

# A Chemical-Physical Procedure to Reduce Levels of Potentially Toxic Elements (PTEs) in Municipal Sewage Sludges

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## Abstract

The current waste policy in EU aims at reducing the amounts of sludges to be disposed in landfill, encouraging their energy reuse (e.g. energy source, fertilizers, etc.). In this perspective a reduction of potentially toxic elements (PTEs) and water is welcome, in view of a more sustainable reutilization of sludges, e.g. in agriculture. Aim of this work was to set up a chemical-physical procedure, named modified Fenton process (patent n° PC2012A000008 of 22/03/2012), which was able to improve the reduction of some PTEs (Zn, Ni, Cu, Pb, Cd and Cr) and water in municipal sewage sludges from anaerobic digestion, better than a conventional Fenton process, avoiding significant decreases of total organic carbon (TOC).

**Keywords:** Municipal sewage sludge; Potentially toxic elements; Fenton reaction; Sludge dewatering

## Introduction

During the last 20 years sewage sludge production has increased from 6.5 M tons of dry solids (DS) in 1992 (EU-15) to 9.8 M tons of DS in 2006 (EU-27-All member States) (EC 2006 [1] with forecasted values exceeding 13 M tons of DS up to 2020 (Milieu Ltd., WRC and RPA) [2]. On average, the preferred final destination of sludges remains landfill (38%), followed by recycling (24-25%), incineration (20-22%) and composting (15-18%). The waste policy (Directive 2008/98/EC) [3] has pointed out that, in order to minimise the negative effects of the generation and management of wastes on human health and the environment, all member States should reduce the use of resources and favour the practical application of the waste hierarchy a) prevention b) preparing for re-use c) recycling d) other recovery (e.g. energy recovery) e) disposal. The following actions should be improved: removing metals by chemical or microbiological leaching, dewatering, to reduce sludge volumes and relative costs, preserving acceptable levels of organic matter in treated sludges for their profitable future reuse. Municipal sludges originate from processes of treatment of wastewaters in which physical-chemical processes are involved, so they tend to concentrate PTEs (Milieu Ltd., WRC and RPA) [2] with increased potential risks for the environment and human health [4]. In order to efficiently reduce PTEs in sewage sludges, the suggested approaches are the control of the point or the diffuse sources and the extractive removal [5]. For the latter, the chemical leaching with use of inorganic or organic salts is employed, which consists of four steps: solubilisation of the PTEs; separation of the water-phase containing the mobilized PTEs and the sludge particles; removal of sludge particles from the leachate containing PTEs and precipitation of PTEs present in the leachate and their subsequent removal [4]. The extraction is frequently preceded by an oxidation treatment, known as classic Fenton reaction, where H<sub>2</sub>O<sub>2</sub>, activated by iron salts at pH of 2.5-3.0, has proved to be more effective, than H<sub>2</sub>O<sub>2</sub> alone, in the destruction of toxic organics in wastewaters [6]. Moreover Fenton's reagent was observed to improve sludge dewaterability (Neyens and Baeyens) [7]; this is an important feature in that it allows high saving-powers and a more sustainable reuse of sludges. Numerous are the studies concerning the effects of Fenton's oxidation process on the reduction of organic contaminants in wastewaters and landfill leachates [8-10] but few concern PTEs reduction and dewatering.

The aim of this work was to set up a chemical-physical procedure, called modified Fenton treatment (patent n° PC2012A000008 of 22/03/2012), performed on municipal sludges from anaerobic digestion, to improve the reduction of some PTEs levels, to increase the dewatering efficacy, with a low TOC decrease, respect to a classic Fenton treatment.

## Materials and Methods

### Reagents and instrumentation

The following reagents, pure for analysis (Carlo Erba, Milano, Italy), were used: HCl 37% (m/v), HNO<sub>3</sub> 65% (m/v), H<sub>2</sub>SO<sub>4</sub> 96% (m/v), H<sub>2</sub>O<sub>2</sub> (40% m/v), Fe<sub>2</sub>SO<sub>4</sub> × 7H<sub>2</sub>O. Multi element standard solutions were prepared by dilution with distilled water, containing the same quantities of acids as the samples. The distilled water used had a conductivity ≤ 0.1 μS cm<sup>-1</sup> (residual at evaporation <1 ppm). The following instruments were used: pH-meter CRISON mod. Basic 20 meter (Barcelona, Spain); stove mod. PID system (MPM Instruments, Bernareggio, MB, Italy); CN elemental analyser (mod. Vario Max CN Macro Elementar Analyzer, Hanau, Germany); open digester system (Digiprep mod. Jr, SCP SCIENCE, Baie d'Urfé, QC H9X 4B6, Canada) (time=120 minutes; temperature=95°C); inductively coupled plasma optical emission spectrometer PerkinElmer Optima 2100 DV simultaneous ICP-OES (PerkinElmer Life and Analytical Sciences, Shelton, CT, USA), equipped with an AS-93 plus autosampler, a concentric glass (Meinhard) with Cyclonic Spray Chamber (Table 1).

### Sample preparation and methods of analysis

The municipal sewage sludges was obtained from an anaerobic

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**Received** February 12, 2015; **Accepted** March 20, 2015; **Published** March 27, 2015

**Citation:** Baffi C, Cella F, Fumi I, Trevisan M (2015) A Chemical-Physical Procedure to Reduce Levels of Potentially Toxic Elements (PTEs) in Municipal Sewage Sludges. J Biofertil Biopestici 6: 153. doi:10.4172/2155-6202.1000153

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Perkin Elmer Optima 2100 DV Simultaneous ICP	
Frequency	40 MHz, free-running
Incident power	1400 W
Reflected power	<5 W
Ar gas flow rate:	
Plasma	15.0 L min <sup>-1</sup>
Auxiliary	0.20 L min <sup>-1</sup>
Nebulizer	0.70 L min <sup>-1</sup>
Peristaltic pump	1.20 mL min <sup>-1</sup>
Nebulizer	Concentric glass (Meinhard) with cyclonic spray chamber
Autosampler	AS 93plus

Table 1: ICP-OES Instrumental operating parameters.

wastewater treatment plant (full capacity of 163,000 equivalent inhabitants) sited in Piacenza, Italy. Samples were collected in polypropylene bottles, shipped cold, and kept at 4°C before use. Sampling, pH and Total Solids (TS) determination were carried out according to the National Official Methods for sewage sludges (IRSA CNR, 1985) [11]. Before analysis of PTEs and carbon, the sample was dried at 105°C overnight, homogenized and ground to 0.2 mm for PTE analysis and to 0.5 mm for total C analysis. For PTE determination (Cd, Cr, Cu, Ni, Pb and Zn) an aqua regia digestion (1:3=HNO<sub>3</sub>:HCl) was performed in an open digestion system. 0.50 g of sample was weighed and put in contact with 14 mL of aqua regia, at T=95°C for approx. 120 minutes; the digests were brought to a final volume of 50 mL, filtered by paper (Schleicher and Schuell n° 589 Blue ribbon ashless) and analyzed for metal contents by inductively coupled plasma emission spectrometry. Total Carbon (TC) was determined by sample combustion on a CN elemental analyser on about 0.250 g of sludge sample; Inorganic Carbon (IC) was determined according to the Official Methods of Soil Analysis (MIPAF G.U.R.I) [12]. Total Organic Carbon content (TOC) was calculated by the subtraction of inorganic carbon from total carbon: TOC=TC-IC. The values of the main chemical-physical parameters of the sludge are shown in Table 2.

### Experimental procedures

To compare the efficacy of the proposed procedure vs. the conventional Fenton method, a RBD (Randomized Block Design) experiment was set up in laboratory; three treatments plus a control were arranged, with five replicates.

A first treatment, called P, was performed with use of H<sub>2</sub>O<sub>2</sub> alone; it consisted in putting in contact 80 g of H<sub>2</sub>O<sub>2</sub> to an aliquot of 1.6 kg of sludge for different times (60 min and 180 min). The mixtures were brought to a value of 7% of TS in order to facilitate subsequent operations such as filtering etc. Then the samples were submitted to vacuum filtration on a Buchner funnel (diameter 90 mm) on extra-rapid filter paper Whatman 41 for 8 minutes, followed by 5 minutes on a press. Determination of TS, PTEs and TOC were carried out on the residues of the filtration, called samples P<sub>1</sub> and P<sub>3</sub>; the former refers to a contact time of 60 min, the latter to a contact time of 180 min with H<sub>2</sub>O<sub>2</sub>.

A second treatment, called R, concerned the use of the classic Fenton's reaction. 80 g of H<sub>2</sub>O<sub>2</sub> and 22.85 g of FeSO<sub>4</sub> × 7H<sub>2</sub>O (Fe<sup>2+</sup> concentration equal to 3.58 mg g<sup>-1</sup> DS and H<sub>2</sub>O<sub>2</sub> equal to 62.5 mg g<sup>-1</sup> DS with a ratio Fe<sup>2+</sup>/ H<sub>2</sub>O<sub>2</sub> of 0.057) were added to an aliquot of 1.6 kg

of sludge. Aliquots of H<sub>2</sub>SO<sub>4</sub> (50% v/v) were also added to reach pH 3.0 (classic Fenton oxidation); this mixture was brought to a value of 7% TS, as in the case of the first treatment. pH determinations were made on samples, named R<sub>1</sub> and R<sub>3</sub>, in virtue of different contact times with H<sub>2</sub>O<sub>2</sub> (the former refers to 60 min; the latter to 180 min). These samples were submitted to vacuum filtration on a Buchner funnel (diameter 90 mm) on extra rapid filter paper Whatman 41 for 8 minutes, followed by 5 minutes on the press under a pressure ranging between 0 and 15 bars for 5 minutes. Determinations of TS, PTEs and TOC were carried out on the residues of the filtration (called R<sub>1</sub> and R<sub>3</sub>).

A third treatment, called Q, concerned the procedure with use of modified Fenton's reaction. 80 g of H<sub>2</sub>O<sub>2</sub> and 22.85 g of FeSO<sub>4</sub> × 7H<sub>2</sub>O (Fe<sup>2+</sup> concentration equal to 3.58 mg g<sup>-1</sup> DS and H<sub>2</sub>O<sub>2</sub> equal to 62.5 mg g<sup>-1</sup> DS with a ratio Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub> of 0.057) were added to an aliquot of 1.6 kg of sludge. Aliquots of H<sub>2</sub>SO<sub>4</sub> (50% v/v) were also added to reach pH 3.0 (classic Fenton reaction), then others were added to reach pH 2.0; this mixture was brought to a value of 7% of TS, as seen before. pH determinations were carried out on Q<sub>1</sub> and Q<sub>3</sub> samples, referring to contact time with H<sub>2</sub>O<sub>2</sub> of 60 min and 180 min., respectively. Then Q<sub>1</sub> and Q<sub>3</sub> samples were submitted to vacuum filtration on a Buchner funnel (diameter 90 mm) on extra-rapid filter paper Whatman 41 for 8 minutes, followed by 5 minutes on the press (pressure of 0-15 bar for 5 minutes). Determinations of TS, PTEs and TOC were carried out on the residues of the filtration. A treatment, called O, was prepared as a control and it had no treatment with H<sub>2</sub>O<sub>2</sub>, no press, no filtration and it was brought to a value of 7% of TS. All information concerning experimental data design is shown in Table 3.

### Statistical data analysis

IBM SPSS vs. 19.0 software (2010) was used to carry out statistical data processing.

parameter	Measure units	value
pH		8.10
Total moisture	%	80.29
Total solids (TS)	%	19.71
Residue at 550°C	%	48.28
Lost to calcination	%	51.72
Total organic carbon (TOC)	% on DS	28.86
Total Cd	mg kg <sup>-1</sup> DS	3.05
Total Cr	mg kg <sup>-1</sup> DS	194
Total Cu	mg kg <sup>-1</sup> DS	612
Total Ni	mg kg <sup>-1</sup> DS	125
Total Pb	mg kg <sup>-1</sup> DS	82.0
Total Zn	mg kg <sup>-1</sup> DS	1031

Table 2: Mean values of chemical-physical parameters of the sludge.

Treatment	sample	Contact time with H <sub>2</sub> O <sub>2</sub> min	pH	H <sub>2</sub> O <sub>2</sub> added (% of sludge weight)
O*	O	---	8.04	0
P	P <sub>1</sub> P <sub>3</sub>	60	7.97	5
		180	8.09	5
R	R <sub>1</sub> R <sub>3</sub>	60	3.34	5
		180	3.32	5
Q	Q <sub>1</sub> Q <sub>3</sub>	60	2.02	5
		180	2.06	5

\*O: control (no treatment); P: addition of H<sub>2</sub>O<sub>2</sub> alone; R: classic Fenton's treatment; Q: proposed modified Fenton's treatment.

Table 3: Experimental design with treatments and values of pH and added H<sub>2</sub>O<sub>2</sub>.

## Results

### Yields of leached PTEs

Table 4 shows the data relative to the leached aliquots of PTEs from sludge, which are calculated as percentage variation ( $\Delta$ PTE%) with respect to the values observed for the control treatment (O). The outcomes of a statistical comparison (one-way ANOVA + LSD test) are also reported.

Very low or no decreases are observed for the treatment with  $H_2O_2$  alone ( $P_1$  and  $P_2$ ); the pH of this treatment is 7.97 and 8.09 respectively, very close to that of the control (8.04).

When pH levels decreased, following Fenton's treatment, the values of leached PTEs increased, for both  $R_1$  and  $R_3$ , which show similar pH values (3.34 and 3.32 respectively). With regard to this, a more prolonged contact time for  $H_2O_2$  ( $R_3$ ) proves better than a shorter time ( $R_1$ ) for obtaining higher values of leached PTEs: -68.8 vs. -66.9 for Zn; -52.1 vs. -51.6 for Ni; -12.9 vs. -8.73 for Cu; -3.45 vs. -3.20 for Cd. This treatment did not prove suitable for Pb and Cr, in that no decrease was observed for the leached aliquots.

When the modified Fenton treatment was applied, further decreases were observed with respect to the classic Fenton reaction for all investigated PTEs but, in some cases (Zn, Cu and Cr) the highest values were observed for the lower contact time ( $Q_1$  at pH=2.02) respect to the longest contact time ( $Q_3$  at pH 2.06). In fact, for these three PTEs the leached values were: for Zn (-76.9 for  $Q_1$ ; -73.1 for  $Q_3$ ); for Cu (-33.4 for  $Q_1$ ; -19.0 for  $Q_3$ ); for Cr (-4.14 for  $Q_1$ ; -3.04 for  $Q_3$ ). On the contrary, Ni, Cd and Pb showed higher leached values for the longer contact time with  $H_2O_2$  ( $Q_3$ ) than with the shorter time ( $Q_1$ ), with the following values: for Ni (-62.2 for  $Q_1$ ; -62.5 for  $Q_3$ ); for Cd (-17.0 for  $Q_1$ ; -21.2 for  $Q_3$ ); for Pb (-3.44 for  $Q_1$ ; -3.51 for  $Q_3$ ).

### Dewatering efficiency

Table 5 shows the mean percentage values of Total Solids (TS %) and dewatering (%) which were much affected ( $P < 0.01$ ) by treatments.

The dewatering values were calculated as the percentage difference with respect to the control (treatment O). The addition of  $H_2O_2$  alone gives rise to TS values (range 27-29%) similar to the control (26.8%) with very low dewatering values (-0.65%; -2.96%). Fenton's reactions proved to be better than  $H_2O_2$  alone, with values of TS ranging from 37.8% to 44.2% and dewatering values from -15.0% to -23.8%; a contact time of 60 min proved to be as good as 180 min. The modified Fenton treatment proved to be better than classic Fenton for obtaining better TS values (range 44.0-44.2% vs. 37.8-38.1%) and for better dewatering percentages (range: -23.5; -23.8% vs. -15.0; -15.5%).

### Total organic carbon (TOC)

Table 6 shows data concerning TOC contents in sludge (expressed as  $g\ kg^{-1}\ DS$ ). When  $H_2O_2$  alone is used, no appreciable variation of TOC with respect to the control is observed (28.05  $g\ kg^{-1}\ DS$ -28.19  $g\ kg^{-1}\ DS$  vs. to 28.24  $g\ kg^{-1}\ DS$ ). In presence of Fenton's reactions a reduction of TOC is observed (range 25.64-26.57  $g\ kg^{-1}\ DS$ ) compared to the control (28.24  $g\ kg^{-1}\ DS$ ). The modified Fenton treatment gives higher values of TOC with respect to the classic Fenton (range 26.23  $g\ kg^{-1}\ DS$ -26.57  $g\ kg^{-1}\ DS$  with respect to 25.64  $g\ kg^{-1}\ DS$ -26.07  $g\ kg^{-1}\ DS$ ) with a value of 26.57  $g\ kg^{-1}\ DS$  for  $Q_3$  (180 min of contact time), significantly higher ( $P < 0.01$ ) than the values observed for the other treatments ( $R_1$ ,  $R_3$  and  $Q_1$ ) which employed Fenton's reaction.

Samples	$\Delta$ Zn %	$\Delta$ Ni %	$\Delta$ Cu %	$\Delta$ Cd %	$\Delta$ Pb %	$\Delta$ Cr %
P1	0.51 A*	-0.41 A	-0.02 B	0.39 A	-1.76 AB	1.18 B
P3	2.66 A	1.74 A	5.41 A	-0.16 A	0.26 AB	3.52 AB
R1	-66.9 B	-51.6 B	-8.73 C	-3.20 A	1.33 AB	3.21 AB
R3	-68.8 B	-52.1 B	-12.9 D	-3.45 A	1.94 A	5.31 A
Q1	-76.9 C	-62.2 C	-33.4 F	-17.0 B	-3.44 B	-4.14 C
Q3	-73.1 BC	-62.5 C	-19.0 E	-21.2 B	-3.51 B	-3.04 C

\* In this and the following tables statistical comparisons are intended for columns; capital letters point out significant ( $P < 0.01$ ) differences among means

Table 4: Mean values of percentage variations of PTEs leached; statistical comparisons following One-way ANOVA + LSD test.

samples	Total Solids %	Dewatering %
O	26.8 A	----
P1	29.0 B	-2.96 B
P3	27.3 AB	-0.65 A
R1	37.8 C	-15.0 C
R3	38.1 C	-15.5 C
Q1	44.0 D	-23.5 D
Q3	44.2 D	-23.8 D

Table 5: Mean values of percentages of Total Solids (TS) and dewatering; statistical comparisons following One-way ANOVA + LSD test.

samples	TOC ( $g\ kg^{-1}\ DS$ )
O	28.24 E
P1	28.19 ED
P3	28.05 D
R1	26.07 B
R3	25.64 A
Q1	26.23 B
Q3	26.57 C

Table 6: Mean values of Total Organic Carbon (TOC) content ( $g\ kg^{-1}\ DS$ ); statistical comparisons following One-way ANOVA + LSD test.

## Discussion

### Yields of leached PTEs

Working conditions for pH, ferrous ion and hydrogen peroxide concentrations were established when Advanced Oxidation Processes (AOP), such as Fenton or Fenton-like systems, were successfully employed to remove organic contaminants from wastewaters; a recent review, dealing with iron-free Fenton-like systems for activating  $H_2O_2$ , was published [13] which concerned the removal of organic pollutants

with high chemical stability and/or biodegradability. The setting up of the above mentioned parameters is still valid when Fenton or Fenton-like systems are applied before the extraction of heavy metals and/or PTEs from wastewaters [4]; here other chemical-physical processes (e.g. speciation) have to be held into consideration, together with the type of extraction (sequential, single) and the type of extractant (single acid, mixture of acids, chelating agents).

The reduction of pH alone, although sometimes allows instant metal solubilisation, as observed for Zn [14], failed for the majority of PTEs unless supported by an increase in the sludge Oxygen Reduction Potential (ORP); this could be caused by biological and chemical oxidation, obtained by  $H_2O_2$  addition [15]. The  $H_2O_2$  addition alone fails to reduce metal contents in a neutral environment and needs more acidic conditions through the use of different acids ( $H_2SO_4$ , HCl,  $HNO_3$ , etc.).

The pH is considered a key factor for the efficiency of Fenton and Fenton-like reactions, which consist in the activation of  $H_2O_2$  by ferrous ( $Fe^{2+}$ ) ions to generate hydroxyl radicals ( $HO\bullet$ ) via a complex reaction sequence (Fenton) [16-18]. The need for strictly acidic conditions is necessary for all AOP, such as Fenton's systems, because they are essential for preventing iron precipitation. The efficacy of the Fenton and Fenton-like processes to degrade organic compounds in wastewaters reaches its optimum at a pH of about 3 [7] and it is reduced at higher and lower pH levels.

At higher pH levels, the oxidation efficiency of Fenton's reagent may decrease because ferric ions could form  $Fe(OH)_3$  [19], which will not react with  $H_2O_2$ , because of its low activity [20]. The ferric ions in the solution that can react with  $H_2O_2$  are reduced with the reaction as follows:  $Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^+$ . This reaction is the rate-limiting step. Moreover, at high pH levels, the auto decomposition of  $H_2O_2$  is accelerated.

At very low pH levels, in presence of high  $H_2O_2$  concentrations, the formation of  $FeOOH^{2+}$  will slow down which consequently causes the production rates of ferrous ions and hydroxyl radicals to decrease as well. The earlier reaction may delay the Fenton reaction. Moreover at very low pH levels, an iron complex species  $[Fe(H_2O)_6]^{2+}$  exists, which reacts more slowly with hydrogen peroxide than the other species [21]. This phenomenon was also influenced by the concentration of ferrous ion present. In addition, the peroxide becomes solvated in the presence of high  $H^+$  ion concentrations to form stable oxonium ions  $[H_3O_2]^+$ . Oxonium ions make hydrogen peroxide more stable and reduce its reactivity with ferrous ions [22,23].

If Fenton or Fenton-like reactions are used in procedures with metal or PTE extraction, the above mechanisms are still valid, together with considerations concerning metal speciation and kinetics, due to different extraction procedures and types of extractant.

Our results strengthen the assumption of very low efficacy of  $H_2O_2$  use alone (pH about 8.0) for all investigated PTEs (Zn, Ni, Cu, Cd, Pb and Cr) both with 60 min and 180 min of contact time with  $H_2O_2$ . The use of classic Fenton's reaction improved the leached quotas much more than  $H_2O_2$  alone, by virtue of lower pH levels (3.34 for  $R_1$  and 3.32 for  $R_3$ ). The most leached PTEs were Zn (about 67%) and Ni (about 51%); at a lesser extent Cu (8-12%) and Cd (3.2-3.4%); no leaching was observed for Pb and Cr. The leached quota increased with increased contact times for  $H_2O_2$ , from  $R_1$  to  $R_3$ , for all PTEs.

The modified Fenton procedure, carried out at a further lower pH (pH  $\approx$  2.0), improved all quotas of the leached PTEs, with respect to

the classic Fenton procedure. This agrees with results of other authors (Lake) [24,25] About an increased extractability of metals following progressive acidification steps.

These results are consistent with those observed in trials made on extractability of metals (Zn, Cu, Cd and Pb), carried out on an anaerobically digested sludge with the use of three different acids: nitric acid, citric acid and oxalic acid [4]. For some PTEs (Ni, Cd and Pb) a longer contact time with  $H_2O_2$  allowed higher leached quotas, as occurred in the classic Fenton procedure. The amounts of Zn and Cr were slightly higher for lower times. The behaviour of Cu for which a sharp decrease of leached quota was observed for longer contact times was unusual. This could be explained, as observed by other authors (Marchioretto) [4], by the fact that Cu presents high affinity for organic complexes and a more prolonged contact time would have promoted the formation of Cu soluble complexes, more extractable with organic acids (e.g. citric or oxalic acid) than with  $HNO_3$ . These authors observed a percentage of 40.5% of Cu extracted by  $HNO_3$  at a pH=1.0, higher than our result (33.4% at pH=2.2). Low values of leached Pb and Cr were observed in this trial for the modified Fenton procedure in comparison with no values for the classic Fenton. A chemical leaching with HCl at a pH level of 1 should probably be adopted; this would allow a solubilisation of almost 100% of Pb and also provide the best extraction yield for Cr (72%) [4]. The low values of leached Pb were probably due to the formation of insoluble  $PbSO_4$  following the treatment with  $H_2SO_4$ ; a further acidification step with the use of HCl is probably needed to allow a complete Pb dissolution. For Cr, in order to increase the leached quota, the use of a closer digestion system (e.g. microwave oven) would be preferable instead of the open system used.

### Dewatering efficiency

The temperature, hydrogen peroxide concentration, pH and reaction time affect the dewaterability of the sludges [26]. Positive effects of Fenton's peroxidation on dewaterability of sludges were observed [7,27,28]. Fenton's reagent is known to have different treatment functions, depending on the  $H_2O_2/FeSO_4$  ratio [29]. When the amount of  $Fe^{2+}$  employed exceeds that of  $H_2O_2$ , the treatment tends to have an effect of chemical coagulation; when the two amounts are reversed, the treatment tends to have the effect of chemical oxidation [7,30,31]. In this study classic and modified Fenton reactions (respectively at pH 3.0 and 2.0) were performed in the presence of 3.58 g  $Fe^{2+}$   $kg^{-1}$  DS and with 62.5 g  $H_2O_2$   $kg^{-1}$  DS (ratio  $Fe^{2+}/H_2O_2$  equal to 0.057) which gave better dewatering results in preliminary trials than other tested ratios (0.028, 0.114 and 0.228) obtained by varying the amounts of  $H_2O_2$  added. The employed ratio (0.057) allowed us to obtain satisfactory results (about 23% of water reduction for modified Fenton and approx. 15% for classic Fenton). Good results were obtained by adding 1.67 g  $Fe^{2+}$   $kg^{-1}$  DS and 25 g  $H_2O_2$   $kg^{-1}$  DS (ratio  $Fe^{2+}/H_2O_2$  equal to 0.067) after proving other ratios with additions of quantities of  $H_2O_2$  variables in the range 5-50 g  $H_2O_2$   $kg^{-1}$  DS [26]. Good dewater ability results were also obtained with a lower ratio  $Fe^{2+}/H_2O_2$  (0.016) by using 20 g  $Fe^{2+}$   $kg^{-1}$  DS and 125 g  $H_2O_2$   $kg^{-1}$  DS [32]. In our study a time of 60 min proved to be good enough for dewatering, similar to times of 80 min [32], 60-90 min [26] and 30 min [9].

### Total organic carbon (TOC)

When  $H_2O_2$  alone is used no appreciable loss of TOC was observed (less than 1% 0); this agrees with observations of Authors (Neyens and Bayens) [7] in which the use of  $H_2O_2$  alone was not effective for decreasing high concentrations of certain refractory contaminants. The reduction of TOC was more pronounced (-8.44 on average) for

classic Fenton than for modified Fenton (-6.51% on average), both values being low, less than 10%. In general higher reduction values of organics are observed with the application classic Fenton to wastewater treatment. The reason for this can be found considering that classic Fenton process includes two steps: a 1<sup>st</sup> step where oxidation takes place at low pH (2.5-3.0) and a 2<sup>nd</sup> step where coagulation is observed at higher pH values; this last process (here not present) is retained to have a primary role in the selective removal of organics [7]. Moreover the modified Fenton treatment revealed more efficient than classic Fenton in maintaining high TOC values, in particular after 180 m of contact ( $Q_3$ ) time respect to a lower time (60 min) ( $Q_1$ ).

## Conclusions

This laboratory study highlights the importance of more acidic conditions (pH=2.0) to improve the efficacy of the classic Fenton reaction applied as a pre-treatment to the chemical leaching concerning PTEs contained in a municipal anaerobic sewage sludge. In this study a modified Fenton treatment, carried out at pH 2.0, proved to be more reliable than classic Fenton (approx. pH 3.0) in decreasing the contents of Zn, Ni, Cu and Cd, in increasing dry solids with a higher dewaterability percentage and in preserving higher amounts of TOC. Further research is needed to improve Pb and Cr removal aliquots.

## Acknowledgements

The Authors thank Mrs. Marina Modenesi (IREN, Municipal Purification Plant of Piacenza) for her kindness in supplying basic materials.

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