Assessment of TiO$_2$ photoactivity on the lead removal: kinetic and mechanistic processing

Anca Peter, Anca Mihaly-Cozmuta, Camelia Nicula and Leonard Mihaly-Cozmuta

ABSTRACT

Removal of lead ions from aqueous solutions, in the presence and in absence of commercial TiO$_2$, under UV-light was studied. The influence of catalyst mass, concentration of Pb(II) ions and of citric acid in the starting solution as well as the impact of illumination conditions on the removal rate were also investigated. The results were fitted on the pseudo-first order, pseudo-second order and Elovich kinetic models, Weber-Morris intraparticle and liquid film diffusion models, in order to establish the photoreduction mechanism. The Pb removal rate increased in time by a combined linear-exponential mechanism. The catalyst had a positive influence on the removal rate at the start of the photoreduction. At a low concentration of Pb(II) ions (20 mg/L), the amount of photoreduced Pb(II) ions was proportional to the concentration of the citric acid solution, but at high concentrations (240 mg/L), the correlation was inversely proportional. The rate limiting steps in the removal of lead were both the photoreduction on the TiO$_2$ surface and the diffusion through the film surrounding the catalyst particle. The lead removal was significantly influenced by the mobility and by the concentration of the species in solution.

Key words | citric acid, kinetic and mechanistic processing, lead removal, titanium dioxide, working parameters

INTRODUCTION

Pollution of the environment by heavy metals has received considerable attention. Heavy metals are non-biodegradable in the environment and can accumulate in living tissues. Lead is one of the most toxic pollutants (Chenthamarakshan & Rajeshwar 2000; Kanki et al. 2004; Kabra et al. 2007, 2008; Mishra et al. 2007; Canterino et al. 2008; Duma & Ayranci 2010; Peter et al. 2014). Photo-assisted deposition from aqueous solutions and wastewaters by photocatalysis is an efficient method used to remove lead and other metals from polluted areas, as compared with other investigated methods such as biological, ion-exchange, liquid–liquid extraction, precipitation and adsorption processes (Chen et al. 2015; Zhuang et al. 2015; Abdullah et al. 2016; Afzali & Fayazi 2016; Cho et al. 2016; Khani et al. 2016; Moharram et al. 2016; Rajput et al. 2016; Sdiri et al. 2016). This is thermodynamically feasible, as a result of the fact that the potential of reduction for Pb (~0.13 eV) is less negative than the energy of the conduction band of TiO$_2$ (~0.3 eV) (Kabra et al. 2008). The literature studies (Mishra et al. 2007) indicate that the titania based mixed oxides mediated UV/visible light photocatalytic method can also be developed as a green waste water treatment process for the complete removal of toxic metal ions like lead within a relatively short period of time. Kabra et al. (2007, 2008) have demonstrated that the photodeposition of Pb(II) is favorable at pH 4 and is independent from the concentration of citric acid used as scavenger. Mishra et al. (2007) have also demonstrated that the addition of a hole scavenger in the photoreduction of lead in the presence of titania mixed with other oxides (10 wt%) increases the activity many fold. Canterino et al. (2008) have demonstrated that the system reactivity does not depend either on the pH (in the 2.0–3.5 range) or on the ionic strength of the solution and that the nature of anionic species can influence the Cu(II) photoreduction. Chenthamarakshan & Rajeshwar (2000) have described the photocatalytic reduction of metal ions in organic-loaded aqueous TiO$_2$ suspensions. Murruni et al. (2007, 2008) have tested the effects of different electron
donors on the efficiency of Pb(II) removal under nitrogen over TiO2 (Degussa P-25) and they have demonstrated that the main identified product in all cases was zero-valent Pb, in the form of colloidal particles. Additionally, Murruni and his research team (2007) have tested the removal of Pb(II) ions also on platinized TiO2 and they have shown that the reductive mechanism of Pb(II) is a minor route, because direct reduction by conduction band electrons to Pb(I) is not favorable due to thermodynamic constraints. The efficiency of removal is due to the fact that Pt acts as an electron acceptor, increasing the reactivity of electrons and allowing the single electron transfer (Murruni et al. 2007, 2008).

The aim of this study was to test the influence of some working conditions on the removal rate of the photoreduced Pb(II) ions, to establish the photoreduction/adsorption mechanism and the route of ionic species migration to the catalyst surface.

**METHODS**

**Experimental**

The TiO2 used as catalyst was purchased from Carlo Erba, a Spanish supplier. The catalyst mass was 0.05 g and 0.1 g, respectively. Solutions of lead nitrate (Merck) with two different concentrations of Pb(II) ions (20 and 240 mg/L) were prepared as Pb(II) source. Solutions of citric acid (Merck) with five different concentrations (1.93 × 10⁻⁴ mol/L, 2.89 × 10⁻⁴ mol/L, 3.86 × 10⁻⁴ mol/L, 15.44 × 10⁻⁴ mol/L and 30.88 × 10⁻⁴ mol/L) were also prepared. The work conditions for each type of the experiment are included in Table 1.

The detailed structural characterization of TiO2 (X-ray diffraction and Fourier transform infrared spectroscopy) is included in our previous study (Peter et al. 2014).

A volume of 400 mL solution containing Pb(II) ions and citric acid solution (v:v = 1:1) was introduced in the UV Laboratory Reactor System, which is an immersion-type photochemical reactor with circulation pump, providing a complete mixing of the reaction liquid. The irradiation is effected by means of a medium pressure UV lamp (150 Watt), operated by utilizing a vertically arranged combination tube (immersion tube/cooling tube combination) immersed into the reaction liquid. The recirculation rate was 0.875 L/min. The working temperature was 20 °C. The concentration of Pb(II) ions which remained in solution was spectrometrically determined by using a Perkin Elmer Atomic Absorption Spectrometer AAS 800. Experiments of adsorption (dark + catalyst) and of photolysis (light only) were also performed. All the experiments were repeated three times and the standard deviation was determined.

The amount of removed Pb (II) ions was determined as follows:

$$\text{Pb (II) ions}_{\text{removed}}(\%) = \frac{C_i}{C_o} \times 100$$  (1)

### Table 1 | Process code and characteristics, initial pH and concentration of PbOH⁺ and Pb₂OH³⁺ species

<table>
<thead>
<tr>
<th>Process code</th>
<th>Process characteristics</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>PbOH⁺</th>
<th>Pb₂OH³⁺</th>
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<td>20 mg/L, Pb(II) ions, 0.05 g TiO₂, 1.93 × 10⁻⁴ mol/L citric acid, photocatalysis</td>
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<td>3.2</td>
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<td>10⁻⁸.72</td>
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<tr>
<td>8</td>
<td>240 mg/L, Pb(II) ions, 0.05 g TiO₂, 30.88 × 10⁻⁴ mol/L citric acid, photocatalysis</td>
<td>3.2</td>
<td>2.9</td>
<td>10⁻⁷.43</td>
<td>–</td>
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<tr>
<td>9</td>
<td>240 mg/L, Pb(II) ions, 0.05 g TiO₂, 15.44 × 10⁻⁴ mol/L citric acid, adsorption</td>
<td>3.5</td>
<td>3.1</td>
<td>10⁻⁷.12</td>
<td>10⁻⁸.72</td>
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<td>10</td>
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<td>13</td>
<td>20 mg/L, Pb(II) ions, 2.89 × 10⁻⁴ mol/L citric acid, photolysis</td>
<td>4.4</td>
<td>3.5</td>
<td>10⁻⁷.33</td>
<td>–</td>
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</table>
where \( c_t \) is the concentration of removed Pb at time \( t \) (mg/L), \( c_0 \) is the initial concentration of Pb (mg/L).

To evaluate the hydro-chemical equilibrium species, Hydra and Medusa software were used (freeware available from the Royal Institute of Technology, Sweden). To obtain the profiles of the equilibrium species in solution, only the initial concentration of Pb(II) ions must be inserted.

**Modeling of photoreduction and adsorption data**

The results were fitted on pseudo-first order, pseudo-second order and Elovich kinetic models, Weber-Morris intraparticle and liquid film diffusion models.

**Pseudo-first order kinetic model**

The integrated (from \( t = 0 \) to \( t \) and from \( q_t = 0 \) to \( q_e \)) equation is expressed in (Equation (2)) (Peter et al. 2014):

\[
\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]

(2)

where \( q_t \) (mmol/g) is the amount of removed Pb(II) ions at time \( t \) (min), \( q_e \) (mmol/g) is the amount of removed Pb(II) ions at equilibrium and \( k_1 \) (min\(^{-1}\)) is the apparent rate constant. The parameters \( q_e \) and \( k_1 \) were calculated from the intercept and slope of the representation \( \log(q_e - q_t) = f(t) \).

**The pseudo-second order kinetic model**

This model is based on the capacity of the TiO\(_2\) and/or light to remove the Pb(II) ions. The integrated form (from \( t = 0 \) to \( t \) and from \( q_t = 0 \) to \( q_e \)) of the equation is (Equation (3)) (Peter et al. 2014):

\[
\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} \cdot t
\]

(3)

where \( k_2 \) is the apparent rate constant (g/mmol min). The parameters \( q_e \) and \( k_2 \) were determined from the slope and intercept of the graph.

**Elovich model**

By fitting the results on the Elovich model, information regarding the removal process (chemical or physical) can be detected. The integrated form of the equation (\( q_t = 0 \) at \( t = 0 \)) was (Peter et al. 2014):

\[
q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t
\]

(4)

where \( a \) is the initial removal rate (mmol/g min), related to the chemisorption rate; \( b \) is the constant related to the surface coverage with Pb(II) ions (Teng & Hsieh 1999). Parameters \( a \) and \( b \) were determined from the intercept and slope of \( q_t \) versus \( \ln t \).

**The intraparticle diffusion Weber-Morris kinetic model**

This model (Trgo et al. 2006; Apiratikul & Pavasant 2008; Mihaly Cozmuta et al. 2012, 2014) can be formulated using the Morris-Weber equation and is expressed as:

\[
q_t = k_p \cdot t^{0.5} + I_d
\]

(5)

where \( k_p \) is the initial rate of the intraparticle diffusion (mmol g\(^{-1}\) min\(^{-0.5}\)) and \( I_d \) is the constant (having the same unit as \( q_t \)).

The two parameters can be established from the intercept and slope, respectively, of the plot of \( q_t \) versus \( t^{0.5} \). If \( I_d = 0 \), the intraparticle diffusion was considered as the rate limiting step, while at \( I_d > 0 \), the rate of diffusion through the film is higher than that of the intraparticle diffusion. The increase in \( I_d \) means that the resistance of the liquid layer that surrounds the TiO\(_2\) particle over the Pb(II) ion diffusion is high (Mihaly-Cozmuta et al. 2014).

The coefficient of the intraparticle diffusion of lead ions in TiO\(_2\) particles is calculated as:

\[
D_e = \pi \left( \frac{d_p \cdot k_p}{12 \cdot q_e} \right)^2
\]

(6)

where \( D_e \) is the effective diffusion coefficient (cm\(^2\) min\(^{-1}\)) and \( d_p \) is the average diameter of TiO\(_2\) particles (18 × 10\(^{-6}\) cm, determined by scanning electron microscopy (SEM) analysis included in our previous study (Peter et al. 2015)).

Establishing whether the film diffusion or the intraparticle diffusion is the rate limiting step is made possible by using the \( I_d \) constant in the following equation:

\[
RC(\%) = 100 \frac{I_d}{q_e}
\]

(7)

where \( RC(\%) \) is the relative coefficient for the intraparticle diffusion and \( q_e \) is the removal capacity at equilibrium obtained from the experiments. The higher \( RC \) would
indicate the film diffusion as a rate limiting step, whereas the lower RC indicates that the intraparticle diffusion step is the rate limiting step (Mihaly-Cozmuta et al. 2014).

The liquid film diffusion model

The kinetic model of the lead ions through the film at the TiO2 particle surface is determined by the relation:

$$\ln \left(1 - \alpha_t\right) = -\frac{D}{r^2} - \frac{3 \cdot D \cdot c}{r \cdot \delta \cdot c_{ex}} \cdot t$$

where $\alpha_t$ is the fraction of Pb(II) ions bounded at time $t$ (dimensionless), $D$ is the diffusion coefficient of the lead ions through the film at the TiO2 particle surface (cm$^2$/s), $r$ is the mean radius of the particles (9 × 10$^{-9}$ m), $c$ and $c_{ex}$ are the concentration of Pb(II) ions in solution (mmol/L) and respectively the concentration of removed ions on TiO2 (mmol/L), $\delta$ is the thickness of the film, estimated to be 10$^{-5}$ m. The relative diffusion coefficient ($D$) was calculated from the slope of $\ln(1 - \alpha_t) = f(t)$, by considering $c/c_{ex} = 1$ (Peter et al. 2013).

RESULTS AND DISCUSSION

Influence of TiO2 mass

Variation of photoreduced Pb(II) ions as a function of the mass of catalyst was illustrated in Figure 1. In the first 90 minutes of photoreduction, the amount of the removed Pb(II) ions increased as the mass of catalyst increased from 0.05 g to 0.1 g, due to the availability of the active sites from the catalyst surface to the Pb(II) ions. This behavior is confirmed by results of Mishra et al. (2007), who studied the photocatalytic reduction of lead over titania-based binary oxide materials.

After 30 minutes of photo-reduction, the amount of removed Pb(II) ions by photoreduction on 0.1 g catalyst was two times greater than that deposited on 0.05 g TiO2. After 90 minutes, the amount of the removed Pb(II) ions in the two processes was equal and, furthermore, the percent of removed lead became greater by deposition on the lowest amount of TiO2 investigated. After 180 minutes, the amount of removed Pb(II) ions on 0.05 g catalyst was 1.4 times greater than that deposited on 0.1 g TiO2. Mishra et al. (2007) have explained the decrease in the removed Pb(II) ions with the increase of the mass of catalyst based on the decrease of the volume of the suspension after a certain amount of catalyst is added, due to the scattering of incident light. Another explanation is the fact that the TiO2 particles are completely covered by the hydrated Pb(II) ions, thus the UV light cannot penetrate the film at the solid surface to activate the catalyst.

Influence of concentration of citric acid solution

The variation of photoreduced Pb(II) ions as a function of the concentration of citric acid solution, acting as hole scavenger, is presented in Figure 2. The amount of Pb(II) ions removed was directly proportional to the concentration of
citric acid solution, during 90 minutes of photoreduction. The results are confirmed by the literature data (Kanki et al. 2004; Chenthamarakshan & Rajeshwar 2000; Mishra et al. 2007; Canterino et al. 2008). It has been demonstrated that, under UV light, as the concentration of Na-formate goes up from 50 to 200 ppm, the amount of Cd(II) ions removed grows 22.4%. Kanki et al. (2004) have demonstrated that when the concentration of the sacrificial agent is smaller than that of the metallic ion, the increase of the removed metal is exponential. The mechanism was applied also in this case, because the concentration of Pb(II) ions (20 mg/L = 9.66 × 10⁻⁵ mol/L) was smaller than that of the solutions of citric acid (Figure 2).

After 90 minutes of photoreduction, no difference is noticeable between the two investigated concentrations of citric acid solution (2.89 × 10⁻⁴ mol/L and 3.86 × 10⁻⁴ mol/L, respectively) on the photoreduction rate. After 180 minutes of photoreduction, the Pb(II) ions were completely removed in both processes. Thus, it can be concluded that the concentration of citric acid solution of 2.89 × 10⁻⁴ mol/L is appropriate and sufficient for the complete removal of the 20 mg/L Pb(II) ions from a solution of lead nitrate, by photoreduction under UV light.

### Influence of the illumination conditions

The variation of photoreduced Pb(II) ions as a function of the illumination conditions is presented in Figures 3 and 4. When the concentration of initial solutions of Pb(II) ions and of citric acid was 20 mg/L and 2.89 × 10⁻⁴ mol/L, respectively, the biggest amount of Pb(II) was removed in the process in which both UV light and catalyst (TiO₂) were used (Figure 3). The lowest amount of Pb(II) ions was removed in the photolysis process (UV light only), thus evidencing the positive influence of the TiO₂ on the photoreduction rate.

Figure 4 shows the variation of the removed Pb(II) ions as a function of both illumination conditions and concentration of the citric acid solution, at 240 mg/L initial concentration of Pb(II) ions. The highest amount of Pb(II) ions (22.3%) was removed during the photocatalytical process. The comparison of the black and red profiles in Figure 4 reveals that, at an initial concentration of 240 mg/L of Pb(II) ions, the amount of Pb(II) ions removed is inversely proportional to the concentration of citric acid solution. This means that, in order to obtain the best photoreduction rate, the concentration of the citric acid used as hole scavenger shall be less than 15.44 × 10⁻⁴ mol/L. By doubling the concentration of citric acid solution from 15.44 × 10⁻⁴ mol/L to 30.88 × 10⁻⁴ mol/L, the amount of Pb(II) ions removed decreases.

When the experiments were performed in the dark, the adsorption rate of Pb (II) ions also decreased as the concentration of citric acid was doubled.

Kabra et al. (2008) have also shown that the amount of Pb(II) ions removed by photoreduction decreased by ∼3% when the concentration of citric acid solution increased from Pb: citric acid = 1:1 (molar ratio) to Pb: citric acid = 1:3 (molar ratio), after 8 h of solar light exposure. This behavior...
can be explained by the fact that citric acid molecules are decomposed, thus generating intermediary products of decomposition containing oxygen that inhibit the Pb(II) reduction (Murruni et al. 2007, 2008). By analyzing Figures 2 and 4, it can be observed that at low concentrations of Pb(II) ions (20 mg/L), the amount of removed Pb(II) ions increases as the concentration of citric acid and the coefficient of diffusion through the film at the TiO2 surface increase (D is $1 \times 10^{-14}$ cm$^2$/s for $1.95 \times 10^{-4}$ mol/L citric acid, $2.7 \times 10^{-14}$ cm$^2$/s for $2.89 \times 10^{-4}$ mol/L citric acid and $3 \times 10^{-14}$ cm$^2$/s for $3.86 \times 10^{-4}$ mol/L citric acid) (Table 2). At low concentration of Pb(II) ions, the coverage of the TiO2 surface with adsorbed molecules of citric acid, with products of citric acid oxidation, with hydroxylated Pb and with reduced Pb particles is smaller than in the case of higher concentration of Pb(II) ions. Thus, the TiO2 surface was less agglomerated compared with the situation when a higher concentration of initial Pb(II) ions was used. The reaction products resulting after the oxidation of citric acid are rapidly desorbed from the TiO2 surface, leaving free spaces for the adsorption of other citric acid molecules.

At relatively high concentrations of Pb(II) ions (240 mg/L), the dependence is inversely proportional, e.g. the amount of removed Pb(II) ions and the coefficient of diffusion (D is $2.4 \times 10^{-14}$ cm$^2$/s for $15.44 \times 10^{-4}$ mol/L citric acid and $1.3 \times 10^{-14}$ cm$^2$/s for $30.88 \times 10^{-4}$ mol/L citric acid) decreases as the concentration of citric acid solution increases. In this situation, two mechanisms can be considered, one was presented above and is related to the formation of intermediary products of decomposition containing oxygen, which inhibit the lead reduction, and another one is given by the fact that the TiO2 surface is agglomerated and the desorption of the reaction products is diminished by the affinity of citric acid molecules to be adsorbed onto the surface, thus the renewal degree of the TiO2 surface is significantly reduced. A third explanation is that, at high concentration of citric acid, the pH is low, the concentration of protons is high and that of the Pb(II) hydro-complexes is low, thus decreasing the mobility of the ionic species through the film at the TiO2 surface and reducing the photoreduction rate. No significant differences in the amount of Pb(II) ions deposited in the processes occurring in the dark and in the light without catalyst can be observed, as seen in Figure 4.

Influence of the concentration of initial solution of Pb(II) ions

The variation of photoreduced Pb(II) ions as a function of the concentration of the starting solution of Pb(II) ions is presented in Figure 5. The mixture containing the high concentration of Pb(II) ions in solution also contained a high concentration of citric acid molecules. As the concentration of the initial solution of Pb(II) ions was enhanced from 20 to 240 mg/L, the concentration of citric acid solution has been increased in order to assure the needed amount of the hole scavenger during the photocatalysis experiments. At the initial concentration of 20 mg/L, the amount of Pb(II) ions removed was double the amount removed when the concentration was 12 times higher. This result contradicts the literature data studied (Chenthamarakshan & Rajeshwar 2000; Kanki et al. 2004; Mishra et al. 2007; Canterino et al. 2008; Peter et al. 2014), but an interpretation can be made. This variation was corroborated with the values of the coefficient of diffusion through the film at the TiO2 surface (D is $8.2 \times 10^{-14}$ cm$^2$/s at 20 mg/L and $2.4 \times 10^{-14}$ cm$^2$/s at 240 mg/L). The highest amount of removed Pb(II) ions was obtained when the coefficient D was high, meaning that the Pb(II) ions cross quickly through the diffusion film as they are reduced on the catalyst surface. In contrast, the lowest amount of removed Pb(II) ions was obtained when the coefficient D was low, meaning that the Pb(II) ions are restrained through the diffusion film because of agglomeration. Thus, a diffusion tangle appears, leading to a diminished concentration of Pb(II) ions onto the catalyst surface and thus, a decrease in the removal rate. Moreover, the diffusion coefficient is not influenced by the initial concentration of Pb(II) ions (Trgo et al. 2006; Apiratikul & Pavasant 2008; Mihaly Cozmuta et al. 2012, 2014), but on the type and concentration of the ionic species assigned in solution at the two different initial concentrations of Pb(II) ions (Figure 6). Increasing the concentration of Pb(II) ions means increasing the type and concentration of the hydroxylated species. These species have different mobility, leading to different diffusion rates. Thus, in practice, in order to completely remove the Pb(II) ions with a concentration higher than 20 mg/L, by photoreduction, the dilution of the solution up to 20 mg/L is recommended.

Mechanism of photoreduction and data modeling

Figure 6 illustrates the species existing in solution at two concentrations of Pb(II) ion solution. At 20 mg/L (96.6 µmol/L) Pb(II) ions, PbOH$^+$ and Pb$^{2+}$ species are the major presence in solution and at 240 mg/L (1.16 mmol/L) Pb(II) ions, the majority consists of Pb$^{2+}$, PbOH$^+$ and Pb$_2$OH$^{3+}$ species. The concentration of these species, apart from Pb$^{2+}$, as well as the initial and final
<table>
<thead>
<tr>
<th>Process code</th>
<th>Removed Pb(II) ions (mg/g%)</th>
<th>Pseudo-first kinetic model</th>
<th>Pseudo-second kinetic model</th>
<th>Elovich model</th>
<th>Intraparticle Weber-Morris diffusion model</th>
<th>Liquid film diffusion model</th>
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<tr>
<td></td>
<td>(q_e^a) (mmol/g)</td>
<td>(k_1^b) (min(^{-1}))</td>
<td>(R^c)</td>
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<td>(b^f) ((\text{mmol/g min}))</td>
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<td>0.028</td>
<td>0.944</td>
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\(q_e^a\) – amount removed Pb(II) ions at equilibrium.

\(k_1^b\) – apparent rate constant of the pseudo-first order kinetic model.

\(R^c\) – correlation coefficient.

\(k_2^d\) – apparent rate constant of the pseudo-second order kinetic model.

\(a^e\) – initial rate of Pb(II) ion removal.

\(b^f\) – non-dimensional coefficient related to the TiO2’s surface coverage with Pb(II) ions.

\(k_p^g\) – initial rate of the intraparticle diffusion (mmol g\(^{-1}\) min\(^{-1}\)).

\(D_k^h\) – constant used to examine the relative significance of the two transport mechanisms of the Pb(II) ions (intraparticle and film diffusion).

\(D_w^i\) – intraparticle diffusion coefficient.

\(RC^j\) – relative coefficient.

\(D^k\) – film diffusion coefficient.
values of pH are listed in Table 1. It can be observed that the pH decreased at the end of all the performed experiments (photocatalysis, photolysis and adsorption, respectively), as in the results showed by Murruni et al. (2007, 2008).

The highest concentration of PbOH$^+$ and/or Pb$_2$OH$_3$$^+$ species appears in processes 3, 7, 9, 11 (described in Table 1). Another important factor influencing, in a positive way, the amount of the removed Pb(II) ions is that the mobility of the lead hydroxylated species in solution and in the film at the surface is higher than that of Pb$^{2+}$ ions (Mihaly Cozmuta et al. 2012). The volume of the lead hydroxylated species is higher than that of Pb$^{2+}$ ions, although the Pb$^{2+}$ ions, due to their high electrical charge, are surrounded by a greater number of water molecules, become more voluminous and their capacity to pass through the film and subsequently, their reduction onto the surface are diminished.

Figure 7 summarizes the mechanism of photoreduction of Pb(II) ions in solution. The ions (Pb$^{2+}$, PbOH$^+$ and Pb$_2$OH$_3$$^+$) from the solution cross the film surrounding the TiO$_2$ particle (the process is governed by the diffusion film model) and arrive at the surface. Then, the ions are dehydrated (the dehydration energy is 1,480 kJ/mol (Trgo et al. 2006) and are adsorbed onto the surface. Separately, the UV light, having a higher energy than that of the gap energy ($E_g \sim 3.2$ eV), activates the TiO$_2$ particle and generates electrons (e$^-$) and holes (h$^+$). The electrons are transferred from the valence band (VB) into the conduction band (CB), leaving in the VB, holes (h$^+$). The electrons in the CB reduce the adsorbed dehydrated Pb$^{2+}$ to Pb$^0$, which remains on the surface. The holes in the VB oxidize the citric acid molecules adsorbed on the surface. The resulting products are desorbed from the TiO$_2$ surface. The role of the citric acid is to reduce the recombination rate of the charge carriers (electrons and holes), by fixing the scavening of the photogenerated holes.

During photolysis, the UV light energy needed to split the water molecule is $\sim 2.76$ eV. The water molecule is cleaved, under UV light, into hydrogen and hydroxyl radicals (Papoutsakis et al. 2013). Then, the hydrogen radicals reduce the lead ions to metallic lead particles and the hydroxyl radicals oxidize the citric acid molecules.

The reason for using the adsorption-related kinetics models in order to explain the photoreduction process is that the photoreduction mechanism is a sum between the

![Figure 5](image1.png)

Figure 5 | Variation of photoreduced Pb(II) ions as a function of the initial concentration of Pb(II) ion solution (each point is the average of three measurements accompanied by the standard deviation).

![Figure 6](image2.png)

Figure 6 | Species formed in the solution at the beginning of the process at (a) 20 mg/L Pb(II) ions and (b) 240 mg/L Pb(II) ions as a function of pH.
needed adsorption of the lead ions onto the surface and the reduction reaction in reality.

The correlation coefficients for the pseudo-first kinetic model (Table 2) were between 0.709 and 0.993, meaning that the results are fitted on this kinetic model and that the variation of the removed Pb(II) ions is linear in the first 45 minutes of the process, a fact that can be observed also in Figure 8. This behavior can also be observed by analyzing the representation \( \log(q_e - q_t) \) versus time \( t \) from the pseudo-first order kinetic model (Figure 8). The results were also fitted on the pseudo-second kinetic model. The correlation coefficients were in the 0.872–0.999 range. This means that the variation of the removed Pb(II) ions is exponential between 45 and 180 minutes of the process. The exception is the photolysis at 240 mg/L Pb(II) ions, \( 15.44 \times 10^{-4} \) mol/L citric acid, where the correlation coefficient was 0.290. The representation \( t/q_t \) versus \( t \) obtained by fitting the experimental data with the pseudo-second order kinetic model is presented in Figure 9.

The conclusion is that the variation profile of the removal of Pb(II) ions by photoreduction or adsorption is mixed, e.g. linear at the beginning of the process and exponential afterwards up to the end. The average values of the correlation coefficient for both kinetic models were also

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**Figure 7** | Mechanism of photoreduction of Pb(II) ions in solution, in the presence of citric acid as sacrificial agent.

**Figure 8** | Representation of \( \log(q_e - q_t) \) versus \( t \) obtained by fitting the experimental data with pseudo-first order kinetic model.
determined. The average $R^2$ for the pseudo-first kinetic model is 0.933 and for the pseudo-second model is 0.903, meaning that the results are better fitted on the pseudo-first kinetic model than on the pseudo-second model.

The values of the parameter $a$ in the Elovich model, related to the chemisorption rate, are relatively low for all the processes and vary directly proportionally with the amount of removed Pb(II) ions (Table 2). The value of parameter $a$ increases as the concentration of citric acid solution increases, demonstrating the positive role of the sacrificial agent at low concentrations of Pb(II) ions. The representation $q_t$ versus $\ln t$ obtained by fitting the experimental data with the Elovich model is presented in Figure 10. At a high concentration of Pb(II) ions (240 mg/L) the parameter $a$ decreases as the citric acid concentration increases. By comparing the values of removed Pb(II) ions in the photocatalysis and adsorption processes, it can be observed that the parameter $a$ is higher for adsorption than for photocatalysis, suggesting that the rate of the photocatalytical process is lower than that of the adsorption, being the rate limiting step. The values of parameter $b$, related to the surface coverage, are inversely proportional to those of parameter $a$, suggesting that Pb(II) ions and citric acid molecules adsorbed onto the TiO$_2$ surface are stationary before the reduction and oxidation, respectively.

The results were also fitted to the intraparticle Weber-Morris and film diffusion models (Table 2). The values of intraparticle diffusion coefficient ($D_p$) are lower (of the $10^{-17}$ order of magnitude) in comparison with those of film diffusion (order of magnitude $10^{-14}$), suggesting that the diffusion of Pb(II) species and of citric acid molecules in the particle is almost stopped and that all the photochemical processes occur at the TiO$_2$ surface. Moreover, the values of the intraparticle rate diffusion ($k_p$) are low, demonstrating the fact that ionic species do not penetrate the catalyst particles. The values of $I_d$ are higher than 0, thus demonstrating that the rate of film diffusion is higher than that of intraparticle diffusion. The representation $q_t$ versus $t^{0.5}$ obtained by fitting the experimental data with the intraparticle diffusion Weber-Morris kinetic model, is presented in Figure 11 and $\ln (1-a_t)$ versus $t$ is obtained by fitting the experimental data with the liquid film diffusion model in Figure 12.

The point of zero charge of commercial TiO$_2$ was found to be $pHpzc$ lower than 7 (~6.3 pH) (Preoanin & Kallay 2006; Gavriloaiei & Gavriloaiei 2008). Moreover, by taking into consideration that the working pH is in the range
3–5, the surface of the titanium dioxide particle is positively charged. The lead ions are also positively charged, thus a weak adsorption occurs, revealed by the low film diffusion coefficients (10^{-14} order of magnitude) (Table 2), compared with the values determined for other processes (adsorption for example) (Mihaly-Cozmuta et al. 2014). The dissociation rate of citric acid molecules is diminished at the working pH, however weak adsorption of citrate ions onto TiO2 surface can also be noticed. The positive role of citric acid is demonstrated by the results in Figure 2.

Based on these results, it can be concluded that both photoreduction on the TiO2 surface and diffusion through the film surrounding the catalyst particle of the Pb(II) are rate limiting steps and influence the removal rate, but the reaction mechanism is more significantly influenced by the processes induced by the charge carriers generated by the UV activation of the catalyst compared with the diffusion processes.

**CONCLUSIONS**

We have investigated the removal of Pb(II) ions from aqueous solutions, in the presence of commercial TiO2 as catalyst and of citric acid as a hole scavenger. The amount of removed Pb(II) ions increases as the mass of catalyst increases, at the start of the photoreduction, but the variation is inversely proportional after 100 minutes of process. The amount of Pb(II) ions removed was biggest by photocatalytical reduction in comparison with adsorption or photolysis. At low concentrations of Pb(II) ions (20 mg/L), the amount of removed Pb(II) ions varies directly proportionally with the concentration of citric acid solution, but at high concentrations (240 mg/L), the correlation is inversely proportional. At low concentrations of Pb(II) ions (20 mg/L), the optimum concentration of citric acid solution, in order to maximize the amount removed, is 2.89 × 10^{-4} mol/L. The amount of removed Pb(II) ions increases as the concentration of the initial solution of Pb(II) ions decreases from 240 mg/L to 20 mg/L. The variation of the amount of removed Pb(II) ions is linear at the starting of the process and exponential at the end. The rate limiting steps in the lead removal are photoreduction on the TiO2 surface and diffusion through the film surrounding the catalyst particle. No intraparticle diffusion of the species inside the TiO2 particle took place. The amount of the removed Pb(II) ions is significantly influenced also by the mobility and concentration of the species in solution.

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