



Wet oxidation of process water from hydrothermal carbonization of biomass with nitrate as oxidant

Patrizia Stutzenstein^{a,b,*}, Barbara Weiner^a, Robert Köhler^a, Christoph Pfeifer^b, Frank-Dieter Kopinke^a

^a Helmholtz-Centre for Environmental Research – UFZ, Department of Environmental Engineering, Permoserstr. 15, 04318 Leipzig, Germany

^b University of Natural Resources and Life Sciences, Department of Material Sciences and Process Engineering, Muthgasse 107/I, 1190 Vienna, Austria

HIGHLIGHTS

- Nitrates are investigated as oxidants in wet oxidation (time & temperature varying).
- Iron(III) nitrate shows same DOC- and COD-reductions as oxygen during wet oxidation.
- Dosage of iron(III) nitrate is simple, it is used effectively compared to oxygen.
- Recalcitrant, chlorinated compounds can be eliminated by iron(III) nitrate.
- Nitrates decomposition at hydrothermal conditions follows first order kinetic.

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ABSTRACT

Wet oxidation of a wastewater highly contaminated with biogenic organic compounds was investigated with nitrates as oxidant. Iron(III) nitrate proved to be a powerful oxidant at a relatively low treatment temperature of 120 °C. 50% of the chemical oxygen demand (COD) and 30% of the dissolved organic carbon (DOC) could be eliminated within the first hour of reaction. Iron(III) ions significantly support the nitrate based wet oxidation under mild reaction conditions. It may function as catalyst and/or co-oxidant. Iron oxides/hydroxides precipitate after cooling the reaction medium. However, the resulting iron sludge can be re-dissolved in HNO₃ and recycled as oxidant. Oxidation efficiency with this mixture was enhanced significantly compared to oxidation with HNO₃ only. At 200 °C similar DOC and COD reductions are achieved with Fe(NO₃)₃ and with HNO₃. At 120 °C Fe(NO₃)₃ outperforms HNO₃ clearly. This points to a nitrate activation by iron(III) which is effective already at low temperatures. 3-Chlorophenol as a representative of chlorinated aromatic pollutants could be completely eliminated by the nitrate-based hydrothermal oxidation under mild reaction conditions (2 h at 120 °C). Thus, wet oxidation using nitrate as oxidant can be feasible for elimination of recalcitrant pollutants at relatively low temperatures of 120 °C.

1. Introduction

Wet oxidation (WO) is the oxidation of dissolved or suspended compounds under hydrothermal conditions in water by an oxidant. Usually, molecular oxygen (O₂) from air or in pure form is used as oxidant to degrade organic compounds in aqueous waste streams that are too dilute for incineration and too concentrated or recalcitrant for microbial treatment [1]. Due to the broad applicability and low price of the oxidant several commercial WO plants have already been established [2]. The main operational costs are caused by the oxygen demand [3]. In addition, reaction temperature, pressure and reactor

material are also significant cost factors. Catalysts are usually added to enable lower oxidation temperatures thus reducing operation and equipment costs [4]. Within the present study, the applicability of nitrates as alternative oxidant for process water from hydrothermal carbonization (HTC) of biomasses is investigated. Nitrate activation and decomposition are examined. According to its standard reduction potential $E_0^H(W)NO_3^- = +0.74 V$ ($2 NO_3^- + 12H^+ + 10 e^- = N_2(g) + 6 H_2O$) [5], compared to dissolved oxygen $E_0^H(W)O_2 = +0.77 V$ ($O_2(aq) + 4H^+ + 4 e^- = 2 H_2O$) [5], nitrate is supposed to be an effective oxidizing agent under acidic conditions [6]. It is easy to handle, available in large amounts and moderate in cost. Most nitrates have

* Corresponding author at: University of Natural Resources and Life Sciences, Department of Material Sciences and Process Engineering, Muthgasse 107/I, 1190 Vienna, Austria.
E-mail address: patrizia.stutzenstein@boku.ac.at (P. Stutzenstein).

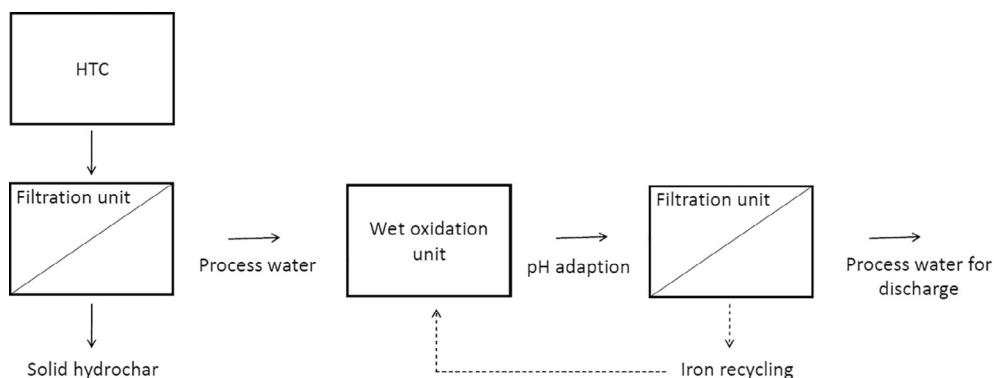


Fig. 1. Flow-chart of the combination of an HTC unit with a wet oxidation unit. The dotted line indicates a possible route for recycling of iron salts used within the process.

high water solubilities such that they can be used in sufficiently high concentrations for wastewaters with high chemical oxygen demand (COD). There are several studies on nitrate decomposition under near-critical or supercritical conditions, but little information on subcritical WO with nitrate can be found in the literature [6–8]. Imamura applied wet air oxidation on an aqueous acetic acid solution (5000 ppm) with various metal nitrates as catalysts (5 mM) at 235 °C [9]. A fourfold increase in total organic carbon (TOC) removal was achieved when copper(II) nitrate was added, compared to the non-catalytic regime. When turning off the oxygen supply, Imamura reported an ongoing decomposition of acetic acid when copper(II) nitrate was present. He proposed the following reaction scheme: $\text{AcOH} + \text{Cu}(\text{NO}_3)_2 \rightarrow \text{RO}_x (+\text{CO}_2) + \text{CuO} \downarrow + \text{NO} + \text{NO}_2$. CuO precipitated during the reaction and NO + NO₂ were detected in the gas phase [9]. This proves that nitrate acts as an oxidizing agent being able to oxidize even the recalcitrant acetic acid. However, the applied hydrothermal conditions were severe. Cox et al. aimed at destroying nitrate thermochemically with different reducing agents (ammonia, formate, urea, glucose, methane and hydrogen) at 200–350 °C [10]. Best results were obtained in acidic solution (pH = 4) at high temperatures. Temperatures of ≥ 250 °C were necessary for significant nitrate conversion within 2 h. N₂ and N₂O (20–30 mol%) were the main reduction products, whereas NO and NO₂ were not observed [10].

The aim of the present study is to apply WO on process water from HTC. The large amount of highly contaminated process water is a bottleneck of the HTC process, which is a thermochemical process converting organic feedstocks into coal-like products (hydrochars) at temperatures between 180 and 250 °C under autogenous pressures. Hydrochars can be used as a storable energy carrier, for soil amelioration or just for carbon sequestration [11]. HTC input materials may have high water contents (> 60%), making feed materials with originally high water contents, like sewage sludge, especially suitable for HTC. However, input water and reaction water make process water the main mass flow, containing high contents of water soluble organic compounds [11]. Due to its high organic load, the process water must be treated before discharge. It still contains high amounts of nutrients, hence it has the potential to be used as a liquid fertilizer. However, an inhibitory effect on seed germination has been reported [13]. Poerschmann et al. reported that the most abundant compounds in the process water of distillers spent grain are phenols and volatile fatty acids [12]. Various organic compounds that were reported to be present in the process water, such as phenols, furfurals, and volatile organic acids, can inhibit germination [13]. Riedel et al. showed that WO is a useful process to further degrade organic pollutants in the process water [14]. Process waters from different feed materials were oxidized and dissolved organic carbon (DOC) and COD reductions around 40 and 55%, respectively, were reported [14]. After oxidation the samples usually contain high concentrations of short chain organic acids, such as acetic acid which are good substrates for anaerobic degradation [15]. A better biodegradability is reported for oxidized waste streams as

compared to HTC process waters [16]. Reza et al. used copper oxide as an alternative solid oxidizing agent for WO of a HTC process water at 260 °C for 30 min. The authors report similar TOC reduction as for oxidation with molecular oxygen (2.5 MPa) and showed that recycling of formed Cu(0) to CuO is possible [17]. However, copper ions are toxic to the environments, thus this process will not be applicable for waste treatment plants [3].

In the present study, we investigate various nitrates as alternative dissolved oxidants to molecular oxygen for the treatment of process water from HTC of sewage sludge. According to their reduction potentials $\text{NO}_3^- (\rightarrow \text{N}_2)$ and $\text{O}_2 (\rightarrow \text{H}_2\text{O})$ are similarly strong oxidants in aqueous solution. The standard free enthalpy changes per transferred electron $\Delta G^0(\text{W})$ are -71 vs. -78 kJ mol^{-1} , respectively, at pH = 7 and -120 vs. -118 kJ mol^{-1} , respectively, at pH = 0 [10]. Due to their moderate market price between that of technical oxygen and hydrogen peroxide (economic considerations see below), nitrates have the potential as oxidants for industrial application. Furthermore, it is easier to dose water-soluble nitrates than pressurized oxygen. Combining a wet oxidation unit with an HTC unit makes direct discharge of HTC process water to a sewage plant possible (see Fig. 1). The objective of this work is to investigate the effectiveness but also the usefulness of different nitrate salts as oxidizing agents for HTC process waters. The effect of iron concentration, pH value, reaction time and temperature were studied. 3-Chlorophenol was oxidized as a model component to explore the potential of nitrates for destruction of chlorinated aromatic pollutants.

2. Materials and methods

2.1. Process water from hydrothermal carbonization

The process water used as feed material for oxidation experiments was derived from HTC of sewage sludge (wastewater treatment plant Nordkanal in Kaarst, Germany) at 210 °C for 4 h. It was separated from solid materials by filtration and stored at 4 °C prior to use.

2.2. Wet oxidation

Oxidation was conducted in in-house built steel autoclaves ($V = 30 \text{ mL}$, $d_{\text{inner}} = 24 \text{ mm}$), filled with glass inserts ($d_{\text{inner}} = 10\text{--}12 \text{ mm}$, $h = 55 \text{ mm}$) and equipped with magnetic stirring bars. The inserts were filled with a mixture of the HTC process water (1 mL) and the desired amount of nitrates (see chemicals section). The glass inserts were placed into the autoclaves, the autoclaves were closed and heated in an GC oven to the desired temperature and reaction time. The reaction mixture was continuously stirred. Then, the autoclaves were cooled down to room temperature. The reaction slurry was filtered through a folded paper filter (MN 619, Machery-Nagel, Germany). The filtrate was stored at 4 °C. The solid residue was dried at 105 °C for 24 h. All experiments were conducted at least in duplicate.

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