Bioresource Technology 146 (2013) 126–134

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Microwave-assisted chemical oxidation of biological waste sludge: Simultaneous micropollutant degradation and sludge solubilization

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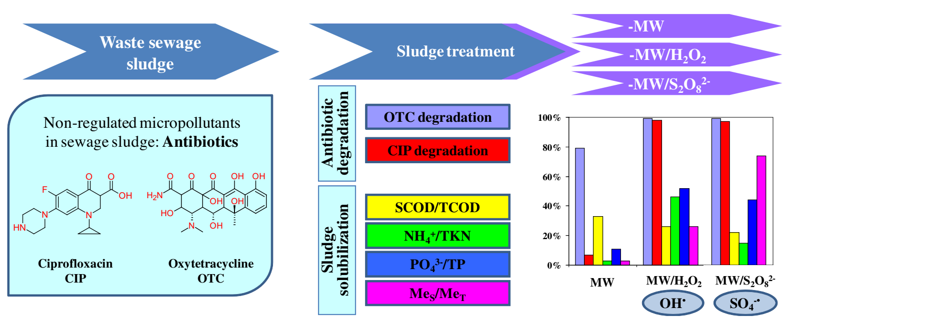
HIGHLIGHTS

- Comparison of MW/H_2O_2 and $MW/S_2O_8^{2-}$ for sludge treatment.
- Oxidant dosing is crucial for recalcitrant antibiotic degradation.
- $MW/S_2O_8^{2-}$ offers effective treatment at shorter periods and lower temperatures.
- 40–75% metal solubilization and enhanced filterability of sludge with $MW/S_2O_8^{2-}$.
- $MW/S_2O_8^{2-}$ oxidizes solubilized ammonia to nitrate.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 May 2013
Received in revised form 5 July 2013
Accepted 11 July 2013
Available online 19 July 2013

Keywords:
Biological waste sludge
Antibacterial micropollutants
Microwave
Advanced oxidation processes
Sludge treatment

ABSTRACT

Microwave-assisted hydrogen peroxide (MW/H_2O_2) treatment and microwave-assisted persulfate ($MW/S_2O_8^{2-}$) treatment of biological waste sludge were compared in terms of simultaneous antibiotic degradation and sludge solubilization. A 2^3 full factorial design was utilized to evaluate the influences of temperature, oxidant dose, and holding time on the efficiency of these processes. Although both MW/H_2O_2 and $MW/S_2O_8^{2-}$ yielded $\geqslant$97% antibiotic degradation with 1.2 g H_2O_2 and 0.87 g $S_2O_8^{2-}$ per gram total solids, respectively, at 160 °C in 15 min, $MW/S_2O_8^{2-}$ was found to be more promising for efficient sludge treatment at a lower temperature and a lower oxidant dosage, as it allows more effective activation of persulfate to produce the $SO_4^{\cdot-}$ radical. Relative to MW/H_2O_2, $MW/S_2O_8^{2-}$ gives 48% more overall metal solubilization, twofold higher improvement in dewaterability, and the oxidation of solubilized ammonia to nitrate in a shorter treatment period.

1. Introduction

The presence of a wide variety of emerging micropollutants in sewage sludge (Oncu Bilgin and Balcioglu Akmehmet, 2013a; Stasinakis, 2012; Clarke and Smith, 2011) has increased concerns regarding sludge disposal on land. Challenges associated with the ever-growing volumes of sludge produced from biological wastewater treatment processes in combination with the motivation to recycle the valuable constituents of sludge have brought land application as a means of reusing biosolids in a beneficial way to the forefront. To minimize the potential risk of pathogens and heavy metals in the environment, waste sludge needs to be stabilized prior to land application. However, conventional stabilization methods such as anaerobic or aerobic digestion and composting cannot destroy many nonregulated organic micropollutants as a result of strong sorption on particulate matter (Stasinakis, 2012).

Currently, studies dealing with waste sludge management are aimed at improving the efficiency of the biological stabilization process (Carrere et al., 2010) and the physical properties of the waste sludge (Li et al., 2008) and at recovering valuable nutrients in the sludge (Tyagi and Lo, 2013). For these purposes, various mechanical, thermal, and chemical processes have been used. However, removal of micropollutants from waste sludge has only been investigated in a limited number of studies (Oncu Bilgin and

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http://dx.doi.org/10.1016/j.biortech.2013.07.043

Balcioglu Akmehmet, 2013b; McNamara et al., 2012; Carrere et al., 2006), and it requires significant care. During sludge treatment, the degradation efficiency of organic micropollutants is known to be rather low and dependent on their thermal stability (McNamara et al., 2012) and their strong tendency to sorb on sludge (Oncu Bilgin and Balcioglu Akmehmet, 2013b; Carrere et al., 2006).

Among various organic micropollutants, antibacterial substances deserve specific attention because they spread into the environment in an uncontrolled way, and this is thought to increase the rate of the development of antibacterial resistance in microorganisms (Oncu Bilgin and Balcioglu Akmehmet, 2013a). Therefore, secondary pollution is created. Moreover, antibiotics, and in particular those from the tetracycline and fluoroquinolone groups, have been detected in sludge at concentrations of milligram per kilogram (Oncu Bilgin and Balcioglu Akmehmet, 2013a). As for ciprofloxacin, an antibiotic from the fluoroquinolone group, a sludge concentration of 97.5 mg/kg was detected (SFT, 2007), and long-term persistence in soil was reported (Golet et al., 2003). A recent study demonstrated that environmental concentration of ciprofloxacin and tetracycline could exert selective pressure and increase the prevalence of resistant bacteria in soil (Tello et al., 2012).

Of the sludge treatment processes, microwave (MW) technology has attracted much interest lately, as it can rapidly and homogeneously heat a sample, which allows effective sludge disintegration, conditioning, and pathogen destruction (Wu, 2008). This technology can be utilized as a stand-alone pretreatment process for sludge solubilization or in combination with chemical oxidation to provide further improvement in sludge disintegration and nutrient recovery (Tyagi and Lo, 2013). In a number of studies, it was demonstrated that hydrogen peroxide, the most commonly used reagent for oxidation, synergistically enhances the solubilization of sludge in MW/H_2O_2 treatment (Tyagi and Lo, 2013; Eskicioglu et al., 2008; Wong et al., 2007). Without MW assistance, it is possible to use hydrogen peroxide and persulfate to enhance sludge dewaterability (Zhen et al., 2012a–c); however, as far as it is known, neither the influence of MW treatment on the fate of micro-organic pollutants in waste sludge nor the combined application of persulfate with MW for sludge treatment have been investigated. Given that the effect of MW irradiation on the desorption of organic pollutants (Wu et al., 2008) is known and that the strong oxidative power of hydrogen peroxide and persulfate on the degradation of organics in solid matrices is also known (Uslu Otker and Balcioglu Akmehmet, 2009), the benefits of a combined process are clear.

In this study, the degradation of sorbed antibacterial micro-organic pollutants in sewage sludge was investigated during MW/H_2O_2 and MW/$S_2O_8^{2-}$ treatments, which were performed in laboratory-scale experiments under different conditions. For this purpose, two antibacterial micropollutants that are commonly detected in sludge, that is, the antibiotics oxytetracycline (OTC) and ciprofloxacin (CIP), were added to the sludge to study the effects of selected operational parameters and their interactions on the efficiency of the applied processes. The efficiency of MW/H_2O_2 and MW/$S_2O_8^{2-}$ on the solubilization of metals as a regulated micropollutant group and on the solubilization of organic matter and nutrients was also studied. Furthermore, efforts were made to recognize the contribution of a radical mechanism during the combined MW treatment and chemical oxidation.

2. Methods

2.1. Preparation of antibiotic-contaminated sewage sludge

The secondary sewage sludge used in this study was obtained from the recirculation line of a municipal wastewater treatment plant (500,000 population equivalent) located in Istanbul, Turkey. The plant employs an anaerobic–anoxic–oxic biological process and operates with a sludge age of about 20 days. The physicochemical parameters of the raw sludge samples and their mean values over the course of the experiments are listed in Table 1.

After concentrating the sludge by centrifugation, the total solid concentration was adjusted to 10.0 ± 0.1 g/L by following a previously described procedure (Oncu Bilgin and Balcioglu Akmehmet, 2013b). In the treatment experiments, synthetically contaminated secondary sewage sludge was used, and the sludge was spiked with both antibiotics, OTC ($C_{22}H_{24}N_2O_9 \cdot HCl$, >95%) and CIP ($C_{17}H_{18}FN_3O_3 \cdot HCl$, 99%), by taking into account the concentrations of these antibiotics already present in the sludge. In the majority of the experiments, the concentration of the antibiotic was 2 mg/g total solids (TS). However, the performance of the treatment processes was also tested with an environmentally relevant antibiotic concentration of 0.08 mg/g TS. Prior to the sludge treatment experiments, the antibiotic-spiked sludge was equilibrated to provide >95% CIP and OTC sorption, which was verified by dissolved and total antibiotic analyses.

2.2. Treatment of sewage sludge with MW/H_2O_2 and MW/$S_2O_8^{2-}$

The treatment of sewage sludge was performed with a bench-scale microwave irradiation system (Berghof, Speedwave MWS-3, 2.54 GHz), which had the capacity to accommodate up to 12 TFM vessels (each with a volume of 60 mL) and could be operated at a maximum temperature, power, and pressure of 230 °C, 1450 W, and 4000 kPa, respectively. After the addition of either hydrogen peroxide, H_2O_2 (30% w/w), or sodium persulfate, $Na_2S_2O_8$ (>98%), to 25 mL of the sludge sample, the samples were treated in closed vessels under predetermined experimental conditions. The temperature of the sludge samples placed in the MW system was increased at a rate of 10 °C/min. Separate experiments in which no oxidant was added were also performed under the same MW conditions.

Of the treatments applied to the sludge, only the MW/H_2O_2 treatment consisted of a preheating stage. Before dosing hydrogen peroxide, all of the samples were heated at 120 °C for 15 min to destruct the biological enzymes in the sludge, whereby undesirable consumption of hydrogen peroxide would be prevented (Wang et al., 2009). In all of the experiments, no effort was made to adjust the pH of the sludge. At the end of the treatment period and before carrying out subsequent analyses, the vessels were inserted in an ice bath without opening the caps and cooled to room temperature to avoid evaporation.

2.3. Experimental design

To explore the effects of the selected variables on the efficiency of the MW/H_2O_2 and MW/$S_2O_8^{2-}$ treatments, a 2^3 full factorial

Table 1
Characteristics of raw secondary sewage sludge.

Sludge properties		Metals	
Parameter	Value	Metals	Sludge concentrations (mg/kg DS)
TS (g/L)	12.2 ± 0.3	Ni	321 ± 8
VS/TS (%)	57 ± 5	Cr	605 ± 12
TCOD (g/L)	10.4 ± 0.1	Cu	544 ± 85
SCOD (mg/L)	105 ± 7	Zn	909 ± 98
TKN (mg/L)	430 ± 7	Cd	BLD
NH_4^+	1.0 ± 0.4	Pb	BLD
NO_3^-	4.2 ± 0.3	Fe	13,877 ± 97
TP (mg/L)	847 ± 32	Mn	563 ± 67
PO_4^{3-} (mg/L)	61.0 ± 9.5		
pH	6.5–7.0		
Alkalinity (g/L)	1.5		

BLD, below limit of detection.