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The treatment of greywater from a restaurant by electrosynthesized ferrate (VI) ion

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ABSTRACT

Greywater reuse is an attractive alternative to sustainable water management, especially in water scarcity situations. This study sought to determine the treatment efficiency of electrochemically produced ferrate(VI) in greywater, assessing ferrate(VI) dose requirements and pH effect. Greywater originating from a restaurant was employed in this research. The treatment efficiency was investigated with regard to the chemical oxygen demand (COD), total organic carbon, turbidity, surfactants, and anions removal. The optimum performance was achieved with 75 mg/L of ferrate(VI) dose at pH 7. The settling characteristics of the treated greywater were also investigated. After treatment, larger particles and zeta potential values closer to zero were observed. Electrochemically produced ferrate(VI) showed promising performance for greywater treatment.

Keywords: Greywater; Coagulation; Ferrate(VI); Oxidation; Particle size; Surfactant; Zeta potential

1. Introduction

Water scarcity, poor water quality and water-related disasters are worldwide problems which need to be resolved to guarantee a water supply which is safe for human use. In order to reverse the non-sustainable tendency of increasing surface and ground water extraction and to satisfy the rising demand for fresh water, some changes must be made to decrease potable water consumption. Mitigating this water scarcity problem is closely linked to greywater management.

Greywater is wastewater from baths, showers, hand basins, dishwashers, washing machines, laundries and kitchen sinks. Reuse and recycling of greywater is receiving more and more attention due to low levels of contaminating pathogens and nitrogen [1–9]. The published literature indicates that the typical volume of greywater varies from 90 to 150 L/p/d in developed countries depending on lifestyles, living standards, population structures (age, gender), customs and habits, and greywater constitutes 50–80% of the total household wastewater [10]. It can be reused for several applications including toilet flushing, car washing and garden irrigation which do not require water of drinking quality, thus reducing potable water consumption. Such reuse of greywater for non-potable applications can substantially reduce potable water consumption.

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Since greywater is a reflection of household activities, its main characteristics strongly depend on consumer habits, living standards and the type of chemicals used [11]. The pollution of greywater due to personal care products, detergents, dirty clothes and body dirt is generally assessed by such indices as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total organic carbon (TOC), turbidity and nutrients (nitrogen and phosphorus) [12]. The source of greywater is highly significant for its reuse potential. Greywater is defined as high load and low load according to its pollutant concentration. High-load greywater includes wastewater coming from kitchens, washing machines and dish washers and presents a complex chemical composition including pollutants such as detergents, soaps, personal care products and other chemicals [10,13–15]. Low-load greywater is sourced from bath, shower and wash-basin wastewater, and it includes naturally lower concentrations of pollutants than high-load greywater, domestic wastewater and blackwater.

Technologies applied for greywater treatment include physical, chemical and biological systems. Most of these technologies are preceded by solid-liquid separation step as pre-treatment and followed by a disinfection step as post-treatment. The disinfection step is used to meet the microbiological requirements. It is known that physical treatments alone are not efficient to remove organic matters and pathogens [16–18]. Advanced oxidation processes (AOPs) are effective in meeting the reuse standards of greywater [19,20]. However, cost-effectiveness is a challenge in real scale applications. Chen et al. found that electrocoagulation was a feasible process for treating restaurant wastewater with around 70% COD and 94% oil and grease removal [21].

Ferrate(VI) exhibits many advantages because of its dual function as an oxidant and a coagulant. Ferrate (VI) is a strong oxidant. Ferrate(VI) species have reduction potentials of 2.20 V in acidic conditions, which are greater than those of ozone and are the strongest of all oxidants/disinfectants that are used for water and wastewater treatment [22]. During the oxidation reaction, Fe(VI) is reduced to a non-toxic by-product, Fe (III), which is a well-known coagulant in water and wastewater treatment. Therefore, ferrate(VI) is one of the most powerful, multipurpose, environmentally friendly water and wastewater treatment chemicals. Ferrate(VI) has been used effectively for wastewater treatment so far by many researchers [23–25]. Due to its unique properties, ferrate(VI) production methods are rather important. These methods can be divided into three main categories: wet chemical synthesis, dry chemical synthesis and electrochemical synthesis. Of these three, the electrochemical method has several advantages, such as simplicity, safety and the absence of hypochlorite. The electrochemical method is also a more cost-effective process, as it does not require expensive chemicals.

The objective of this study was to evaluate greywater treatment by electrosynthesized ferrate(VI) in terms of COD, TOC, turbidity, anions (SO_4^{2-}, NO_3^-, NO_2^-, PO_4^{3-} and F^-) and anionic surfactant methylene blue active substance (MBAS) removal for its potential utilization in real scale applications. This is the first time when electrosynthesized ferrate(VI) ion has been used for greywater treatment.

2. Materials and method

2.1. Greywater and sampling

Greywater was collected from the kitchen of a restaurant located in Mikkeli, Finland. Samples were taken on Mondays at 11 am, which was the busiest time in the restaurant, during three months period (October 2013–December 2013), stored at 4˚C and then analysed within 48 h. Raw greywater was analysed each time after collection, and standard deviations for each pollutant were calculated. The characterization of the greywater is summarized in Table 1.

2.2. Analytical methods

COD was measured according to Standard Methods [26] using Dr Lange cuvette tests (LCK 114) in conjunction with a Hach spectrophotometer (Hach Lange DR-2800) at the wavelength of 420 nm, and turbidity was measured using a 2100P ISO turbidimeter (Hach, Germany). TOC measurements were taken using a TOC analyser (TOC-V_{CPH}, Shimadzu, Japan) calibrated with standard potassium hydrogen phthalate solutions. The pH was determined using a WTW Inolab Multi 9310 IDS pH meter.

Anionic surfactant, such as MBAS, was analysed with Dr Lange cuvette tests (LCK 332) based on Standard Methods [26] with a Hach spectrophotometer (Hach Lange DR-2800). The reference compound for this method was sodium dodecyl benzene sulphonate. Anions (nitrate, nitrite, sulphate, phosphate and fluorine) were analysed using a high-performance liquid chromatographer (HPLC) (Schimadzu, Japan). The used anion columns were IC SI-50 4E and SI-90G (Shodex®) with the size of 4 × 250 mm, and conductivity detector was CDD- 10Avp. 3.2 mM Na_2CO_3 + 1 mM $NaHCO_3$ was used as eluent. The flow was 0.7 ml/min and the temperature was 25˚C. The transmission ^{57}Fe Mössbauer spectra were recorded using a Mössbauer

Table 1
The characteristics of greywater and standard deviations of pollutants (initial pH 11.7)

Parameter	Concentration	Standard deviation
COD (mg/L)	984.60	6.4
TOC (mg/L)	388.70	0.51
Turbidity (NTU)	303.07	4.55
Anionic surfactant (MBAS) (mg/L)	14.55	2.45
SO_4^{2-} (mg/L)	43.09	0.47
NO_3^- (mg/L)	24.28	0.32
NO_2^- (mg/L)	0.63	0.60
PO_4^{3-} (mg/L)	1.28	0.39
F^- (mg/L)	2.13	0.22

spectrometer in a constant acceleration mode with a $^{57}Co(Rh)$ source. Zero velocity of the Mössbauer spectra is referred to the centroid of the metallic iron foil spectrum at room temperature. The measurements were carried out at the temperature of 100 K in a zero external magnetic field.

The zeta potential (ZP) measurements of the particles in the suspensions were determined from their electrophoretic mobility based on the Smoluchowski model using a Nano-ZS Zetasizer (Malvern, USA). Dynamic light scattering measurements of the particle hydrodynamic diameter were also taken using a Nano-ZS Zetasizer (Malvern, USA). The cell was washed with deionized water and ethanol before measuring. All measurements were taken at 25˚C. Each result was an average of three readings.

2.3. Experimental setup and procedure

Firstly, ferrate(VI) was generated by electrochemical method in a rectangular plexiglas reactor and used simultaneously for the treatment procedure. NaOH (CAS number: 1310-73-72) was used for alkaline media at a concentration of 20 M. The electrodes were made of high-purity iron plates. The active total surface area (S_{total}) of the electrodes was 81.25 cm^2, and the applied current density was 1.47 mA cm^{-2}. Constant direct current was supplied by a GW Instek PSP-405 Programmable DC power source. The electrolyte was stirred with a magnetic stirrer. These conditions were optimum for ferrate(VI) generation according to the findings of our previous study, and the recoveries of the method for ferrate(VI) measurement can be also found in this study [27]. Ferrate(VI) concentration was measured using Perkin Elmer Lambda 45 UV/VIS Spectrophotometer at the wavelength of 505 nm.

Secondly, 1 L of the greywater to be treated was placed in the jar tester. Ferrate(VI) was dosed into the jar. Next, the pH was adjusted to 2 and then modified to the final pH (4, 5, 6, 7, 8, 9 and 10) with the buffers. The buffers used in this study included the following: $C_8H_5KO_4$ (CAS number: 877-24-7)–HCl (CAS number: 7647-01-0) solution (pH 4); $C_8H_5KO_4$–NaOH solution (pH 5); KH_2PO_4 (CAS number: 7778-77-0)–NaOH solution (pH 6, 7 and 8); $Na_2B_4O_7{\cdot}10H_2O$ (CAS number: 1303-96-4)–HCl solution (pH 9) and $Na_2B_4O_7{\cdot}10H_2O$–NaOH solution (pH 10). A rapid mix at 400 rpm for 30 s was applied. The sample was then flocculated for 20 min at 30 rpm and allowed to settle for an additional 60 min. The schematic diagram of the process is given in Fig. 1.

The experiments were conducted using different ferrate(VI) doses (2, 5, 10, 20, 50, 75 and 100 mg/L). This range of Fe(VI) doses was chosen according to the preliminary studies. At the end of each experiment, the treated water was filtered through 0.45 μm cellulose acetate membrane syringe filters (VWR) for the measurements. ZP and particle size distribution (PSD) measurements were carried out without filtering the sample.

The settling test was conducted in a stoppered and graduated acrylic cylinder with a height of 300 mm and a diameter of 200 mm, and settling times were recorded with a stopwatch. First, the cylinder was filled with flocculated greywater. The cylinder was inverted 10

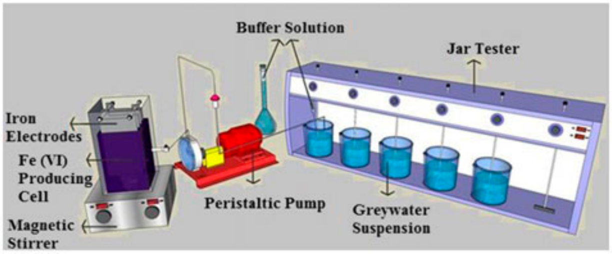

Fig. 1. The schematic diagram of greywater treatment system.

times to ensure uniform particle distribution. The cylinder was then placed upright, and the height of the interface between the water and the settling solid bed was measured over time. The interface height of the flocculant-containing suspension was measured as a function of time, and the results were plotted.

All experiments were triplicated and the average was taken.

3. Results and discussion

3.1. Organics degradation and physical impurities

To evaluate the performance of greywater treatment by ferrate(VI) in terms of percentage improvement of water quality and removal of organics and physical impurities, parameters such as COD, TOC and turbidity were considered. The result indicates that all the water quality parameters are improved significantly after treatment, as shown in Fig. 2(a) according to the applied ferrate(VI) dose. Ferrate(VI) in a concentration range of 2–100 mg/L was added to greywater samples. The experiments were conducted at pH 7 and temperature 25°C. Low COD removal (37%) occurred with 2 mg/L of ferrate(VI), indicating low oxidation of the contaminants in the greywater. Significant COD removal (in the range of 70–89%) was observed with 20 mg/L ferrate(VI) and its extent concentrations. While only 50% COD removal efficiency with UV disinfection process [28] and less than 80% COD removal with electrocoagulation process [29] were gained for greywater from restaurants, with a ferrate(VI) dosage of 100 mg/L, the COD level in the water was reduced to 105 mg/L, corresponding to 89.3% COD removal by ferrate(VI). As seen in Fig. 2, there were no such removal difference between applied ferrate(VI) doses of 75 and 100 mg/L. Thus, most contaminants were oxidized during the ferrate (VI) treatment.

TOC was removed in the range of 21.6–61.7% according to the applied ferrate(VI) dose as seen in Fig. 2(a).

Fig. 2 also shows the efficiency of turbidity removal by the ferrate(VI) process. Turbidity removal was between 97 and 99.9% according to the applied ferrate(VI) dose. Relatively low ferrate(VI) concentration (2 mg/L) already appeared to be fairly efficient for the turbidity removal, and the per cent of removal was almost unchanged for all doses applied.

The pH range of 4–10 was chosen to evaluate the pH effect on the ferrate(VI) process (Fig. 2(b)). A ferrate(VI) dose of 75 mg/L was used. This concentration (75 mg/L) was chosen because there were no difference in the removal efficiencies for 75 and 100 mg/L ferrate(VI) doses, and it was determined as an optimum dose according to the results of preliminary studies. Although pH appeared to have a minor effect on the effectiveness of TOC removal, COD reduction was greater in the pH range of 6–9. The highest COD removal efficiencies were obtained at pH 7 and 8 as 88.8 and 87.6%, respectively. Turbidity removal efficiency ranged from 87.93 to 99.56%. It was clear that all pH values were effective for turbidity removal with the ferrate(VI) process.

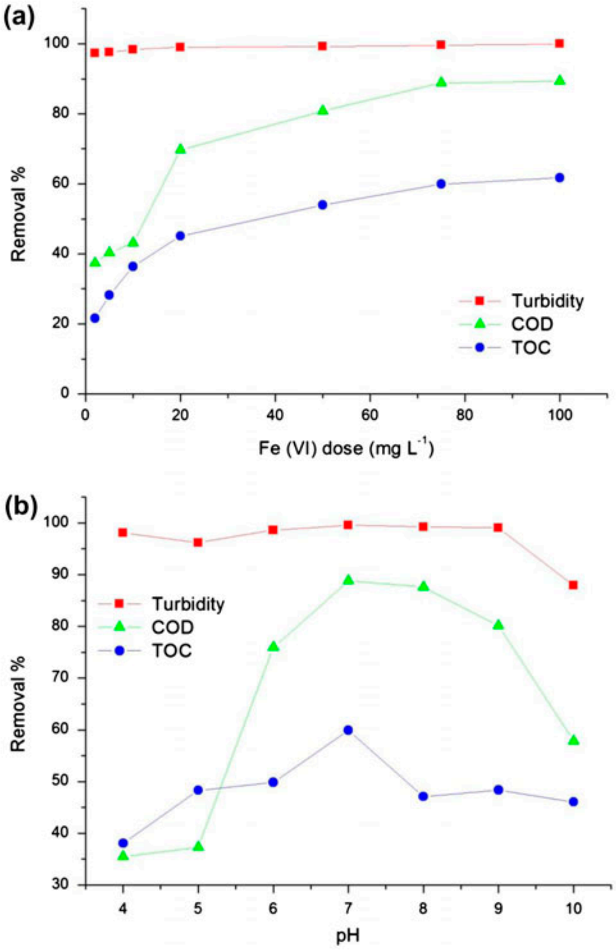

Fig. 2. Turbidity, COD and TOC removal efficiencies according to (a) applied Fe(VI) dose at pH 7 and (b) the change of pH at 75 mg/L Fe(VI) dose.

These results differ from those for AOPs, which are more effective under acidic conditions [30–32]. The decomposition of organics at this pH range may be explained by the higher redox potential and higher stability of ferrate(VI). Also, the ferrate(VI) process reaches the maximum sorption capacity between pH 7 and 8, as the by-product of ferrate(VI) degradation, $Fe(OH)_3$, occurs, and organics are coagulated by Fe(III) precipitates. Thus, degradation is of no way the major process by which compounds are removed from wastewater treatment plants, and hence the sorption mechanism may also intervene in the process [33]. In the light of this knowledge, the most efficient pH for greywater treatment by electrosynthesized ferrate(VI) was pH 7–8.

3.2. Surfactant degradation

Fig. 3 shows the anionic surfactant degradation according to the ferrate(VI) dosage and pH changes. The results demonstrated that there was more than 98% degradation of these types of compound. When a ferrate(VI) dose applied was between 20 and 100 mg/L, MBAS concentration was reduced to 0.63–0.23 mg/L, respectively. The consumed amount of MBAS increases with increasing concentrations of ferrate(VI).

Dependency between pH and surfactant removal can be seen in Fig. 3. It reaches its maximum value at pH 6 (96.08%). The removal per cent is lower in both acidic (pH 4 and 5) and basic conditions (pH 9 and 10). This can be attributed to the efficiency of ferrate (VI) species at mid-range pH (6–8). $HFeO_4^-$ is the dominant species at mildly acidic and neutral conditions and it is known that, as a protonated form of ferrate (VI) ($HFeO_4^-$), it reacts faster than the unprotonated species (FeO_4^{2-}) [34,35]. $HFeO_4^-$ can oxidize surfactants easily. Yet FeO_4^{2-} is dominant at pH 8, at which the coagulation effect also occurs, providing efficient removal. It must be pointed out that surfactants are usually amphiphilic organic compounds, meaning that they contain both hydrophobic and hydrophilic groups (their tails and heads, correspondingly). Therefore, when $Fe(OH)_3$ particles occur in the ferrate(VI) process, hydrophobic surfactant adsorbs onto the solid particles. By flocculation–coagulation, the particles collide and aggregate in hydrophobic–hydrophobic association and can be removed from greywater.

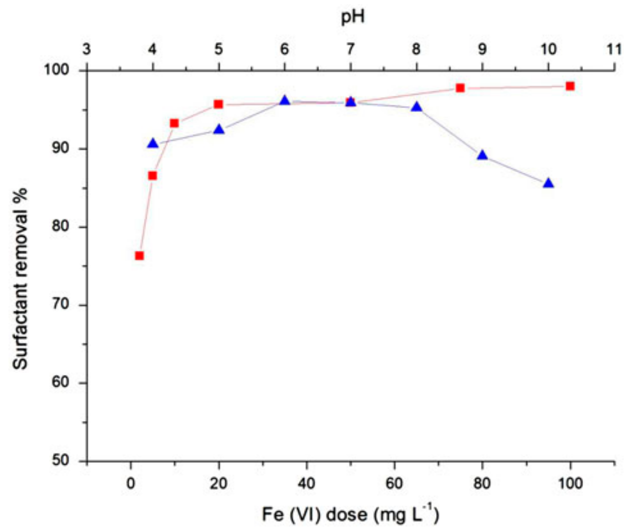

Fig. 3. Surfactant removal efficiencies (■ shows the effect of Fe(VI) dose and ▲ shows the effect of pH).

Surfactants may have negative effects if they are present in irrigation water. It is recommended that the concentration of anionic surfactants should not exceed 1 mg/L [16]. According to our results, Fe(VI) at the 75 mg/L dose is capable of leaving only 0.33 mg/L of surfactant in treated greywater.

3.3. Anion removal

The concentrations of anions in greywater samples after treatment are shown in Fig. 4, which shows that the ferrate(VI) process is highly efficient for the removal of all anions as above 65% removal efficiency was provided with 75 mg/L Fe(VI) dose. The benefit was clearly observed in the removal of anions. The treatment process achieved a stable removal efficiency of 98.7, 93.2, 73.9, 69.1 and 66.2% for PO_4^{3-}, F^-, SO_4^{2-}, NO_2^- and NO_3^-, with the 75 mg/L ferrate(VI) dose, respectively.

The significant effect of pH on the removal of anions can be seen in Fig. 4(b). At pH 4 and 5, efficiency was lower than in the range of pH 7–9. This was due to the production of $Fe(OH)_3$ in the treatment process. As far as iron hydroxide has the characteristic of sweeping floccules with a large surface area, this is beneficial for the rapid adsorption of soluble anions. However, PO_4^{3-} and F^- anions removal was greater than the other anions as NO_3^-, NO_2^- and SO_4^{2-} anions and are much more soluble than PO_4^{3-} and F^- [36]. Sweeping floccules which occurs with degraded Fe (VI) can easily remove those insoluble anions [37].

Such behaviour can be explained by that just formed colloidal particles combine with anions (An) and make granules, which aggregate much more quickly due to neutralization of their charges. The mechanism can be presented by means of the following scheme.

At the first stage of coagulation, the particle $Fe(OH)_3/FeO^+$ is being formed. It adsorbs (n-x)An- and generates a granule. Then diffusive layer with xAn- is being formed, that implies the occurrence of the particles' isoelectric points (see Fig. 5).

All this causes the colloidal particles gluing and growth of their size, which result in the more effective removal of anions from the solution.

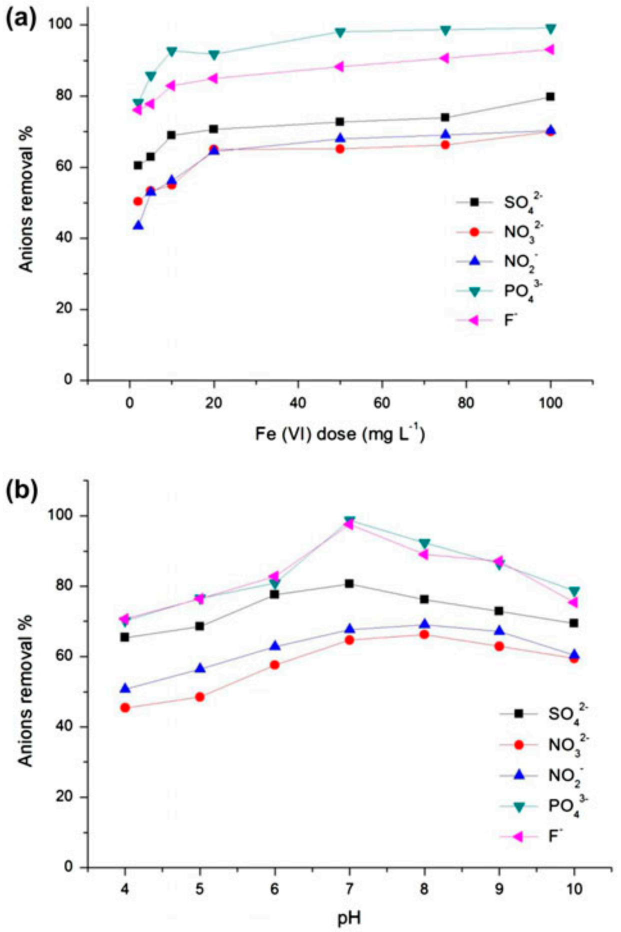

Fig. 4. Anions (F$^-$, Cl$^-$, NO_2^-, NO_3^-, PO_4^{3-} and SO_4^{2-}) removal efficiencies according to (a) applied Fe(VI) dose at pH 7 and (b) the change of pH at 75 mg/L Fe(VI) dose.

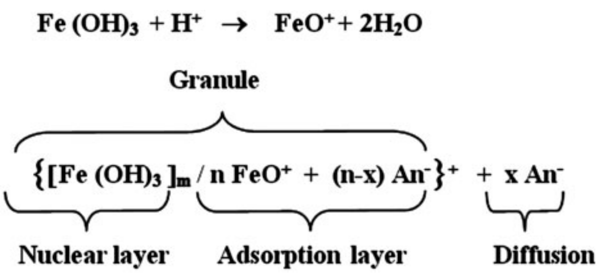

Fig. 5. Coagulation stages and generation of a granule.

3.4. Reactivity of Fe(VI) in greywater suspension

It is well known that ferrate(VI) is unstable in aqueous solution, and will quickly reduce to Fe(III) or insoluble end-product, $(Fe(OH)_3)$. Mössbauer spectroscopy was used to determine the oxidation states of iron in greywater suspension after the treatment. The Mössbauer spectrum determines the parameters including isomer shift (δ), which varies with the valence of iron in the sample [38]. Fig. 6 shows spectra of iron species in greywater sample after the treatment. This spectrum shows that the Fe(VI) was partially reduced to doublets of Fe(III). As seen in Fig. 6, the values of the isomer shift (δ) were highly sensitive to the oxidation state (OS) of iron, and δ values decreased with an increase in OS. Only Fe(III) was identified as a reaction final product of the Fe(VI) (not Fe(II)). The great amount of Fe(VI) was consumed in greywater sample.

While Fe(VI) reacted with pollutants in greywater, various reactions take place between Fe(VI) and pollutants. These reactions consist of the generation of Fe (V) and Fe(IV) via 1-e$^-$ and 2-e$^-$ transfer processes, production of radical species which can also generate Fe(V) and Fe(IV) species, further reactions of Fe(V) and Fe(IV) with contaminants and as well as Fe(III) formation, self-decompositions of Fe(VI), Fe(V), and Fe (IV) species (Fe(II) and Fe(III) formation) and reactions of ferrates with reactive oxygen species, $O_2^{\cdot-}$, and H_2O_2, produced from self-decompositions [39].

3.5. ZPs and PSD

Fig. 7 shows raw greywater particle size and the floccule growth profile with the dose of 75 mg/L ferrate(VI) at pH 7 and the 75 mg/L change of pH. The coagulation effect of the ferrate(VI) decomposition changes the PSD. After coagulation, much larger

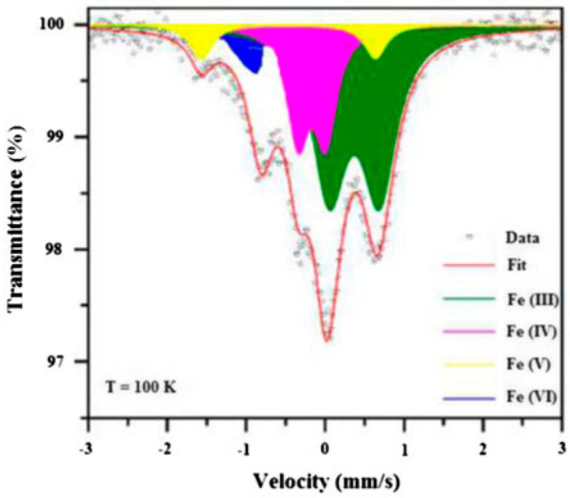

Fig. 6. Mössbauer spectra of Fe(VI), Fe(V), Fe(IV), and Fe (III) species formed together during disproportionation of ferrate(IV) in greywater sample (spectrum measured at 100 K).

particles were observed, with an average size of over 500 nm, to be compared with 59 nm before treatment. This was due to higher $Fe(OH)_3$ precursor mass production leading to a higher collision frequency.

At pH 7, ambient conditions become almost favourable for the $Fe(OH)_3$ precipitation and approached sweep coagulation, and therefore, they cause an acceleration in the floccules growth at the later stages.

ZP varies from −3.65 to −0.99 mV. This indicates that the solution was at rapid coagulation or flocculation according to D4187-82 ASTM ZP of Colloids in Water and Wastewater. The applied ferrate(VI) dose has a significant effect on ZP values reaching values of isoelectric points at a ferrate(VI) dose of 75 mg/L. Charge reversal is not observed during further increase of the ferrate(VI) dose up to 100 mg/L. Increasing ZP indicates also that during the process, charge neutralization occurs together with sweep coagulation and adsorption.

Variation of the floccules' ZP as a function of pH is shown in Fig. 7. It can be seen that the floccules' ZP increases gradually during the process for all applied pH values. Larger floccules and ZP values closer to zero were observed at pH 7 and 8, as removal efficiencies were higher at these pH values. This is because $HFeO_4^-$ reacts with compounds more rapidly than FeO_4^{2-} does. Density functional theory calculations on the reactivity of ferrate(VI) with compounds have shown that protonated ferrate(VI) has a larger spin density on the organic compounds than unprotonated ferrate(VI), which increases the oxidation ability of protonated ferrate(VI) [40]. Furthermore, ferrate(VI) yields Fe(II) and Fe(III) as reduced products, and different numbers of oxygen atoms are being transferred to form oxidized products.

3.6. Settling characteristics of flocculated greywater suspension

The settling characteristics of flocculated particles are an important indicator of the performance of sludge settling which influences the effluence quality of a secondary settling tank. Variations of the coagulation performance according to ferrate(VI) dose were investigated in terms of settling velocity and PSD. The flocculation efficacy for five different ferrate(VI) doses is presented in Fig. 8.

Effect of the ferrate(VI) dose was found to be remarkable. The plot of the interface height as a function of settling time indicates that settling velocity increases with increasing ferrate(VI) dose, although no such differences were observed between 75 and 100 mg/L doses of ferrate(VI). This result is compatible with the other experimental data obtained.

Fig. 9 exhibits PSD profiles for raw and treated greywater with different ferrate(VI) doses. As indicated previously, coagulation affects positively the PSD. While an average particle size was 0.025 μm before Fe (VI) treatment, 0.58 μm average particle size was provided after the treatment which was 23-fold greater than raw greywater's. Friedler et al. indicated that average particle size in greywater suspension increased to 0.5 μm from 0.064 μm by $FeCl_3$ coagulation which was 8-fold greater than raw greywater's [41]. There is a clear difference between PSD profiles for each ferrate(VI)

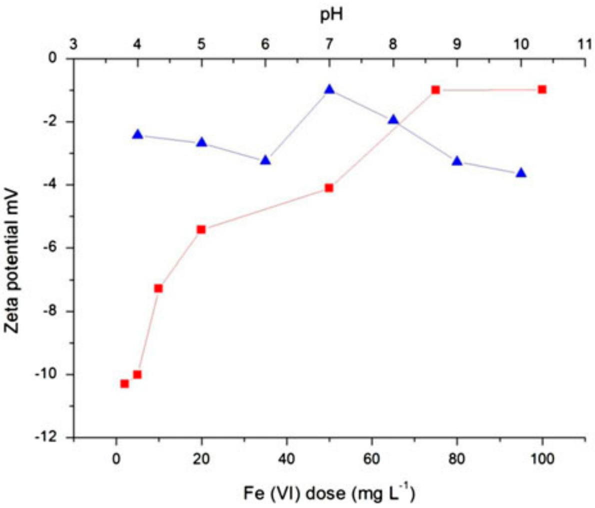

Fig. 7. The change of ZP (■ shows the effect of Fe(VI) dose and ▲ shows the effect of pH).

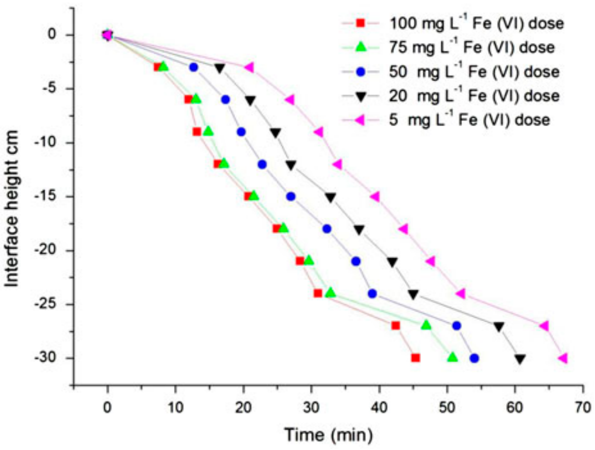

Fig. 8. Settling times of particles in treated greywater suspension by different ferrate(VI) dosage.

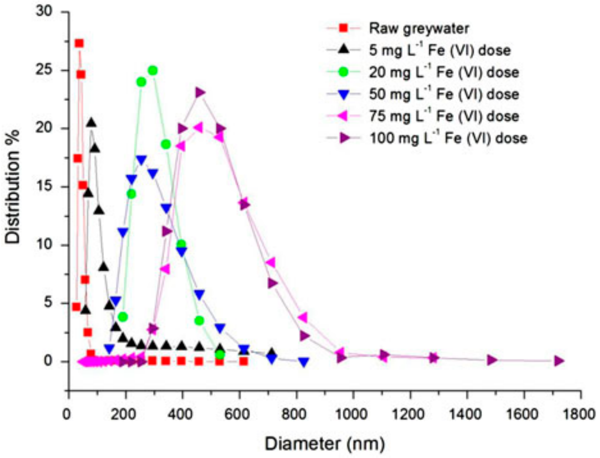

Fig. 9. Effect of ferrate(VI) dosage on particle size number distributions.

dose used in the experiments. Larger particles are observed for increased ferrate(VI) doses.

The results indicate that the closer proximity of the ferrate(VI) decomposition by-product, $Fe(OH)_3$ particles, due to increasing concentration, results in higher collision frequency, which enhances the flocculation process. The dependence of floccules' size on the dose of ferrate(VI) shows a similar parabolic trend for 75 and 100 mg/L.

3.7. Reuse potential of treated greywater

Among the recent guidelines, very few reuse guidelines are particularly made for greywater recycling. These guidelines generally focus on the healthy and environmental impacts and are often established by local authorities. In 2006, the World Health Organization (WHO) released a guideline for greywater reuse for restricted and non-restricted agricultural irrigation. The guideline only outlines the microbiological requirements without considering the other physical and chemical parameters. Different reuse types need different water quality conditions and therefore need different treatments changing from simple processes to advanced ones.

The assessment for the potential of reusing treated greywater from a restaurant by presented system, results of quality parameters were compared with regulatory documents from literature and different countries (see Table 2) as there is no specific greywater reuse regulation in Finland.

As it can be seen in Table 2, pH, COD, turbidity and surfactant concentration of treated greywater were in accordance with the quality parameters defined in the checked documents. Almost all values fall within those reported in literatures consulted about greywater reuse systems. But TN concentration (as NO_3^- and NO_2^-) was too high. Besides TP concentration was in agreement with the literature if only PO_4^{3-} concentration takes into consider. It can be said that treated greywater can be used for toilet flushing and landscape irrigation for water conservation.

3.8. Operating cost of greywater treatment by Fe(VI)

One of the most important parameters that affect the application of any method of water and wastewater treatment significantly is the operating cost (OC). The OC included material (mainly electrodes) cost, utility (mainly electrical energy) cost, chemicals cost (NaOH in this case) as well as labour, maintenance and other fixed costs. In this study, energy, electrode material and chemicals costs were taken into account as major cost items, in the calculation of the OC as €/m^3 of the greywater treated.

The major OC of Fe(VI) process was associated with electrical energy consumption during the process. The electrical energy required to Fe(VI) synthesis via Fe electrodes was calculated in terms of kWh/m^3 using the equation given as follows:

$$C_{\text{energy}} = \frac{Uit_{\text{process}}}{V} \tag{1}$$

where U is an average cell potential (V) in the ferrate (VI) producing cell; i is a current (A) passed for a duration of operating time t_{process} (h) and V is the volume (m^3) of the NaOH solution in the cell.

Electrode consumption was calculated theoretically and experimentally. Calculation of theoretical electrode consumption is given in Eq. (3):

$$C_{\text{electrode,theo}} = \frac{it_{\text{process}M_w}}{zFV} \tag{2}$$

where i is a current (A) passed for a duration of operating time t_{process} (s); M_w is the atomic weight of anode material (55.85 g/mol), z is the number of electrons involved in the oxidation/reduction reaction (z_{Fe} = 2); F is the Faraday's constant (96,485 C/mol) and V is the volume (m^3) of the NaOH solution in the cell.

In the overall assessment, total OC was calculated according to Eq. (3):

$$\text{Operating cost } \left(OC_{\text{Fe(VI)}pro}, €/m^3\right) = aC_{\text{energy}} + bC_{\text{electrode}} + cC_{\text{chemicals}} \tag{3}$$

Table 2
Average parameters of treated greywater from the presented system and standards in different countries and literature

		Goals for treatment					
Parameter	Treated greywater by Fe(VI)	[a]Literature A, B	[b]Spain A	[c]USA A, B	[d]Portugal A, B	[e]Australia A	[f]Japan B
pH	7.2	6–9	6–9	6–9	–	6–9	6–9
COD (mg/L)	105	24–118	<160	–	–	–	–
TSS (mg/L)	–	4.4–27.3	–	5	10	–	–
TP (mg/L)	0.017 (as PO_4^{3-})	≤0.05	–	–	–	–	–
TN (mg/L)	7.71 (as NO_3^- and NO_2^-)	≤1	–	–	–	–	–
Total coliform (CFU/100 mL)	–	0	0	–	1,000	<4	<10
Faecal coliform (CFU/100 mL)	–	0	0	N.D.	10,000	<1	<10
Surfactant (anionic) (mg/L)	0.23	≤1	–	–	–	–	–
Turbidity (NTU)	0.3	≤2	–	–	–	–	–

[A] Toilet flushing and laundry.
[B] Landscape irrigation.
[a] [17,42,43].
[b] [44].
[c] [45].
[d] [28].

Table 3
OCs for Fe(VI) producing and greywater treatment by Fe(VI)

Parameters	Value	Cost (€/m^3)
Current density, I_d (mA/cm^2)	1.47	–
Current, i (A)	0.12	–
Process time, $t_{process}$ (h)	1.5	–
Average voltage, V_{ave} (V)	1.716	–
Energy consumption, C_{energy} (kWh/m^3)	1.0296	0.074
Theoretical electrode consumption, $C_{electrode,\ theo}$ (kg/m^3)	0.627	0.53
Experimentally electrode consumption, $C_{electrode,\ exp}$ (kg/m^3)	0.556	0.47
Chemicals consumption, $C_{chemicals}$ (€/kg)	0.0188	15.04
[a]Cost for Fe(VI) producing, $OC_{Fe(VI)\ pro,theo}$	–	15.644
[b]Cost for Fe(VI) producing, $OC_{Fe(VI)pro,exp}$	–	15.587
Cost for greywater treatment, $OC_{treated\ greywater}$	–	~0.156

[a] Theoretical electrode consumption was considered.
[b] Experimental electrode consumption was considered.

where C_{energy} is electrical energy consumption, kWh/m^3; $C_{electrode}$ is consumption of iron electrodes, kg electrode/m^3; and $C_{chemicals}$ is consumption of chemicals, kg/m^3 for Fe(VI) synthesis as mentioned. Unit prices, a, b and c given for the Finnish Market, December 2013 were as follows: a is electrical energy price (0.072 €/kWh), b is electrode material price for Fe (0.85 €/kg), c is chemical price for NaOH (0.0188 €/kg).

According to the calculations and prices given above, OC was found as 15.644 €/m^3. This represents the cost for 1 m^3 ferrate(VI) production. In the experiments, 1 L greywater was treated using 10 mL of produced Fe(VI) solution. This volume ratio (100/1) provided Fe(VI) concentration of 75 mg/L which was determined as optimum conditions. So that, 1 m^3 greywater can be treated using 0.01 m^3 produced Fe (VI) solution which means that 1 m^3 of treated greywater costs 0.156 €/m^3 by electrosynthesized ferrate(VI). The summary of costs for greywater treatment can be seen in Table 3.

According to other feasibility studies for greywater treatment, OC of biological treatment plants varies between 0.1158 and 0.7491 €/m^3. The average value was found as 0.2200 €/m^3 [47]. According to another study conducted in India, for greywater reuse system, which consists of primary (synthetic sponge and sedimentation tank), secondary (sand filtration) and tertiary treatment (aeration and chlorination), the OC was found as 0.1347 €/m^3 [48].

4. Conclusions

Greywater reuse is a potential method of reducing potable water consumption, which, in turn, reduces wastewater discharge to public sewage systems and treatment plants. The environmental and economic benefits of this approach are significant. This restaurant case study evaluated the use of electrogenerated ferrate(VI) for greywater treatment.

The present investigation shows that ferrate(VI) has a potential for greywater reuse. 89% COD, 56% TOC and 99.9% turbidity removal were gained with a 75 mg/L dosage of ferrate(VI). Surfactant concentration reduced from 14.5 to 0.33 mg/L with the same dosage. Ferrate(VI) was successful in removing anions. Increased ferrate(VI) dosage has a positive effect on PSD and ZP. The pH had a significant impact on removal efficiencies, PSDs and ZP. The optimum ferrate(VI) dose was found to be 75 mg/L, and the optimum pH was 7 for restaurant greywater treatment.

Besides the high oxidation capacity of ferrate(VI), its coagulation and flocculation abilities cause the formation of Fe(III) ion, or ferric hydroxide, while oxidizing pollutants. Thus, greywater purification by ferrate(VI) is a feasible process, as its dual function (oxidation/coagulation) meets reuse standards. Treated greywater can be used for toilet flushing and/or landscape irrigation. Besides the assessment of OC shows that electrochemical ferrate(VI) production for greywater treatment is an affordable process. As a consequence, this electrochemical method is cost effective in practice.

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