

ENHANCED COAGULATION WITH PRE-OXIDATION FOR THE REMOVAL OF ARSENIC FROM GROUNDWATER

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Abstract

One of the most wide-spread problems with current drinking water resources globally is the natural presence of arsenic in groundwaters. The aim of this work was to investigate the removal of arsenic by a variety of combined oxidation/coagulation processes, in order to identify and optimise the most critical process parameters. The most significant gains made by both preoxidation steps were observed in the techniques which combined aluminum and ferric chloride based coagulation. The most efficient coagulation treatment investigated involved application of preozonation at a dose of 7.5 mg O₃/l with subsequent combined coagulation with PACl–FeCl₃ (30 mg Al/l and 10 mg FeCl₃/l).

Introduction

Throughout South-East Europe, groundwaters are commonly used as sources for drinking water. Within the Pannonian Basin, the groundwaters are naturally contaminated with particularly high concentrations of arsenic, which poses a severe challenge for public water utilities. The extremely negative impact of chronic arsenic exposure on human health led the World Health Organisation to recommend a maximum allowable concentration (MAC) of 10 µg As/l for drinking water (WHO, 2011). Meanwhile, in parts of Vojvodina, the groundwaters can contain as much as 250 µg As/l, and it is estimated that almost 1 million people in Vojvodina are currently supplied with drinking water which contains arsenic concentrations which exceed 10 µg/l (Agbaba et al., 2015). Given the negative health effects of chronic arsenic exposure, there is thus not just a legal, but also a social imperative to reduce the As concentrations to acceptable legally defined levels. The process of removing As from water is made more complicated by the other water constituents present, which may either indirectly reduce effectiveness of removal mechanisms, or compete directly for adsorption sites. NOM is particularly significant here, as it is known to play a key role in the mobility of As from the mineral layers surrounding aquifers into the water phase. In this context, there is a critical need for research relating to new drinking water treatment technologies, capable of sustainably treating a wide variety of source waters, and providing chemically and microbiologically safe drinking water.

The aim of this work was to investigate the removal of arsenic by a variety of combined oxidation/coagulation processes, in order to identify and optimise the most critical process parameters.

Experimental

For these experiments, groundwater from Zrenjanin was used which contains average As concentration of 134±4.5 µg/l, as well as high NOM (DOC=9.85±0.99 mg C/l) and alkalinity (745±12 mg CaCO₃/l). All coagulation experiments were carried out by jar tests. Coagulation was carried out with rapid stirring at 120 rpm for 2 min, after which flocculation was conducted

with slow mixing at 30 rpm for 30 minutes. MagnaflokLT27 flocculant was dosed at 0.2 mg/l. After the mixing was finished, samples were settled for 60 minutes, after which the supernatant was separated. Water samples were filtered through a 0.45 μm membrane filter and analyzed for total arsenic concentrations. The following coagulants were used: a 4% solution of iron (III) chloride in doses of 50–200 mg FeCl_3/l (0.1–2.0 mmol/l); a 1% solution of polyaluminium-chloride (PACl) in doses from 2.5 to 30 mg Al/l (0.1–2.0 mmol/l); and 1% $\text{Al}_2(\text{SO}_4)_3$ in doses from 2.5 to 30 mg Al/l (0.1–2.0 mmol/l). Possible improvements to the coagulation process using different coagulant and oxidant combinations were investigated. The following doses of hydrogen peroxide or ozone were investigated with the coagulant combinations in Table 1 below: H_2O_2 doses: 2.5, 5.0, 7.5, 10.0 mg $\text{H}_2\text{O}_2/\text{l}$; O_3 doses: 2.5, 5.0, 7.5, 10.0 mg O_3/l . Arsenic concentrations were determined either by inductively coupled plasma mass spectrometry (ELAN 5000, PerkinElmer-SCIEX) or graphite furnace atomic adsorption spectroscopy (AAnalyst 700, PerkinElmer). The PQL was 0.5 $\mu\text{g As}/\text{l}$.

Results and discussion

Enhanced coagulation with preoxidation using hydrogen peroxide: Hydrogen peroxide doses of 2.0–10 mg $\text{H}_2\text{O}_2/\text{l}$ were applied prior to coagulation with FeCl_3 , PACl, $\text{Al}(\text{SO}_4)_3$ and their combinations (PACl/ FeCl_3 and $\text{Al}(\text{SO}_4)_3/\text{FeCl}_3$). The arsenic removal results for the coagulants are shown in Figure 1.

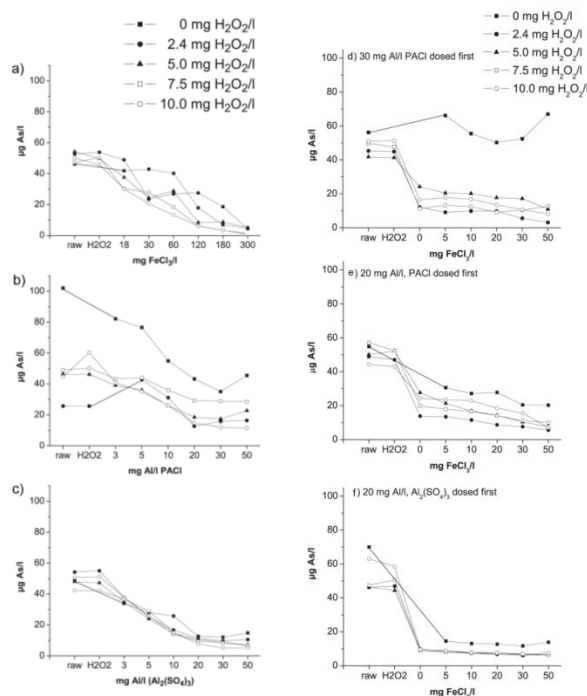


Figure 1. Effect of hydrogen peroxide oxidation on the removal of As by coagulation

The preoxidation step with hydrogen peroxide did not overcome the weak affinity of PACl for arsenic sufficiently enough for this technique to be a practical solution for arsenic removal, as the MAC for As was not satisfied. However, significant gains were made in the As removal efficacy of FeCl_3 , while coagulation by $\text{Al}_2(\text{SO}_4)_3$ was also improved. These gains were expected, as the results of the speciation study show that As(V) is more readily removed by coagulation than As(III), a conclusion supported by many authors (Cui et al., 2015). The PACl– FeCl_3 combination which applied 30 mg Al/l needs doses of 5 mg FeCl_3/l and 2.4 mg $\text{H}_2\text{O}_2/\text{l}$ in order to achieve As

levels below the 10 $\mu\text{g As/l}$ MAC. The best removal was achieved with the same conditions but with a 30 mg FeCl_3/l dose. However, the As removal gains made in comparison to the 5 mg FeCl_3/l dose are not significant enough to justify application of the increased dose from an economic standpoint, especially considering the considerably larger volume of waste sludge that would be produced. As could be expected, the PACl– FeCl_3 combination with the lower Al dose (20 mg Al/l) was less effective than the 30 mg Al/l dose. Reducing the PACl dose from 30 mg Al/l to 20 mg Al/l meant that 4 times more FeCl_3 was required, with the same 2.4 mg $\text{H}_2\text{O}_2/\text{l}$ dose, to reduce As below 10 $\mu\text{g/l}$. Finally, none of the $\text{Al}_2(\text{SO}_4)_3$ – FeCl_3 doses investigated were able to achieve arsenic concentrations of less than 10 $\mu\text{g/l}$ without preoxidation (Figure 1b). However, 2.4 mg $\text{H}_2\text{O}_2/\text{l}$ sufficiently enhanced coagulation with 20 mg Al/l and 5 mg FeCl_3 to achieve satisfactory water quality, with the preoxidation step increasing coagulation efficacy by almost 10%. Further increasing the FeCl_3 and H_2O_2 doses did not result in improvements in the arsenic removal.

Enhanced coagulation with preoxidation using ozone: Ozone doses of 2.0–10 mg O_3/l (0.2–1.0 mg $\text{O}_3/\text{mg DOC}$) were chosen for investigation, based on previous research (Tubić et al., 2010). The results of the experiments with preozonation prior to coagulation with PACl, $\text{Al}_2(\text{SO}_4)_3$ and FeCl_3 , as well as the PACl– FeCl_3 combination, are shown in Figure 2.

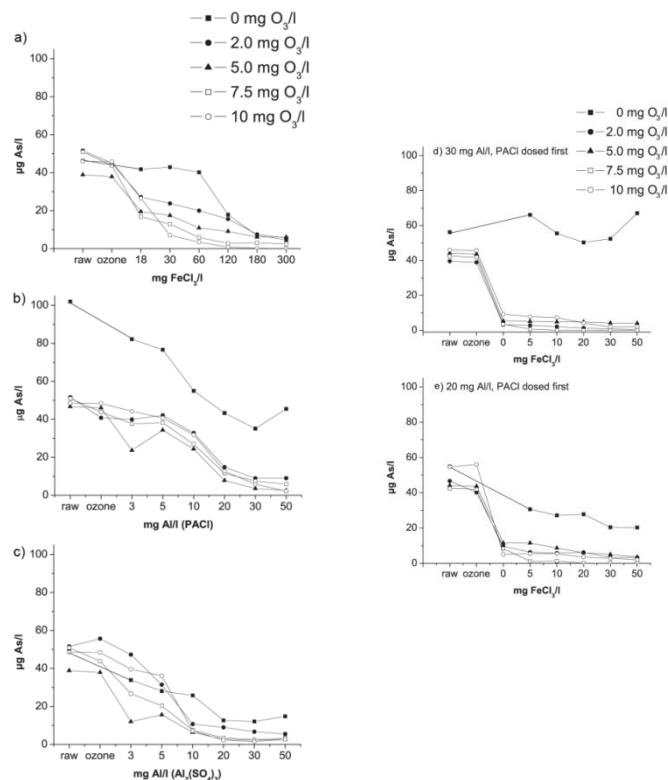


Figure 2. Effect of pre-ozonation on the removal of As by coagulation: (a-c) single coagulants (d-e) combined coagulants

Without preozonation, a 180 mg FeCl_3 dose is required to satisfy the MAC for arsenic. With preozonation, arsenic concentrations of less than 10 $\mu\text{g/l}$ were obtained by either i) dosing 10 mg O_3/l prior to just 30 mg FeCl_3/l , or ii) dosing 5 mg O_3/l with 120 mg FeCl_3 (Figure 2a). Although it is unlikely to be economically viable, preozonation with 10 mg O_3/l prior to 180 mg FeCl_3/l coagulant dose resulted in complete arsenic removal ($<0.5 \mu\text{g/l}$). In the case of

PACl, preozonation with a dose of 5 mg O₃/l increased the percentage removal of As at a dose of 20 mg Al/l by 25%, sufficient to bring the concentration to less than 10 µg As/l. Preozonation dramatically improved the performance of Al₂(SO₄)₃ coagulation for As removal. With the preoxidation step, applying a 5 mg O₃/l dose together with 10 mg Al₂(SO₄)₃/l was sufficient to remove As down to 6.4 from 38.9 µg/l. Given its superior impact on the removal of arsenic, it can be concluded that ozone, which is a strong oxidising agent which reacts faster than H₂O₂, is the most effective agent for oxidising arsenic containing molecules, and is therefore a very good choice for implementation together with single-coagulant coagulation during the water treatment process. This conclusion is supported by the literature (Sharma and Sohn, 2009). The final set of treatments investigated was preozonation prior to different PACl–FeCl₃ combined coagulant doses (30 and 20 mg Al/l). At 30 mg Al/l, preozonation at 2 mg O₃/l already reduces As concentrations below 10 µg/l without the addition of FeCl₃ (Figure 2b). At the lower 20mgAl/l dose, a higher dose of 10 mg O₃/l was required to achieve satisfactory drinking water quality without the addition of FeCl₃. Addition of 5 mg FeCl₃/l allows the ozone dose to be reduced to 2 mg O₃/l, whilst still maintaining satisfactory water quality. Of the combined coagulation treatments investigated, the most effective coagulation treatment for the removal of arsenic applied preozonation at a dose of 7.5 mg O₃/l, with subsequent combined coagulation with PACl–FeCl₃ at doses of 30 mg Al/l and 10 mg FeCl₃/l.

Conclusion

Preoxidation with hydrogen peroxide or ozone before combined coagulation increased the efficiency of the coagulation processes sufficiently that lower coagulant doses could be applied to reduce residual As concentrations below the analytical limits of detection. Preoxidation with hydrogen peroxide was capable of reducing the coagulant demand of the already very effective FeCl₃ process, and also improved the efficacy of Al₂S(O₄)₃ coagulation. However, it was not able to overcome the poor affinity of PACl for As to achieve As concentrations below 10 µg/l. In contrast, ozone proved to be a much more effective arsenic-oxidising agent. The most significant gains made by both preoxidation steps were observed in the techniques which combined aluminum and ferric chloride based coagulation. As such the most efficient coagulation treatment investigated for removing As below the MAC involved application of preozonation at a dose of 7.5 mg O₃/l with subsequent combined coagulation with PACl–FeCl₃ at doses of 30 mg Al/l and 10 mg FeCl₃/l. This FeCl₃ dose is an order of magnitude lower than the doses required by coagulation alone, resulting in not just a more economic treatment process, but also in the generation of much smaller amounts of more concentrated arsenic-bearing sludge.

Acknowledgements

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