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Effect of recycling overhead gases on pollutants degradation efficiency in gas-phase pulsed corona discharge treatment

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ABSTRACT

In the present study, pollutant degradation efficiency was investigated by recycling of overhead gases from gaseous phase to aqueous phase in gas-liquid interface pulsed corona discharge reactor. Methylene blue (MB) was used as a model pollutant and its degradation was compared by recycling and non-recycling of oxygen, air and argon gases. The degradation rate constants of MB were 0.28 and 0.23 min^{-1} in recycled condition which was decreased to 0.22 and 0.21 min^{-1} in non-recycled condition in oxygen and argon gas, respectively. On contrary, in air medium, comparatively higher MB degradation rate (0.21 min^{-1}) was achieved in non-recycled condition compared to recycled condition (0.11 min^{-1}). The long-lived reactive oxygen species (ROS) such as hydrogen peroxide and ozone were quantified in both conditions. We observed that the concentration of ozone present in the aqueous solution was slightly higher in recycling conditions as compared to that of non-recycled condition in all the gases. Moreover, higher hydrogen peroxide concentration was detected in recycled condition (185 and 168 mg/L) compared to non-recycled condition (112 and 40 mg/L) in the presence of oxygen and argon, respectively, and vice-versa in air medium. The economic comparison revealed that up to 33% of electrical energy could be saved by recycling overhead oxygen gas.

1. Introduction

Water pollution is garnering major attention not only for its impact on water availability and quality, but also for its adverse effects on humans and aquatic ecosystem. Apart from microbiological contamination, the voracious consumption and introduction of new chemicals discharged by various industries such as textile, pharmaceutical manufacturing, tannery, paint, printing, cosmetics manufacturing etc, are on rise. Various chemical laden effluent by industries causes significant environment damage and human diseases [1–4].

Several conventional methods such as coagulation/flocculation [5], adsorption [6], biological treatment [7], and different advanced oxidation processes (AOPs) like ozonation [8], fenton oxidation [9], photofenton [10] and photo-catalytic degradation [11,12] have been implemented to treat the various organic pollutants from industrial effluent. However, many of these techniques are having some limitations. Conventional treatment methods are not effective in removing complex organic pollutants from industrial wastewater. Also, many pollutants are resistant to biological degradation, which results in the membrane fouling/damage (due to deposition and reactivity of the pollutants on the surface or within the pore of the membrane) and incomplete mineralization [13]. Though AOPs have the potential to remove these pollutants from industrial wastewater, the treatment costs of these technologies are relatively higher and required large consumption of chemicals/catalysts [14,15]. Hence, researchers worldwide are still trying to find an optimized technique to reduce the impact of industrial discharges to the environment.

In recent time, plasma technology has emerged as one of the new advanced oxidation processes (AOP) for the treatment of organic compounds in water, sterilization of water, synthesis materials and nanoparticles, energy generation and application in medicines [16–27]. Corona discharge is one such method, which is widely being used recently by various researchers for the plasma generation to treat various organic pollutants and pathogens from water [28–33]. Typical corona discharge requires two asymmetrical electrodes; first, the electrode having very high curvature (such as needles and wires) and the second electrode having lesser curvature such as a plate. This configuration creates a very high electric field and very sharp voltage pulse in duration of nanoseconds to microseconds. Plasma can be generated either by high voltage electric discharge directly inside the water

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(electrohydraulic discharge) or as a discharge in the air above the water. High voltage corona discharge in air or water generates plasma, which is a mixture of highly reactive oxygen species (ROS) like hydroxyl radical, ozone, hydro peroxyl, hydrogen peroxide and atomic oxygen, which then reacts with the organic contaminants and breaks them into innocuous compounds [16,34,35].

Direct corona discharge (electrohydraulic discharge) has its own pros and cons; direct interaction of the reactive species to the pollutants is advantageous whereas the concentration gradient that forms due to the low rate of transport in the liquid phase stands as the disadvantage [36,37]. Similarly, diffusion of reactive species from gas phase to bulk liquid is the major limitation of gas phase electrical discharge [38] and this shortcoming was avoided by developing hybrid gas-liquid reactor [39–42]. In hybrid system, high voltage reactor is submerged in the liquid and ground electrode is suspended in the gas phase. The benefit of this reactor is that the discharge could also happen in gas phase and liquid phase, intensifying the reactive species formation and thus resulting in an efficient pollutant removal by dissolving reactive species in the liquid. However, in hybrid gas-liquid discharges, a part of ROS generated in gaseous phase discharge may not diffuse and react with the pollutants present inside liquid. The recycling of ROS from overhead gaseous phase to liquid phase would increase the degradation efficiency of the corona discharge based plasma reactors.

Therefore, the objective of the present study is to recycle the ROS present in overhead gaseous phase to aqueous phase in order to further improve the pollutant degradation. Methylene blue (MB) was used as a model pollutant and its degradation was compared by recycling and non-recycling of overhead gases in the reactor. Though, some of the studies have discussed about the MB degradation in gas phase plasma treatment [32,42–46], the insight into efficient utilization of gas-phase ROS for the MB degradation is lacking. Thus, in this study an attempt was made for the efficient utilization of overhead gas-phase ROS for the MB degradation in gas phase corona discharge reactor. An economic comparison between recycling and non-recycling condition of the pulsed corona discharge treatment was also performed.

2. Materials and methodology

2.1. Reagents and apparatus

Methylene blue (99% purity, Paxmy chemicals, India) was used as a model organic pollutant. Titanium(IV) Oxysulfate-sulfuric acid (Sigma Aldrich, India) and Ozone kit (Prerna Laboratory, Pune, India) was used for the analysis of H_2O_2 and O_3, respectively.

2.2. Experimental set up and reactor configuration

The experimental set up used in the present study is as shown in Fig. 1. For generation of high voltage an AC source was used, which consisted of a discharge-free test transformer (100 kV, 5 kVA) and the AC source was converted to a DC source using a high voltage diode (140 kV, 20 mA, 100 kΩ). The continuous DC source was converted to pulse by means of a Rotating Spark Gap (RSG), wherein the shape of the pulse was recorded by using an oscilloscope (HP 54645A, 100 MHz). The pulse voltage and injected current in the reactor was recorded using a voltage probe (EP–50 K, PEEC, Japan) and current probe (Pearson Electronics, USA, model no – 101), respectively.

The corona discharge was produced by using a multiple-needle and plate arrangement. The reactor consists of an electrode made of iron with nine streamers attached to a circular plate and the tip of each streamer needle had a radius of curvature of 50 μm. The electrode was connected to the high voltage DC source. The bottom of the reactor was a plane electrode, which was grounded. The high voltage electrode was also adjustable in its pitch using a screw arrangement so that the electrode distance can be adjusted (increased or decreased) from the water surface. One pitch rotation was equivalent to 1 mm distance. Therefore, the distance between tip of the needles and water surface can be adjusted 1 mm by one rotation of screw rod. The reactor chamber was formed using cylindrical glass of diameter 4.5 cm and height of 6 cm. The two electrodes were provided with ports and valves to facilitate the entry and exit of required gases (Ar, O_2 and Air), recycling of gases as well as for sample collection. Gas was recycled as forced system. Fresh gases were continuously introduced during the experiment, which could develop pressure in the head space above the liquid inside the reactor. A tube was connected from the head space to the bottom part of the electrode for the recycling. Due to the pressure gradient developed between the head space and liquid, the gases were recycled through bottom part of the reactor. A hole was provided at the center of the ground (bottom) electrode, through which recycled gas was introduced to the reactor. The reactor was provided with a water jacket in order to maintain constant temperature during the span of the experiment. The reactor was filled with 50 mL of sample solution methylene blue (MB) or water. The tip of the streamer was maintained at a height of 5 mm from the surface of the sample solution for the production of surface corona discharge. The reactor was sealed properly to prevent leaks of gases using a gasket and septum. The hard-flexible tube made up of teflon was used for the recycling experiments. The extra built pressure was released during each sampling (after 2 min of treatment time). There no condensation in the tube was observed during the experiment. The length, diameter and thickness of the tube was 10 cm, 6 mm and 1 mm, respectively. The temperature of the tube was around 30–40 °C.

2.3. Experimental procedure

Different batch experiments were performed for the degradation of MB and to measure the concentration of H_2O_2 and O_3 in recycled and non-recycled conditions. In recycled condition, the headspace gases were recycled back to aqueous phase by opening valve. For MB degradation, 50 mL sample solution of MB with 50 mg/L concentration was used as the sample and was treated in the reactor for a total duration of 10 min. Samples were collected at intervals of 2 min to measure the residual MB concentration in both recycling and non-recycling conditions. Similarly, various experiments were carried out in deionized water (50 mL) and concentrations of H_2O_2 and O_3 were measured. A constant flow rate of 50 mL/min of different gases (Oxygen, pure air and Argon) was purged during the experiments. Gases were introduced perpendicular to the liquid surface above 3 cm of the plasma region. The uniform gaseous environment can be expected due to 3 cm air gap. The system was purged for 5 min with a very high flow rate of gases before experimentation. All the batch experiments were performed at an applied voltage of 16 kV with a pulse frequency of 25 Hz. The solutions were manually mixed during each sampling (after each 2 min) in both recycling and non-recycling condition. All the experiments were performed in deionized water of initial pH 7 and conductivity of 18 μS/cm. The MB degradation efficiency and energy consumption for the present treatment method were determined using Eqs. (1) and (2) [18,19].

$$\%\ Degradation(\eta) = \left(1 - \frac{C_t}{C_0}\right) \times 100 \tag{1}$$

$$W_p = \int_{t=0}^{t=T} U(t) I(t) dt \times f \tag{2}$$

where C_0 (mg/L) was the initial MB concentration and C_t (mg/L) was the MB concentration at treatment time 't'. W_p is the input power (kW), which was calculated by recording instantaneous voltage, U(t); and current I(t) over the one cycle. 'f' was the applied pulsed frequency in Hz.