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Use of Fenton reaction for the treatment of leachate from composting of different wastes

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Abstract

The oxidation of leachate coming from the composting of two organic wastes (wastewater sludge and organic fraction of municipal solid wastes) using the Fenton's reagent was studied using different ratios $[Fe^{2+}]/[COD]_0$ and maintaining a ratio $[H_2O_2]/[COD]_0$ equal to 1. The optimal conditions for Fenton reaction were found at a ratio $[Fe^{2+}]/[COD]_0$ equal to 0.1. Both leachates were significantly oxidized under these conditions in terms of COD removal (77% and 75% for leachate from wastewater sludge composting and leachate from organic fraction of municipal solid wastes, respectively) and BOD_5 removal (90% and 98% for leachate from wastewater sludge composting and leachate from organic fraction of municipal solid wastes, respectively). Fenton's reagent was found to oxidize preferably biodegradable organic matter of leachate. In consequence, a decrease in the biodegradability of leachates was observed after Fenton treatment for both leachates. Nevertheless, Fenton reaction proved to be a feasible technique for the oxidation of the leachate under study, and it can be considered a suitable treatment for this type of wastewaters.

Keywords: BOD_5 removal, COD removal, Composting, Fenton reaction, Leachate.

1. Introduction

Solid waste management is becoming a global problem in developed countries. In recent years, the international policy on management of organic wastes has been increasingly directed towards recycling. There are different technologies to recycle organic wastes and composting is often presented as a low-technology and low-investment process to convert organic wastes to an organic fertilizer known as compost [1]. In Europe, huge amounts of organic municipal solid wastes and sludge are managed in composting facilities where these materials are processed. One of the main problems associated with the treatment of organic wastes in composting facilities is the management and treatment of leachates, which present a high organic load and cannot be stored in the plant.

Among chemical processes the Advanced Oxidation Processes (AOPs) has been used to reduce the organic load or toxicity of different waters and wastewaters [2,3]. AOPs are based on the generation of hydroxyl free radicals, which have a high electro-chemical oxidant potential. Among AOPs the Fenton's reagent [4] has been efficiently used as a chemical process for wastewater treatment and pre-treatment [5]. The Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions.

A wide variety of Fenton's reagent applications have been reported, such as treatment of textile wastewaters [2,6], reduction of Polynuclear Aromatic Hydrocarbons (PAH) in water [7], removal of Adsorbable Organic Halogens (AOX) from pharmaceutical wastewater [8], or treatment of paper pulp manufacturing effluents [9]. Among them, application of the Fenton reaction for the treatment of leachates has been recently reported and different conditions for the Fenton reaction have been studied [10-11]. However, these results have been obtained with landfill leachate, which is inherently different from composting leachate due to the aerobic conditions of the process and the use of “fresh” and “young” wastes. To our knowledge, there are no studies published on the use of the Fenton reaction to treat leachates from composting processes.

The objective of this work is to study the utilization of the Fenton reaction for the treatment of leachates coming from the composting of two typical organic wastes: wastewater sludge (WS) and organic fraction of municipal solid wastes (OFMSW). The efficiency of the Fenton process is evaluated in terms of reduction of organic matter load.

2. Materials and methods

2.1. Leachate collection

Different samples of leachates from the composting of wastewater sludge (mixed with pruning wastes) and source-selected organic fraction of municipal solid waste were collected from the composting plant of Jorba (Barcelona, Spain) during the period January-June of 2005. The results of the characterization of leachates (Table 1) are presented as average values with standard deviation. A complete description of the plant and the composting process can be found in [12].

2.2. Analytical procedures

Analytical procedures for the determination of chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), pH and electrical conductivity were conducted according to Standard Methods [13].

2.3. Fenton reaction

Fenton reaction was performed at 25ºC and atmospheric pressure. In all the experiments, the ratio $[H_2O_2]/[COD]_0$ (g/g) (total COD) was fixed to 1 whereas the ratio $[Fe^{2+}]/[COD]_0$ (mol/mol) was fixed at 0.5, 0.1 and 0.05. Concentrated hydrogen peroxide (33%, Panreac, Barcelona, Spain) was used to minimize the dilution effect associated to H_2O_2 addition (this dilution effect was considered in the calculation of BOD_5 and COD removal). pH of all samples prior to Fenton reaction was fixed to 3 by adding concentrated sulphuric acid. No precipitation was observed after pH adjustment. All the experimental conditions were performed in triplicate. Fenton reaction was concluded after 60 min, when no reaction was visually observed. A detailed description of the experimental procedure used to carry out the Fenton reaction can be found in [14].

2.4. Data analysis

Statistical significance of replicate values was carried out by means of F-test (variance analysis) and Student's t-test (mean analysis) both at 5% level of probability.

3. Results and discussion

3.1. Leachate characterization

The characterization of leachates from WS and OFMSW composting are shown in Table 1. As expected, both leachates presented a very high level of COD and BOD_5, whereas the ratio BOD_5/COD was around 0.5, which corresponded to a high level of biodegradability of the organic matter. These results are higher than those found in leachates from landfill, which usually present values of COD from 5 to 10 g/l and low values of biodegradability (ratio BOD_5/COD around 0.1) [10,11]. One possible explanation for this fact is that composting leachates consist of particulate and dissolved organic matter from fresh and young wastes instead of landfill leachate that is a mixture of different aged materials. The high levels of BOD_5 found (in the case of sludge composting even higher than that of dissolved COD) indicates that a significant amount of particulate organic matter is also degradable. This is often found when respiration tests are carried out with solid wastes or slurries [15]. Nevertheless, the values found for composting leachates are in the range of liquid streams that are being currently treated by AOPs [13,16]. Moreover, given the high values of COD and BOD_5, a biological process to treat composting leachates will not probably achieve legal requirements of water quality. In relation to pH, however, it must be pointed that the values found in WS and OFMSW leachates are far from those considered optimal for Fenton reaction, which is usually carried out at pH values below 4 [5].

3.2. BOD_5 and COD reduction by Fenton reaction

Fenton reaction was carried out on WS and OFMSW leachate samples at different levels of the ratio $[Fe^{2+}]/[COD]_0$ (0.5, 0.1 and 0.05), whereas the ratio $[H_2O_2]/[COD]_0$ (g/g) was fixed to 1. These experimental conditions were selected since they are commonly used in Fenton reaction. For instance, Kurt et al. [17] and Kim et al. [18] used a ratio $[H_2O_2]/[COD]_0$ equal to 1 for the treatment of different leachates and showed no significant differences in COD removal when this ratio was modified around the stoichiometric theoretical value (2), whereas the optimal ratio $[Fe^{2+}]/[COD]_0$ show a high variability in different studies treating different wastewaters [5,14,17,18].

Table 2 show the results of COD removal found for Fenton reaction. In both WS and OFMSW leachates the optimal ratio $[Fe^{2+}]/[COD]_0$ was 0.1, which produced a COD removal of 77 and 75% for WS and OFMSW, respectively. However, it must be pointed that precipitation of hydrated ferric oxides was observed when using high Fe^{2+} concentrations. In this case, it is probable that some of the COD removal may be associated to co-precipitation and not properly to Fenton reactions. Nevertheless, these results are in accordance to those found for landfill leachate [10,11], demonstrating the suitability of the Fenton reaction for the treatment of leachates from solid wastes with a high content of organic matter.

To study the effect of Fenton reaction on the biodegradability of composting leachates, the BOD_5 removal was studied for the optimal conditions found for COD reduction ($[Fe^{2+}]/[COD]_0 = 0.1$). Results are shown in Table 2. BOD_5 removal for both leachates was very high (90 and 98 % for WS and OFMSW respectively). In particular the results for BOD_5 removal were higher than those of COD removal. This can be also observed in the values of the final ratio BOD_5/COD, which clearly decreased after Fenton treatment (Table 2). One possible hypothesis for this is the fact that Fenton's reagent is likely to oxidize preferably biodegradable organic matter, which is also the major constituent of organic load found in composting leachates. These results are different from those recently found with mature landfill leachates, where Fenton treatment produces an increase in leachate biodegradability (increase in the ratio BOD_5/COD from 0.13 to 0.42) [19]. In this case, it is probable that mature landfill leachates are composed of more recalcitrant organic molecules and consequently a Fenton process can break down or rearrange molecular structures of organic matter and convert the non-biodegradable organics to more biodegradable forms. In the case of composting leachates, however, the organic compounds of leachate are mostly biodegradable and the Fenton process is likely to oxidize these compounds. Anyway, the results presented in this work demonstrate the suitability of the Fenton process to reduce organic load of composting leachates with extremely high values of COD and BOD_5.

Obtained results point that, since composting leachates have a relatively high BOD_5/COD ratio, the global treatment process should be composed of a first biological process with a posterior treatment with Fenton reaction. Fenton reaction could be proposed therefore as a post-treatment for the composting leachate, which have been previously treated by biological (aerobic or anaerobic) treatment. Contrarily, with landfill leachate, the Fenton reaction should be included in the treatment sequence as a pre-treatment [19].

4. Conclusions

From the data here presented, we can conclude that:

1) Leachate from the composting process of two typical organic wastes (WS and OFMSW) has been characterized in terms of organic load. The values found for both COD and BOD_5 were extremely high.

2) The optimal conditions for Fenton reaction were found at a ratio $[Fe^{2+}]/[COD]_0$ equal to 0.1 when the ratio $[H_2O_2]/[COD]_0$ was maintained to 1. Both leachates were significantly oxidized under these conditions in terms of COD removal (77% and 75% for WS and OFMSW leachate, respectively) and BOD_5 removal (90% and 98% for WS and OFMSW leachate, respectively).

3) Fenton reaction was found to oxidize preferably biodegradable organic matter of leachates, resulting in a significant reduction of the ratio BOD_5/COD for both leachates.

4) Fenton reaction proved to be a feasible technique for the oxidation of the leachate under study, and can be considered a suitable treatment for this type of wastewaters. The use of Fenton reaction, given the high biodegradability of composting leachate,

should be proposed as a post-treatment after biological treatment. The resulting effluent may be treated in a municipal wastewater treatment plant.

5) Further research on the use of the Fenton reaction to treat composting leachates should be focused on the improvement of the effectiveness of the organic matter removal by changing experimental conditions or by using other AOPs. The study of the oxidation of specific organic compounds found in composting leachate would be also of interest.

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References

1. R.T. Haug, The Practical Handbook of Compost Engineering, Lewis Publishers, Boca Raton, Florida, 1993.
2. M. Pérez, F. Torrades, X. Doménech, J. Peral, Fenton and photo-Fenton oxidation of textile effluents, Wat. Res. 36 (2002) 2703-2710.
3. L. Guzzella, D. Feretti, S. Monarca, Advanced oxidation and adsorption technologies for organic micropollutant removal from lake water used as drinking-water supply, Wat. Res. 36 (2002) 4307-4318.
4. H.J.H. Fenton, Oxidation of tartaric acid in the presence of iron, J. Chem. Soc. 65 (1894) 899-910.
5. E. Neyens, J. Baeyens, A review of classic Fenton’s peroxidation as an advanced oxidation technique, J. Hazard. Mater. B98 (2003) 33-50.

6. S.F. Kang, C.H. Liao, M.C. Chen, Pre-oxidation and coagulation of textile wastewater by the Fenton process, Chemosphere 26 (2002) 923-928.

7. F.J. Beltrán, M. González, F.J. Rivas, P. Alvarez, Fenton reagent advanced oxidation of polynuclear aromatic hydrocarbons in water, Water Air Soil Poll. 105 (1998) 685-700.

8. C. Hölf, S. Sigl, O. Specht, I. Wurdack, D. Wabner, Oxidative degradation of AOX and COD by different advanced oxidation processes: a comparative study with two samples of a pharmaceutical wastewater, Wat. Sci. Technol. 35 (1997) 257-264.

9. M. Pérez, F. Torrades, J.A. García-Hortal, X. Doménech, J. Peral, Removal of organic contaminants in paper pulp treatment effluents under Fenton and photo-Fenton conditions, Appl. Catal. B: Environ. 36 (2002) 63-74.

10. H. Zhang, H.J. Choi, C.P. Huang, Optimization of Fenton process for the treatment of landfill leachate, J. Hazard. Mater. B125 (2005) 166-174.

11. F.J. Rivas, F. Beltrán, F. Carvalho, B. Acedo, O. Gimeno, Stabilized leachates: sequential coagulation–flocculation + chemical oxidation process, J. Hazard. Mater. B116 (2004) 95-102.

12. R. Barrena, E. Pagans, G. Faltys, A. Sánchez, Effect of inoculum dosing on the composting of source-selected organic fraction of municipal solid wastes, J. Chem. Technol. Biotechnol. 81 (2006) 420-425.

13. APHA, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, USA, 1998.

14. N. San Sebastián, J. Fíguls, X. Font, A. Sánchez, Pre-oxidation of an extremely polluted industrial wastewater by the Fenton’s reagent, J. Hazard. Mater. B101 (2003) 315-322.

15. R. Barrena, F. Vázquez, M.A. Gordillo, T. Gea, A. Sánchez. Respirometric Assays at Fixed and Process Temperatures to Monitor Composting Process. Bioresource Technol. 96 (2005) 1153-1159.

16. M. Ahmadi, F. Vahabzadeh, B. Bonakdarpour, E. Mofarrah, M. Mehranian, Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation, J. Hazard. Mater. B123 (2005) 187-195.

17. U. Kurt, M.T. Gonullu, Y. Avsar, E. Arslankaya, Research on Treatability of Young Landfill Leachates by Fenton's Reaction, in: ISWA 2002 World Environmental Congress & Exhibition, 8-12 July, Istanbul, 2002, pp. 901.

18. S.M. Kim, S.U. Geissen, A. Vogelpohl, Landfill leachate treatment by a photoassisted fenton reaction, Wat. Sci. Technol. 35 (1997) 239-248.

19. J. Lopes, P. Peralta, Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates, J. Hazard. Mater. B123 (2005) 181-186.

Tables

Table 1: Characterization of leachate from organic fraction of municipal solid waste and wastewater sludge.

Parameter	Leachate from wastewater sludge composting	Leachate from municipal solid waste composting
Total COD (g/l)	132 ± 8	177 ± 8
Dissolved COD (g/l)	65 ± 6	117 ± 2
BOD_5 (g/l)	71 ± 1	87 ± 2
Ratio BOD_5/COD	0.54	0.49
pH	7.11 ± 0.03	6.16 ± 0.02
Elec. conductivity (mS/cm)	47.1 ± 0.4	51.6 ± 0.5
Colour	black	dark brown

Table 2: BOD_5 and COD removal obtained by the Fenton's Reaction for the leachate under different conditions.

Sample	Experimental conditions $[Fe^{2+}]/[COD]_0$	Total COD removal (%) *	BOD_5 removal (%)	Final ratio BOD_5/COD
Leachate from wastewater sludge composting	0.5	74 ± 10 a	-	-
	0.1	77 ± 8 a	90 ± 2	0.23
	0.05	58 ± 6 b	-	-
Leachate from municipal solid waste composting	0.5	57 ± 11 c	-	-
	0.1	75 ± 8 d	98 ± 2	0.04
	0.05	59 ± 5 c	-	-

* Different letters indicate significant statistical difference.