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The impact of ferrous iron/heat-activated persulfate treatment on waste sewage sludge constituents and sorbed antimicrobial micropollutants

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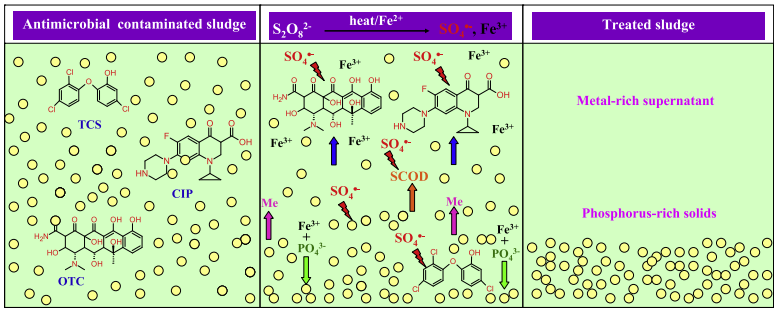
HIGHLIGHTS

- Investigation of Fe^{2+}/heat-activated persulfate for sludge treatment.
- Sulfate radical mechanism promotes degradation of sorbed antimicrobials.
- Complexation of zwitterionic antibiotics with Fe^{3+} promotes their desorption.
- Remarkable degree of micropollutant and metal removal from waste sewage sludge.
- Addition of Fe^{2+} enhances solubilization of the metal and the recovery of phosphorus.

GRAPHICAL ABSTRACT



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ABSTRACT

The fate of the antimicrobial micropollutants oxytetracycline (OTC), ciprofloxacin (CIP), and triclosan (TCS) as well as that of the different constituents of sludge during treatment with ferrous iron and heat activated persulfate (Fe^{2+}/heat/$S_2O_8^{2-}$) was investigated with full factorial experimental design methodology. Owing to a sulfate radical mechanism, considerable degradation of the micropollutants was achieved in the sludge. Iron promoted the degradation of the zwitterionic OTC and CIP antibiotics, recovered the phosphorus in the solid phase of the sludge, and enhanced the solubilization of the metal. The average degradation rates of OTC, CIP, and TCS were 95%, 84%, and >99%, respectively, whereas the overall rate of solubilization of the metal and the rate of precipitation of phosphate were 53% and 74%, respectively with $S_2O_8^{2-}$ = 22.7 mM and $Fe^{2+}/S_2O_8^{2-}$ = 0.5 at 75 °C in 120 min.

1. Introduction

Land application of biosolids is a common means of handling waste sewage sludge, and it enables both the management of large sludge quantities and the recycling of valuable nutrients. However, owing to the widespread utilization of various human-made products by modern society, biosolids also contain a vast cocktail of organic micropollutants [1,2]. Many organic micropollutants are sequestered in the sludge as a result of sorption during wastewater treatment [3]. Although sorbed micropollutants in sludge have not received much interest because of expected environmental risk minimization by fixation in the solid phase [2], their release through the land application of biosolids can pose a threat to the environment and public health. Of specific concern are antimicrobial compounds, the spread of which in the environment can cause ecotoxicological effects in organisms and, more importantly, can increase the prevalence of antimicrobial resistance [4]. Recent studies suggest that concurrent contamination of soil with other organic micropollutants may influence the fate of the sorbed antimicrobials. For example, it was reported that soil irrigation with surfactant-rich wastewater can lead to leaching of oxytetracycline (OTC) [5]. Moreover, even if bound to the solid phase, antimicrobial

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compounds can still retain their bioactivity [6] and continue to assist resistance development in soil microorganisms [7]. These facts suggest that preventive measures should also be taken to remove sorbed micropollutants in sludge to encourage the use of biosolids on land.

Chemical oxidation processes, especially advanced oxidation processes (AOPs), have already been used to treat sludge to accelerate the anaerobic digestion of waste sludge [8], to improve sludge dewaterability [9,10], and to reduce waste-sludge volumes; however, the fate of organic micropollutants including pharmaceuticals, polyaromatic hydrocarbons, polychlorinated biphenyls, and phthalates during application of these processes has been investigated in only a few studies [11–19]. The majority of the AOPs investigated for sludge treatment are based on the use of hydrogen peroxide (H_2O_2) as the oxidant for the generation of the hydroxyl radical (HR), which can nonselectively oxidize a wide variety of sludge components. However, this process can cause rapid consumption of the oxidants by sludge constituents without achieving degradation of the target micropollutants, especially in the presence of large amounts of organic matter [17]. As opposed to the HR, the sulfate radical (SRA), which can be obtained by activation of persulfate with various agents, exhibits high reactivity towards certain (e.g. carboxylic, anilinic, and phenolic) functional groups [20] and is more suitable for the removal of target micropollutants in complex matrixes with a high organic content [17]. Degradation of antimicrobial compounds in water and wastewater by peroxydisulfate and peroxymonosulfate activated with various agents has been explored in different studies (e.g. for antibiotics [21–23]). Recently, microwave (MW) activated peroxydisulfate (PDS) was applied to waste sludge to destruct two antimicrobials, OTC and ciprofloxacin (CIP) [17]. Although MW is an excellent aid for the activation of PDS in relatively short periods of time [17,23] and although it can also result in the desorption of certain micropollutants, the concurrent fast desorption of organic matter from the sludge induces a competitive influence on the oxidation of micropollutants [17]. Activation of PDS with iron at ambient temperature is another alternative, and this treatment system was shown to enhance the dewaterability of waste sludge [9,10]. In addition, Zhen et al. [24] demonstrated the effectiveness of the simultaneous application of heat at mild temperatures up to 80 °C with Fe^{2+} for persulfate activation in enhancing sludge dewaterability. It was also shown that this way of combined use of iron and heat for the activation of persulfate can accelerate and enhance micropollutant degradation and mineralization in aqueous medium [25,26]. A similar approach for the effective degradation of sorbed micropollutants in sewage sludge can be promising for the production of a safe sludge matrix.

In light of the above-mentioned facts, this study aimed to investigate the potential of persulfate oxidation for the degradation of antimicrobial micropollutants that exhibit different sorption behavior in waste sewage sludge. Two zwitterionic antibiotics, that is, OTC, ciprofloxacin (CIP), and a hydrophobic antibacterial, that is, triclosan (TCS), were selected as model micropollutants on the basis of their frequent detection rates and the aforementioned environmental risks. The simultaneous solubilization of secondary sewage sludge and the contribution of free radicals on micropollutant degradation were also investigated in this study.

2. Materials and methods

2.1. Preparation of antimicrobial contaminated sludge

Secondary sewage sludge was obtained from a municipal wastewater treatment plant in Istanbul that has a wastewater treatment capacity of 500,000 population equivalent (average flow of 100,000 m^3/d). The physico-chemical characteristics of the raw secondary waste sludge were: pH 6.6 ± 0.3, total solids (TS) = 16.8 ± 0.1 g/L, total COD (TCOD) = 10.6 ± 6.8 g/L, total phosphorus (TP) = 954.5 ± 98.3 mg/L (n = 6) (Table S1, Supplementary data). While the sludge contained high concentrations of organic carbon and nutrients, very little of these were present in the soluble form.

Prior to the experiments, the TS content of the sludge was adjusted to a constant value to maintain consistency throughout the experiments, as in the case of previous studies [16,17]. For this purpose, the sludge was thickened and then diluted to an average TS concentration of 10 g/L by using either distilled water or aqueous solutions of OTC (Sigma), CIP (Mp. Biomedicals), and TCS (Irgasan, Sigma). By taking into account the concentrations of the target micropollutants already present in the sludge, their initial concentrations were adjusted to 1 mg/L, which corresponds to 100 mg/kg TS in the sludge, by spiking. Then, the sludge was equilibrated in a temperature-controlled water bath at 200 rpm and 25 ± 5 °C for 90 min to ensure homogeneous distribution and >95% micropollutant sorption.

2.2. Treatment of sewage sludge

The oxidizing agent used for sludge treatment was PDS. All treatment experiments were performed in polytetrafluoroethylene (PTFE) tubes (50 mL capacity) under temperature-controlled conditions. Unless otherwise noted, the treatment period for all experiments was 120 min. Treatment was initiated by the successive addition of doses of Fe^{2+} ($FeSO_4{\cdot}7H_2O$, Sigma–Aldrich) and PDS ($Na_2S_2O_8$, Sigma–Aldrich) to the sludge (25 mL), which was heated to the desired temperature prior to the addition of the chemicals. No effort was made to adjust the pH of the sludge. At the end of each experiment, the tubes were immersed in an ice bath before opening the caps to avoid evaporation and then the samples were immediately analyzed.

A priori and on the basis of a literature survey on PDS treatment [9,10,24,27,28], three factors were considered: temperature, oxidant dose, and the molar ratio of $Fe^{2+}/S_2O_8^{2-}$. The effectiveness of the treatment was evaluated in terms of micropollutant degradation and sludge solubilization. Considering that this work was performed with real sludge samples, experimental design methodology with a full factorial design was used to obtain the maximum realistic information with the minimum number of experiments. For each of the three factors, two levels were examined (2^3) (Minitab 17 statistical software, Minitab Inc.), which were coded as high (+) and low (−), and the center point was denoted 0. A total of 19 random experiments were performed, including replicates for each corner point and three replicates at the center point. The experimental range and the levels of the independent variables are given in Table 1.

Preliminary experiments were accomplished to determine the extreme values (i.e., corner points) of the variables shown in Table 1.

2.3. Analytical methods

2.3.1. Micropollutant extraction and analysis

Micropollutant extraction from both the liquid phase and the solid phase was performed after centrifugation of the sludge

Table 1
Independent variables and their levels used in the 2^3 full factorial design for sewage sludge treatment with Fe^{2+}/heat/$S_2O_8^{2-}$.

Experimental factors	Symbol	Level (−)	Level (0)	Level (+)
Temperature (°C)	*A*	40.0	57.5	75.0
$S_2O_8^{2-}$ dose (mM)	*B*	8.0	15.4	22.7
$Fe^{2+}/S_2O_8^{2-}$ (molar ratio)	*C*	0.50	0.87	1.25