



Removal of metals and phosphorus recovery from urban anaerobically digested sludge by electro-Fenton treatment

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ABSTRACT

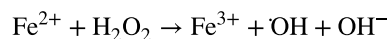
To our knowledge, this work presents the first application of electro-Fenton (EF) process to sludge washing. Suspensions of anaerobically digested sludge (0.50 wt%) from a municipal wastewater treatment facility were electrolyzed with addition of Na₂SO₄ and Fe²⁺ at pH 3.0, using a stirred tank reactor with a boron-doped diamond (BDD) or RuO₂-based anode and an air-diffusion cathode that produced H₂O₂. The effect of the sludge content in suspensions and applied current density (*j*) was examined. High quantities of Cr, Pb, Cd, Zn, Fe and P were leached at pH 3.0, whereas Cu showed the opposite trend. Aeration only enhanced Pb and Zn leaching, whereas the use of Fenton's reagent with 15 mM H₂O₂ solubilized 16.0% Cr, 23.0% P, 42.6% Fe and 56.0% Pb, with total leaching of Cd, Cu and Zn. EF with BDD anode at high *j* caused total precipitation of Cr, Pb and Fe, 40% Cd leaching and total solubilization of Cu and Zn. The RuO₂-based anode enhanced the entrapment of Cr, Fe and P in the solid fraction of the sludge, but promoted a high transport of Cd, Cu and Zn to the liquid phase. P recovery was about 74%–79% in all EF treatments. The soluble organic carbon increased in most cases except for EF with BDD, where it decreased markedly, in agreement with the high oxidation power of this anode. The sludge dewaterability was largely improved in all treatments, attaining up to 97%, consistent with the scission of many extracellular polymeric components.

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1. Introduction

Municipal wastewater treatment facilities (WWTs) produce large amounts of anaerobically digested sludge from mixed urban and industrial effluents, needing proper management or valorization before disposal (Zhu et al., 2013; Krüger and Adam, 2015). Management of a large portion of the produced sludge is based on incineration or landfilling, but the real challenge is to ensure conditioning to serve as raw material for fertilizers, thus giving added value to its high content in nutrients like nitrogen and phosphorus (Ito et al., 2013; Zhang et al., 2017). However, anaerobically digested sludge contains hazardous materials such as pharmaceuticals, endocrine disruptors and metals as a result of ineffective wastewater treatment, thereby requiring some additional step to minimize their content before agricultural usage (Ito et al., 2013; Fontmorin and Sillanpää, 2017). In the case of metals, it has been shown that their removal depends on the chemical structure of the substances contained in the solid fraction of the sludge as well as on the nature of its matrix (Tyagi et al., 1997; Fuentes et al., 2004; Krüger and Adam, 2015; Fang et al., 2016).

Different methods have been utilized to wash urban anaerobically digested sludge regarding metal content. They include acidification (Yoshizaki and Tomida, 2000; Stylianou et al., 2007; Deng et al., 2009; Kuan et al., 2010; Ottosen et al., 2013), chemical treatment (Ren et al., 2015; Wu et al., 2015), hydrolysis (Suárez-Iglesias et al., 2017), wet oxidation (Suárez-Iglesias et al., 2017), bioleaching (Yoshizaki and Tomida, 2000; Zhu et al., 2013), electro dialysis (Ebbens et al., 2015) and electrokinetics (Tang et al., 2017, 2018). Furthermore, advanced oxidation processes (AOPs) such as chemical Fenton-based processes have also been applied to improve metal leaching from sludge (Neyens and Baeyens, 2003; Neyens et al., 2004; Ito et al., 2013; Fontmorin and Sillanpää, 2017; Xiong et al., 2018). Fenton's reagent, a mixture of Fe²⁺ and H₂O₂, is added to the sludge to produce the strong oxidant hydroxyl radical (\bullet OH) via the well-known Fenton's reaction (1) (Tyagi et al., 1997; Schaum et al., 2008; Brillas et al., 2009):



(1)

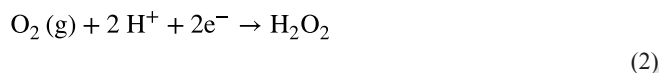
The optimum pH for reaction (1) is 2.8. Its rate depends on various factors, mainly the Fe²⁺ and H₂O₂ concentrations and ratio. In the presence of organic matter, iron ions can form complexes that react very slowly with \bullet OH. The main action of \bullet OH is the disintegration

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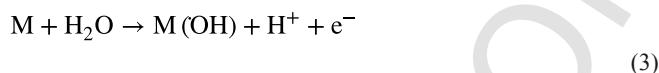
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of extracellular polymeric substances (EPS) contained in the solid fraction of the sludge, with the subsequent release of metals and other compounds (Yoshizaki and Tomida, 2000; Du et al., 2015; Fontmorin and Sillanpää, 2017). Table S1 summarizes the best performances for the solubilization of elements by selected sludge washing techniques. As can be seen, the best results were obtained using conventional Fenton treatment. Fontmorin and Sillanpää (2017) detailed that, after 1 h of this treatment with 36 mM Fe²⁺ and 360 mM H₂O₂, large amounts of Cd, Cu, Pb and Zn were removed from anaerobically digested sludge at pH 3.0 (see Table S1), with a high increase of dewaterability, consistent with the loss of EPS. Ito et al. (2013) described that the oxidation of insoluble metallic substances of a sludge at pH 2.5 by Fenton-like process using up to 1 g L⁻¹ Fe³⁺ and 10 g L⁻¹ H₂O₂ (with low •OH production from small Fe²⁺ generation) favored Cu leaching as compared to the action of H₂O₂ alone. Moreover, Fe and P were recovered as FePO₄ retained in the sludge, potentially serving as a slow-release fertilizer. However, the treatment of anaerobically digested sludge by Fenton-based electrochemical processes like electro-Fenton (EF) has not been reported so far.

EF consists in the continuous production of H₂O₂ from O₂ reduction at a suitable cathode by reaction (2), which allows working with small amounts of added Fe²⁺ catalyst to reach high efficiency for reaction (1) at optimum pH ~3 (Brillas et al., 2009; Sirés et al., 2014; Martínez-Huitle et al., 2015; Moreira et al., 2017). Typical devices to conduct reaction (2) are equipped with carbonaceous substrates modified with metal oxides (Assumpção et al., 2013), carbon nanotubes (Khataee et al., 2013, 2014), boron-doped diamond (BDD) (Cruz-González et al., 2010, 2012), activated carbon fiber (Wang et al., 2008), carbon felt (Dirany et al., 2012; El-Ghenymy et al., 2014; Yahya et al., 2014) and carbon-polytetrafluoroethylene (PTFE) O₂- or air-diffusion electrodes (Thiam et al., 2015; Galia et al., 2016; Steter et al., 2016).

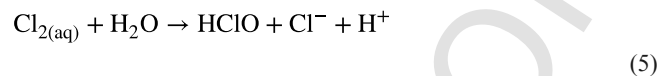


The homogeneous •OH formed from Fenton's reaction (1) acts in the whole solution volume. In addition, when an undivided electrochemical cell is utilized, heterogeneous hydroxyl radical (M(•OH)) is originated at the surface of anode M from water discharge at high current or voltage via reaction (3) (Boye et al., 2002; Panizza and Cerisola, 2009):



The reactivity of M(•OH) depends on the nature of the anode material. The use of a non-active thin-film boron-doped diamond (BDD) electrode yields great quantities of such radical, as a result of its large O₂-evolution overpotential and its lower BDD-•OH interaction. It has been demonstrated that EF with BDD anode typically causes a faster oxidation of organic molecules (Vasudevan and Oturan, 2014; Martínez-Huitle et al., 2015; Moreira et al., 2017). Conversely, active dimensionally stable anodes (DSA®) like those based on RuO₂ generate low amounts of M(•OH), but they are able to accumulate a high concentration of other strong oxidants like active chlorine (Cl₂/HClO) in acidic matrices from the anodic oxidation of Cl⁻ ion via reactions (4) and (5) (Randazzo et al., 2011; Sirés et al., 2014; Galia et al., 2016; Steter et al., 2016). The action of active chlorine enhances the removal of organics, but with production of chloro-derivatives that are usually more recalcitrant than the parent molecules (Galia et al.,

2016; Steter et al., 2016; Ridruejo et al., 2018).



This work aims to examine the removal of metals from anaerobically digested sludge, along with the possible P recovery. Sludge suspensions in water were treated by EF using a cell equipped with a BDD or RuO₂-based anode and an air-diffusion cathode. Chemical treatments by acidification, aeration and Fenton's reagent were also studied to better explain the performance of the EF process.

2. Materials and methods

2.1. Reagents

Concentrated sulfuric, hydrochloric and nitric acids were of analytical grade, purchased from Panreac and Acros Organics. Sodium sulfate and heptahydrated Fe(II) sulfate were of analytical grade, supplied by Fluka. Analytical grade hydrogen peroxide 30% (w/w) was purchased from Sigma-Aldrich. All the solutions were prepared with ultrapure water from a Merck Millipore Milli-Q system with resistivity >18.2 MΩ cm. Chemicals used for analysis were of analytical grade from Fluka and Acros Organics.

2.2. Collection and pre-treatment of sludge samples

Three anaerobically digested sludge samples (S1, S2 and S3) were collected from an urban WWTF located in Gavà (Barcelona, Spain) and stored at +4 °C in a refrigerator before use. Suspensions of 150 mL containing 0.10 or 0.50 wt% of the sludge were prepared with addition of 0.050 M Na₂SO₄ as background electrolyte. The mixture was then introduced into the cell and acidified to pH 3.0 with sulfuric acid. After that, 0.50 mM Fe²⁺ was added as catalyst and the suspension was stabilized for 20 min under vigorous stirring with a magnetic PTFE bar at 700 rpm, keeping the temperature at 30 °C.

2.3. Chemical and electrochemical systems

An open, undivided, double-jacketed cylindrical glass cell thermostated at 30 °C with recirculating external water was employed for all the chemical and electrochemical trials. A scheme of the setup for the latter kind of experiments is shown in Fig. S1. The magnetic stirring of the suspension in the cell was always maintained at 700 rpm during the 60 min of each treatment. In EF, 3 cm² electrodes separated 1 cm were introduced in the cell. The anodes were a BDD thin film on a Si wafer (3 cm × 1 cm) or a DSA®-Cl₂ (RuO₂-based, 3 cm × 1 cm) coating on a Ti plate, supplied by NeoCoat and NMT Electrodes, respectively. The cathode was a carbon-PTFE air-diffusion electrode (circle of ca. 1 cm diameter) supplied by Sainergy Fuel Cell, placed at the bottom of a propylene cylindrical tube, as reported elsewhere (Thiam et al., 2015; Steter et al., 2016). Compressed air was injected at a flow rate of 1 L min⁻¹ through its inner dry side, in order to achieve continuous H₂O₂ production at its wet side. An AMEL 2051 potentiostat-galvanostat was used as power source to provide a constant *j* for electrolysis, with connection to a Demestres 601BR digital multimeter as voltmeter for monitoring the cell voltage. Before the ex-

periments, the surface of the BDD and RuO₂-based anodes was cleaned and the air-diffusion cathode was activated in 0.050 M Na₂SO₄ at $j=100\text{ mA cm}^{-2}$ for 180 min. All treatments were made in duplicate and average results are reported with the corresponding standard deviations.

2.4. Analytical procedures

To determine the composition of the collected sludge, about 5 g of each sample were freeze-dried on a VirTis lyophilizer at $-58.7\pm 2.0^\circ\text{C}$ and 17 mTorr for seven days. Once determined the dry sludge mass, the total solid concentration (TS, in g kg^{-1}) was obtained as the dry mass/total mass ratio. The content of C was determined by elemental analysis of the dry sludge samples. Cd, Cu, Cr, Pb, Zn, Fe and P contained in each sample were quantified after digestion of 0.5 g of dry sludge in 8 mL of a HCl/HNO₃ (3:1, v/v) mixture on a microwave digester (Milestone, Ethos Plus), programmed to rise its temperature up to 200 °C in ~10 min and hold for 15 min. The resulting solution was diluted when required to avoid the interference of other metals (method ISO 11466). The concentration of the above elements was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Perkin Elmer Optima 3200 L spectrometer and ICP-mass spectrometry (ICP-MS) using a Perkin Elmer Elan 6000 ICP. Both techniques were also employed to measure the concentration of the same elements present in the liquid phase of the initial and treated suspensions. Prior to the ICP-OES and ICP-MS analyses, all the suspensions were filtered with 0.45 μm syringe filters and the resulting clear mixed with 1% (v/v) of HNO₃.

The soluble Fe²⁺ was determined by mixing 1 mL of suspension, filtered with 0.45 μm cellulose syringe filters, with 1 mL of 0.2% (v/v) 1,10-phenanthroline and 1 mL of 0.1 M sodium acetate/0.1 M acetic acid buffer (pH~4), followed by dilution to 10 mL with Milli-Q water. The same steps were made to obtain the total dissolved iron ions, but adding 0.5 mL of 1% (v/v) hydroxylamine hydrochloride before dilution to 10 mL. In each case, the Fe²⁺ concentration was measured from the absorbance of its complex with 1,10-phenanthroline at $\lambda=510\text{ nm}$ using a Shimadzu 1800 UV-Vis spectrophotometer at 25 °C (method ASTM E394).

Cr, Pb, Cd, Cu, Zn, Fe and P concentrations in the liquid phase are expressed as mg per kg of TS. The total organic carbon (TOC, in mg C L^{-1}) of the liquid phase was determined by injecting 50 μL of filtered aliquots (with 0.45 μm cellulose syringe filters) into a Shimadzu VCNS TOC system, with $\pm 1\%$ reproducibility. The capillary suction time (CST) of the sludge for dewaterability determination was measured with a 304 M CST from Triton Electronics Ltd., using standard CST filter papers. Cl⁻ concentration was determined as previously reported (Thiam et al., 2015).

The morphological and surface composition characterization of dry sludge was made by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) using a Microscope-JEOL JSM-7100F coupled with an Inca 250 detector from Oxford Instruments. The SEM images were obtained at a voltage of 20 kV. To carry

out these analyses, the lyophilized sludge was sputtered with gold and supported on carbon substrates the day before.

3. Results and discussion

3.1. Characteristics of the anaerobically digested sludge samples

Table 1 summarizes the composition analysis of the three collected sludge samples. Higher TS concentration of ca. 38 g (kg raw sludge)⁻¹ can be observed in sample S1, as compared to samples S2 and S3, which contain about 32 g (kg raw sludge)⁻¹. The larger amount of dry residue (i.e., solid fraction) in sample S1 was also in agreement with the greater C content and hence, EPS components. Metals and P concentrations tended to be higher in samples S2 and S3, although with analogous relative contents in all cases. Cd was the less abundant metal, ranging between 1.4 and 1.9 mg (kg TS)⁻¹, followed by Pb from 18 to 56 mg (kg TS)⁻¹ and Cr from 41 to 104 mg (kg TS)⁻¹. A higher content was found for Cu, attaining up to 513 mg (kg TS)⁻¹, whereas it was slightly superior for Zn with up to 616 mg (kg TS)⁻¹. Fe clearly was the most abundant metal in all samples. Similarly, high contents of P from 32.6 to 41.0 g (kg TS)⁻¹ were determined, showing the potential interest of the sludge as a fertilizer source for use in agriculture.

Fig. 1a shows an SEM micrograph of the dry sludge obtained from sample S1. A rough surface with laminar protuberances can be seen, suggesting the existence of crystalline compounds. Analogous features were observed by SEM for the samples S2 and S3 (not shown). The EDX analysis shown in Fig. 1b informs about the presence of compounds with major elements like Mg, Ca, P, C and Fe linked to the solid surface. The high O content is indicative of the pre-eminent form of metals and P as oxides and hydroxides. No peaks related to Cr, Pb, Cd, Cu and Zn were detected by this technique due to their very low concentration in the sludge (see Table 1).

3.2. Chemical treatment of anaerobically digested sludge

To study the effectiveness of different treatments for sludge washing, suspensions of 150 mL containing 0.50 wt% of the raw sludge and 0.050 M Na₂SO₄ were prepared. The natural pH was 7.9 and the concentration of elements detected in the liquid phase after 20 min of continuous stirring is shown in Fig. 2a, as an average for samples S1 and S3. As can be seen, Zn and P were not released from the solid fraction of the sludge, whereas small amounts of Cr, Pb, Cd and Cu could be dissolved. Fe was the most soluble metal, reaching near $2.7\times 10^4\text{ mg (kg TS)}^{-1}$. The Fe²⁺ concentration in the liquid phase of the 0.050 wt% suspension of sample S1 determined spectrophotometrically with 1,10-phenanthroline was near $1.89\times 10^4\text{ mg (kg TS)}^{-1}$. Note that a small fraction is due to the addition of $5.2\times 10^3\text{ mg (kg TS)}^{-1}$ Fe²⁺ (0.50 mM) employed to mimic the conditions that will be described below to promote Fenton's reaction (1) (Sirés et al., 2014; Thiam et al., 2015; Steter et al., 2016; Ridruejo et al., 2018). Total soluble iron analysis yielded $2.18\times 10^4\text{ mg (kg TS)}^{-1}$, meaning that only a minor proportion of $2.9\times 10^3\text{ mg (kg TS)}^{-1}$ (13.3%) was re-

Table 1
Total solid (g of dry sludge per kg of raw sludge) and selected elements concentrations (mg per kg of dry sludge (TS)) obtained for the samples tested in this work.

Sample	TS (g kg ⁻¹)	Cr (mg (kg TS) ⁻¹)	Pb	Cd	Cu	Zn	Fe	P	C
S1	38.1±2.3	41±1	18±1	1.4±0.1	313±10	417±12	25,628±373	32,661±247	13,992±195
S2	32.2±0.2	103±4	48±3	1.9±0.1	517±19	561±17	67,533±790	41,010±352	11,782±160
S3	31.5±0.5	104±2	56±2	1.4±0.1	513±13	616±16	71,120±860	36,836±326	9455±120

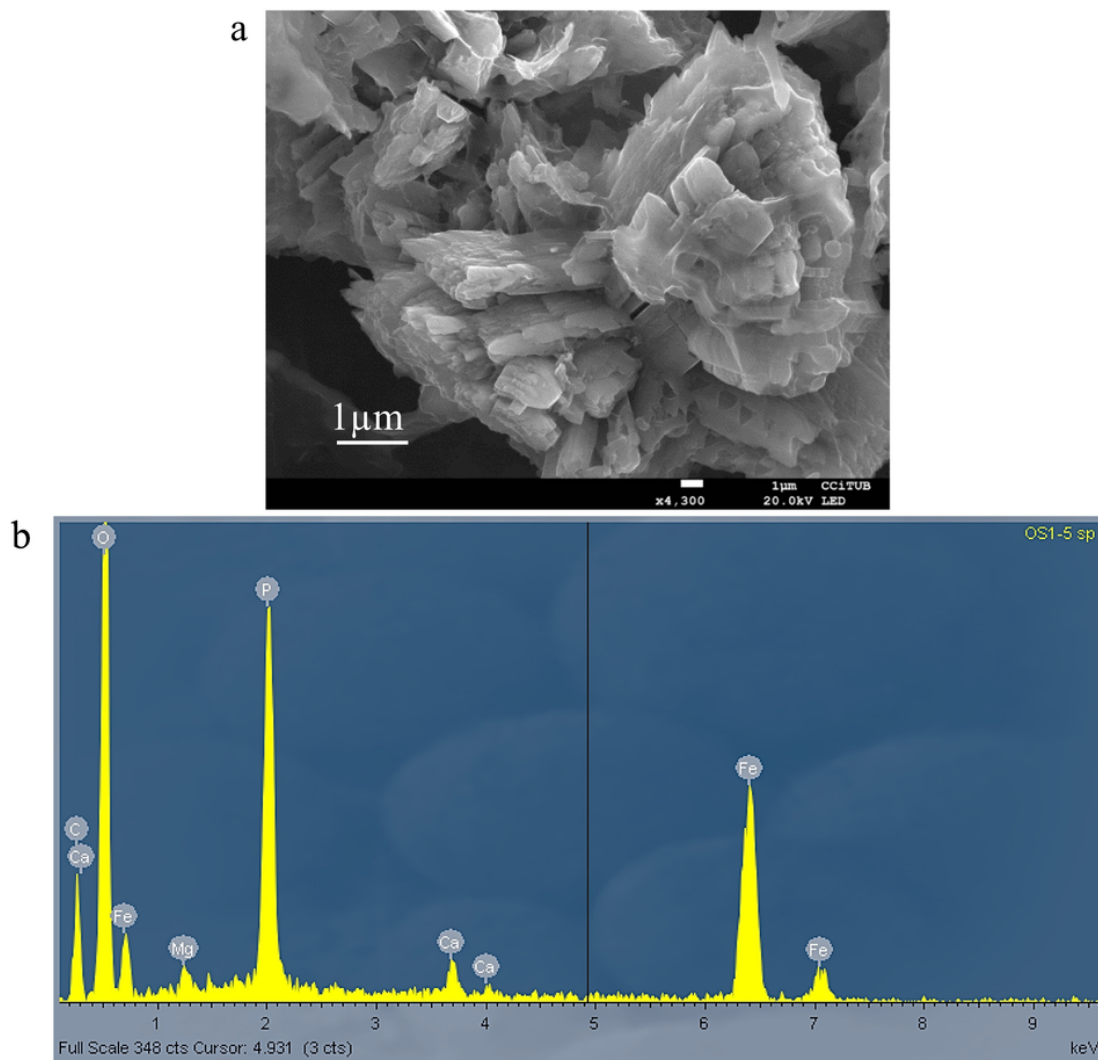


Fig. 1. (a) SEM image (300 \times) and (b) EDX analysis of the dry sludge sample S1.

lated to Fe^{3+} . The great total Fe content leached to the liquid phase can be related to the existence of some complexes between iron ions and soluble organic matter. Additionally, the liquid phase contained a high Cl^- concentration of $375.9 \pm 22.7 \text{ mg L}^{-1}$, which is a significant parameter envisaging the application of Fenton-based electrochemical treatments since the production of active chlorine species can play a relevant role.

A first chemical treatment of the above suspension consisted in a simple acidification to pH 3.0 with sulfuric acid, i.e., mimicking the optimum pH conditions to perform the Fenton-based processes. Fig. 2b presents the concentration of the elements at such pH in the liquid phase, as an average of samples S1 and S2 in the presence of 0.50 mM Fe^{2+} and after stirring for 20 min. Note that leaching of Pb and Cd to the liquid phase was very poor. Comparison of Fig. 2a and b allows establishing that for most of the elements, acidification enhanced their solubilization, especially for Zn and P that were insoluble at circum-neutral pH. This can be related to the leaching of: (i) free ions from insoluble oxides or hydroxides (for example, Zn^{2+} from neutralization of insoluble $\text{Zn}(\text{OH})_2$), or (ii) soluble metal and P complexes upon protonation or scission of hydrolyzed EPS in acidic medium (Stylianou et al., 2007; Deng et al., 2009; Kuan et al., 2010). Worth noting, acidifi-

cation at pH 3.0 was only detrimental for Cu, whose concentration in the liquid diminished by about 50%, suggesting that Cu^{2+} rather forms insoluble complexes with organics under acidic conditions.

Later, the effect of direct aeration of the prepared 0.50 wt% suspensions with 0.050 M Na_2SO_4 and 0.50 mM Fe^{2+} at pH 3.0 was investigated. The change of elements concentration after 60 min of bubbling compressed air at a flow rate of 0.75 L min^{-1} through a suspension of the sludge sample S1 is illustrated in Fig. 3. Under such mild oxidation conditions, only Pb and Zn contents rose 4.25- and 1.74-fold as compared to their initial values, without any substantial modification for the other metals and P. This suggests that the saturated O_2 in the liquid phase is able to promote the oxidation of some insoluble Zn- and Pb-organic complexes, releasing soluble Zn^{2+} and Pb^{2+} ions.

The last chemical method examined was the conventional Fenton process, which was used for the treatment of analogous suspensions with 0.50 wt% sludge and 0.50 mM Fe^{2+} , using 15 mM H_2O_2 . Fig. 4 exemplifies the variation of elements concentration for the sample S3 at 20 and 60 min, although similar tendencies were obtained for the other samples. As a first remarkable finding, Cu leaching was substantially enhanced, up to 22.4-fold at 20 min as compared to the initial concentration shown in Fig. 2b after conditioning. Sludge washing was also good for Cd (6.5-fold increase in the liquid phase), Pb (5.1-fold)

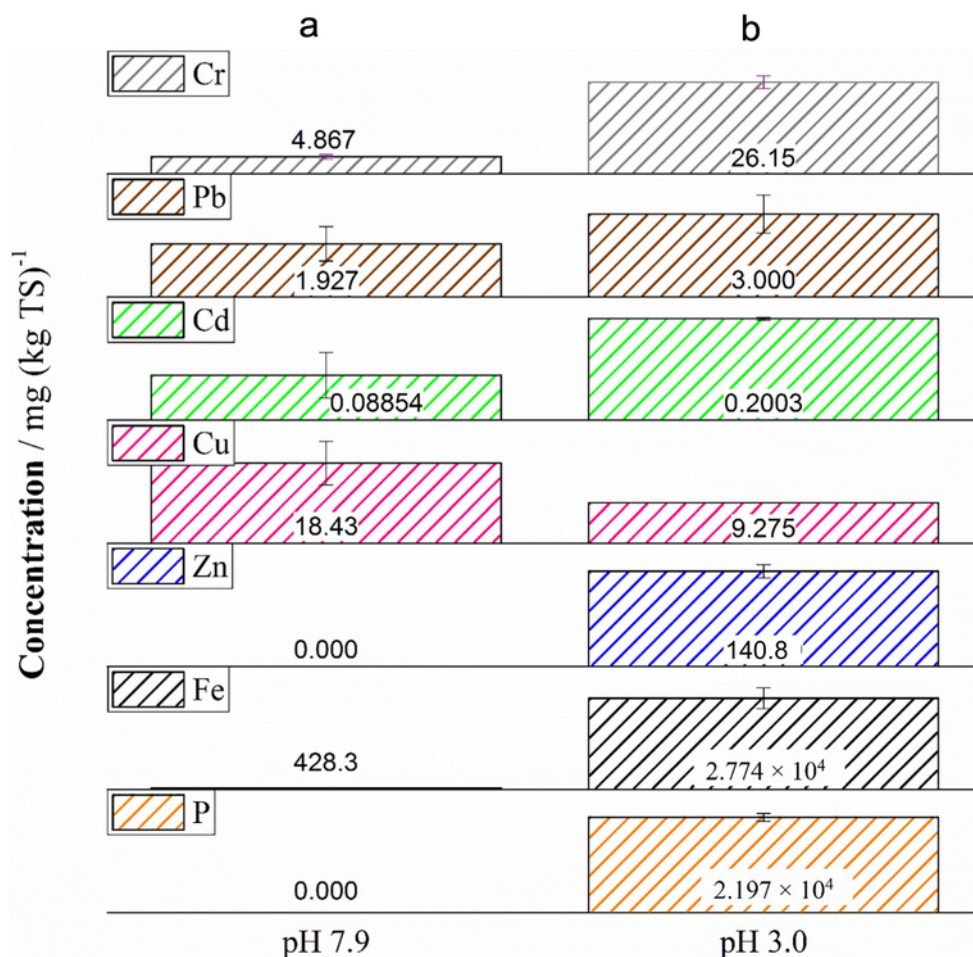


Fig. 2. Elements concentration (in liquid phase) after 20 min of continuous stirring at 700 rpm and 30 °C for 150 mL of a 0.50 wt% anaerobically digested sludge suspension with 0.050 M Na₂SO₄ and 0.50 mM Fe²⁺. (a) Natural pH 7.9, as an average for samples S1 and S3, and (b) adjusted to pH 3.0 with H₂SO₄, as an average for samples S1 and S2.

and Zn (3.7-fold). In contrast, the soluble Fe only rose 1.4-fold, whereas the Cr and P content in the liquid was strongly reduced, close to 62% and 65%, respectively. At 60 min, Fig. 4 depicts that further leaching was only noticeable for Cu and Zn, with a slight insolubilization of Pb. At the end of the treatment with the chemical Fenton's reagent, and based on the data of Table 1, the percentage of solubilization was 16.0% for Cr, 23.0% for P, 42.6% for Fe (which includes the 0.50 mM Fe²⁺ used as catalyst), 56.0% for Pb and about 100% for Cd, Cu and Zn. The almost total solubilization of the three latter metals has also been reported in earlier work using a mixture of 36 mM Fe²⁺ and 360 mM H₂O₂ for the treatment of a non-diluted anaerobically digested sludge (Fontmorin and Sillanpää, 2017). It is also noticeable the large P recovery in the solid fraction, related to the precipitation of insoluble phosphate salts, in agreement with Ito et al. (2013).

Apart from added H₂O₂ and produced •OH from Fenton's reaction (1), other weak oxidants can contribute to the solubilization/insolubilization mechanisms of metals and P during Fenton's treatment. For example, since Cl⁻ is present in the liquid phase of the suspension, as pointed out above, radical chlorine (Cl•) can be produced as follows

(Liao et al., 2001; Bruguera-Casamada et al., 2017):



The role of oxidants during the change in elements concentrations can be explained via different routes. The significant leaching of metallic ions like Cd²⁺, Cu²⁺ and Zn²⁺ can be mainly explained by the oxidative scission of organic metal-complexes, which are linked to the solid fraction sludge before the treatment. In addition, the formation of soluble complexes of such metals with humic and fulvic acids that remain stable in the liquid phase cannot be disregarded (Town et al., 2012). On the other hand, the oxidation of initially soluble metallic ions to superior valence states that promote their insolubilization is feasible. This can explain the reduction of soluble Pb content during the Fenton's reagent treatment, which can be ascribed to the partial conversion of Pb²⁺ into insoluble forms like PbO₂ and PbSO₄. The loss of P in the liquid phase can be associated with the release of PO₄³⁻ from the oxidation of soluble P-complexes, which can precipitate as salts of Fe³⁺ or alkaline ions (e.g., Ca²⁺), as previously proposed (Ito et al., 2013; Ottosen et al., 2013; Ebberts et al., 2015).

The TOC of the liquid phase of the suspension increased from 180.7 ± 6.2 to 196.0 ± 5.6 mg CL⁻¹ upon Fenton's treatment. This rise

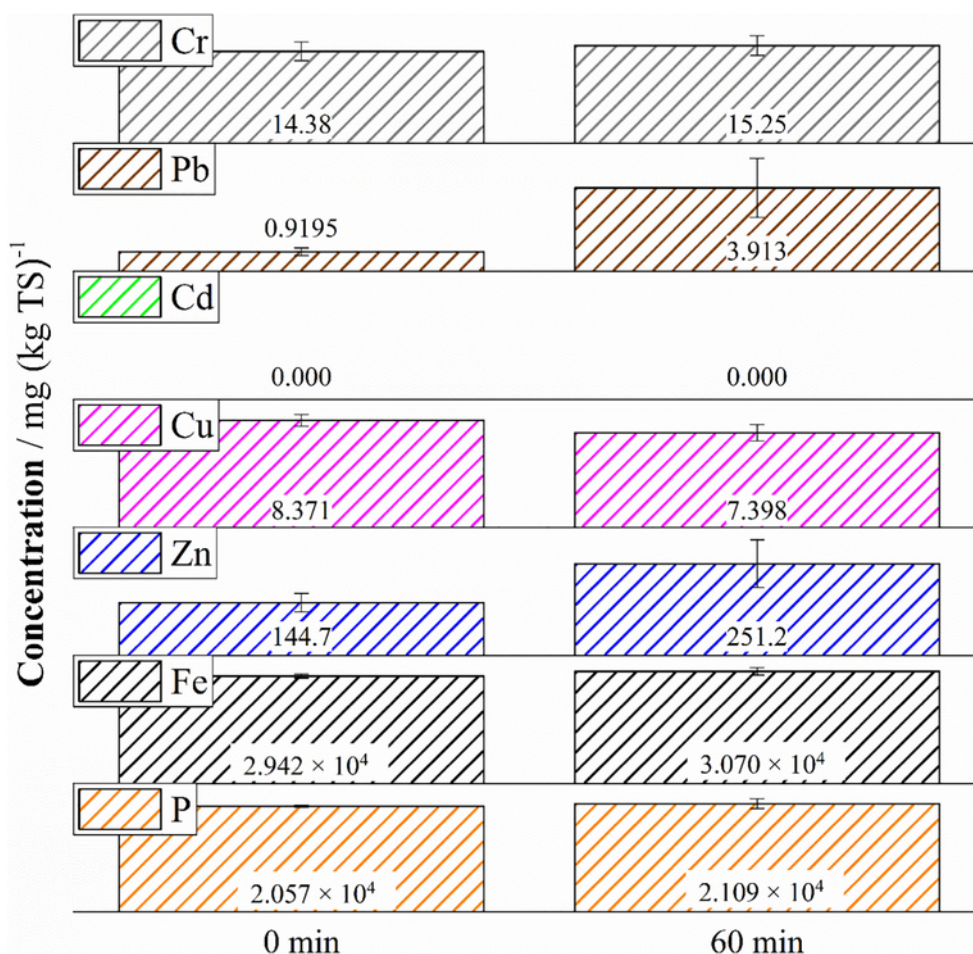


Fig. 3. Change of elements concentration after 60 min of aeration with compressed air bubbled at flow rate of 0.75 L min^{-1} for 150 mL of a 0.50 wt% anaerobically digested sludge suspension of sample S1, with $0.050 \text{ M Na}_2\text{SO}_4$ and 0.50 mM Fe^{2+} . The suspensions were previously conditioned at pH 3.0 and 30°C for 20 min.

in 8.5% of organics confirms the release of soluble humic and fulvic acids due to the oxidation of the organic matter adsorbed on the solid fraction of the sludge. Such acids can complex several metallic ions, enhancing their solubilization. On the other hand, the CST of the sludge was reduced by about 91%, from an initial value of $156.2 \pm 5.4 \text{ s}$ to a final one of $14.2 \pm 0.2 \text{ s}$. This is directly correlated with a large improvement of its dewaterability, in agreement with previous reports for conventional Fenton's treatment of this kind of urban sludge (Fontmorin and Sillanpää, 2017).

3.3. Electro-Fenton treatment of anaerobically digested sludge

The EF treatment was performed with 150 mL of stirred sludge suspensions in the presence of $0.050 \text{ M Na}_2\text{SO}_4$ and 0.50 mM Fe^{2+} , at constant j . The experiments were ran after immersing the anode and the air-diffusion cathode, with the air stream injected at a flow rate of 1 L min^{-1} . This prevented the percolation of the liquid through the cathode, although some of the air formed bubbles upon contact with the liquid. Once the power supply was switched on and the current circulated, the cathode produced H_2O_2 continuously from O_2 reduction via reaction (2). The effect of the percentage of TS in suspension, applied j and anode nature (active vs. non-active) on the concentration of the selected elements leached into the liquid phase was examined. An unexpected phenomenon was observed during all the EF treatments. After about 25–40 min of electrolysis, depending on the exper-

imental conditions, the suspension became clearly biphasic due to the accumulation of dark foam on top of the liquid, which remained clear and transparent. This surprising fact, which is not typical during the EF treatment of wastewater, can be related to the following consecutive circumstances: (i) the long chains of the EPS aggregates present in the solid fraction of the sludge were progressively oxidized to shorter molecules upon action of generated oxidants, namely $\text{M}(\bullet\text{OH})$ from reaction (3), $\bullet\text{OH}$ from reaction (1) and active chlorine from reactions (4) and (5), and (ii) the smaller molecules formed were adhered to the surface of the fine gas bubbles emitted by the electrodes (O_2 from the anode and the excess of air flowing through the cathode), thus being transported and maintained over the liquid phase. This is something similar to an electroflotation process (Brillas et al., 2009; Sirés et al., 2014). Note that this evident solid-liquid phase separation was not observed during the chemical treatments studied. Aeration did not oxidize the long EPS aggregates and hence, organic matter could not be adhered to the gas bubbles, whereas the Fenton's reagent was able to oxidize such aggregates to smaller molecules but there was no continuous gas evolution to favor their transport to the surface. In fact, the oxidation of EPS producing a more porous and less dense solid phase is sustained by the improvement of its dewaterability after conventional Fenton treatment, as stated above, since absorbed water is more easily released from the resulting less-compact sludge.

Fig. 5 shows the change of concentration of selected elements after 60 min of EF treatment of a suspension with 0.10 wt% of sample S3 using a BDD anode at $j = 33.3 \text{ mA cm}^{-2}$. The conductivity of this sus-

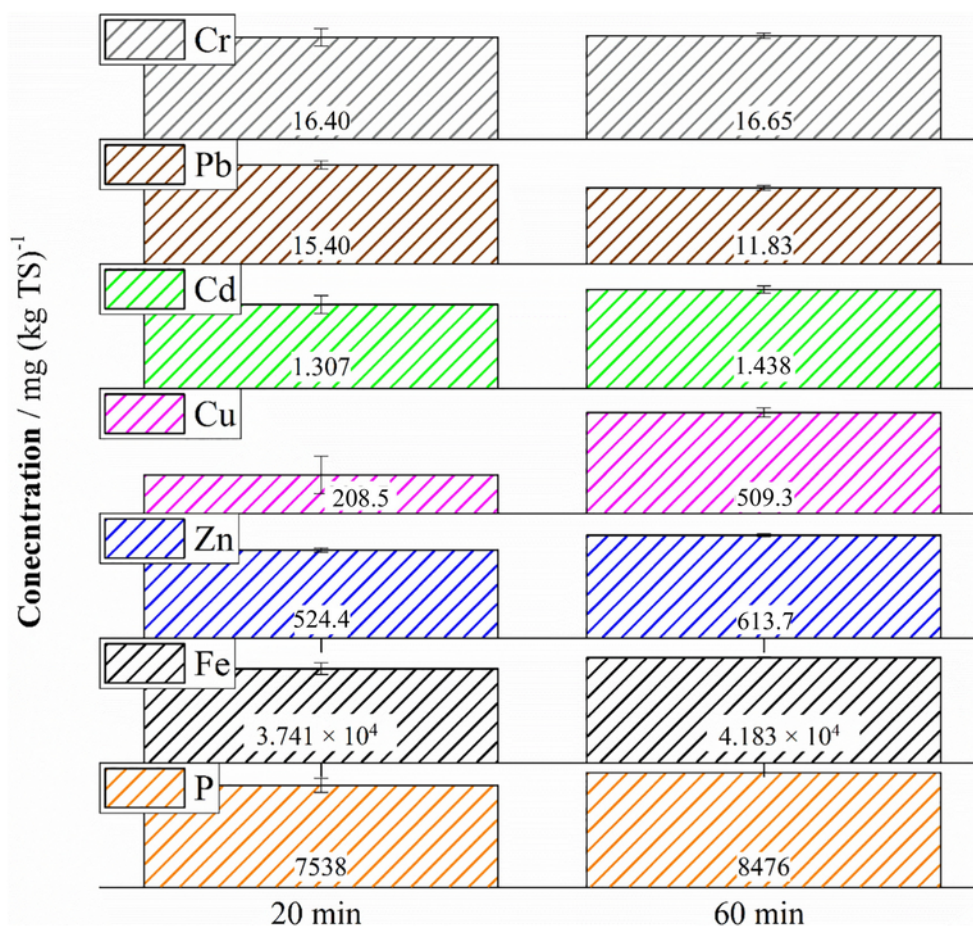


Fig. 4. Elements concentration at 20 and 60 min for conventional Fenton treatment of 150 mL of a 0.50 wt% anaerobically digested sludge suspension of sample S3, with 0.050 M Na_2SO_4 and 0.50 mM Fe^{2+} at pH 3.0, under stirring at 700 rpm and at 30 °C. Trials were made in the presence of 15 mM H_2O_2 , as added reagent to the initial suspension.

pension was $8.1 \pm 0.5 \text{ mS cm}^{-1}$, a value lower than $9.1 \pm 0.2 \text{ mS cm}^{-1}$ found for 0.50 wt%, as expected from the high salts content of the sample. This figure evidences that the amount of Pb was unaffected by the process, whereas the Cr, Fe and P concentrations decreased by 39.6%, 91.7% and 84.2%, respectively. This can be explained by the precipitation of Cr(III)- and Fe(III)-organic complexes, or the insoluble salts of these metals. Their precipitation as hydroxides is less feasible, since at the final pH of 2.5 determined in this trial the corresponding metal ions would be completely soluble. In the case of P, the oxidation from its soluble organic complexes to produce insoluble phosphates like FePO_4 is expected, as stated above (Ito et al., 2013). In contrast, as in the case of Fenton's reagent, Cd, Cu and Zn increased about 2.6–2.9-fold, accounting for 69.0%, 60.2% and 67.5% of their total content in the sludge at the end of EF. These elements, leaching from the oxidation of their complexes with EPS, can form soluble Cd^{2+} , Cu^{2+} and Zn^{2+} ions or complexes with soluble organics like humic and fulvic acids (Town et al., 2012). The soluble TOC increased by 4.6% during the process, from 57.6 ± 4.3 to $60.1 \pm 9.5 \text{ mg CL}^{-1}$, whereas the CST decayed by 63.3%, from 23.2 ± 1.3 to $8.6 \pm 0.4 \text{ s}$.

It is interesting to compare the data of Fig. 5 with those of Fig. 6a, in which a 0.50 wt% suspension of sample S1 was treated under analogous EF conditions. The same trends can be observed for all the elements in both assays, except for Pb. Its content increased 2.07-fold as compared with its initial value, although the final value accumulated in

the liquid only represented about 10% of its total content in the sludge. This is indicative of the oxidation of insoluble Pb(II)-EPS complexes, thus being possible to form soluble Pb(II) complexes with the organics present in the liquid phase. Larger Cr (90.4%) and smaller Fe (88.0%) and P (62.1%) insolubilization can be observed in Fig. 6a. This occurred in concomitance with 59.1-fold, 29.0-fold and 2.3-fold solubilization of Cd, Cu and Zn, corresponding to 29.5%, 99.2% and 83.6% of their total content. The variation in elements concentration of Fig. 5 and Fig. 6a can be due to different contents of metal-organic complexes. In particular, the recovery of P was much greater in the case of 0.10 wt%, which can be ascribed to the lower quantity of complexes of P to be oxidized with release of PO_4^{3-} . Also, Cd was also less solubilized, but the leaching of Cu and Zn was greater probably due to the presence of a larger amount of soluble organics to complex them. Iron analysis of the final liquid revealed that it contained a low amount of Fe^{2+} , i.e., $293.2 \text{ mg (kg TS)}^{-1}$, and a greater quantity of $438.0 \text{ mg (kg TS)}^{-1}$ as Fe^{3+} , although the major part of the soluble total iron detected by ICP (about $7530 \text{ mg (kg TS)}^{-1}$) corresponded to soluble complexes of iron ions with organics.

Fig. 6a–c depicts the change of the elements concentration by EF with a BDD anode at increasing j from 33.3 to 150 mA cm^{-2} . It is noticeable that Cr and Fe contents were gradually reduced in the liquid phase, totally disappearing at the highest j . Precipitation of these metals complexed with organics is expected. Pb was not observed at the highest j , suggesting that the high amounts of oxidants formed are

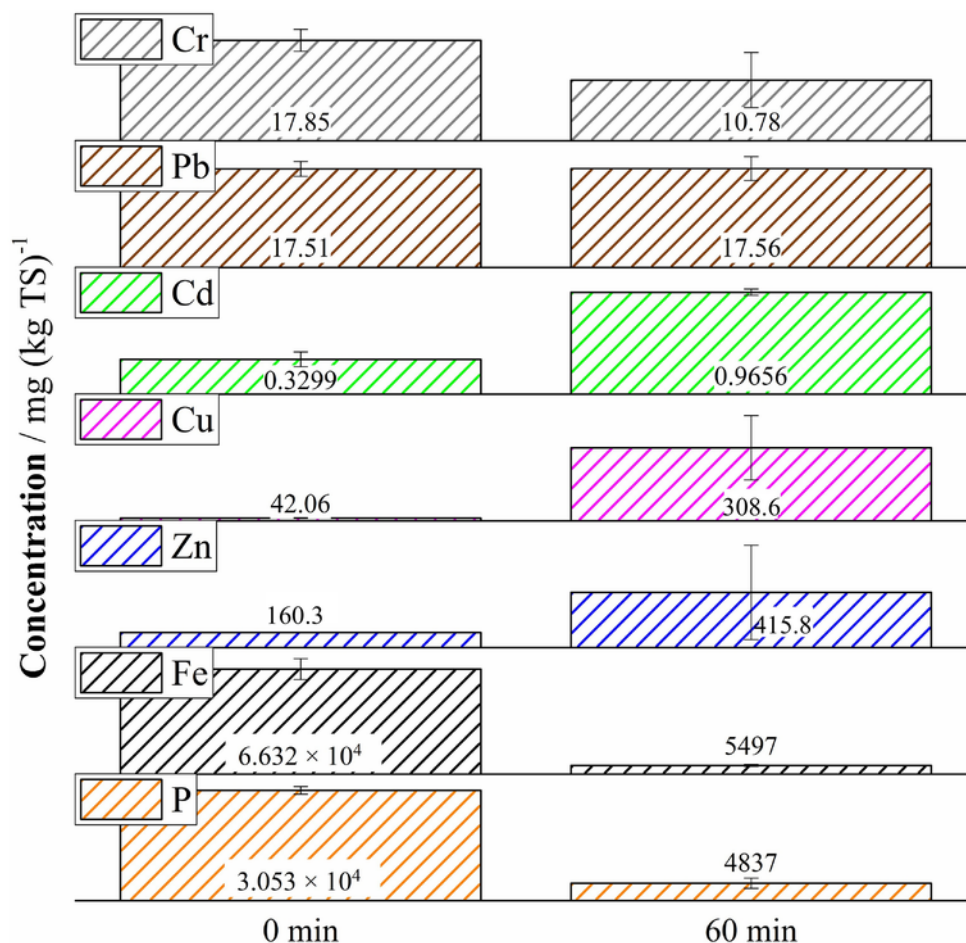


Fig. 5. Change of elements concentration after 60 min of electro-Fenton (EF) treatment of 150 mL of a 0.10 wt% anaerobically digested sludge suspension of sample S3, with 0.050 M Na_2SO_4 and 0.50 mM Fe^{2+} at pH 3.0, under stirring at 700 rpm and at 30 °C. The cell was equipped with a 3 cm² boron-doped diamond (BDD) anode and a 3 cm² air-diffusion cathode. A current density (j) of 33.3 mA cm⁻² was applied to the suspension previously stabilized for 20 min.

able to transform it into PbO_2 . The maximum Cd leaching was 40%, whereas similar recovery of P up to about 74% of its total content was obtained regardless of the j value applied. In contrast, Cu and Zn became 100% soluble at $j=150$ mA cm⁻². In these assays, TOC in the liquid phase was gradually reduced by 12% to 19%, whereas the dewaterability rose from 86% to 97%. The application of j values of 33.3, 100 and 150 mA cm⁻² corresponded to increasing specific charges of 0.67, 2.01 and 3.01 Ah L⁻¹, yielding energy consumptions of 4.4, 30.2 and 51.7 kWh m⁻³. Therefore, it is preferable to operate at low j values.

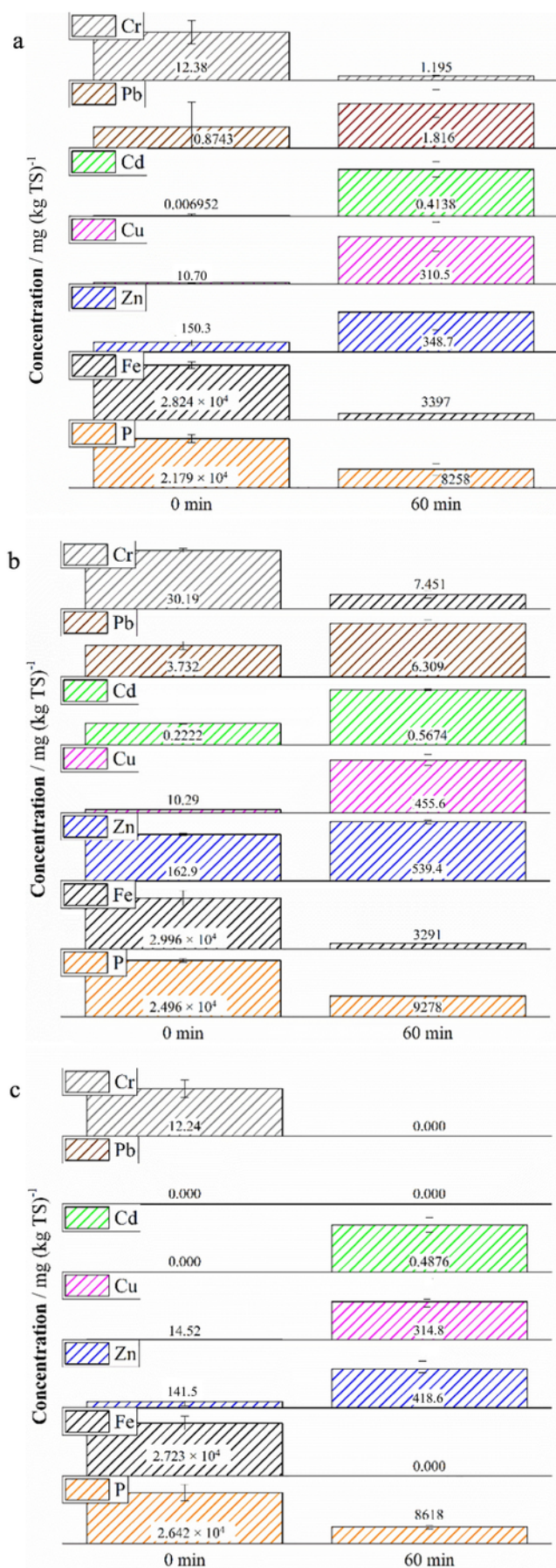
The EF study was comparatively made with a 0.50 wt% suspension of sample S1 using an active RuO_2 -based anode at $j=33.3$ mA cm⁻², and the results obtained are depicted in Fig. 7. The main difference between this anode and the non-active BDD is the proportion of $\text{M}(\bullet\text{OH})$ and active chlorine generated as oxidants. While a RuO_2 -based anode favors the production of active chlorine with low amounts of $\text{RuO}_2(\bullet\text{OH})$ species, the opposite occurs for BDD, which promotes the formation of the strong oxidant BDD($\bullet\text{OH}$) over active chlorine (Thiam et al., 2015; Steter et al., 2016; Ridruejo et al., 2018). Compared to Fig. 6a for BDD, after 60 min of electrolysis, Fig. 7 shows a significant larger decay of Cr, Fe and P concentrations, a similar solubilization of Pb, and a smaller concentration of soluble Cd, Cu and Zn. This means that active chlorine species destroy to larger extent the soluble organic complexes of the three former elements, whereas they attack more slowly the insoluble organics

linked to the three latter metals. In the case of P, for example, near 77% was recovered in the solid fraction using the Fenton's reagent where $\bullet\text{OH}$ is the pre-eminent oxidant (see Fig. 4), whereas it underwent a slightly higher precipitation up to 79.0% in EF when active chlorine was predominant from the RuO_2 -based anode (see Fig. 7). This significant amount of P recovered as FePO_4 can act as a slow-release fertilizer. Note that no active chlorine was detected in the liquid phase during the EF assays from *N,N*-diethyl-*p*-phenylenediamine colorimetric analysis (Steter et al., 2016), indicating its fast consumption by reaction with H_2O_2 and organics. Data of Fig. 4 for the conventional Fenton treatment also corroborate the very positive action of $\bullet\text{OH}$ to solubilize pre-eminent Cu and Zn, as found for EF regardless of the anode used although with better results for BDD.

It should be mentioned that at the end of EF with a RuO_2 -based anode, dewaterability was enhanced to attain 94%, similar to that determined using BDD. In contrast, the TOC of the liquid phase increased by 13%, in contrast to the gradual abatement found with BDD. This can be accounted for by the expected greater oxidation power of the latter anode to mineralize the organic matter.

4. Conclusions

Acidification of a 0.50 wt% urban anaerobically digested sludge suspension to pH 3.0 promoted the leaching of P and selected metals, except Cu that remained partially precipitated in the solid fraction.



Aeration only favored the solubilization of Pb and Zn. The use of Fenton's reagent allowed the oxidation of organic metal-complexes by \bullet OH, leading to the insolubilization of Cr and P, with total leaching of Cd, Cu and Zn. EF with a non-active anode like BDD at high j was very effective as sludge washing technique to totally remove the latter two metals. This Fenton-based electrochemical treatment also allowed the total precipitation of Cr, Pb and Fe. Comparative use of a RuO₂-based anode led to greater production of active chlorine species. This favored a larger decay of Cr, Fe and P concentrations in the liquid phase, but a smaller enhancement of Cd, Cu and Zn solubilization. The P recovery in the solid phase was about 74%–79% by conventional Fenton and EF treatments, being slightly superior with the RuO₂-based anode. An irregular evolution of the soluble TOC was found, increasing in most cases except for EF with a BDD anode, where it decreased due to the higher mineralization power of BDD(\bullet OH). The CST measurements of the sludge showed a great improvement of its dewaterability because of the scission of EPS, yielding a less-compact sludge.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.06.337>.

Fig. 6. Elements concentration quantified at 0 and 60 min of electrolysis for the EF treatment of 150 mL of 0.50 wt% anaerobically digested sludge suspensions under the same conditions of Fig. 5 with a BDD/air-diffusion cell. Applied j : (a) 33.3 mA cm⁻² using sample S1, (b) 100 mA cm⁻² using sample S3 and (c) 150 mA cm⁻² using sample S1.

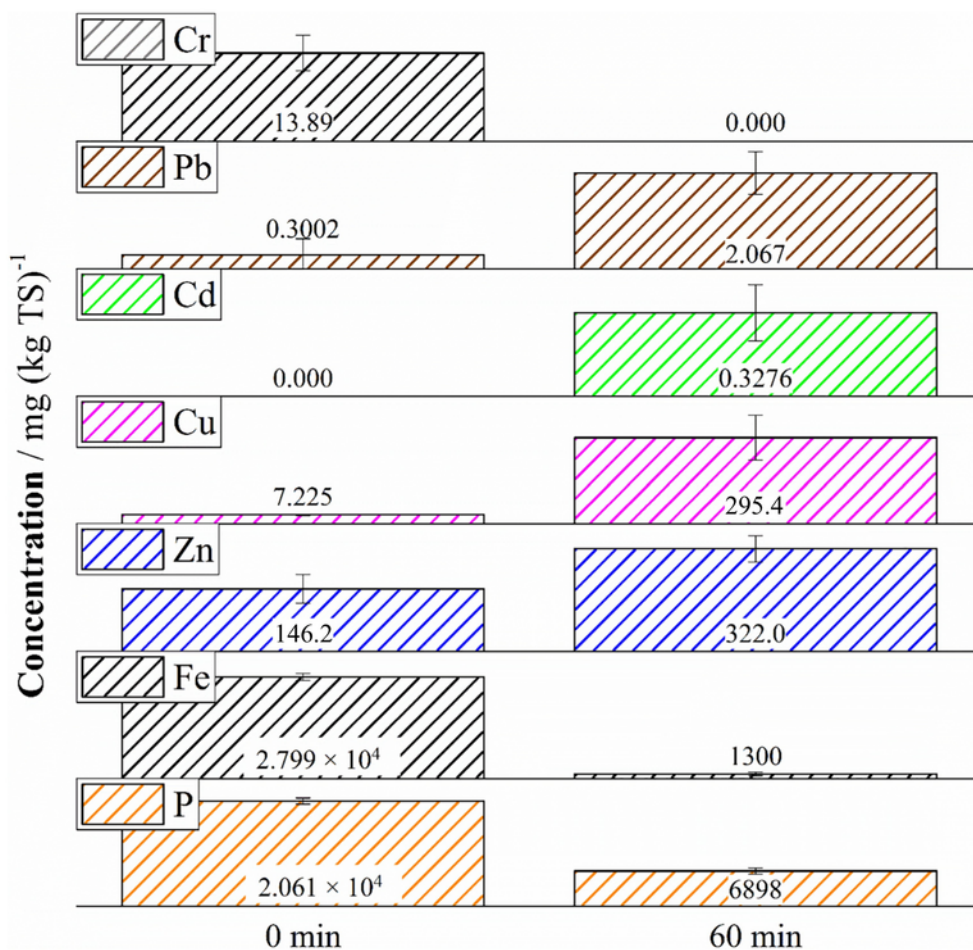


Fig. 7. Elements concentration at 0 and 60 min of electrolysis for the same suspension of sample S1 shown in Fig. 6 operating under similar EF conditions, but using a 3 cm² RuO₂-based anode at $j=33.3$ mA cm⁻².

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