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## Cr(VI) reduction by microsecond pin-to-pin discharges generated in an aqueous solution

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### ABSTRACT

The total reduction of Cr(VI) by microsecond pin-to-pin electric discharge generated in aqueous solution has been reported. [Cr(VI)] and [H<sub>2</sub>O<sub>2</sub>] were measured simultaneously by UV-vis absorption spectroscopy during the process. The kinetics of the Cr(VI) reduction resulting from the discharges is found to be pseudo zero order rate. The influence of the electron properties has been studied by varying the applied voltage and the electrode gap showing a better reduction for a higher electric field. In addition pH and conductivity of the solution have been measured before and after the process. The analysis of the chemical kinetics has been completed by varying the pulse duration of the discharge. The results show that the reduction occurs both during the plasma and the post plasma phases. It is also noted that the increase of the pulse duration involves a better Cr(VI) reduction, a higher [H<sub>2</sub>O<sub>2</sub>] production and a more important change in conductivity.

**KEYWORDS:** electrical discharge, water depollution, Cr(VI) removal

### 1. Introduction

Hexavalent chromium Cr(VI) pollution in water represents a current health and society issue worldwide since this compound is a CMR agent (Carcinogenic, Mutagenic and Reprotoxic). This pollution is mainly related to industrial applications in many fields such as energy production, waste and wastewater managements, paints and pigments, metal plating, tanning and steel industries [1, 2]. The effluent from these industries can contain Cr(VI) at concentrations ranging from tenths to hundreds of mg/L. These values are much higher than the recommended dose thresholds. Chromium emission limits in the aquatic environment are mainly regulated on a national scale (no universal regulation), depending on the source of pollution, the receiving water body and the chromium speciation. As an example for drinking water, the European Union and the United States of America have set the above limit to 0.05 mg/L and 0.1 mg/L of total chromium respectively, whereas World Health Organization suggests 0.05 mg/L for Cr(VI) [1].

Different techniques are considered to remove Cr(VI) from wastewaters either using chemical treatment (chemical reduction, adsorption, ion exchange, electrocoagulation), biological approaches (biosorption, bioaccumulation, bioreduction, phytoremediation) or physical processes (permeable

reactive barriers, solidification) [3-5]. Most of them involve the reduction process of Cr(VI) to the less mobile and less toxic form Cr(III). Most techniques reach high removal efficiency (>90%) but few of them report a total removal which represents a limitation since heavy metals are highly toxic even at very low concentration [6]. Moreover, none of these techniques has become dominant since they all involve different pros and cons. For example, biological methods are considered as potential and eco-friendly but the processes take a lot of time to be completed [2, 4, 5].

Among the physico-chemical methods, plasma in interaction with liquid can be considered as a promising remediation technology since first studies show encouraging results [7-18]. For example, Wang *et al.* reported that the energy efficiency of Cr(VI) reduction in glow discharge plasma (GDP) is higher than those in semiconductor photocatalysis and comparable to that in electrolytic reduction with Fe electrode [16]. But to the best of our knowledge, no plasma-liquid interaction (PLI) techniques has reported a total removal of Cr(VI), only *almost* 100% of reduction is reported [11, 13, 17]. One of the main drawback of these processes is the pseudo 1<sup>st</sup> order kinetics that involves an exponential decay of [Cr(VI)]. As a consequence the initial decrease of [Cr(VI)] is fast but the total removal is not obtained. As an example, some works reported a decrease by a factor of two of the initial [Cr(VI)] concentration in about 2 min but a horizontal asymptote is reached after 3 min of process corresponding to a non-zero concentration [7, 18].

It is known that discharges above or inside a solution results in the formation of reactive species in the liquid phase such as H<sub>2</sub>O<sub>2</sub>, •H, •OH or solvated electrons. A list of reactions have been detailed in several papers [18-20] and examples are reported in **Table 1** (reactions 1-4). These species can be involved in the redox processes between Cr(VI) and Cr(III). Some of the main reduction mechanisms of Cr(VI) by PLI discussed in the literature have been reported in **Table 1** [7, 11, 17, 21]. Reactions are reported by considering either the ion global form of Cr(VI) (Reaction 5) or the more specific forms (Reactions 6-12). Indeed Cr(VI) exists in solution with different speciation according to pH including H<sub>2</sub>CrO<sub>4</sub>, HCrO<sub>4</sub><sup>-</sup>, CrO<sub>4</sub><sup>2-</sup> and CrO<sub>7</sub><sup>2-</sup> [2, 5]. The removal of Cr(VI) is known to be more efficient in an acidic environment. This effect could be attributed to three reasons [14]: (i) The pH of the solution affects the existing form of Cr(VI) in the solution, and the oxidation potential of Cr(VI) increases when the pH decreases, then facilitating the reduction process ; (ii) Under acidic conditions, the amount of H<sup>+</sup> ions is increased, which enhances the reducing efficiency of the process (reactions 7, 10 and 12) ; (iii) Under acidic conditions, Cr(VI) in solution can be slowly reduced to Cr(III) by the H<sub>2</sub>O<sub>2</sub> produced by PLI (reactions 8 and 11).

$\text{H}_2\text{O} \rightarrow \bullet\text{H} + \bullet\text{OH}$	Reaction 1
$\text{H}_2\text{O} \rightarrow \text{H}^+ + \bullet\text{OH} + \text{e}_{\text{aq}}^-$	Reaction 2
$\bullet\text{OH} + \bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$	Reaction 3
$\text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+$	Reaction 4
$\text{Cr(VI)} + 3 \bullet\text{H} \rightarrow \text{Cr(III)} + 3\text{H}^+$	Reaction 5
$\text{HCrO}_4^- + 7\text{H}^+ + 3\text{e}_{\text{aq}}^- \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$	Reaction 6
$\text{HCrO}_4^- + 3\bullet\text{H} + 4\text{H}^+ \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}$	Reaction 7
$2\text{HCrO}_4^- + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{O}_2 + 8\text{H}_2\text{O}$	Reaction 8

$\text{CrO}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	Reaction 9
$\text{CrO}_7^{2-} + 8 \text{H}^+ + 6 \cdot\text{H} \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	Reaction 10
$\text{CrO}_7^{2-} + 3\text{H}_2\text{O}_2 + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{O}_2 + 7\text{H}_2\text{O}$	Reaction 11
$\text{CrO}_4^{2-} + 5 \text{H}^+ + 3 \cdot\text{H} \rightarrow \text{Cr}^{3+} + 4 \text{H}_2\text{O}$	Reaction 12

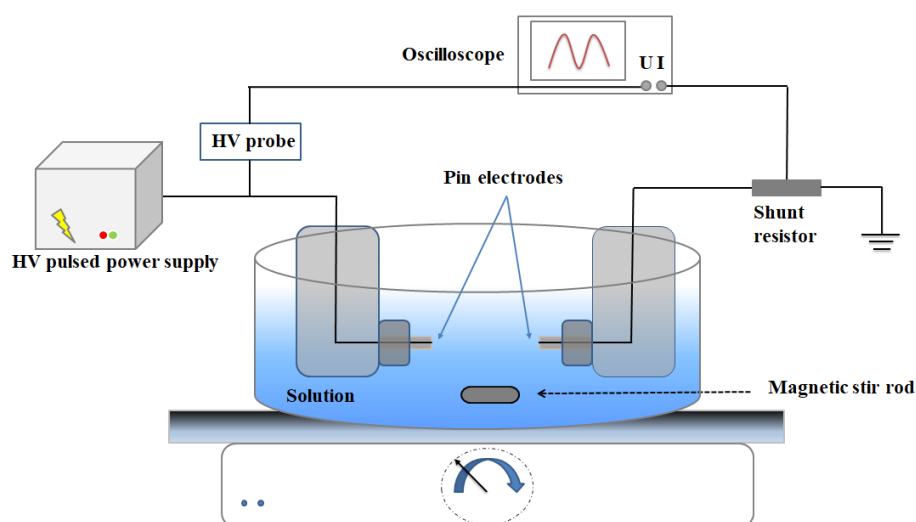
**Table 1** Examples of mechanisms involved in Cr(VI) reduction by PLI process in aqueous solution [7, 11, 17-21]

Despite several studies that have reported the feasibility of Cr(VI) reduction by PLI, the total removal is still challenging as well as the identification of the reactions mechanisms for Cr(VI) reduction [21].

This work reports a plasma in liquid process able to completely reduce Cr(VI) in solution. Moreover, parametric studies on the applied voltage and the interelectrode gap is performed in order to better understand the mechanisms mainly responsible for Cr(VI) reduction. In addition to [Cr(VI)] measurements, chemical analyses of the solution have been performed reporting the variation of the pH and the conductivity as well as the hydrogen peroxide concentration during the PLI process. Finally, the pulse duration is varied to provide new insights into kinetics analysis of Cr(VI) reduction.

## 2. Experimental set up

A description of the plasma set-up has been previously detailed in [22, 23]. A general schematic of the microsecond plasma system in liquid using a pin-to-pin configuration is shown in **Fig. 1**. The high voltage pulsed power supply consists of a low inductance capacitor ( $C = 1 \text{ nF}$ ) charged by a 30 kV DC high voltage power supply (Ultravolt 30A24-P30) through a 30 k $\Omega$  resistor, and a fast-high voltage solid-state switch (Behlke HTS 301-03-GSM). The 200  $\mu\text{m}$ -diameter electrodes are in platinum (Pt). The tips of the electrodes do not protrude from the insulator in the solution.



**Fig. 1** Experimental set-up of pin-to-pin discharge in liquid (side view)

Electrical measurements are performed using a HV probe (LeCroy PMK 20 kV, 1000:1, 100 MHz), a shunt current ( $R=10 \text{ }\Omega$  connected to Lecroy PP023 probe) and an oscilloscope (HDO9104 - 1GHz, Teledyne LeCroy). Typical voltage and current waveforms are reported in **Fig. S1** and values of

injected energy are also provided in **Table S1**, in supplementary file. Readers can refer to [22, 24] for the description of the electrical signals. In summary, two main regimes of discharge can be identified using the electrical signals: one regime only reports a transient current corresponding to the plasma formation at the electrode tips (bush-like structures) whereas the other one involves a breakdown (resulting from the plasma connection across the gap) which results in voltage drop and current peak as well as strong light emission (see **Fig. S2**, in supplementary file). It is noted that the distribution of the two discharge regimes during the process is monitored thanks to a dedicated data processing program. For both regimes the plasma discharge occurs during the first 10  $\mu\text{s}$  according to both light emission and current signals. More specifically the charges are mainly injected during the first ten microseconds for no breakdown and even faster for breakdown since the breakdown phenomenon is not measured after 4  $\mu\text{s}$ . From 10  $\mu\text{s}$  to the end of the pulse duration, the voltage is about 1-2 kV and the current is too small to be detected by the acquisition system ( $<1$  mA).

Cr(VI) solution with a concentration equal to 50 mg/L ( $\pm 0.3$  mg/L) is prepared by dissolving 0,1414 g of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) in 1 L of distilled water. Then 94 mL of this solution is then mixed with 6 mL of acid  $\text{H}_2\text{SO}_4$  0,1 M. The resulting properties of the initial solution used for all the experiments are:  $[\text{Cr(VI)}]_0 = 47$  mg/L ( $\pm 0.3$  mg/L);  $V = 100$  mL, conductivity  $\sigma = 4$  mS/cm, and  $\text{pH} = 2.3$ -2.4. We choose to work in acidic aqueous solution ( $\text{pH} \approx 2$ ) since it is known to provide a better Cr(VI) removal as discussed previously. With the initial conditions used in this work ( $[\text{Cr(VI)}]_0 = 47$  mg/L and  $\text{pH} = 2.4$ ), the major initial form of Cr(VI) is hydrogen chromate ( $[\text{HCrO}_4^-]_0 = 8.96 \times 10^{-4}$  mol/L) and the second one is dichromate ( $[\text{Cr}_2\text{O}_7^{2-}]_0 = 3.21 \times 10^{-5}$  mol/L) (estimated by the software Visual Minteq, <https://Vminteq.Lwr.Kth.Se/>)

In this paper all the results will be discussed in terms of [Cr(VI)], including all the forms of the species. The measurements of Cr(VI) concentration have been performed every 15 minutes during the treatment process by sampling 2 mL of the treated solution and using UV-vis absorption spectrophotometry at 350 nm (AvaSpec-2048 XL, Avantes). Moreover additional measurements using DPC (1,5-diphenylcarbazide), a reagent forming a complex with Cr(VI) that ensures selectivity and lower detection limit [25], are also performed periodically to confirm the results for low concentrations.

The concentration of  $\text{H}_2\text{O}_2$  is measured by a colorimetric method using ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) [26]. The method is based on measuring the absorption at 440 nm of the complex  $\text{NH}_4[\text{VO}(\text{O}_2)\text{SO}_4]$  formed by the reaction between  $\text{H}_2\text{O}_2$  and  $\text{NH}_4\text{VO}_3$  under acidic conditions. The measurements are performed every 15 minutes by mixing 2 mL of the treated solution with 1 mL of 0.06 M  $\text{NH}_4\text{VO}_3$ . We note that this method allows measuring  $[\text{H}_2\text{O}_2]$  and [Cr(VI)] simultaneously.

Measurements of [Cr(VI)] and  $[\text{H}_2\text{O}_2]$  have been repeated several times for the same experimental condition and the corresponding standard deviation is calculated (example for [Cr(VI)] in **Fig. S3** in supplementary file). The corresponding values are reported as error bars in the figures.

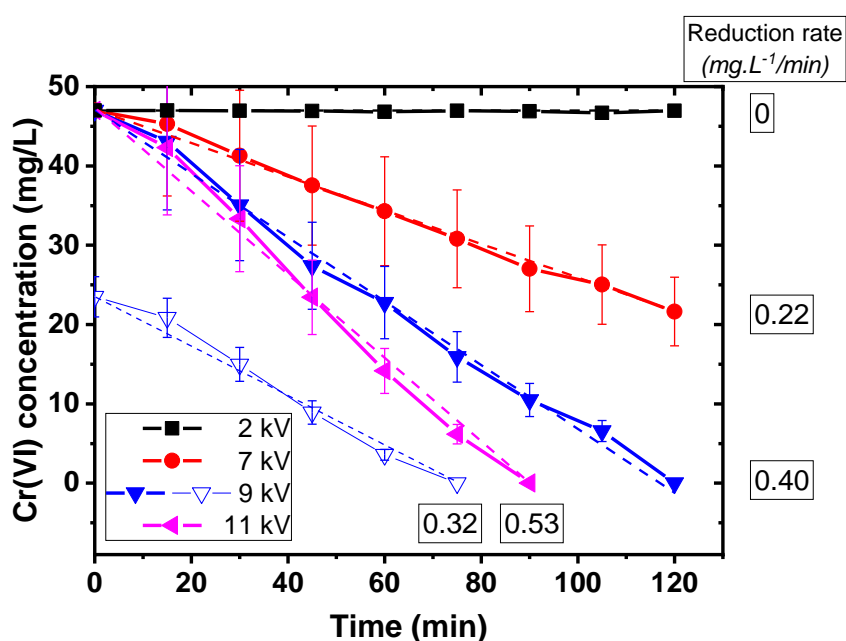
The measurements of the conductivity and the pH of the treated solution are performed before and after the process using dedicated probes (SensION+ EC71, HACH and SensION MM340, HACH, respectively). The experiments are performed at room temperature and only a slight increase in liquid temperature is reported after 2 h of process.

Different initial parameters are changed within this study: the inter-electrode distance is equal to either 2 or 5 mm using micrometer control system; the applied voltage is changed from  $U = 2$  kV to 11 kV and the pulse duration varies from  $\Delta t = 10 \mu\text{s}$  to 1 ms. The repetition rate of the process is constant and equal to 50 Hz. The process duration is defined to be equal to maximum 2 hours.

### 3. Results and discussions

#### 3.1 Kinetics of the Cr(VI) reduction

For all the conditions used in the frame of this work (changing the applied voltage, the pulse duration or the gap), it is reported that the evolution of Cr(VI) concentration during PLI process is linear with time (coefficient of determination  $R^2 > 0.98$ ). As an illustration, **Fig. 2** shows the results obtained for different applied voltages.



**Fig. 2** Time evolution of Cr(VI) concentration according to the applied voltage for 2 mm gap obtained during pin-to-pin discharges in Cr(VI) solution (47 mg/L,  $\sigma=4$  mS/cm, pH=2.3)  $V = 100$  mL,  $\Delta t = 500 \mu\text{s}$ , electrodes length =  $0 \pm 10 \mu\text{m}$ ,  $f = 50$  Hz. The empty symbols refer to  $[\text{Cr(VI)}]_0 = 23.5$  mg/L ( $\sigma=4$  mS/cm, pH=2.3)

This linear trend is very different from other evolutions reported in the literature for Cr(VI) reduction by PLI which have shown exponential decay [7, 11, 17, 18]. These works generally refer to first order kinetics which involves that (i) the reverse process (oxidation) occurs along with the reduction process and (ii) the rate of reduction is related to the initial concentration of Cr(VI) [7]. In this work, the linear evolution refers more to pseudo-zero order mechanism. In accordance with this result, it is also observed in **Fig. 2** that the reduction rate does not strongly depend on the initial concentration of Cr(VI) when it is divided by two: it is equal to  $0.4 \text{ mg.L}^{-1}/\text{min}$  for 47 mg/L and to  $0.32 \text{ mg.L}^{-1}/\text{min}$  for 23.5 mg/L.

It is known that two general conditions can result in zero-order rates [27]:

- Only a small part of the reactants are in a configuration (place or state) in which they are able to react, and this amount is continually supplied from a larger pool (as for catalyze). We can consider

that this effect happens if Cr(VI) is reduced at the interface between the gas phase and the liquid, the interface acting like the catalyst for the reactivity limitation.

- For multi-components process, the concentration of one reactant is much greater than those of other(s). This assumption is possible if Cr(VI) reduction is directly related to H<sub>2</sub>O (aqueous solution) or to species produced in abundance by H<sub>2</sub>O dissociation.

Then considering a pseudo-zero order assumption, the kinetics of Cr(VI) concentration can be written as:  $\frac{d[\text{Cr(VI)}]}{dt} = -K$  with  $K$  the rate constant of the reduction process. Of course the rate constant is effective, including the concentrations of species generated by the discharge that participate in the reduction process [7]. The measurements show that the reduction rate increases with the applied voltage, from 0.21 mg.L<sup>-1</sup>/min at 7 kV to 0.53 mg.L<sup>-1</sup>/min at 11 kV (**Fig. 2**). It is to notice that no reduction is observed for 2 kV, suggesting that electrolysis effect alone cannot reduce Cr(VI) (also shown by [17]). Moreover it is observed that Cr(VI) is totally reduced in 120 min of PLI process (with gap = 2 mm and pulse duration = 500 μs) at 9 kV and in 90 min at 11 kV.

The distribution of breakdown/no breakdown discharge changes with the applied voltage (**Table S2** in supplementary file). As expected, the number of breakdowns increases with the applied voltage. Additional measurements are performed by changing the interelectrode gap from 2 to 5 mm in order to avoid breakdown phenomenon. In this case, Cr(VI) reduction is still significant (**Fig. S4** in supplementary file), *e.g.* the reduction rate is equal to 0.39 mg.L<sup>-1</sup>/min for 10 kV. These new result show that breakdown does not play a main role in Cr(VI) reduction. Moreover it is observed that increasing the gap from 2 to 5 mm leads to slightly decrease the reduction rate. As an example for applied voltage of 9 kV, the reduction rate decreases from 0.4 to 0.35 mg.L<sup>-1</sup>/min for 2 and 5 mm respectively.

Results obtained by changing the gap and the applied voltage suggest that electric properties of the plasma has an influence on Cr(VI) reduction mechanisms. To go further, additional measurements dedicated to the chemical analysis of the process, such as pH, conductivity and [H<sub>2</sub>O<sub>2</sub>] are discussed hereafter.

### 3.2 pH evolution

In this work, the maximum variation of pH observed after two hours of process is an increase of 0.1 (from 2.3 to 2.4) which corresponds to an increase in [H<sup>+</sup>] equal to 1 mM. In acid conditions Cr(VI) reduction can either consume or produce H<sup>+</sup>, by reactions 6-8 and 5 (**Table 1**) respectively [10, 12, 15, 17]. However it is noted that changes in pH at values around 2 might be affected by buffer capacity of water, so the variation in pH could not be directly related to variation in [H<sup>+</sup>]. In our conditions the pH variation is not directly related to the Cr(VI) reduction since the same increase of 0.1 is observed for a Cr(VI) reduction rate equal to 0.21 mg.L<sup>-1</sup>/min (7 kV) and 0.53 mg.L<sup>-1</sup>/min (11 kV). The increase in [H<sup>+</sup>] during plasma discharge in aqueous liquid can also be related to other processes as reactions 2 and 4 (**Table 1**).

This result is consistent with the literature showing that hydronium ions are deeply involved into Cr(VI) chemistry. It is reported that the variation of the pH during the Cr(VI) reduction does not depend on the plasma type (above or inside the liquid) but it relies on the initial pH of the solution: for acid solution, the pH slightly increases whereas for initial pH>5, the pH of the solution decreases during the process [11, 12, 17].

### 3.3 Change in solution conductivity

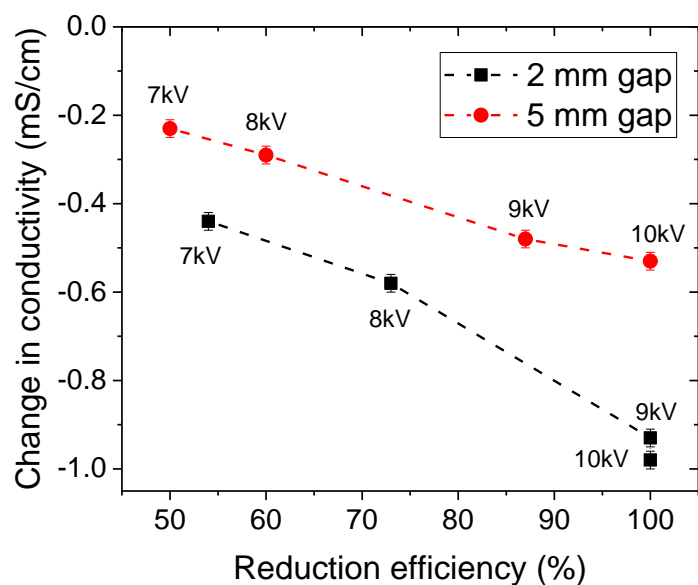
At the beginning of the experiments, the solution conductivity is about 4 mS/cm. After two hours of plasma process, the conductivity decreases significantly depending on the experimental conditions. This result has been also observed in other papers for above and inside liquid processes, *e.g.* in [17] the conductivity decreases from 5 to 4.6 mS/cm after 20 min of GDP in Cr(VI) solution.

**Fig. 3** reports the change in conductivity after 2 hours of process in relation to the reduction rate for 2 and 5 mm gaps. It shows that the decrease of the conductivity is more important for high reduction rate, but no direct relationship is observed. Indeed, a given reduction rate is related to different changes in conductivity depending on the gap. As an example, for a reduction rate equals to about 0.2 mg.L<sup>-1</sup>/min, the change in conductivity is equal to -0.23 and -0.44 mS/cm for 5 and 2 mm respectively (at 7 kV). The decrease of the solution conductivity is related to the global chemical activity initiated by the plasma, not only the Cr(VI) reduction.

Wang *et al.* assumed that, because the mobility of H<sup>+</sup> is much higher than that of Cr<sup>3+</sup>, the decay of the solution conductivity is a consequence of the production of Cr<sup>3+</sup> (due to Cr(VI) reduction) and the decrease of [H<sup>+</sup>] (pH increase) [17]. This correlation between the variations of pH and conductivity is not observed in our conditions since the variation of the pH is always close to 0.1 whereas the change in conductivity varies from -0.23 to -0.99 mS/cm. However the mobility of chromium in aqueous fluids strongly depends on its oxidation state. In contrast to Cr<sup>3+</sup> species, Cr(VI) is considered to be relatively mobile [28] [29] so the reduction of Cr(VI) in Cr(III) can result in the decrease of the solution conductivity. This assumption can only explain partially the results observed in **Fig. 3** since a total reduction of Cr(VI) does not involve the same final conductivity. Indeed, it is noted that reduction efficiency of 100% is obtained at 10 kV for both gaps but with very different changes in conductivity, being equal to -0.53 and -0.98 mS/cm for 5 and 2 mm respectively.

**Fig. 3** shows that the decrease of the conductivity is more important with high applied voltage and low interelectrode gap, *i.e.* with high electric field. For example, at 5 mm gap the variation of the conductivity is equal to -0.23 mS/cm for 7 kV and -0.53 mS/cm for 10 kV. It is also observed that for 10 kV the variation changes from -0.53 to -0.98 mS/cm when the gap decreases from 5 to 2 mm. These results confirm that the reaction mechanisms strongly depend on the electron properties initially generated by the discharge.





**Fig. 3** Change in solution conductivity according to the reduction efficiency after pin-to-pin discharges in Cr(VI) solution (47 mg/L,  $\sigma=4$  mS/cm, pH=2.3)  $V = 100$  mL,  $\Delta t = 500$   $\mu$ s, electrodes length =  $0 \pm 10$   $\mu$ m,  $f = 50$  Hz, duration of 120 min

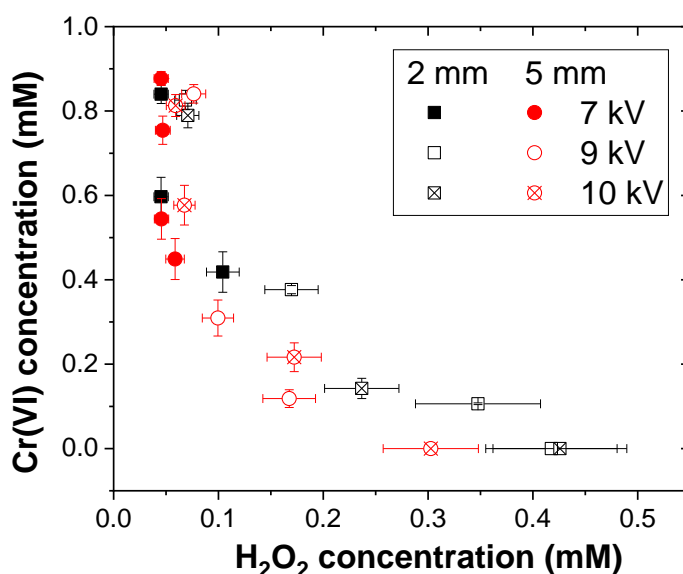
The chemistry activated by the plasma is complex and results in the production and the consumption of a lot of other species that can also modify the conductivity. The electric discharge initiates the generation of reactive oxidizing or reducing species such as  $\cdot\text{H}$ ,  $\cdot\text{OH}$ ,  $\text{H}_2\text{O}_2$ ,  $e_{aq}^-$ . These species can diffuse in the liquid phase and induce oxidation/reduction reactions with dissolved elements. To give a first insight of the chemical activity, simultaneous measurements of  $[\text{H}_2\text{O}_2]$  and  $[\text{Cr(VI)}]$  have been performed for different experimental conditions.

### 3.4 Measurements of $\text{H}_2\text{O}_2$ concentration

The species that are the most effective in reducing Cr(VI) have not been identified yet, but some works assume that  $\text{H}_2\text{O}_2$  can play a major role [9, 12, 21]. Although  $\text{H}_2\text{O}_2$  and Cr(VI) reactions are quite slow and require acidic medium (**Table 1**),  $\text{H}_2\text{O}_2$  is very interesting to monitor because it is a long lived specie and one of the major products formed in aqueous solution by PLI. The literature highlights the role of  $\text{H}_2\text{O}_2$  in Cr(VI) reduction for PLI above liquid showing that hydrogen peroxide plays a major role but it is not the sole factor [9, 12, 21]. However comparisons between Cr(VI) and  $\text{H}_2\text{O}_2$  concentrations have never been presented for direct PLI in Cr(VI) solution. Some studies have been performed in more complex solutions including phenol [15] or arsenic [14], which leads to more difficult chemical analysis. In this work, the concentration of  $\text{H}_2\text{O}_2$  and Cr(VI) are measured simultaneously by UV-Vis absorption method (as detailed in section 2).

**Fig. 4** shows the relation between  $[\text{Cr(VI)}]$  and  $[\text{H}_2\text{O}_2]$  for different applied voltages and gaps (in molar concentration). For a given condition, four measurements are presented corresponding to different sampling times (15, 45, 90, and 120 minutes). It is shown that the higher values of  $[\text{H}_2\text{O}_2]$ , the lower Cr(VI) concentrations. We note a good agreement with the literature [13, 14, 30] showing that the reduction of Cr(VI) in an acidic environment increases when the concentration of  $\text{H}_2\text{O}_2$  increases.

We also note that the relationship between  $[\text{Cr(VI)}]$  and  $[\text{H}_2\text{O}_2]$  is not linear. For example,  $\text{Cr(VI)}$  concentration decreases significantly (from 0.9 mM to about 0.4 mM) despite very low  $\text{H}_2\text{O}_2$  concentrations (less than 0.1 mM). In particular, for 7 kV half of the  $\text{Cr(VI)}$  is reduced after 120 minutes for both gaps, and the concentration of  $\text{H}_2\text{O}_2$  is equal to about 0.1 mM for 2 mm and 0.05 mM for 5 mm. Moreover, for 10 kV we can observe that  $[\text{Cr(VI)}]$  is completely removed when  $[\text{H}_2\text{O}_2]$  is about 0.3 mM for 5 mm gap, while in the case of 2 mm, the complete removal of  $\text{Cr(VI)}$  is achieved when  $[\text{H}_2\text{O}_2]$  is about 0.42 mM. These phenomena can be explained by the fact that  $\text{H}_2\text{O}_2$  is not the only species involved in the reduction of  $\text{Cr(VI)}$ . As an example, Chandana *et al.* have reported that in acidic medium,  $\text{Cr(VI)}$  reduction depends on both  $\text{H}_2\text{O}_2$  and  $\text{H}^+$  [12].



**Fig. 4** Evolution of  $\text{Cr(VI)}$  concentration according to  $\text{H}_2\text{O}_2$  concentration measured after pin-to-pin discharges in  $\text{Cr(VI)}$  solution (47 mg/L,  $\sigma=4$  mS/cm,  $\text{pH}=2.3$ )  $V = 100$  mL,  $\Delta t=500$   $\mu\text{s}$ , electrodes length =  $0\pm 10$   $\mu\text{m}$ ,  $f = 50$  Hz

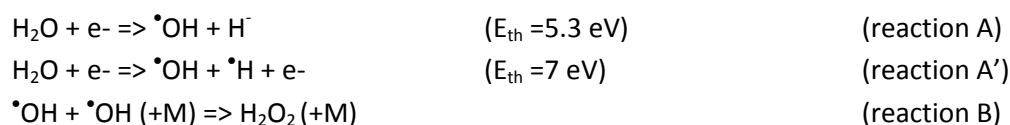
To go further on this assumption, measurements of  $[\text{H}_2\text{O}_2]$  without  $\text{Cr(VI)}$  in solution have been performed in the same experimental conditions. Results have been given after 30 min of discharges (at 9 kV – 50 Hz) (**Fig. S5** in supplementary file). The concentration of  $\text{H}_2\text{O}_2$  is about 10 times higher when there is no  $\text{Cr(VI)}$  in the initial solution:  $[\text{H}_2\text{O}_2]=0.68$  mM without  $\text{Cr(VI)}$  and 0.057 mM with  $\text{Cr(VI)}$  ( $\Delta[\text{H}_2\text{O}_2]=0.62$  mM). It confirms that  $\text{H}_2\text{O}_2$  is consumed by  $\text{Cr(VI)}$  reduction. But during the same duration,  $[\text{Cr(VI)}]$  decreases by only 0.23 mM. If considering that Reaction(8) of Table 1 is the main pathway for  $\text{Cr(VI)}$  reduction, this decrease of  $[\text{Cr(VI)}]$  would be related to a consumption of about 0.35 mM of  $\text{H}_2\text{O}_2$ , which is very low comparing to 0.62 mM. This result confirms that there are several processes taking place simultaneously in  $\text{Cr(VI)}$  reduction.

### 3.5 Discussion

To complete the analysis of the reduction process, the pulse duration is varied from 10  $\mu\text{s}$  to 1 ms. **Fig. 5** presents the reduction rate (and also the corresponding reduction efficiency after 2 hours) according to the pulse duration. It is shown that the reduction rate increases significantly with the pulse duration for the two gaps (2 and 5 mm).

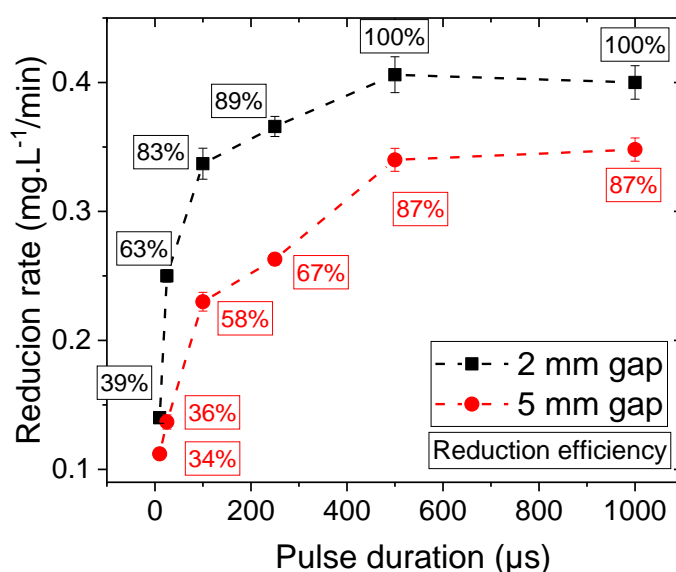
As shown in **Fig. S2**, whatever the regime discharge (breakdown or no breakdown) the charges are mainly delivered into the discharge during the first microseconds. As a consequence the pulse duration of 10  $\mu\text{s}$  ensures that the whole plasma phase is taken into account despite the variability of the experiments. The plasma phase generates reactive species which can diffuse into the solution and be responsible for Cr(VI) reduction. For 10  $\mu\text{s}$  the reduction efficiency is close to 35% and the reduction rate is about 0.1-0.15  $\text{mg}\cdot\text{L}^{-1}/\text{min}$  for the two gaps (**Fig. 5**). Despite the short duration of the plasma, its effect is significant on Cr(VI) reduction (almost 40% of efficiency). The gap has only a slight effect on the process; the short gap provides a slight better reduction. Reducing the gap changes the electric field and then the electron properties of the plasma, *e.g.* presence of breakdowns has been reported for 2 mm gap (**Table S2**). Although consequences on the chemical activity are expected, no direct effect of the gap is observed on the reduction rate during 10  $\mu\text{s}$ -long discharges.

Between 10 and 25  $\mu\text{s}$  the reduction process strongly depends on the gap, it is higher for 2 mm than for 5 mm, the reduction efficiency being equal to 63% and 36% respectively. The chemistry during this post-plasma phase mainly involves long-lived species (such as  $\text{H}_2\text{O}_2$ ). The production of these species depends on the gap so it can be assumed that their production depends on the electric field. Moreover, these species are significantly produced after 10  $\mu\text{s}$  so they should result from multi-steps mechanisms. An example of such mechanisms could be the succession of reaction A or A' and reaction B:



Primary reactions A and A' both involve electrons as reactants but have different threshold energy (about 5.5 and 7 eV respectively [31]). Their reaction rate depends on both the electron energy and the electron density, therefore it depends on the electric field. It can be assumed that for 5 mm gap, the low electric field involves mainly reaction A whereas at 2 mm the higher electric field involves higher electron density and more reaction A' which results in a higher production of  $\cdot\text{OH}$ . Then secondary reactions (B) take place which results in higher production of  $\text{H}_2\text{O}_2$  for 2 mm gap, and then higher Cr(VI) reduction.

From 25  $\mu\text{s}$  to 1000  $\mu\text{s}$ , the reduction rate continues to increase with the pulse duration showing quite parallel evolution for both gaps. It can be assumed that the chemical mechanisms are the same for both gaps. As a consequence the additional effect previously identified for 2 mm gap has no longer effect. It is possible that the very low current delivered by the DC power supply during this time interval (< 1 mA, not quantifiable in our experimental conditions) and/or the low applied electric field (high voltage < 2 kV) promote Cr(VI) reduction by low energy mechanisms. But it should be reminded that no reduction effect is obtained for applied voltage equal to 2 kV (**Fig. 2**). Then these low energy mechanisms should involve species previously produced during the plasma phase.

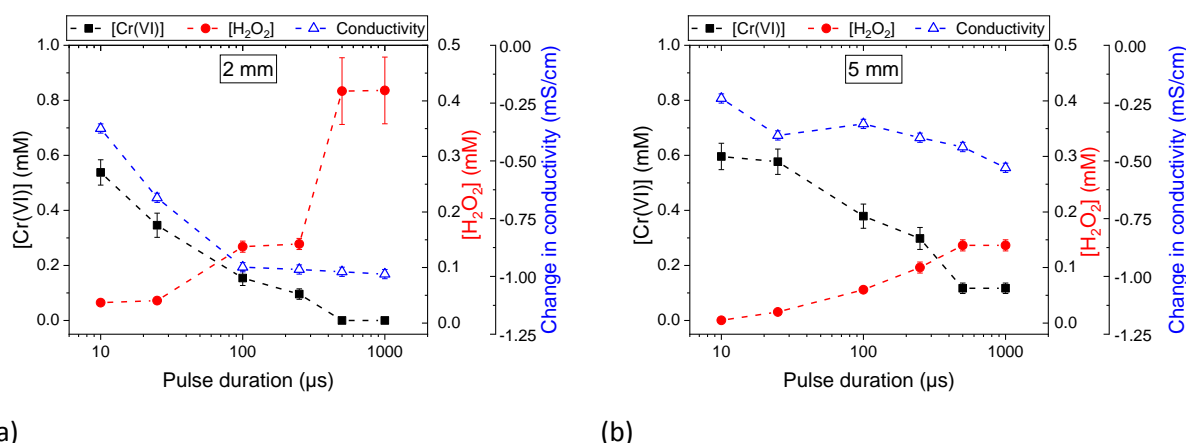


**Fig. 5** Reduction rate of Cr(VI) according to the pulse duration after pin-to-pin discharges in Cr(VI) solution (47 mg/L,  $\sigma=4$  mS/cm, pH=2.3) V = 100 mL, U= 9 kV, electrodes length =  $0\pm 10$   $\mu$ m, f = 50 Hz, duration of 120 min

**Fig. 6** presents a comparison between the evolutions of [Cr(VI)], [H<sub>2</sub>O<sub>2</sub>] and the change in conductivity for different pulse durations. First, it is observed for the two gaps that with longer pulse duration, H<sub>2</sub>O<sub>2</sub> concentration increases and the decrease in conductivity is higher. These results confirm that the reactivity of the solution changes with the pulse duration and also that the variation depends on the gap, being higher for 2 mm than for 5 mm.

Regarding the conductivity, the main difference between 2 and 5 mm is observed for short pulse durations ( $\Delta t < 100$   $\mu$ s): for 5 mm gap, the variation of the conductivity is quite constant ( $\approx 0.35$  mS/cm) whereas for 2 mm gap a strong variation is observed (from -0.35 to -0.1 mS/cm). On the opposite, for [H<sub>2</sub>O<sub>2</sub>] the difference between 2 and 5 mm gaps appears for long pulse duration. For  $\Delta t > 250$   $\mu$ s, [H<sub>2</sub>O<sub>2</sub>] remains lower than 0.15 mM for 5 mm gap while it increases to 0.4 mM for 2 mm gap.

To summarize, the increase of the pulse duration involves a better Cr(VI) reduction, a higher [H<sub>2</sub>O<sub>2</sub>] production and a more important change in conductivity. But no direct relationship between the three parameters can be easily highlighted. Due to the high complexity of the intertwined mechanisms involved in plasma process, the variation of the conductivity cannot be related to species production or consumption.



**Fig. 6** Evolution of  $[H_2O_2]$ ,  $[Cr(VI)]$  and change in conductivity according to pulse duration for (a) 2 mm gap and (b) 5 mm gap – for pin-to-pin discharges in Cr(VI) solution (47 mg/L,  $\sigma=4$  mS/cm, pH=2.3)  $V = 100$  mL,  $U=9$  kV, electrodes length =  $0\pm 10$   $\mu\text{m}$ ,  $f = 50$  Hz, duration of 120 min

#### 4. Conclusion

The results of this study prove that microseconds electrical discharge in solution can totally remove dissolved Cr(VI). The simultaneous measurements of  $[Cr(VI)]$  and  $[H_2O_2]$  are reported for the first time for this experimental configuration, *i.e.* direct discharge in aqueous Cr(VI) solution. Additional measurements of pH and conductivity complete the chemical analysis of the process. Time evolution of  $[Cr(VI)]$  shows a linear behavior reflecting pseudo-zero order rate which is different from first order systematically reported by the literature. This result involves that the oxidation process is negligible which is in accordance with the total Cr(VI) removal obtained in this work. Increasing the applied voltage and decreasing the gap result in increasing the reduction rate of Cr(VI) and  $[H_2O_2]$ . These variations are also related to higher decrease of the conductivity. On the contrary, the slight pH increase does not depend significantly on the experimental conditions. These results highlights the significant influence of the electric properties of the plasma on chemical mechanisms and so on the Cr(VI) reduction.

To complete the analysis of the kinetics, the influence of the pulse duration on the chemical properties of the solution has been studied. The increase of the pulse duration involves a better Cr(VI) reduction, a higher  $[H_2O_2]$  production and a more important change in conductivity. Moreover it has been shown that despite the short duration of the plasma phase ( $<10$   $\mu\text{s}$ ), its effect is significant on Cr(VI) reduction leading to maximum 40% of reduction efficiency. In addition the post plasma stage is also very efficient for Cr(VI) degradation since the reduction rate increases from about  $0.15$   $\text{mg}\cdot\text{L}^{-1}/\text{min}$  to  $0.4$   $\text{mg}\cdot\text{L}^{-1}/\text{min}$  when the pulse width rises from 10 to 500  $\mu\text{s}$ .

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