New mechanistic insight in plasma based water treatments

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Abstract: The study of the mechanisms of decomposition of organic contaminants in water induced by atmospheric plasma requires particular strategies. These include the kinetic description of the pollutant removal, the identification of oxidation intermediates and products, the determination of the reactive species involved, the investigation of the effect of the experimental variables of the solution and of the applied discharge. Some case studies in which this strategy allowed to obtain new mechanistic insight are presented and discussed.

Keywords: atmospheric plasma, organic contaminants, advanced oxidation.

1. Introduction

The application of cold plasma for the decomposition of organic contaminants in water is a very promising technique, which is proposed as an advanced oxidation process for eliminating residual persistent pollutants after the conventional water treatment processes [1-4]. Many different lab scale plasma reactors have been designed and used for this purpose and classified based on whether the discharge occurs into the water, in the air above the water or in air bubbles which are mixed with the water [2]. Moreover, also considering the same reactor type with regard to the above mentioned classification, many are the experimental parameters which can influence the degradation process, including notably: reactor geometry, electrodes material and configuration, power supply and discharge regime. Other important variables deal with the chemical nature and composition of the solution to be treated, such as: initial concentration of the pollutants, pH, presence of salts and other additives. The gas used to produce the plasma influences both the discharge features and the chemical processes taking place in the system, determining the energy of the process, the time required for its completion and the possible formation of byproducts. The volume of the solution and the distance of the liquid from the electrodes are still additional variables which influence the global process. Our research group has long been interested in finding correlations between the discharge regimes applied and the ensuing outcome of the treatments. Specifically, the degradation efficiency of the primary pollutant and of its metabolites, the extent of mineralization of organic carbon and the mechanisms involved in the process are analysed and studied [5-12]. The investigations are generally carried out by comparative evaluations: dc corona discharge *vs* dielectric barrier discharge (dbd) [9,10], ultrapure water *vs* tap water or water buffered at different pHs [6], discharge in air *vs* discharge in Ar. The model organic pollutants chosen for these studies are molecules representative of different classes of water contaminants (pharmaceuticals, pesticides, PFAs,..). The understanding of their oxidation mechanism is the first objective of our studies. In addition, organic compounds, the oxidation mechanisms of which are already known, are used as molecular probes to obtain information on the reactive species which cannot be measured directly.

2. Experimental

Schematics of the reactors designed and built in our lab are shown in Figure 1.

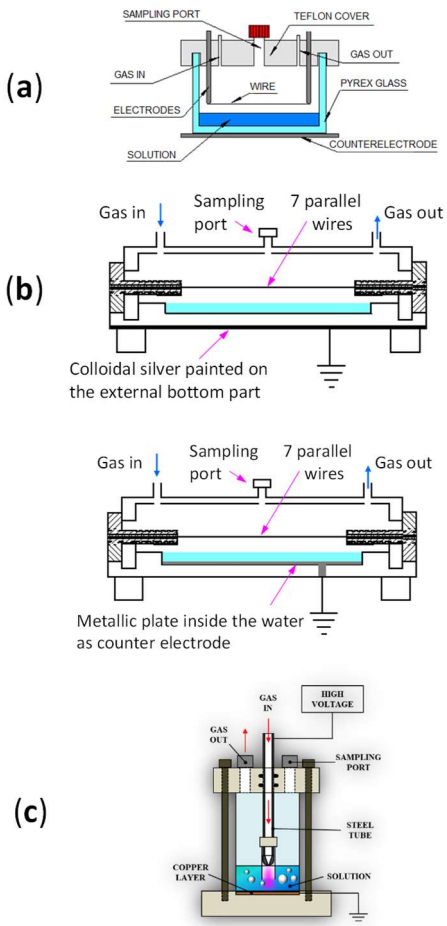

Fig. 1. Prototypes reactors employed at the Dept. of Chemical Sciences of University of Padova.

Reactor **a** is a small dbd prototype, in which an ac voltage of 18-21 kV and 50 Hz of frequency is applied to two parallel wires located above the aqueous solution [5]. Reactor **b** was born as a scale-up of reactor **a** with larger dimensions and seven parallel wires instead of two as high voltage electrode. Reactor **b** has the additional feature of

two interchangeable bases which allow to apply a +dc or a –dc corona discharge instead of the dbd [9-10]. Reactor **c** is another example of a device which allows to use different electrode configurations and thus to compare different discharge regimes without changing the geometry of the reactor [11]. Further elaborations of these prototypes are currently under development and testing in our lab. Common features of the experimental procedure employed with all these devices are i) the presence of a constant flow of the discharge gas during operation, which allows for the continuous renewal of the gaseous environment in which the plasma is produced, and ii) the saturation of the discharge gas with humidity prior to its entrance in the reactor in order to prevent water evaporation and thus concentration of the aqueous solution subjected to the treatment. The process efficiency is determined by monitoring the reaction progress, i.e. the pollutant conversion (C/C_0, where C and C_0 are the pollutant concentration at time t and time zero) as a function of the treatment time (or input energy). Depending on the reactor size, these experiments are carried out either by sampling the same solution, after briefly interrupting the discharge, at selected treatment times (used with large volume reactors) or by performing a series of experiments in batch, by treating in each experiment a fresh portion of solution for a different reaction time. In all cases plots of C/C_0 *vs* time (or *vs* energy) are used to obtain the process kinetic parameters.

3. Results and Discussion

One of the case studies which will be considered in the talk, deals with the effect of pH on the decomposition efficiency of a common pollutant, phenol, and of a contaminant of emerging concern (EOC), the herbicide metolachlor. In a previous study carried out with reactor **a** [6], it was observed that the removal of phenol was faster in tap water than in ultrapure water. In consideration of the composition of tap water, the effect of different possible factors was investigated to explain these findings: conductivity, traces of iron, traces of residual active chlorine from the depuration process operated in the aqueducts of Italian cities, bicarbonate anions and their buffer effect on pH. The effect of each variable was investigated separately and it was concluded that the increase in the rate of the process observed in tap water was due to the buffering of pH at a value of about 7 due to bicarbonate anions, while in the case of ultrapure water the pH rapidly decreases during the treatment due to the formation of nitric acid. In the case of phenol, pH affects the dissociation equilibrium of the molecule. However, also the concentration of the reactive species can be influenced by pH, thus, considering the high concentration of ozone produced in reactor **a**, the decomposition of ozone in water with the consequent formation of hydroxyl radical was taken into account. To investigate on this question, *tert*-butanol was used as probe, exploiting the fact that it does not react with ozone. It was verified that at pH 7, characteristic of tap water, ozone is not decomposed. This result was confirmed by analysing the effect of tap water on the plasma induced decomposition of metolachlor in reactor **a**: since this compound has no strong acid-base properties, its decomposition is not influenced by pH and thus by tap water (Figure 2). Thus, if the removal rate of phenol in reactor **a** is increased with the increase of pH, this is due only to the higher concentration of phenoxide anion, which is more reactive than undissociated phenol with ozone.

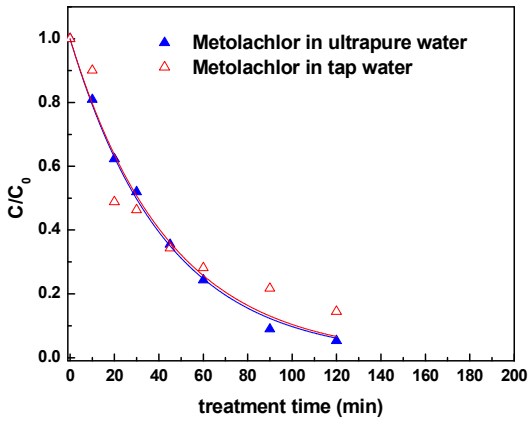

Fig. 2. Decomposition of metolachlor in solutions prepared in ultrapure and tap water ($C_0 = 1 \cdot 10^{-4}$ M) in reactor **a**.

When the same experiments were carried in reactor **c**, the relative rates of phenol decomposition in ultrapure and tap water was opposite with respect to that observed in reactor **a**: the process was faster in ultrapure than in tap water. The same result was observed with metolachlor, the decomposition in tap being considerably slowed down with respect to ultrapure water. The different characteristics of ultrapure and tap water were again considered and their effects were tested individually in specific experiments using reactor **c**, as was done previously with reactor **a**. The results of these experiments show that the opposite effects observed with the two reactors are due to the different relative concentrations of the reactive species generated in water in reactor **a** and reactor **c** and in the different equilibria in which these species are involved.

An organic molecule which is both a contaminant which we are interested to decompose by atmospheric plasma but which can also be considered an excellent probe in this type of mechanistic studies is perfluorooctanoic acid (PFOA), a second case studies. This compound belongs to the class of perfluoroalkyl substances (PFAs), highly persistent compounds in the environment and resistant to traditional wastewater treatments [13]. For these reasons, for their ability to bioaccumulate and for their potential adverse effects on human health, PFAs, among which PFOA in particular, are nowadays closely monitored and their production has been almost completely interrupted. Nevertheless, they will persist in the environment for years

and years. Lacking of hydrogen atoms, PFAs are unreactive with OH radicals [14], a characteristic which is rare in the case of organic compounds and which further underlines the important role of OH radical among the reactive species present in cold plasma. We have, indeed, ascertained that most cold plasmas which are generally effective in the decomposition of many different classes of organic compounds, such as the plasma produced in reactor **b** by dc- corona discharge, are not able to significantly decompose PFOA (Figure 3).

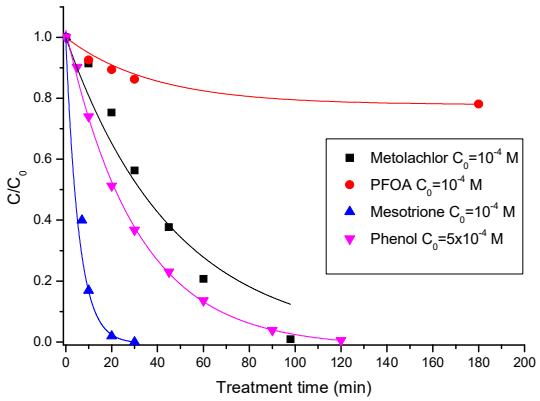

Fig. 3. Decomposition of metolachlor, PFOA, mesotrione and phenol in solutions prepared in ultrapure water in reactor **b** energized by –dc corona discharge.

Thus, the development of a new system is underway in our lab guided by the study of the decomposition mechanism of PFOA. The objective of the work is the production of a plasma rich of reactive species capable of attacking PFOA.

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