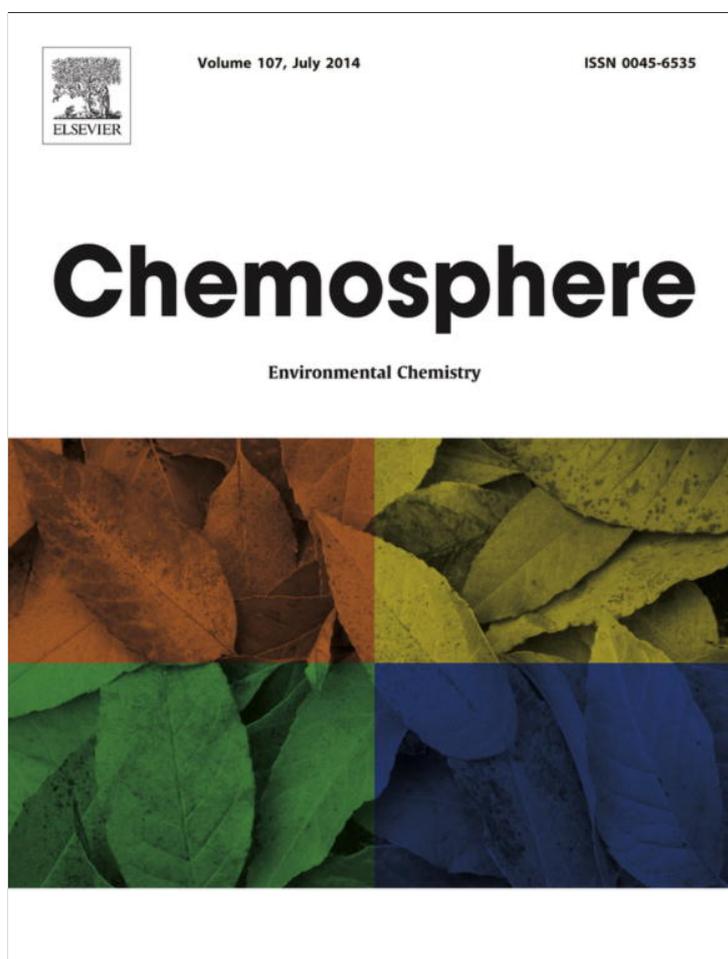


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Plasmacatalytic removal of lead acetate assisted by precipitation



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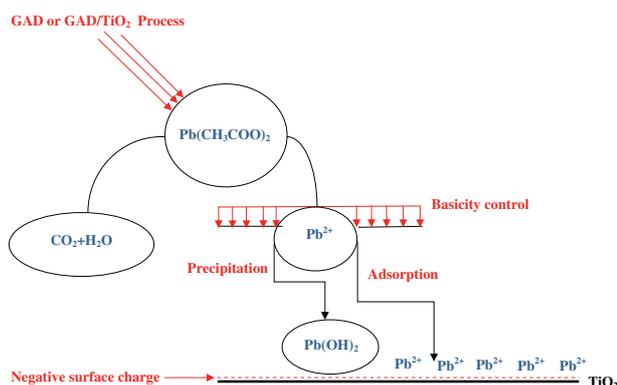
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HIGHLIGHTS

- Lead acetate molecule is more toxic than lead ions.
- Lead acetate is soluble in water but it weakly ionises in this aqueous medium.
- We degraded separately lead acetate molecules in water by GAD and GAD/TiO₂.
- The released Pb²⁺ ions were removed by precipitation process.

GRAPHICAL ABSTRACT

'GAD-precipitation' and 'GAD-TiO₂-precipitation-adsorption' mechanisms.



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ABSTRACT

The Gliding Arc Discharge (GAD) is an efficient non-thermal plasma technique able to degrade organic compounds dispersed in water at atmospheric pressure. The degradation of the organometallic lead acetate (PbAc) in aqueous solution was performed by two distinct plasmageneous processes: GAD and GAD/TiO₂.

The global oxidation of the organic matter was followed by Chemical Oxygen Demand (COD) and the mineralization was determined by the Total Organic Carbon (TOC). The Pb²⁺ ions released during the degradation process were measured by Atomic Absorption Spectroscopy (AAS).

For 2 h of GAD treatment, the degradation rate of PbAc (10 mM) reached 83% and for the same duration of GAD/TiO₂ process ([TiO₂] = 1 g L⁻¹), it reached 93%.

The release of Pb²⁺ ions in the solution was respectively of 95% and 57% for GAD and GAD/TiO₂ processes. The released Pb²⁺ ions were removed by precipitation process in a basic medium at pH = 11.1.

A reaction mechanism was proposed to explain the PbAc molecule degradation and the Pb²⁺ elimination.

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1. Introduction

Lead acetate is used as a mordant in textile printing, dyeing, in varnishes, in preparing other lead compounds, etc. (Lyman

et al., 1982; Suleman et al., 2011) however it can be very harmful to health: by damaging vital organs (Fu and Boffetta, 1995), suppressing cellular processes (Chakravarthi et al., 2012) or causing cancers (Damstra, 1977).

The works of Noyes and Whitcomb (1905) have shown that the molecule is highly soluble in water, but it is slightly ionised in this medium. According to the same works and others (Gobom, 1963; Kagaya et al., 1997; Agency for Toxic Substances and Disease Registry, 2007), the small degree of ionisation seems to be related to the spontaneous formation of complex anion in aqueous solution.

It is commonly known that the organic form of lead is more toxic than its mineral form (Gobom, 1963; Jiraroj et al., 2006); and since lead acetate releases a small amount of Pb^{2+} ions; it is necessary to ionise this molecule by using Advanced Oxidation Processes (AOPs). Some of these processes such as photocatalysis (TiO_2/UV) were reported to remove efficiently EDTA complexes of Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Fe^{2+} , Mn^{2+} , Cd^{2+} and Pb^{2+} ions from water (Kagaya et al., 1997; Madden et al., 1997; Davis and Green, 1999; Vohra and Davis, 2000).

Stemmler et al. (2001) have also degraded Zn-EDTA and Fe-EDTA complexes by ozonation but the Zn^{2+} and Fe^{2+} released in water were not eliminated. The works of Pirkanniemi et al. (2007) showed that the photolysis in presence of H_2O_2 (H_2O_2/UV) is an efficient process to degrade the same compounds.

According to the mentioned works, it is obvious that AOPs can be used to degrade the organometallic molecules in order to release the metal ions. The latter can be eventually eliminated after the oxidation process by a simple chemical precipitation.

The Gliding Arc Discharge (GAD) has emerged as an important electrical AOP leading to the degradation of most of organic pollutants such as: synthetic dyes (Abdelmalek et al., 2004, 2006; Yan et al., 2008), wastewaters from polymer industries (Ghezzar et al., 2008), endocrinal disruptor (Abdelmalek et al., 2008) and phenol (Yan et al., 2005).

To make the electric treatment more efficient, the GAD was coupled with the TiO_2 particles as photocatalyst to degrade an anthraquinonic dye (AG25) (Ghezzar et al., 2007), a surfactant (Marouf-Khelifa et al., 2008) and industrial liquid wastewaters (Ghezzar et al., 2009).

To our knowledge, the electrical techniques have never been applied to the degradation organometallic compounds. In this work, we propose to degrade lead acetate (PbAc) in aqueous solution by different GAD processes. The Pb^{2+} ions released during the plasmageneous treatments were eliminated by precipitation process at a basic medium.

2. Experimental

2.1. Material

The organometallic anhydrous lead acetate ($C_4H_6O_4Pb = 325.3 \text{ g mol}^{-1}$) was purchased from SIGMA-ALDRICH society. Its solubility in water is of 456 mg L^{-1} at 20°C , forming slightly ionised $Pb(C_2H_3O_2)_2$ (Noyes and Whitcomb, 1905).

The photocatalyst used is the titane dioxide TiO_2 (P-25, ca. 80% anatase, 20% rutile; BET area, ca. $50 \text{ m}^2 \text{ g}^{-1}$; particles average size, ca. 30 nm) was supplied by Degussa Co.

2.2. Apparatus

The experimental GAD apparatus used is presented in Fig. 1. The reactor shape is cylindrical with the dimensions of (length $L = 20 \text{ cm}$, width $l = 10 \text{ cm}$, diameter $D = 10 \text{ cm}$). An electric arc forms between two diverging electrodes raised to a convenient voltage difference at the minimum gap. A special transformer (9 kV; 100 mA) provides the electric power. The arc is pushed away

from the ignition point by the feeding gas flow and sweeps along the maximum length of the electrode gap and so, forming a large plasma plume. A new arc then appears and develops according to the same procedure.

The plasma plume is disposed close enough to the target liquid (volume $V = 500 \text{ mL}$). It wipes the liquid surface, and allows the chemical reactions to take place at the plasma-solution.

Pyrex reactor is equipped with a cooling system to avoid evaporation. With an adequate cooling, the temperature in the reactor is of 30°C and the loss in volume is negligible (1–2%).

The treatment is done in closed system fixing the functioning parameters. The gas flow is fixed at $Q = 900 \text{ L h}^{-1}$, the divergence between the electrodes $e = 2 \text{ mm}$, the diameter of the nozzle $\varnothing = 1 \text{ mm}$ and the distance between the electrodes and the target liquid surface $d = 3 \text{ cm}$.

2.3. Procedure and analysis

A volume of 180 mL of PbAc aqueous solution (10 mM) was introduced into the GAD reactor. The evolution of the GAD treatment in batch mode was followed for various exposure times t (0, 10, 20, 30, 60 and 120 min). In the case of GAD/ TiO_2 treatment, different amounts of TiO_2 are added to the PbAc solution to obtain: 0.25, 0.5, 1, 1.25 and 1.50 ppm of the photocatalyst dose. The suspension was stirred for 30 min in dark to reach the adsorption equilibrium, which is established between the solution and the TiO_2 surface. Before analysis, aliquots of the suspensions were collected to be centrifuged and filtered through 0.45 mm Millipore filters to remove catalyst TiO_2 particles.

The degradation was followed by the analysis of Total Organic Carbon (TOC) (Shimadzu 5000a) and the Chemical Oxygen Demand (COD) (Collectif AFNOR, 1999). Sulfamic acid was used to remove nitrite ions formed during the plasma-treatments (Collectif AFNOR, 1999). The ionic lead released was analysed by Atomic Absorption Spectroscopy (AAS) of flame using a Thermo Solar S spectrophotometer.

The pH and the Ox/Red potential were systematically measured after each treatment using a Consort multi-parameter-analyser.

All chemicals were of analytical grade and used without further purification. Each solution was prepared by dissolving the commercial chemical product in distilled water.

3. Results and discussion

3.1. Comparison study of GAD and GAD/ TiO_2 degradation of PbAc

In order to establish the degree of PbAc oxidation and mineralization, we followed the COD and TOC evolution in function of time. Both techniques are complementary to one another to illustrate the detoxification level of water.

This study is based on the treatment of lead acetate in water (10 mM) which was separately exposed to GAD and GAD/ TiO_2 processes. TiO_2 photocatalyst has a high oxidation potential as shown in the paragraph below.

3.1.1. Mechanism of TiO_2 photocatalyst

In previous works (Ghezzar et al., 2007, 2009; Marouf-Khelifa et al., 2008), we showed that the GAD process can be combined with the TiO_2 particles in order to produce more and more hydroxyl radicals. Indeed, the UV rays emitted by plasma (Moreau et al., 2008) excite the surface of TiO_2 . Consequently, conduction band electrons, valence band holes and $\cdot\text{OH}$ radicals are formed (Bouzaida et al., 2004). It is known that the efficiency of the photocatalytic process depends on the optimal dose of TiO_2 .

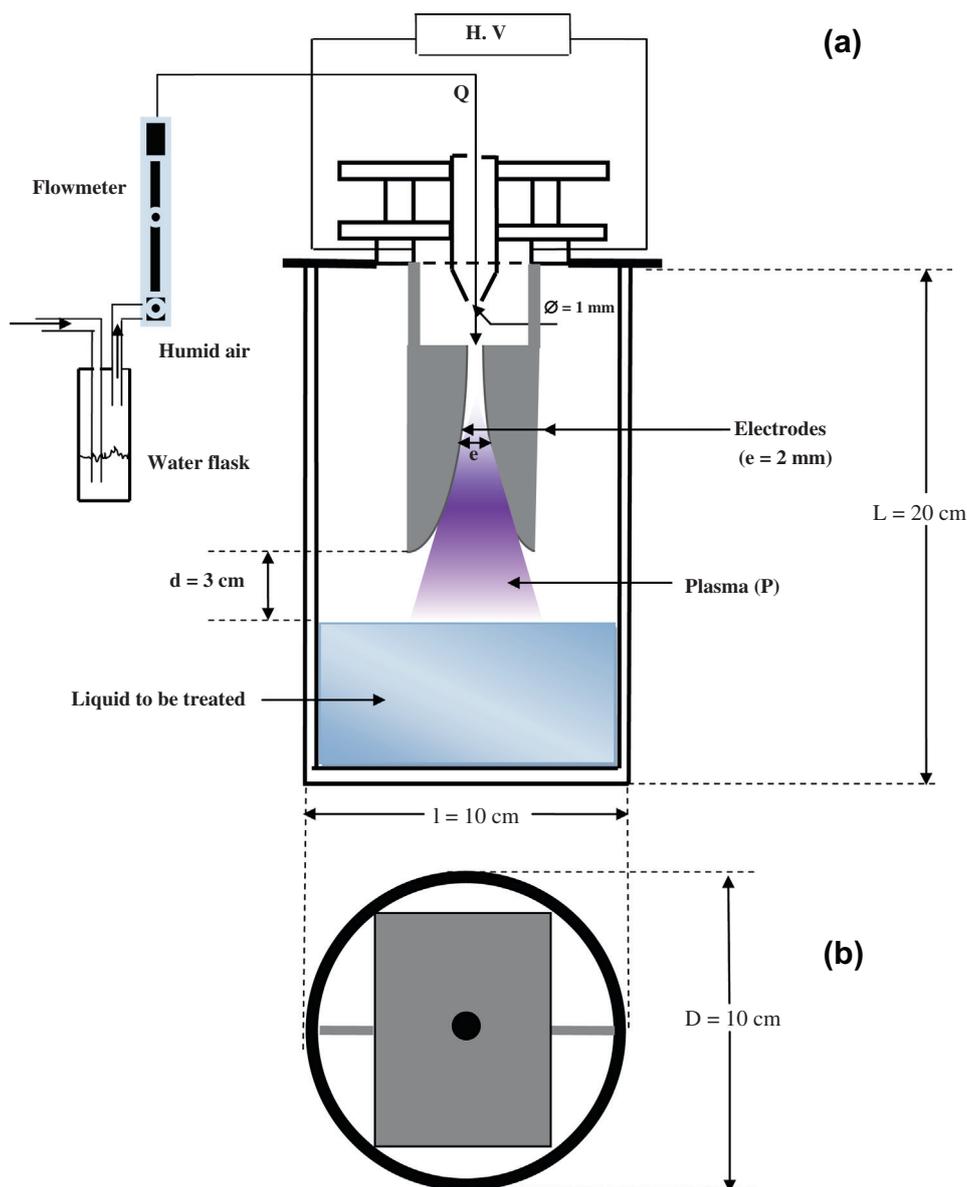


Fig. 1. Gliding Arc Discharge apparatus: (a) front view, and (b) top view.

3.1.2. Catalyst optimisation

Fig. 2 shows the variation of the TOC and the COD abatements as a function of photocatalyst dose. We noticed that the degradation rate increased proportionally to the dose: the degradation rate reached 70% after 30 min of treatment in presence of 1 g L^{-1} of TiO_2 . Beyond this dose, the rate decreased to 61% for the same exposure time.

This phenomenon may be explained both by a screening effect of excess particles which masks part of the photosensitive surface; and by the scattering of the light which reduces the amount of photons produced by the discharge that normally must be absorbed by the catalyst (Bouzaida et al., 2004).

In this work, the plasma-catalytic process GAD/ TiO_2 will be realised at the optimal dose of TiO_2 which is of 1 g L^{-1} .

3.1.3. TOC and COD studies

Figs. 3 and 4 show respectively the COD and TOC evolution of PbAc treated separately by GAD and GAD/ TiO_2 processes.

It is important to mention that at the natural pH of 6.1 and in dark ambience, the removal rate of PbAc was of 2.5%. At pH = 1.2,

this rate increased slightly to 5.1% due to the electrostatic changes on the TiO_2 surface.

The analyses by TOC or COD show that a time exposure of 120 min led to a degradation rate of 82% by GAD against 93% by GAD/ TiO_2 process. The presence of photocatalyst has then improved the plasma chemical treatment. This can be explained by the availability of the $\cdot\text{OH}$ radicals produced simultaneously from plasma and TiO_2 particles.

The decrease in the TOC indicates the progress of mineralization (Li et al., 2013). It can be explained by the conversion of PbAc to other weak molecules. Lyman et al. (1982) reported that the degradation of organic compounds could be divided into three distinct stages: primary, acceptable and ultimate. Primary TOC degradation brings about structural change in the parent compounds which may improve biodegradability, acceptable TOC degradation reduced the toxicity to satisfactory levels, and ultimate TOC degradation resulted in complete mineralization of organic compounds to carbon dioxide, water and other inorganics. COD will change accordingly over the TOC degradation stages. The decrease of COD accounts for the mineralization

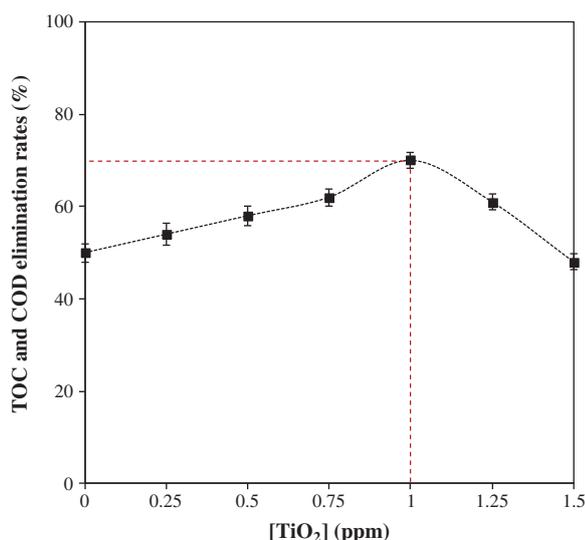


Fig. 2. Variation of the TOC and COD elimination rate as a function of concentration of photocatalyst. The error bars indicate the standard deviations (SD).

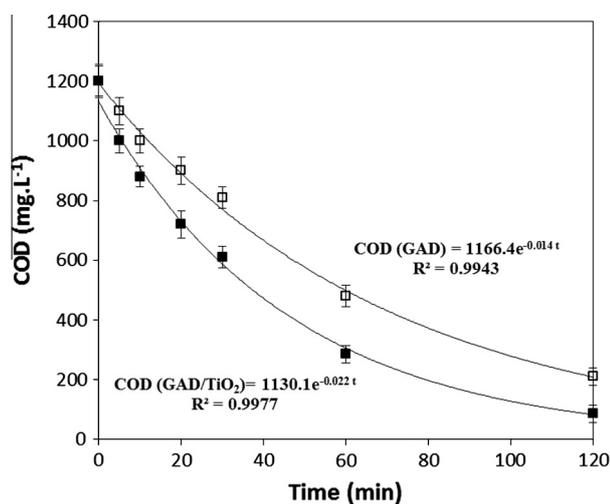


Fig. 3. PbAc (10 mM) COD kinetic: (□) GAD, (■) GAD/TiO₂. The error bars indicate the standard deviations (SD).

process and means that the starting molecule is oxidized to mineral ions (Li et al., 2013).

In order to understand the degree of carbon mineralization of the PbAc molecule, the ratio COD/TOC was studied in this work. Bristol et al. (2001) report that the determination of COD/TOC ratio is evident. The two parameters are useful independently and their ratio is an excellent indicator of the organic loading present in water.

Fig. 5 depicts the variation of the COD/TOC ratio versus the treatment time. Initially ($t = 0$), the ratio was equal to 3.05. At the end of the treatment ($t = 120$ min) it reached the values of 3 and 3.1 respectively for the GAD and GAD/TiO₂ processes. The degradation ratio remained relatively constant along the treatment. This shows the good correlation between the two parameters during the plasma-degradation process of PbAc pollutant.

3.1.4. Kinetic study

The plasma chemical reaction takes place between the PbAc molecules and ·OH. This leads to the kinetic law given by the next equation:

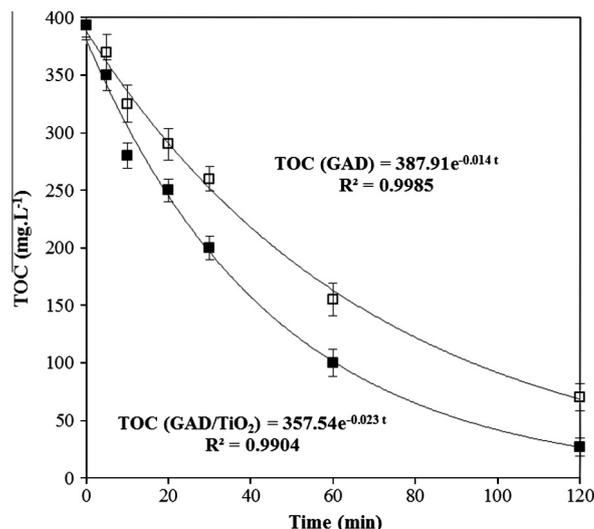


Fig. 4. PbAc (10 mM) COT kinetic: (□) GAD, (■) GAD/TiO₂. The error bars indicate the standard deviations (SD).

$$-\frac{dC}{dt} = kC[\cdot\text{OH}] \quad (1)$$

k is the rate constant (min^{-1}); t the treatment time (min); C the PbAc concentration (μM); $\cdot\text{OH}$ is the $\cdot\text{OH}$ concentration (μM). The $\cdot\text{OH}$ flux driven by the plasma gas being constant implies the constancy of term $k[\cdot\text{OH}] = k_{app}$. The Eq. (1) is written as follows:

$$-\frac{dC}{dt} = k_{app}C \quad (2)$$

The integration of Eq. (2), with the condition $C = C_0$ at $t = 0$, gives:

$$C = C_0 e^{-k_{app}t} \quad (3)$$

k_{app} is the apparent rate constant (min^{-1}).

Whatever the analytic method used TOC or COD, the PbAc degradation rate was of 82% for the GAD process and of 93% for the GAD/TiO₂ catalytic process. The rate constants were equal to 0.014 and 0.024 min^{-1} for GAD and GAD/TiO₂ respectively.

The $\cdot\text{OH}$ driven simultaneously from the plasma and the TiO₂ particles attack selectively regions of high electron density. The nonselective character of these radicals as well as their availability

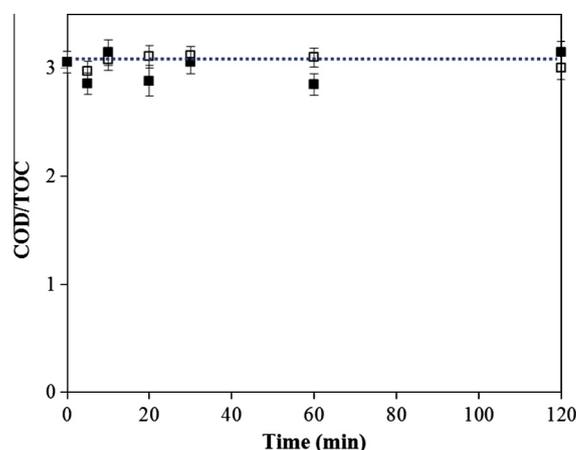


Fig. 5. COD/TOC ratio versus time: (□) GAD, (■) GAD/TiO₂. The error bars indicate the standard deviations (SD).

allow to degrade the chemical σ bonds present in the PbAc molecule.

On this basis, a degradation mechanism is proposed:

- i. Stage 1: degradation of the orbital π in the C=O band by the $\cdot\text{OH}$.
- ii. Stage 2: degradation of the ionic bands in the O–Pb–O molecular part. This type of band has a median energy between the π and σ energy bands.
- iii. Stage 3: degradation of the σ orbital in the C–O and C–H bands. This last stage will allow to form CO_2 , H_2O and probably will liberate the Pb^{2+} ions in the solution.

3.2. Formation and removal of Pb^{2+}

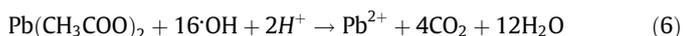
$\cdot\text{OH}$ is principally formed by electron impact on excited water molecules as follows (Brisset and Hnatiuc, 2012):



Other sources probably exist such as the photon impact on hydrogen peroxide as follows (Brisset and Hnatiuc, 2012):



The $\cdot\text{OH}$ radicals produced during the treatments can degrade the PbAc molecule according to the following reaction:



An excess of $\cdot\text{OH}$ radicals would increase the reaction yield according to the law of action mass. The reaction (6) stipulates that the final products of degradation are CO_2 , H_2O and Pb^{2+} . The lead ions released in the solution have been identified and quantified.

3.2.1. Identification of Pb^{2+}

The initial pH of the PbAc aqueous solution (10 mM) is of 6.1. The plasmageneous treatment of 2 h has reduced it to 1.6 for GAD and 1.2 for GAD/TiO₂. In these conditions, the oxidation potentials were of 0.69V/ESH and 0.89V/ESH for GAD and GAD/TiO₂ processes respectively.

pH and oxidation potential measurements allowed the localisation of the lead form associated to the positions (1.6, 0.69 V) for GAD and (1.2, 0.89 V) for GAD/TiO₂. In the diagram Potential (E) versus pH for the metallic lead (Atlas of Eh–pH diagrams, 2005); we can see that the Pb^{2+} ions appear as the only ionic species that can be released during the PbAc plasma-degradation processes.

3.2.2. Evolution of Pb^{2+} during the treatment

Fig. 6 expresses the evolution of Pb^{2+} versus time. During the 2 h of treatment, the concentration of the ions increased from 21 ppm to 1250 ppm for GAD process and attained 750 ppm for GAD/TiO₂ process. The plasma-release kinetic of lead II can be modelled as follows:

$$+ \frac{d[\text{Pb}^{2+}]}{dt} = k_{\text{pb}^{2+}} [\text{Pb}^{2+}]^n \quad (7)$$

The linear profiles obtained in Fig. 6, stipulates that the liberation kinetic is in accordance with the zero order ($n = 0$). The integration of Eq. (5) gives the next equation:

$$[\text{Pb}^{2+}] = k_{\text{pb}^{2+}} t \quad (8)$$

According to the experimental models, the constant rates of Pb^{2+} liberation are 10.2 and 6.1 $\text{mg L}^{-1} \text{min}^{-1}$ for GAD and GAD/TiO₂ respectively.

Theoretically, the maximum of Pb^{2+} concentration which can be liberated in solution is of 1320 mg L^{-1} . However, in the case of GAD process, 95% of this value was attained against only 57% for GAD/

TiO₂ catalytic process. In the plasma-catalytic treatment, a part of Pb^{2+} released in the solution seems to be adsorbed on the TiO₂ surface at pH = 1.2. The same phenomenon was observed by Murruni et al., 2008 at pH = 1.4 during the photocatalysis treatment of PbCl_2 solution in the presence of 1 g L^{-1} TiO₂ dose. In the same context, Chen and Ray (2001) have noticed the adsorption of Pb^{2+} at natural pH = 6 and 2 g L^{-1} TiO₂ dose during the treatment of wastewater by photocatalysis process.

The addition of the TiO₂ particles has good effects on the enhancement of the GAD process. However, the concentration of these ions remains excessively high.

3.2.3. Removal of Pb^{2+} ions by precipitation process

The removal of Pb^{2+} ions released during the GAD treatment of PbAc solutions was carried by precipitation process. Different pHs have been imposed to complete the GAD-treatment. For a pH of 10.2 the elimination of ions attained 70% and for a pH of 11.1 it was total. These results are in agreement with the theoretical study presented by Wang et al. (2009) who have demonstrated that the precipitation of lead II in homogeneous medium is more significant at the pH range of 10.2–11.3.

In the same context, the precipitation allowed the removal of lead ions formed during the treatment of GAD/TiO₂. The PbAc solution treated during 2 h was basified at pH = 8 by NaOH. This complementary chemical treatment has led to the total elimination of the Pb^{2+} . To explain this result we have thought of three phenomena:

i. Precipitation

The Pb^{2+} ions precipitation is possible at basic medium according the following reaction:



A similar approach was used by Jiraroj et al. (2006) who precipitated at pH = 8 the Pb^{2+} ions after the degradation of Pb-EDTA complex by H₂O₂/UV process.

ii. Adsorption

When $\text{pH} > \text{pH}_{\text{pzc}} = 6.8$, the TiO₂ surface is negatively charged according to:



However, when $\text{pH} < \text{pH}_{\text{pzc}} = 6.8$, the TiO₂ surface is positively charged according to:

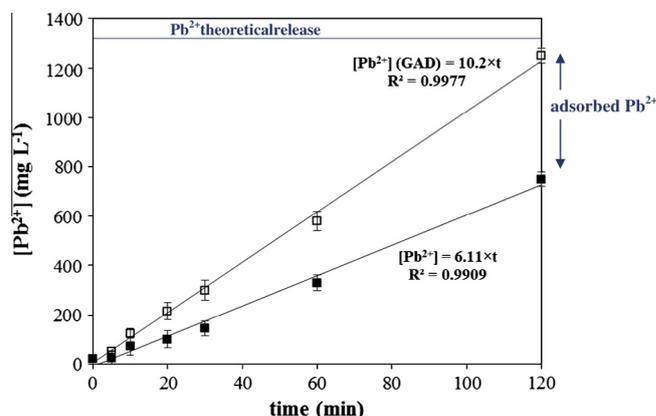


Fig. 6. Pb^{2+} ions release kinetic: (□) GAD, (■) GAD/TiO₂. The error bars indicate the standard deviations (SD).



On the basis of the point of zero charge (pH_{pzc}) of TiO_2 which is equal to pH 6.8, we can explain the adsorption. At $\text{pH} > \text{pH}_{\text{pzc}}$ the surface of titania becomes negatively charged (Eq. (8)) and an electrostatic repulsion between TiO_2 and the PbAc occurs.

Vohra and Davis (2000) mentioned the possible adsorption of the ion on the TiO_2 surface at $\text{pH} = 8$, after the degradation of Pb-EDTA complex by photocatalysis process.

iii. Precipitation/adsorption competition

It is possible that the two phenomena happen simultaneously. In this case, the competition between the precipitation and the adsorption is highly probable.

4. Energy consumption

In order to evaluate the energy consumption, an electrical counter was placed on the GAD apparatus. The electric power consumed was of 0.4 kW for 120 min.

In this context, we have applied the formula (12) proposed by Bolton et al. (2001) to estimate the Electric Energy per Mass (E_{EM}) for a batch electric reactor.

$$E_{\text{EM}} (\text{kW h kg}^{-1}) = \frac{P \times t \times 1000}{V \times M \times (C_i - C_f)} \quad (12)$$

P is the power (kW) of the GAD reactor; V the volume (L) of water treated in the time t (h); M the molar mass (g mol^{-1}) of C ; C_i , C_f is the initial and final concentrations (mol L^{-1}) of C , and the factor of 1000 converts g to kg.

With a degradation rate of 82%, the calculating according the formula (12) gives:

$$E_{\text{EM}} = \frac{0.4 \times 2 \times 1000}{0.5 \times 325.3 \times (0.01 - 0.0082)} \quad \text{i.e. } 2732 \text{ kW h kg}^{-1}.$$

It is well to remember that this power is specific to 1 kg of PbAc . In the case of 1.6265 g (mass dissolved in 0.5 L of water to have 10 mM), the power is of 8.9 kW h.

5. Conclusion

Two distinct Gliding Arc Discharges (GAD and GAD/ TiO_2) were separately used to treat lead acetate (10 mM) in aqueous solution in order to degrade and release the Pb^{2+} ions. The latter were removed by precipitation process at a basic medium.

- For 120 min of GAD process: the degradation was of 82% with a rate constant of 0.014 min^{-1} . This degradation liberated 95% of the Pb^{2+} ions with $10.2 \text{ mg L}^{-1} \text{ min}^{-1}$ rate constant. The released Pb^{2+} was totally precipitated at $\text{pH} = 11.2$.
- For 120 min of GAD/ TiO_2 process: in presence of 1 g L^{-1} of TiO_2 , the degradation increased to 95% with a rate constant of 0.023 min^{-1} . Despite the high rate of degradation, only 57% of Pb^{2+} was liberated with a constant rate of $6.1 \text{ mg L}^{-1} \text{ min}^{-1}$. The high degradation rate of PbAc , suggests that the residual Pb^{2+} was adsorbed on TiO_2 surface. The Pb^{2+} ions were totally eliminated at $\text{pH} = 8$.

Both processes seem to be appropriate for the treatment of organometallic compounds such as lead acetate that is difficultly removed by conventional methods.

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References

- Abdelmalek, F., Gharbi, S., Benstaali, B., Addou, A., Brisset, J.L., 2004. Plasma chemical degradation of azo dyes by humid air plasma: Yellow Supranol 4 GL, Scarlet Red Nylosan F3 GL and industrial waste. *Water Res.* 38, 2339–2347.
- Abdelmalek, F., Ghezzer, M.R., Belhadj, M., Addou, A., Brisset, J.L., 2006. Bleaching and degradation of textile dyes by nonthermal plasma process at atmospheric pressure. *Ind. Eng. Chem. Res.* 45, 23–29.
- Abdelmalek, F., Toress, R.A., Combet, E., Petrier, C., Pulgarin, C., Addou, A., 2008. Gliding Arc Discharge (GAD) assisted catalytic degradation of bisphenol A in solution with ferrous ions. *Sep. Purif. Technol.* 63, 30–37.
- Agency for Toxic Substances and Disease Registry (ATSDR), 2007. Toxicological Profile for Lead (Update). Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.
- Atlas of Eh-pH diagrams, 2005. Intercomparison of thermodynamic databases Geological Survey of Japan Open File. Report No. 419 National.
- Bolton, J.R., Bircher, K.G., Tumas, W., Tolman, C.A., 2001. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems. *Pure Appl. Chem.* 73, 627–637.
- Bouzaida, I., Ferronato, C., Chovelon, J.M., Rammah, M.E., Herrmann, J.M., 2004. Heterogeneous photocatalytic degradation of the anthraquinonic dye, Acid Blue 25 (AB25): a kinetic approach. *J. Photochem. Photobiol. A* 168, 23–30.
- Brisset, J.L., Hnatiuc, E., 2012. Peroxynitrite: a Re-examination of the chemical properties of non-thermal discharges burning in air over aqueous solutions. *Plasma Chem. Plasma Process.* 32, 655–674.
- Bristol, P., John, C., Dan, H., Razvan, R., 2001. The beneficial use of the cod/toc ratio in the treatment of paper manufacturing wastewater. *Water. Environ. Federation Proc. Water. Environ. Federation* 14, 224–237.
- Chakravarthi, S., Haleagrahara, N., Yen Haw, K., Rao, M., 2012. Effects of *Etlingera elatior* extracts on lead acetate-induced testicular damage: a morphological and biochemical study. *Exp. Ther. Med.* 3, 99–104.
- Chen, D., Ray, A.K., 2001. Removal of toxic metal ions from wastewater by semiconductor photocatalysis. *Chem. Eng. Sci.* 56, 1561–1570.
- Collectif AFNOR, 1999. la qualité de l'eau, tome II, Analyses organoleptiques. Mesures physico-chimiques. Paramètres globaux. Composés organiques. NFT 90-102. Groupe Eyrolles S.A AFNOR.
- Damstra, T., 1977. Toxicological properties of lead. *Environ. Health Perspect* 19, 297–307.
- Davis, A.P., Green, D.L., 1999. Photocatalytic oxidation of cadmium-EDTA with titanium dioxide. *Environ. Sci. Technol.* 33, 609–617.
- Fu, H., Boffetta, P., 1995. Cancer and occupational exposure to inorganic lead compounds: a meta-analysis of published data. *Occup. Environ. Med.* 52, 73–81.
- Ghezzer, M.R., Abdelmalek, F., Belhadj, M., Benderdouche, N., Addou, A., 2007. Gliding arc plasma assisted photo-catalytic degradation of anthraquinonic acid green 25 in solution with TiO_2 . *Appl. Catal. B: Environ.* 72, 304–313.
- Ghezzer, M.R., Belhadj, M., Abdelmalek, F., Raïs, A., Addou, A., 2008. Non-thermal plasma degradation of wastewater in presence of titanium oxide by Gliding Arc Discharge. *Int. J. Environ. Waste Manage.* 2, 2458–2470.
- Ghezzer, M.R., Abdelmalek, F., Belhadj, M., Benderdouche, N., Addou, A., 2009. Enhancement of the bleaching and degradation of textile wastewaters by Gliding Arc Discharge plasma in the presence of TiO_2 catalyst. *J. Hazard Mater.* 164, 1266–1274.
- Gobom, S., 1963. The complex formation between lead (II) ions and acetate ions. *Acta Chem. Scand.* 17, 2181–2189.
- Jiraroj, D., Unob, F., Hagège, A., 2006. Degradation of Pb-EDTA complex by a H_2O_2 /UV process. *Water Res.* 40, 107–112.
- Kagaya, S., Bitoh, Y., Hasegawa, K., 1997. Photocatalyzed degradation of metal-EDTA complexes in TiO_2 aqueous suspensions and simultaneous metal removal. *Chem. Lett.* 155–156.
- Li, Y., Hsieh, W., Mahmudov, R., Weia, X., Huang, C.P., 2013. Combined ultrasound and Fenton (US-Fenton) process for the treatment of ammunition wastewater. *J. Hazard Mater.* 244, 403–411.
- Lyman, L.W., Reehl, W.F., Rosenblatt, D.H., 1982. Handbook of Chemical Propriety Estimation Methods Environmental Behaviour of Organic Compounds. ACS, Washington DC, pp. 25–30.
- Madden, T.H., Datye, A.K., Fulton, M., Prairie, M.R., Majumdar, S.A., Stange, B.M., 1997. Oxidation of metal-EDTA complexes by TiO_2 photocatalysis. *Environ. Sci. Technol.* 31, 3475–3481.
- Marouf-Khelifa, K., Abdelmalek, F., Khelifa, A., Addou, A., 2008. TiO_2 -assisted degradation of a perfluorinated surfactant in aqueous solutions treated by Gliding Arc Discharge. *Chemosphere* 70, 1995–2001.
- Moreau, M., Orange, N., Feuilloley, M.G.J., 2008. Non-thermal plasma technologies: new tools for bio-decontamination. *Biotechnol. Adv.* 26, 610–617.
- Murrini, L., Conde, F., Leyva, G., Litter, M.I., 2008. Photocatalytic reduction of Pb(II) over TiO_2 : new insights on the effect of different electron donors. *Appl. Catal. B* 84, 563–569.
- Noyes, A., Whitcomb, W.J., 1905. The solubility of lead sulphate in ammonium acetate solutions. *Am. Chem. Soc.* 27, 747–759.

- Pirkanniemi, K., Metsärinne, S., Sillanpää, M., 2007. Degradation of EDTA and novel complexing agents in pulp and paper mill process and waste waters by Fenton's reagent. *J. Hazard Mater.* 147, 556–561.
- Stemmler, K., Glod, G., Von Gunten, U., 2001. Oxidation of metal-diethylenetriaminepentaacetate (DTPA) complexes during drinking water ozonation. *Water Res.* 35, 1877–1886.
- Suleman, M., Khan, A.A.Y., Zahid Hussain, A., Amir Zia, M., ohaib Roomi, S., Rashid, F., Iqbal, A., Ishaq, 2011. R. Effect of lead acetate administered orally at different dosage levels in broiler chicks. *Afric. J. Environ. Sci. Technol.* 5, 1017–1026.
- Vohra, M.S., Davis, A.P., 2000. TiO₂-assisted photocatalysis of lead–EDTA. *Water Res.* 34, 952–964.
- Wang, Y.Y., Chai, Y., Chang, H., Peng, X., Shu, Y., 2009. Equilibrium of hydroxyl complex ions in Pb²⁺–H₂O system. *Trans. Nonferrous Met. Soc. China* 19, 458–462.
- Yan, J.H., Du, C.M., Li, X.D., Sun, X.D., Ni, M.J., Cen, K.F., Cheron, B., 2005. Plasma chemical degradation of phenol in solution by gas–liquid Gliding Arc Discharge. *Plasma Sources Sci. Technol.* 14, 637–644.
- Yan, J.H., Liu, Y.N., Bo, Zh., Li, X.D., Cen, K.F., 2008. Degradation of gas–liquid Gliding Arc Discharge on Acid Orange II. *J. Hazard Mater.* 157, 441–444.