend NTP methods to a broad scale further research and study is required.

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