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Degradation of chlortetracycline in wastewater sludge by ultrasonication, Fenton oxidation, and ferro-sonication

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ABSTRACT

Residual emerging contaminants in wastewater sludge remain an obstacle for its wide and safe applications such as landfilling and bio-fertilizer. In this study, the feasibility of individual ultrasonication (UlS) and Fenton oxidation (FO) and combined, Ferro-sonication processes (FO) on the degradation of chlortetracycline (CTC) in wastewater sludge was investigated. UlS parameters such as amplitude and sonication time were optimized by response surface methodology (RSM) for further optimization of FS process. Generation of highly reactive hydroxyl radicals in FO and FS processes were compared to evaluate the degradation efficiency of CTC. Increasing in the ratio of hydrogen peroxide and iron concentration showed increased CTC degradation in FO process; whereas in FS, an increase in iron concentration did not show any significant effect ($p > 0.05$) on CTC degradation in sludge. The estimated iron concentration in sludge (115 mg/kg) was enough to degrade CTC without the addition of external iron. The only adjustment of sludge pH to 3 was enough to generate *in-situ* hydroxyl radicals by utilizing iron which is already present in the sludge. This observation was further supported by hydroxyl radical estimation with adjustment of water pH to 3 and with and without the addition of iron. The optimum operating UlS conditions were found to be 60% amplitude for 106 min by using RSM. Compared to standalone UlS and FO at 1:1 ratio, FS showed 15% and 8% increased CTC degradation respectively. In addition, UlS of sludge increased estrogenic activity 1.5 times higher compared to FO. FS treated samples did not show any estrogenic activity.

1. Introduction

Tetracyclines (TCs) are the most commonly used antibiotics in veterinary life for therapeutic and prophylactic purposes. Up to 90% of TCs are excreted as parent compound after administration in all kinds of living systems [1] via urine and feces. Consequently, these TCs have been detected in wastewater (0.3–62 μg/L [2,3]), wastewater sludge (15 μg/kg–7.1 mg/kg [4]), and in animal manure (91 mg/kg [5]), samples. Further usage of this wastewater and biosolids produced from animal manure and wastewater sludge (WWS) containing these residual TCs in irrigation of agricultural fields and as biofertilizer results in contamination of soil. Hence, the land application of biosolids will be the point source for the accumulation of TCs in soil and further leaching into water sources, which cause food chain contamination.

Currently abundance of TCs antibiotic resistance genes were identified in wastewater [6] and also increased levels of TCs antibiotic resistance in the soil after using biosolids of animal manure and biosolids of wastewater treatment plant (WWTP) [7]. Hence, waste management practices seems to be control the accumulation, development and spread of resistance; which has become a major threat to human and environmental ecology owing to toxicity. Consequently, upgrading the existing regulations to improve the efficiency of WWTPs resulted in increased biosolids production [8–10]. Even, biosolids application in soils is ever increasing because of safe and efficient waste disposal and resourceful utilization of fertilizer value of biosolids [11]. So the adoption of advanced oxidation processes (AOPs) for removing residual contaminants including TCs in WWS significantly represent a tool for the production of safe biosolids.

Chlortetracycline (CTC) is the former antibiotic of TCs family and most commonly used in veterinary infections. CTC form complexes with metals which decrease the solubility of CTC and

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also its strong adsorption to organic matrix directly or through metal bridging makes CTC high partitioning into the WWS instead of wastewater [3,12,13]. Even lower biodegradation of CTC in sludge in conventional treatment processes, such as composting and stabilization [14] makes CTC accumulation in biosolids. Furthermore, CTC is the most phototoxic compound among TCs and has showed chlorosis at 100 μg/L in *Lemna gibba* [15]. Considering these, it is necessary to mineralize CTC in WWS before using it in the production of bio-fertilizer. Studies revealed that AOPs are efficient in degrading recalcitrant compounds in complex matrices, such as sludge and soil. Hence, it is necessary to evaluate AOPs to effectively remove organic pollutants including CTC from sludge before its final discharge into the environment.

WWS have high solids concentration and complex matrix; so that it is difficult to apply AOPs efficiently to mineralize toxic compounds including CTC. Mass transfer is the major limiting factor for application of ultraviolet irradiation, ozonation and Fenton oxidation (FO) AOPs in WWS. Ultrasonication (UlS) AOP can overcome this limitation by increasing the solubilization of sludge and this process has been reported to be more efficient in lesser time [17] compared to mechanical, thermal, chemical and biological methods to break down the sludge. But the production of hydroxyl radicals ($OH^{\cdot}$) in UlS is not efficient as ozonation and FO processes for effective mineralization of toxic compounds. Hence, combined UlS AOP with ozonation or FO processes treatment might have the synergistic effect and overcome these problems (decreased mass transfer resistance and boost $OH^{\cdot}$). Among AOPs, FO has more capability to destroy refractory organic pollutants in complex matrixes [18] and studies proved that FO process efficiency was enhanced by sludge reduction and effectiveness in operating cost when coupled with UlS [19]. More importantly, accumulation of CTC in sludge by adsorption to solids directly or by metal bridging to perform sludge solubilization or disintegration to release bound CTC into free form for further effective degradation.

In this context, UlS AOP combined with FO process definitely will have a synergistic impact by solubilization of sludge solids and release and degradation of CTC. Further, the released CTC will be simultaneously degraded by FO process. Combined UlS and FO treatment may not be efficient in complete mineralization of CTC and also form different oxidative by-products as sludge contain diverse contaminants. In order to determine the safety of treatment and formed intermediate compounds, it is desirable to estimate the toxicity of sludge after treatment. The present work aims to evaluate the efficacy of combined UlS and FO process compared to individual treatments in degrading selected antibiotic CTC in WWS. In the first part of this work, optimization of UlS process parameters, such as time and ultrasonic frequency was performed using response surface methodology (RSM). And further combined UlS and FO that is ferro-sonication (FS) process efficiency in degrading CTC was investigated by using optimized UlS parameters in WWS. Individual and combined treatment parameters were explored to determine the synergistic effect of FS on CTC degradation. In the second part, formed degradation products are analyzed and compared; further change in the toxicity of sludge following treatments is measured by using yeast estrogenicity screening (YES) assay and discussed along with degradation products.

2. Material and methods

2.1. Chemicals

Chlortetracycline hydrochloride (99% purity) was purchased from Toronto Research Chemicals (Toronto, Canada). Disodium ethylenediaminetetraacetate (Na_2H_2EDTA, 99%) was purchased from E-bay (Tokyo, Japan). Ammonium hydroxide (NH_4OH, 28–30% w/w) and methanol (HPLC grade, purity > 99.8%) were purchased from Fisher Scientific (Ontario, Canada). The beef extract was purchased from Quelab Laboratories inc. (Montreal). Sodium dibasic phosphate (K_2HPO_4), sodium hydroxide (NaOH, 10 N) and sodium monobasic phosphate (KH_2PO_4) was supplied by Laboratoire MAT Inc. (Quebec, Canada). Calcium chloride anhydrous ($CaCl_2$, >99%), magnesium perchlorate anhydrous ($Mg(ClO_4)_2$, >99%), cupric chloride anhydrous ($CuCl_2$, >99%), urea (>99%), iron sulfate heptahydrate ($FeSO_4.7H_2O$; 99% analytical grade), hydrogen peroxide (H_2O_2; 30%) and chromium nitrate ($(CrNO_3)_3.9H_2O$) were obtained from Fisher scientific (New Jersey, USA). pH of the WWS was adjusted by using H_2SO_4 (10 N) or NaOH (5 M) (Merck, US). N, N-Dimethyl-4-nitrosoaniline (RNO, 97%) was purchased from Sigma-Aldrich (Canada). Milli-Q/Millli-Ro Milli pore system (Milford, MA, USA) was used to prepare HPLC grade water in the laboratory.

2.2. Wastewater sludge sampling and characterization

Wastewater sludge used in this study was collected from Quebec Urban Community (CUQ) WWTP (Sainte-Foy, Quebec City, Quebec, Canada) which has a sewage treatment capacity of 13,140 m^3/h. Sludge samples were collected from sludge thickening source in WWTP and stored under dark conditions at 4 ± 1 °C to prevent degradation of CTC. Basic characterization of sludge, such as pH, total solids (TS), suspended solids (SS), volatile solids (VS), soluble chemical oxygen demand (SCOD) was carried out as per the standard methods [22]. The specific characteristics of WWS used in this study are presented in Table 1.

2.3. Experimental design and optimization by response surface methodology (RSM)

Experimental design and optimization of multivariable system (UlS) was carried out by using RSM. In this study, initial optimization of independent variables (UlS time and amplitude) for optimal response of CTC degradation and its release into the supernatant was obtained by RSM. The responses are displayed in three-dimensional plots as a function of independent factors. Effect of independent variables: sonication time and amplitude of UlS was investigated for degradation in sludge and release of CTC into the supernatant as dependable variables using second order central composite design (CCD). CCD with a quadratic surface is usually appropriate for the process optimization. Independent variables and their experimental range are given in Table 2.

Thirteen experiments were carried out according to the central composite to evaluate two UlS independent variables. The following quadratic (second-order) polynomial equation was used to fit the experimental results (see Appendix A, Eq (1)).

Where y is the predicted response, β_0 is the model intercept; β_i and β_{ij} are the coefficients of linear terms; β_{ii} is the coefficient of the quadratic term; X_i and X_j are the independent variables.

Table 1
Physico-chemical characteristics of wastewater sludge

Parameter	Value
pH	5.7 ± 0.6
Total solids (g/L)	34.57 ± 1.2
Suspended solids (g/L)	31.73 ± 3.6
Total dissolved solids (g/L)	2.84 ± 2.9
Volatile solids (g/L)	20.9 ± 4.2
Total dissolved volatile solids (g/L)	1.22 ± 5.1
Chemical oxygen demand (mg/L)	6558 ± 8.3
CTC in supernatant (mg/L)	BDL
CTC in sludge (mg/kg)	34.22 ± 2.7

CTC: chlortetracycline.