

Current research



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Removing micropollutants and phosphate with ferrate

Alongside ozone, ferrate has emerged as a new option for enhanced wastewater treatment at municipal treatment plants. Both substances oxidize anthropogenic organic micropollutants. Ferrate offers the additional advantage of removing phosphate – by precipitation – at the same time. But what doses of ferrate are required? And is the use of ferrate cost-effective? We report here on initial experience from the Eawag laboratory.

As treated wastewater still contains traces of pharmaceuticals, personal care products and household chemicals, it contributes substantially to water pollution. Since the possibilities for reducing consumption of these products are limited, attention is currently focused on how micropollutants can be eliminated from treated effluents [1]. One strategy involves the addition of a third treatment step at conventional wastewater treatment plants (WWTPs). In this additional step, micropollutants could be removed by oxidation processes. Thanks to the experience accumulated at Eawag over several years in the field of ozonation, it was possible for a large-scale pilot project to be carried out at the Regensdorf WWTP, where ozone was used as an oxidant [2].

A substance representing a potential alternative to ozone is ferrate $[\text{Fe}(\text{VI})\text{O}_4]^{2-}$ – an oxidant and disinfectant containing iron in the +VI oxidation state. Ferrate is particularly attractive because – unlike ozone – it serves not only as an oxidant but also as a precipitant: first, in the form of $\text{Fe}(\text{VI})$, it acts as an oxidant, being reduced to $\text{Fe}(\text{III})$ in the process. $\text{Fe}(\text{III})$, which has already been used for many years in wastewater treatment to precipitate phosphate, is thus a useful, non-toxic decomposition product of ferrate. Another advantage of ferrate is that – as far as is known – no unwanted by-products arise during the oxidation process.

Research on the possible application of ferrate in wastewater treatment began only recently. Eawag has now investigated the

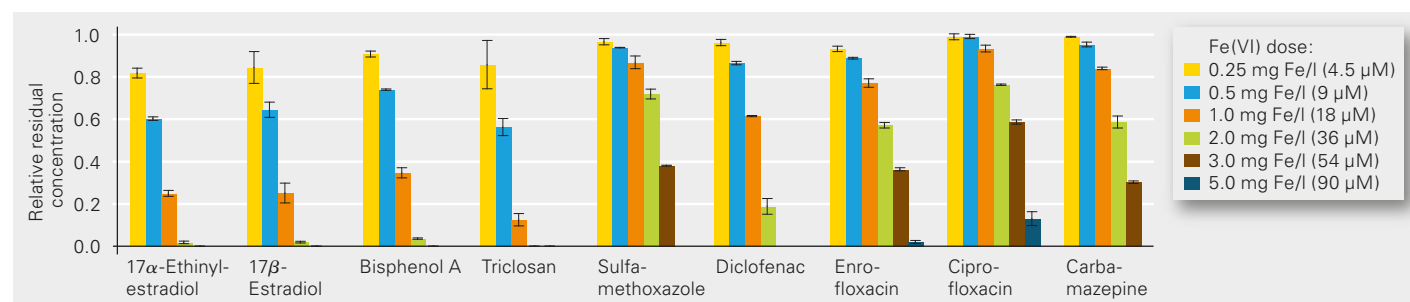
potential of ferrate to oxidize a wide variety of micropollutants in wastewater – also in comparison with ozone – and sought to establish what doses of ferrate are required to remove phosphate from wastewater by precipitation.

Removal of reactive micropollutants from wastewater. The aim of our study was to analyse directly in wastewater the oxidation of as wide a range of micropollutants as possible, with different properties. In a similar manner to ozone, ferrate also attacks electron-rich moieties in the molecules of micropollutants. These include, in particular:

- phenols, contained for example in the endocrine disruptors 17α -ethinylestradiol, 17β -estradiol, bisphenol A and the biocide triclosan;
- amines, found for example in the antibiotics sulfamethoxazole, enrofloxacin, ciprofloxacin and in the analgesic and anti-inflammatory agent diclofenac;
- alkenes (compounds containing double bonds), found for example in the antiepileptic drug carbamazepine.

As Fig. 1 shows, a ferrate dose of around 2 mg Fe/l is sufficient for complete oxidation of substances with phenolic moieties. However, amines and alkenes are only fully oxidized by a ferrate dose of around 5 mg Fe/l ; overall, they are thus less reactive than phenols [3, 4]. In addition, it is known from the literature

Fig. 1: Relative residual concentration of a wide range of micropollutants containing electron-rich moieties in treated wastewater from the Dübendorf WWTP as a function of the ferrate dose.



that ferrate also reacts with other electron-rich moieties such as sulfides and thiols, but this was not investigated in our project.

In the absence of such electron-rich moieties, however, substantially higher doses of ferrate are needed: for example, 15 mg Fe/l was required to achieve 40 % oxidation of the lipid-lowering agent bezafibrate and the contrast medium iopromide, and only 10 % oxidation was achieved with the same dose in the case of the analgesic and anti-inflammatory drug ibuprofen [3] (Fig. 2).

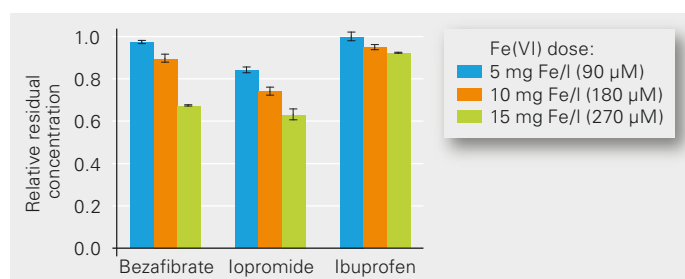
Less efficient than ozone for oxidation of micropollutants.

In recent years, various studies have confirmed that ozone is an effective agent for the oxidation of micropollutants in wastewater. For this reason, it is particularly interesting to compare the two substances as oxidants for wastewater treatment. Figure 3 provides an overview of the oxidation of selected micropollutants containing electron-rich moieties as a function of the dose of ferrate or ozone. Only one of the compounds studied, 17 α -ethinylestradiol, was oxidized roughly equally efficiently by both oxidants. In this case, a dose of 20 μ M (~1 mg/l) ferrate or ozone was sufficient to ensure complete oxidation. All other micropollutants analysed were oxidized less efficiently by ferrate than by ozone. To achieve complete oxidation, about three times more ferrate than ozone was required – e.g. 53 μ M (= 3 mg/l) ferrate versus 20 μ M (= 1 mg/l) ozone for the oxidation of diclofenac [3].

Lower reactivity offset by higher stability. In subsequent studies of the kinetics of oxidation reactions, the rate constants (k values) for the reactions of the micropollutants analysed were found to be three to four orders of magnitude lower for ferrate than for ozone [3]. In fact, on the basis of the preceding experiments, we would have expected the values here to be considerably higher. So how is it to be explained that ferrate is, nonetheless, not much less efficient than ozone in the oxidation of micropollutants?

To understand this, the stability of each of the oxidants in wastewater needs to be taken into account. Ferrate is consumed less rapidly by other components of wastewater and by self-decay than is the case for ozone. For example, it took more than 30 minutes for a ferrate dose of 40–45 μ M to be completely consumed in a secondary effluent from the Regensdorf WWTP – at pH 8 and with a DOC (dissolved organic carbon) concentration of 5 mg/l.

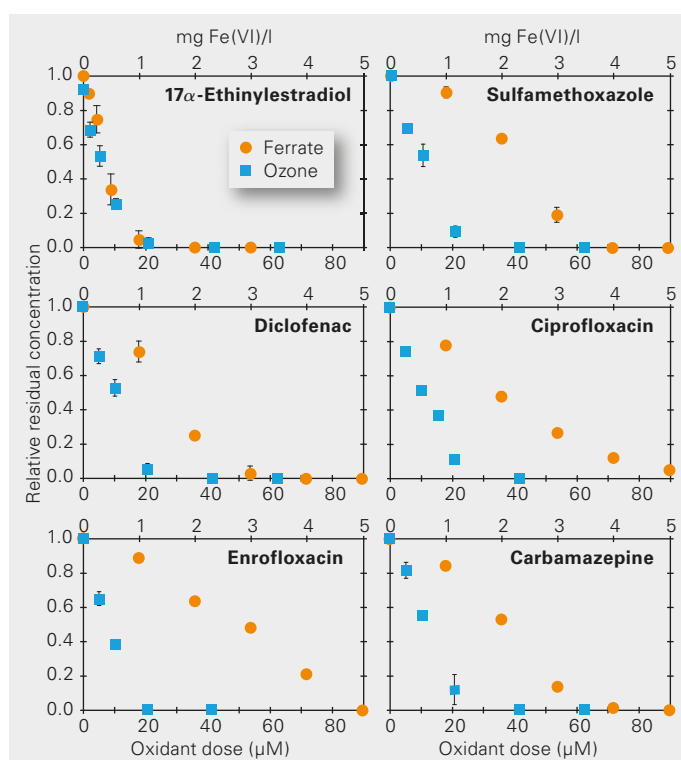
Fig. 2: Relative residual concentration of selected micropollutants lacking electron-rich moieties in treated wastewater from the Dübendorf WWTP as a function of the ferrate dose.



Postdoctoral fellow Yunho Lee measures the Fe(VI) concentration of a test solution.

By contrast, the same dose of ozone was consumed in only 5 minutes. Ferrate is thus present over a longer period and attains a higher exposure value (concentration \times time), thereby largely compensating for its lower reactivity with micropollutants [3]. Our tests also indicated that ferrate should be added to the secondary

Fig. 3: Relative residual concentration of selected micropollutants in treated wastewater from the Dübendorf WWTP after oxidation by ferrate (orange circles) or ozone (blue squares) as a function of the oxidant dose.



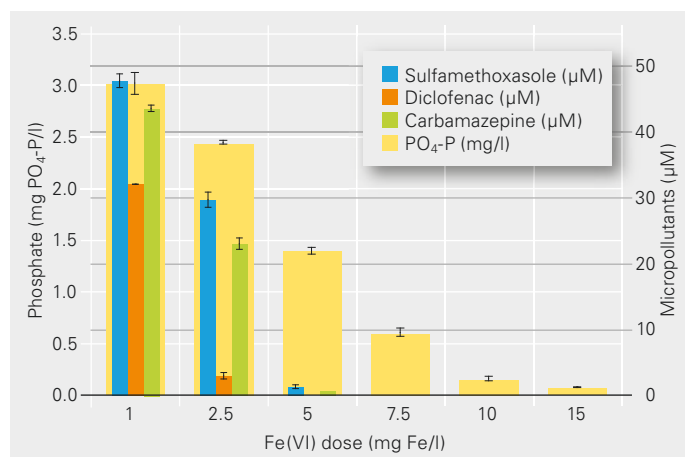


Fig. 4: Oxidation of selected micropollutants and simultaneous phosphate precipitation in treated wastewater from the Dübendorf WWTP as a function of the ferrate dose.

effluent, rather than to wastewater entering the biological treatment step, since here it would be too rapidly consumed as a result of the activated sludge and high DOC concentrations.

Phosphate in wastewater precipitated by the decomposition product Fe(III). In the course of the oxidation of micropollutants and other wastewater constituents, and as a result of self-decay, ferrate [Fe(VI)] is reduced to Fe(III). Fe(III), in turn, has long been used in wastewater treatment for chemical precipitation of phosphate. We wished to determine how much ferrate needs to be added in order to allow phosphate to be removed from wastewater at the same time. In our laboratory tests, we experimented with a phosphate content of 3.5 mg PO₄-P/l, which represents a realistically high concentration of phosphate in a WWTP influent.

In fact, a ferrate dose of 7.5 mg Fe/l is sufficient to reduce the phosphate concentration to below 0.8 mg PO₄-P/l – in accordance with the regulations on wastewater discharges to receiving waters in Switzerland (Fig. 4). This corresponds to approx. 80 % precipitation. The three reactive micropollutants sulfamethoxazole, diclofenac and carbamazepine were almost completely oxidized by a ferrate dose of 5 mg Fe/l. Thus, the ferrate doses required for complete oxidation of reactive micropollutants are lower than those required for phosphate precipitation [3].

Ferrate: a worthwhile option. Overall, our studies showed that ferrate is well suited for the oxidation of micropollutants in wastewater. Although it is somewhat less efficient than ozone in oxidizing micropollutants, it offers the additional advantage of eliminating phosphate. The ferrate doses required for phosphate precipitation are higher than those needed for complete oxidation of reactive micropollutants. It could therefore make sense, in terms of the operating costs of a WWTP, to use ferrate to ensure complete oxidation of reactive micropollutants, while achieving a degree of phosphate precipitation in the process. The remaining phosphate could then be precipitated using Fe(III) or Fe(II), in line with existing practice.

Questions now arise regarding the production and storage of ferrate. As the substance decomposes in contact with water, it cannot be transported or stored in an aqueous solution. In powdered form, ferrate has to be stored in airtight containers to protect it from humidity. Ideally, therefore, it would need to be continuously produced *in situ* (e.g. with the aid of an electrochemical cell) and then added to wastewater. However, preparation of a mixture using powdered ferrate at the WWTP is also conceivable. Treatment plants already performing chemical phosphate precipitation with solutions of Fe(II) and Fe(III) could then also use existing pumps and mixing systems for the application of ferrate.

At present, the use of ferrate is more expensive than the application of ozone. While ozone production costs amount to CHF 1–2 per kilogram, ferrate costs around CHF 18 per kilogram (comparison based on the molecular weight of ozone and ferrate in K₂FeO₄). However, experience has shown that manufacturing costs for chemicals fall dramatically as soon as large-scale production begins. A comprehensive analysis of the costs for ferrate would also have to take into account both the savings arising from simultaneous phosphate removal and the lower investment costs required for the necessary infrastructure, compared with ozone (use of existing feed systems for phosphate precipitation with iron).

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