

Nano-TiO₂ catalyzed UV-LED sample pretreatment method for decomposition of humic substances in natural water samples

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Abstract

A photocatalytic digestion device consisting of an ultraviolet light emitting diode (UV-LED) and a nano-TiO₂ coated catalyst rod was designed and used for the decomposition of humic substances in natural water samples prior to inorganic elemental analysis. The aim was to develop a green sample pretreatment method by utilizing energy efficient and environmental friendly UV-LED technology. The effects of different experimental variables including pH, UV-LED irradiation time, and hydrogen peroxide concentration were studied using a statistical experimental design. Dissolved organic carbon (DOC) removal was studied as the response. Dissolved organic carbon can interfere in some analytical measurements (for example in electrochemical analysis methods) and after digestion, the possible interfering effects are minimized. The recoveries for some spiked elements (As, Bi, Cd, Co, Cu, Ge, Ni, Pb, Sb, Se and Tl) were studied. It was found that in optimal DOC removal conditions, the recoveries for cadmium, cobalt, nickel and selenium were good. However, lower recoveries for some hydride forming elements were observed, indicating element losses, possibly due to adsorption phenomenon.

Keywords:

UV-LED, TiO₂, sample pretreatment, trace element analysis

1. Introduction

Sample preparation is an important step prior to inorganic elemental analysis to ensure reliable analytical results. Even samples in liquid form may need digestion before analysis, since dissolved substances, e.g., humic compounds, may interfere in the determination step [1,2]. Traditional methods like digestion in open vessels with strong mineral acids consume a lot of harmful reagents and are prone to contamination. Microwave-assisted digestion is considered to be more environmental friendly, as the acid consumption is reduced and the decomposition time is shorter. Photocatalytic methods using ultraviolet (UV) radiation and a catalyst go one step further and for some sample matrices it is considered an option with very low reagent and power consumption [3,4].

Digestion of organic material in a water sample with UV irradiation was reported for the first time in 1961 by Beattie et al. [5]. They used a medium pressure mercury vapor lamp to oxidize organic carbon and detected the formed carbon dioxide. Since then, different kinds of digestion apparatuses using UV irradiation have been developed and used in routine analyses. In recent years, ultraviolet light emitting diode (UV-LED) technology has evolved rapidly and UV-LEDs have been used in various applications [6-9]. UV-LEDs are long

lasting, compact in size, robust, efficient, and mercury free [10]. UV-LEDs typically have narrow emission spectra in the UV A range (315-400 nm), which alone is inefficient in breaking bonds between carbon atoms. Titanium oxide (TiO_2) is widely used as an effective and inexpensive catalyst in photocatalytic applications. Traditional UV digestion devices using mercury lamps have been used routinely in analytical chemistry [3] but UV-LED applications are still rare. Daniel et al. (2007) introduced a microfluidic cell with a TiO_2 -modified gold electrode that they used for *in situ* photocatalytic decomposition of organic matter with UV-LED followed by voltammetric analysis.

Natural waters may contain high concentrations of humic substances, which are complex organic compounds formed through degradation of organic matter in soil. Humic substances can bind strongly with chemical elements and interfere in certain analytical measurements, for example, in electrochemical methods or in the hydride generation method [1,2]. Photocatalytic degradation of these substances is already widely studied [12-14] but there are some challenges when applying photocatalytic methods to sample pretreatment in inorganic analysis. The TiO_2 surface can interact with analyte elements depending on pH value, redox conditions, and element speciation. The point of zero charge (pzc) for TiO_2 is around pH 6 at room temperature [15-16]. When the pH is lower than the pzc value, the surface of TiO_2 is positively charged and when the pH is higher, the surface is negatively charged. When photocatalytic degradation is applied in inorganic analysis, organic matter should be effectively digested and the analytes should remain in the solution. The surface charge of TiO_2 affects both the degradation of organic carbon compounds and possible adsorption of ions, e.g., due to electrostatic forces.

Adsorption of humic acids on the surface of TiO_2 has an important role in photocatalytic degradation. At high pH values, humic acids cannot adsorb onto the negatively charged TiO_2 surface and hence the degradation is more effective at lower pH values. However, when the pH is lowered to 2 or below, the solubility of humic acids is poor which inhibits degradation [17]. The maximum adsorption rate is observed at $\text{pH} \sim 3$ [18,19]. On the other hand, in elemental analysis, a low pH is usually preferred. At low pH values, many metal ions are positively charged and are not attracted by the positively charged TiO_2 surface. Some elements, like inorganic forms of arsenic (such as H_2AsO_4^- , HAsO_4^{2-} , H_2AsO_3^- , AsO_4^{3-} or HAsO_3^{2-}), occur as anionic species in aqueous solutions at a wide pH range. These species can adsorb onto a TiO_2 surface at low pH. Pena et al. [20] found that TiO_2 was effective in removing As(III) and As(V) at a pH less than 8, while Dutta et al. [21] showed that adsorption of As(III) and As(V) was strongly dependent on pH, with As(V) being adsorbed in acidic media and As(III) in basic media.

In this study, the nano- TiO_2 catalyzed UV-LED sample pretreatment method was used for the digestion of humic-rich natural water samples. Natural waters (e.g. in Finland) may contain high concentrations of dissolved organic carbon (DOC), which can interfere in certain inorganic analytical measurements. The

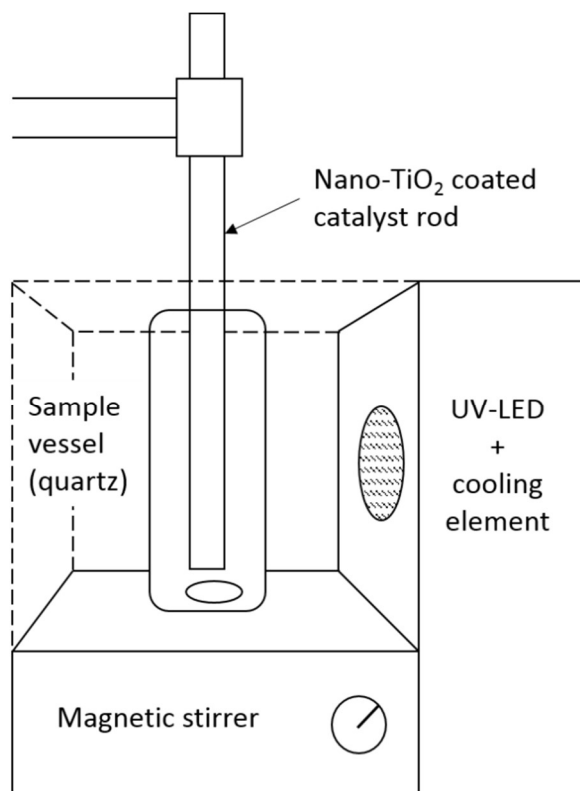
experimental conditions in the UV-LED sample pretreatment were studied to optimize the digestion efficiency of organic matter and the properties of the method were evaluated (e.g., element recoveries). To our knowledge, this type of device has not previously been used for sample digestion in elemental analysis.

Experimental

1.1. UV-LED reactor

The LZC-00U600 UV-LED Emitter (LED Engin, San Jose, USA) was used as a UV light source in a UV-LED reactor constructed in-house (Fig 1). The LZC-00U600 UV-LED is rated for 40 W power handling and its maximum radiant flux is 5.00 W. The reactor consists of a UV-LED, a cooling element to prevent overheating of the LED and a reaction chamber with a magnetic stirrer. 30 mL quartz vessels are used for sample digestion and a glass rod coated with a nano-TiO₂ layer is immersed into the sample solution. The catalytic surface of the rod is easy to regenerate or renew compared to the option of coating the inner surface of the quartz vessels with a TiO₂ layer. The TiO₂ -coated rods were prepared by making a suspension of nano-TiO₂ in ultrapure water. Glass rods were immersed in the suspension to cover them with a thin TiO₂ layer. The coated rods were dried for 30 minutes at room temperature and then calcined at 350 °C for one hour. The rods were cleaned after use by leaching in nitric acid (~5 M) with UV light irradiation for 30 min and rinsed with ultrapure water.

Fig. 1. Schematic of the UV-LED digestion device



1.2. Sample, reagents, and standards

The primary water sample of two liters was taken from a ditch located in Tyrnävä, Northern Finland. The sample was filtered through 0.45 μm filter and preserved with nitric acid (0.5 % v/v). The DOC concentration of the primary sample was roughly 50 mg L^{-1} and the concentrations of the studied elements before spiking were in the sub-micrograms per liter range.

The spike solution containing 2 mg L^{-1} of As, Bi, Cd, Co, Cu, Ge, Ni, Pb, Sb, Se and Tl was prepared by diluting commercial stock solutions. Prior to digestion, the pH of the water samples were adjusted with 2 M HNO_3 (Merck, Germany, p.a.) and 2 M NaOH, (Merck, Germany, p.a.). Nitric acid (Romil, UK, 67-69%, sp.) was used to acidify the samples and standard solutions before ICP-MS measurements. Hydrogen peroxide (Merck, Germany, 30%, p.a.) was used in the sample digestion. Ultrapure water (Millipore Gradient, Millipore Corp., Billerica, MA, USA) was used in all dilutions. Commercial titanium(IV)oxide nanopowder (Aeroxide P25, Aldrich, Germany) was used as a catalyst.

For the experiments, some 220 mL aliquots of the filtered Tyrnävä ditch sample were spiked with 2.5 mL of the spike solution, resulting in added concentrations of 20 $\mu\text{g L}^{-1}$. The pH of the sample was adjusted to a desired level (1, 4 or 7) with HNO_3 and NaOH. After that, the solution was carefully transferred to a 250 mL volumetric flask and finally transferred to a 500 mL polyethylene bottle. Each digestion experiment was carried out with a 20 mL subsample and the desired amount of H_2O_2 was added just before the UV-LED irradiation. After each digestion experiment, the pH was measured again to check if it had the same value as before the experiment. At pH 1 the pH was stable through all the experiments. At pH 4 and 7, there was small variation, which could be due to, for example, the degradation products of humic acids.

1.3. Instrumentation

A Thermo Elemental X7 Inductively coupled plasma mass spectrometer (ICP-MS, Thermo Elemental, Windsford, England) equipped with a concentric glass nebulizer and a Peltier cooled (+3 $^{\circ}\text{C}$) conical spray chamber was used to measure elemental concentrations. A Formacs^{HT} TOC/TN Analyzer (Skalar, Breda, The Netherlands) was used to determine DOC concentrations in water samples.

1.4. Statistical experimental design

Full 2^3 -factorial and central composite face-centered (CCF) designs were used in the screening and optimization experiments, in which the effects of UV-LED irradiation time, hydrogen peroxide concentration, and pH were studied. The levels of H_2O_2 concentrations for the first factorial experiment were selected according to the literature. A small concentration of around 5 mmol L^{-1} is beneficial, while an increase in the concentration does not increase the DOC removal efficiency (Wang 2001). In addition, the first factorial experiment was done at pH 1 because acidic conditions are preferred in elemental analysis to prevent

precipitation of some elements. Furthermore, two identical TiO₂ catalyst rods were used to verify that the catalytic effect is reproducible. The factors and their levels are shown in Table 1.

In the 2³ factorial design, 11 experimental runs were carried out. These runs included three replicates determined at the center point of the design to obtain an estimate of the experimental uncertainty. After the screening phase, the central composite face-centered (CCF) design was used to more closely study the effects of concentration of H₂O₂, UV-LED irradiation time, and pH. The used CCF design consisted of three variables with two levels (high and low), including 3 center points and axial points, centered on the faces of the cube (Table 1).

All experimental runs were carried out in random order. DOC removal efficiency and recoveries of the spiked elements were used as the responses in both studies. Empirical models were fitted to the experimental data using MODDE 9.1 (Umetrics AB 2011) computer software. Statistical validation of the fitted models was carried out with an ANOVA test at a 95% confidence level.

2. Results and discussion

2.1. Screening phase

Six preliminary experimental runs were performed to collect information on the effects of different factors on the DOC removal efficiency (Table 2). Hydrogen peroxide alone had only a minor effect that could be explained by statistical variation. The catalyst alone had a slightly larger effect, which is due to adsorption of organic material on the surface of the catalyst. The white TiO₂ surface turned a mild brownish yellow after 60 min contact with the sample. Photocatalytic oxidation occurs mainly on the surface of the catalyst and adsorption is an important step in the process [19]. Therefore, when the sample is in contact with the catalyst without UV irradiation, the DOC removal is due to adsorption. The UV-LED irradiation without TiO₂ catalyst or H₂O₂ had an effect, but the DOC removal efficiency was quite poor. The catalyst is clearly needed with the UV-LED of 365 nm wavelength.

Table 1. The factors and their levels used in the full 2³-factorial design and in the CCF design.

Experimental design	Factor levels		
	Low	Center	High
Full 2³-factorial design			
H ₂ O ₂ (mmol L ⁻¹)	2	5	8
UV-LED irradiation time (min)	30	60	90
Catalyst*	rod 1	rod 1	rod 2
Central composite face centered design			
H ₂ O ₂ (mmol L ⁻¹)	5	10	15
UV-LED irradiation time (min)	30	60	90
pH	1	4	7

* qualitative factor

Table 2. DOC removal efficiencies* for the preliminary experimental runs (N1-N6) and the screening experimental runs (N7-N16). The experiments were performed at pH 1.

Experimental run	Catalytic rod number	H ₂ O ₂ conc. (mmol L ⁻¹)	UV-LED irradiation time (min)	DOC removal efficiency (%)
Preliminary experiment				
N1	no rod	0	0	0
N2	no rod	5	0	3.8
N3	no rod	0	60	13.5
N4	no rod	5	60	40.0
N5	1	0	60	22.3
N6	1	0	0	6.4
Screening experiment				
N7	1	2	30	42.9
N8	2	2	30	40.8
N9	1	8	30	45.1
N10	2	8	30	47.6
N11	1	2	90	65.5
N12	2	2	90	68.7
N13	1	8	90	73.2
N14	2	8	90	85.3
N15	1	5	60	57.4
N16	1	5	60	60.3
N17	1	5	60	63.6

* $(\text{DOC}_{\text{untreated}} - \text{DOC}_{\text{sample}}) / \text{DOC}_{\text{untreated}} * 100\%$ where $\text{DOC}_{\text{sample}}$ is DOC concentration after the experimental run and $\text{DOC}_{\text{untreated}}$ is DOC concentration of the untreated sample N1.

The first factorial experiment (2³-design) was carried out at pH 1 to identify the effects of the H₂O₂ concentration and the UV-LED irradiation time on the digestion efficiency. In addition, it was studied if the two separate catalytic rods had different effects on the digestion efficiency. The results are presented in Table 2. When the experimental data were analyzed, it was found out that the most important factor for the DOC removal efficiency is UV-LED irradiation time (Table 3). The concentration of hydrogen peroxide has a small but statistically significant positive effect. On the other hand, there was no difference in the results between the two catalyst rods, indicating that the in-house made catalyst rods had similar catalytic activity.

2.2. Optimization phase

Based on the results of the factorial experiment, it was concluded that the UV-LED irradiation time was near optimum for the further studies. On the other hand, the concentration of hydrogen peroxide needed further study to establish the optimal concentration. Moreover, pH was included as a variable in the optimization step. The central composite face-centered (CCF) design was used in the optimization experiments (Table 1).

Table 3. The scaled and centered regression coefficients and their confidence intervals for the fitted models after screening and optimization experiments.

Model term	Coefficient	Std. Err.	Conf. int(±)
Full 2³-factorial design			
Constant	59.4	1.33	3.14
Rod 1	-1.16	1.33	3.14
Rod 2	1.16	1.33	3.14
H ₂ O ₂	4.16	1.50	3.54
UV	14.5	1.50	3.54
Central composite face centered design			
Constant	94.6	1.49	3.24
UV	5.22	1.24	2.71
pH	9.96	1.24	2.71
H ₂ O ₂	1.23	1.24	2.71
pH*pH	-21.9	1.94	4.22

Table 4. DOC removal efficiencies* for the CCF experiment.

Experiment	UV-LED irradiation time (min)	pH	H ₂ O ₂ (mmol L ⁻¹)	DOC removal efficiency (%)
K1	30	1	5	53.5
K2	90	1	5	70.2
K3	30	7	5	72.5
K4	90	7	5	88.2
K5	30	1	15	53.4
K6	90	1	15	71.0
K7	30	7	15	85.2
K8	90	7	15	86.6
K9	30	4	10	94.7
K10	90	4	10	95.5
K11	60	1	10	65.5
K12	60	7	10	80.7
K13	60	4	5	93.9
K14	60	4	15	94.4
K15	60	4	10	94.8
K16	60	4	10	96.3
K17	60	4	10	92.4

* $(\text{DOC}_{\text{untreated}} - \text{DOC}_{\text{sample}}) / \text{DOC}_{\text{untreated}} * 100\%$ where $\text{DOC}_{\text{sample}}$ is DOC concentration after the experiment and $\text{DOC}_{\text{untreated}}$ is DOC concentration of the untreated sample at corresponding pH (1, 4 or 7).

The results are presented in Table 4. When the experimental data were analyzed, it was found out that the significant factors were pH and UV-LED irradiation time (Table 3). In addition, one significant quadratic term pH^2 was included in the model. The results showed that pH is the most important critical factor (Table 4). At pH 4 the DOC removal efficiency was about 95% regardless of the values of the other factors. This result is in good agreement with other published results [18,19]. The irradiation at pH 1 resulted in lower DOC removal efficiency but the increase in the irradiation time improved DOC removal.

According to the screening phase, the added hydrogen peroxide improved DOC removal efficiency. However, in the optimization step the concentration of hydrogen peroxide proved not to have a statistically significant effect. These results indicate that a H_2O_2 concentration between 5-15 mmol L^{-1} does not increase DOC removal efficiency. This is in agreement with Wang et al. (2001) who found that excessive dosage of H_2O_2 does not further improve the degradation of humic acids. Optimal conditions for DOC removal are close to pH 4 and the model predicts DOC removal to be slightly more efficient with increasing irradiation times (Fig 2). According to the literature, pH 3 is the optimum for the degradation of organic carbon [18,19], which is in agreement with this study.

Fig. 2. Response contour plot for DOC removal efficiency. The model is fitted on the basis of the CCF design. H_2O_2 concentration = 10 mmol L^{-1} .

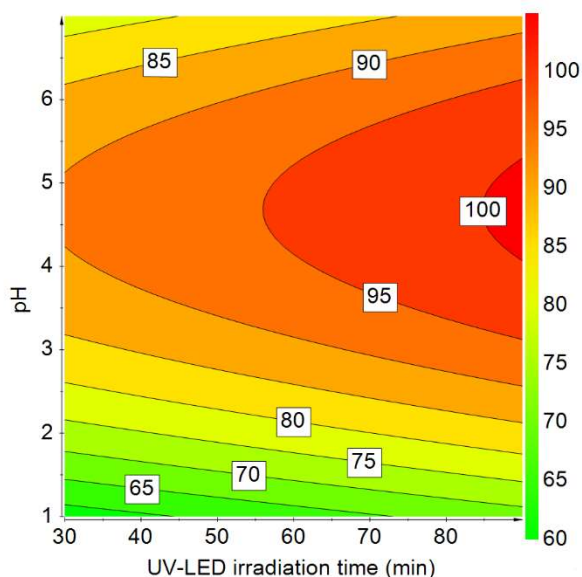
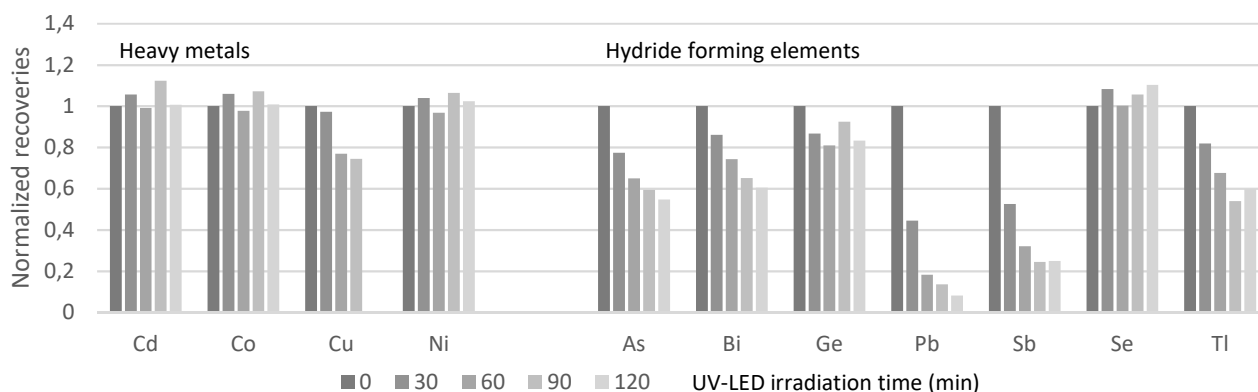


Fig. 3. Normalized recoveries* for the spiked elements at pH 4 as a function of UV-LED irradiation time (H_2O_2 concentration = 10 mmol L^{-1}).



* $c_{\text{sample}}/c_{\text{untreated}}$ where c_{sample} is concentration measured after the experiment and $c_{\text{untreated}}$ is concentration of the untreated spiked sample.

2.3. Recoveries of the spiked elements

It is known that nano-sized metal oxides can adsorb elements from the solution on their surface and they have been used as adsorbents to remove hazardous elements and compounds from water [22,23]. In this study, nano- TiO_2 was used as a catalyst and it might adsorb elements depending on the experimental conditions. The surface of the TiO_2 catalyst is positively charged at pH 4 and it attracts negatively charged species [15,16]. Also, due to photochemical reactions [24], the formation of volatile compounds is possible.

The recoveries for spiked elements were determined in optimal DOC removal conditions at pH 4 as a function of UV-LED irradiation time (Fig. 3). Good recoveries were obtained for cadmium, cobalt, nickel and selenium. The recoveries for Cu, As, Bi, Ge, Pb, Sb and Tl were decreasing with increasing irradiation time. This observation suggests there is a rather slow continuous process that is most likely adsorption onto the TiO_2 surface. Many hydride-forming elements tend to form negatively charged species in aqueous solutions, which are attracted by the positively charged TiO_2 surface below pH 6.

The other possible reasons for the low recoveries are precipitation and the formation of gaseous compounds. It is to be noted that photochemical vapor generation (PVG) using UV radiation and low molecular weight organic (LMW) acids are used in some analytical applications [24,25]. Photochemical vapor generation is possible during the UV-LED irradiation, but the reaction conditions should not favor reduction without LMW acids. In addition, the catalytic rod was leached with nitric acid after the experiments and elements exhibiting low recoveries were found in the leaching solution. Thus, there is evidence of adsorption, though this does not exclude the possibility of PVG. The recoveries presented in Fig. 3 were obtained with a H_2O_2 concentration of 10 mmol L^{-1} . Some additional experiments revealed that for arsenic, antimony, and bismuth the recoveries were dependent on the H_2O_2 concentration and higher recoveries were achieved when the H_2O_2 dosage was

15 mmol L⁻¹. This observation might indicate that with lower H₂O₂ concentrations, photochemical vapor generation may also cause the observed low recoveries.

Selenium species are typically negatively charged and adsorption is expected on a positively charged TiO₂ surface below pH 6. Zhang et al. [26] studied the sorption behavior of selenium ions on titanium oxide particles in aqueous solution and highest adsorption rates (60-100%) were obtained in the pH range of 2–6. However, in our study, selenium recoveries were good and reproducible. The spike solution contained several other elements and it is possible that selenium can interact with metal cations [27] and occur thereafter as positively charged species. Copper is an exception among the heavy metals studied in having decreasing recoveries with increasing irradiation time. It is possible for copper to adsorb onto the TiO₂ surface via surface complexation [28].

3. Conclusions

The in-house constructed UV-LED-based digestion device is well suited for the pretreatment of humic rich natural water samples to decompose dissolved organic matter. The DOC removal efficiency was about 95% at pH 4 after 30 min irradiation time. The sample was spiked with different elements (of As, Bi, Cd, Co, Cu, Ge, Ni, Pb, Sb, Se and Tl) and recoveries were studied in optimal DOC removal conditions. In optimal decomposition conditions the recoveries for cadmium, cobalt, nickel and selenium were good. The recoveries for hydride-forming elements were decreasing when the UV-LED irradiation time was increased. This is probably due to adsorption of different species onto the TiO₂ surface. However, photochemical vapor generation cannot be excluded. For selenium, the recoveries were good and the digestion device could be used for sample pretreatment, for instance, in the analysis of selenium in water samples by the hydride-generation method or electrochemical methods when organic matter has to be digested. The UV-LED digestion device is cheap to construct and it could be easily updated to treat multiple samples at the same time by increasing the number of UV-LEDs. This device has a lot of potential as a green and moderately fast sample pretreatment method, but some more research is needed. The DOC removal efficiency needs to be further improved to approach almost 100% to meet the requirements of, for example, electrochemical methods and we believe that this is possible with further optimization of the digestion process.

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