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Influence of pH and temperature on Cr(VI) removal from a natural water using Fe(II): A pilot and full scale case study

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ABSTRACT

Aqueous Cr(VI) removal using Fe(II) was studied in a natural water as a function of temperature and pH, in kinetic batch experiments and also in a pilot and a full scale study. Temperature and pH strongly influenced the reduction of Cr(VI) by Fe(II). The reaction rate was increased by increasing pH in the range between 6 and 8 commonly encountered in natural waters. At 25°C and pH values higher than 7, maximum Cr(VI) removal was achieved at a reaction time equal or less than 5 min. The reaction followed a second order rate equation $\{-d[\mathrm{Cr(VI)}]/dt = k_{obs}[\mathrm{Cr(VI)}]\,[\mathrm{Fe(II)}][\mathrm{Cr(VI)}]\}$ with $k_{obs}[\mathrm{Cr(VI)}] \geq 1{\times}10^4\ \mathrm{M^{-1}s^{-1}}$. Reaction rate was also increased by increasing temperature from 10°C to 40°C, confirming the endothermic character of the reaction. Dissolved oxygen strongly competed with Cr(VI) in Fe(II) oxidation and batch experiments showed an increase of the reaction ratio [Fe(II)]/[Cr(VI)] from the almost stoichiometric value 3.1 at pH 6 to 25 at pH 8. These reaction ratio values were also verified by the pilot as well as by the full scale experiments. In addition pilot and full scale experiments proved that the sand bed contributed to the oxidation of the excess Fe(II) dose, improving in turn the removal of chromium precipitates. This was attributed to a surface effect due to ferric oxy-hydroxides retained on the sand bed, whose surface hydroxyl groups coordinated with Fe(II) increasing its oxidation rate and removal.

Keywords: Chromate; Ferrous; pH; Temperature; Sand-filter

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1. Introduction

Chromium (Cr) is the 21st most abundant element in the earth's crust and occurs mostly in its trivalent form Cr(III), with the ferrous chromite [(Fe, Mg)Cr_2O_4] to be the principal ore. It enters the water from both natural and anthropogenic sources, with leather tanneries, textile industry, cooling tower blow-down and electroplating factories being the most common anthropogenic sources. Since Cr(III) solubility, at the common pH range 6.5–8.5 of potable water, was determined to be around 10^{-7} M (~5 μg/L) [1], higher naturally occurring chromium concentrations were attributed to Cr(VI) [2] due to natural oxidation of Cr(III) in soils derived from ultramafic [3] and ophiolitic rocks [4]. Our laboratory has determined Cr(VI) concentrations in the range of 5–110 μg/L in water samples derived from ophiolitic rocks all over Greece, even at an altitude as high as 1,700 m of Smolikas

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mountain in spring water samples. Conclusively, Cr(VI) is a common natural pollutant of drinking water which possibly formed through the following process.

It is believed that MnO_2 is likely to be responsible for most Cr(III) oxidation, since oxidation of Cr(III) to Cr(VI) is poor with dissolved oxygen [5], while it is very effective in the presence of MnO_2 [6,7]. The oxidation reaction would occur in three steps [7]:

- Adsorption of Cr(III) onto MnO_2 surface sites
- Oxidation of Cr(III) to Cr(VI) by surface Mn(IV)
- Desorption of the reaction products Cr(VI) and Mn^{2+}

which suggest the following theoretical stoichiometries:

$$Cr^{3+} + 1.5\delta.MnO_2(s) + H_2O \rightarrow HCrO_4^- + 1.5\ Mn^{2+} + H^+$$

$$Cr(OH)_2^+ + 3\beta.MnO_2(s) + 3H_2O \rightarrow HCrO_4^- + 3MnOOH(s) + 3H^+$$

Cr(III) is an essential element for glucose metabolism, amino and nucleic acidic synthesis. In contrast, Cr(VI) is a well known carcinogenic element when inhaled [8], while there is a considerable debate regarding its carcinogenicity when ingested. WHO considers Cr(VI) as a priority pollutant and US EPA and European Community limit total chromium to 0.1 mg/L and 0.05 mg/L, respectively.

The toxicity of Cr(VI) has engendered interest in processes for its removal from both industrial effluents and potable water. Removal of Cr(VI) was studied through its adsorption by iron oxy-hydroxides [9] and ion exchange resins [10]. However, the most effective way to remove Cr(VI) from water is to reduce it to less toxic and less soluble Cr(III). Trickling filter was effectively applied for the biological reduction of Cr(VI) and its removal from industrial wastewater [11]. Other reductants used for the reduction of Cr(VI) to Cr(III) in water samples included activated carbon [12], sodium sulfite-bisulfite [10], amorphous iron sulphide [13], hydrogen sulphide [14], metallic iron [15] even in nanoparticles form [16] and ferrous water soluble salts [17]. Considering, however, that completion of Cr(VI) reduction was achieved within hours or days with all the previously reductants except aqueous Fe(II), only the latter seems to be of practical importance for Cr(VI) reduction. Indeed, it has been observed that the rates of aqueous Cr(VI) reduction by highly soluble Fe(II) salts were significantly fast, with reduction being generally completed within the first 1–2 min after the addition of ferrous iron [10,17–19]. The reduction of aqueous Cr(VI) by aqueous Fe(II) can be described by the overall reaction:

$$Cr(VI)_{(aq)} + 3Fe(II)_{(aq)} \rightarrow Cr(III)_{(aq)} + 3Fe(III)_{(aq)} \qquad (1)$$

The products of Reaction (1) will be co-precipitated as hydroxides in slightly acidic to alkaline solutions under the following scheme, depending on their solution concentrations:

$$xCr(III) + (1-x)Fe(III) + 3H_2O \rightarrow Cr_xFe_{1-x}(OH)_3(s) + 3H^+ \qquad (2)$$

where x can vary between 0 and 1. The solubility of $Cr_xFe_{1-x}(OH)_3(s)$ limits total dissolved chromium concentration, as Cr(III), to values that are less than the preset drinking water maximum contaminant level of 50 μg/L between pH 5 and 11 [17]. However, as Cr(III) is oxidized to Cr(VI) in distribution systems by chlorine compounds, a successful technology is required to effectively remove both Cr(III) and Cr(VI).

The objectives of this study were the evaluation of pH, temperature, dissolved oxygen and Fe(II) dose on the removal of Cr(VI) – achieving values below 1 μg/L – and of the excess of Fe(II) dose using a natural water derived from ophiolitic rocks. These objectives were realized by practicing either batch experiments with filtration through a 0.45 μm pore-size membrane filter or pilot and full scale experiments with filtration through a sand filter.

2. Materials and methods

2.1. Water source

Water samples from underground natural water, which is qualified as drinking water, were collected during spring and autumn of 2008. The quality parameters of this water, during the period of the study, are presented in Table 1. The choice of this water was based on the fact that its physicochemical parameters and the concentration of the anions and cations that influence Cr(VI) removal are typical of the ultramafic-ophiolitic rocks derived natural waters and therefore the results obtained could be applicable to a majority of this type of natural waters.

2.2. Reagents

A 1,000 mg/L Cr(VI) stock solution was prepared from reagent grade $K_2Cr_2O_7$. Working standards were freshly prepared by proper dilution of the stock solution. Water samples were spiked with Cr(VI) by adding the appropriate volume of the working Cr(VI) standards to achieve total Cr(VI) concentrations of 50, 100 and 250 μg/L (0.96, 1.92 and 4.8 μM). Initial and residual Cr(VI) concentrations were determined by the diphenylcarbazide method [20] using a Lambda 2 UV/VIS spectrophotometer version 3.7 Perkin Elmer equipped with 10 cm path-length measurement cells. The detection limit of the method, calculated from 7 replicates of 2–5 μg Cr(VI)/L, was estimated to be 1.4 μg/L. Total initial, as well as residual chromium concentration was determined by graphite furnace atomic absorption spectrophotometry (GFAAS) using a Perkin Elmer instrument, model AAnalyst 800. The detection limit of the method, calculated from 7 replicates of 2–5 μg Cr/L, was also estimated to be 0.8 μg/L.

A 1,000 mg/L Fe(II) stock solution was prepared by diluting 4.95 reagent grade $FeSO_4.7H_2O$ and 2 mL concentration H_2SO_4 in 1 L distilled water. This stock solution was stored in an amber bottle in a cool, dark location. The titer of stock was quantified daily by a 0.01 N stan-

Table 1
Typical physicochemical characteristics of the water used in this study

Physicochemical parameters		Cations (mg/L)		Anions (mg/L)		Trace elements (µg/L)			
pH	7.7	Na^+	20	Cl^-	25	As	<1	Fe	<1
Temperature, °C	17.5	K^+	1.3	HCO_3^-	384	Ba	70	Mn	<1
TDS, g/L	0.38	Ca^{2+}	45	SO_4^{2-}	13	Cd	<0.1	Ni	<1
Suspended solids[1], mg/L	1.1	Mg^{2+}	49	NO_3^-	9	Co	<1	Pb	<1
TOC, mg/L	0.4	Sr^{2+}	0.2	NO_2^-	<0.01	Cr(VI)	33	Se	<1
SiO_2, mg/L	26	NH_4^+	<0.05	PO_4^{3-}	0.2	$Cr_{(tot)}$	35	Zn	15

[1] Particle size distribution, particle/mL

2–3 µm	3–5 µm	5–10 µm	10–15 µm	15–30 µm	30–400 µm	2–400 µm
660	850	420	150	20	—	$2.1×10^3$

dard $KMnO_4$ titrant [20]. Fe(II) doses of 0.5, 1, 2.5, and 5 mg/L (8.92, 17.8, 44.6, 89.2 µM) were used by applying appropriate aliquots of the stock solution to the water samples. Concentrations of the stock solution, as well as, Fe(II) doses were always verified by flame atomic absorption spectrophotometry (FAAS). Residual total iron concentration was determined either by the FAAS at batch and pilot scale experiments or by the GFAAS at full scale experiments using a Perkin Elmer instrument, model AAnalyst 800. The detection limit of the method, calculated from 7 replicates of:

- 2–5 µg Fe/L was calculated 1.5 µg Fe/L for GFAAS,
- 75–300 µg Fe/L was calculated 50 µg Fe/L for FAAS

The pH of the water samples were initially adjusted either with 1 N HCl or 1 N NaOH, in such a way that the addition of Fe(II) dose that followed brought the pH at the selected values, that is 6, 6.5, 7, 7.5 and 8.

Zeta potential measurements were carried out to quantify the magnitude of the electrical charge of precipitates surface and to define the isoelectric point (IEP). The water sample was poured into the electrophoresis cell of a Rank Brothers Apparatus MkII, the electrophoretic velocity was determined through a digital camera and the value of ζ-potential was calculated.

2.3. Procedure

2.3.1. Batch kinetic experiments

Water samples spiked with Cr(VI) were kept for 24 h in a thermostatic cabinet, to achieve equilibrium at the selected temperature (10, 25 and 40°C). This wide range of temperatures was selected for the following two reasons: a) The low temperatures range to simulate natural conditions during winter and b) the higher temperatures to simulate conditions of geothermic origin waters. The ferrous dose was added to the water sample inside the thermostatic cabinet, rapidly mixed at G value of 150 s^{-1} for 2 min, flocculated at G value of 35 s^{-1} for 2, 5, 15, 30 and 60 min and filtered through a 0.45 µm pore-size membrane filter.

2.3.2. Pilot scale experiments

Water samples were spiked with Cr(VI) and kept for 24 h at 20±2°C (room temperature). The pilot system consisted of the following major components: a peristaltic pump for water sample feeding at 25 L/h, a mixing tank V_m = 4 L equipped with a propeller stirrer rotating at 300 rpm and resulting a G value of 200 s^{-1} for 9.6 min, a flocculation tank V_f = 15 L (total reaction time 45.6 min) equipped with a four paddles stirrer rotating at 30 rpm and resulting a G value of 30 s^{-1} for 18 min, a filter column D_{in} = 0.08 m ($S = 5×10^{-3}$ m^2) containing 0.7 m of silica with particle-size of 0.4–0.8 mm and uniformity coefficient 1.6 resulting in filter loading rate 5 m^3/m^2h and a CHEMTRAC PC 2400D particle counter for counting particle size distribution in the treated water. For the addition of ferrous sulphate a peristaltic chemical feed pump was used. Pilot scale experiments were run for at least 6 h.

2.3.3. Full scale experiments

The treatment plant was installed nearby the underground natural water, whose quality parameters are presented in Table 1 and consisted of the following major components:

- A submersible pump for water feeding at 25 m^3/h,
- A flow meter which indicates flow rate, records the total volume of the water treated and also controls the proportional addition of Fe(II), keeping its dose constant independently of the variation of the water flow,
- An in line mixer of Fe(II) and CO_2,
- A tank (V = 100 L) incorporating a stirrer for $FeSO_4 \cdot H_2O$ dissolution (20 g/L) along with the dosing pump (1–5 L/h) for feeding the solution,
- A pH meter controlling CO_2 addition for pH adjustment,

- A flocculation tank of 3.7 m^3 equipped with a two paddles stirrer rotating at 21 rpm and resulting in a total reaction time of about 9 min,
- A filter column D_{in} = 1.8 m (S = 2.55 m^2) containing 0.75 m of silica with particle-size of 0.4–0.8 mm and uniformity coefficient 1.6, resulting in a filter loading rate of about 10 m^3/m^2h.
- A particle counter for counting particle size distribution in the treated water.
- A buffer tank and a pump for feeding the water (25 m^3/h) to a micro-filtration unit,
- A micro-filtration unit with 0.45 μm pore-size filter.
- A backwash system for the sand filter consisting of a 20 m^3 water tank and a pump with a maximum capacity of 110 m^3/h at 2 bar. Backwash water was disposed to the sewage system for treatment at a central wastewater treatment plant.

3. Results and discussion

3.1. Batch experiments

According to Eq. (1) the required molar ratio [Fe(II)]/[Cr(VI)] for complete Cr(VI) removal is equal to 3, if theoretically the oxidation of Fe(II) was exclusively accomplished due to Cr(VI) reduction. However, it is well known that the dissolved oxygen competes with Fe(II) oxidation, which in turn results in a demand for excess Fe(II) addition in order to ensure complete Cr(VI) reduction/removal. The residual Fe(II) concentration should be further oxidized by dissolved oxygen and precipitated as $Fe(OH)_3$ and removed along with $Cr_xFe_{1-x}(OH)_3$ precipitates. Consequently, in an attempt to determine the kinetic parameter of Cr(VI) removal, as well as of the excess Fe(II) dose removal, a wide range of molar ratios [Fe(II)]/[Cr(VI)] was practiced in the batch experiments.

3.1.1. Establishing the experimental conditions

Preliminary experiments were conducted, with a spiked sample containing initial Cr(VI) concentration equal to 100 μg/L (1.92 μM) and using a Fe^{2+} dose equal to 0.5 mg/L (8.92 μM), at pH 6.5, to establish the reaction time at various temperatures. Since during rapid-mixing and flocculation all reactions (reduction, adsorption, co-precipitation) leading to chromium removal are completed, the term "reaction time" includes the sum of "rapid-mixing plus flocculation" time in this paper. The rapid-mixing time of 2 min was selected in accordance to the literature [21]. The results (Fig. 1) showed the following:

- At 25°C, maximum Cr(VI) removal was achieved at a reaction time of 30 min and the reaction obeyed the following second-order rate equation {$-d[Cr(VI)]/dt = k_{obs}[Cr(VI)]\,[Fe(II)][Cr(VI)]$}. The rate coefficient k_{obs}[Cr(VI)] was calculated to be equal to $3.4\times10^3\ M^{-1}s^{-1}$. The use of pore-size filters of 0.2 μm resulted in about the same Cr(VI), Cr(total) and Fe(total) residual concentrations with the 0.45 μm filter, verifying the fact that the latter was equally effective. In view of the above results, a 0.45 μm pore-size membrane filter was used in all subsequent batch experiments.

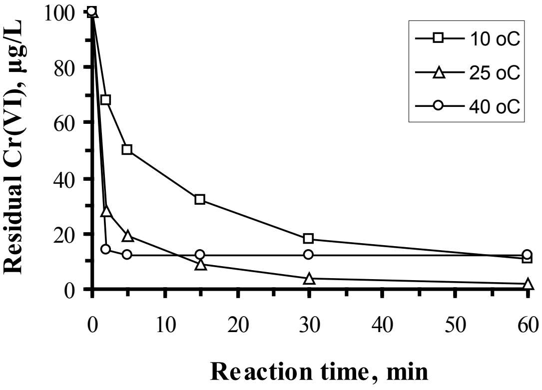

Fig. 1. Cr(VI) removal as a function of the reaction time and temperature at pH 6.5 (Cr(VI) = 100 μg/L and Fe(II) = 0.5 mg/L).

- At 10°C, however, a reaction time of 60 min resulted in about 90% of total Cr(VI) reduction, obviously due to a decrease of the reaction rate (k_{obs}[Cr(VI)] = $5.2\times10^2\ M^{-1}s^{-1}$). Further Cr(VI) removal proceeded at no practically measurable rate.
- At 40°C the reaction was completed at 5 min, reaching a residual concentration of 12 μg Cr(VI)/L (Fig. 1) and a value of $k_{obs}[Cr(VI)]$ =$10.1\times10^3\ M^{-1}s^{-1}$ was estimated.

These results are indicative of the endothermic character of the reaction (Fig. 2), as reported by other researchers

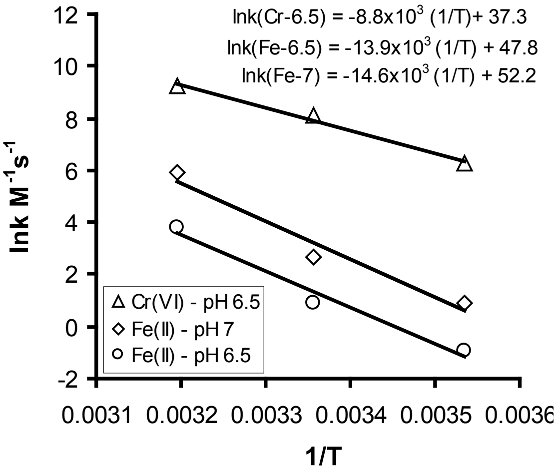

Fig. 2. Relationship between second-order rate coefficient and 1/T for Cr(VI) reduction (Cr(VI) = 100 μg/L and Fe(II) = 0.5 mg/L) and O_2 – oxidation of excess Fe(II) (Cr(VI) = 100 μg/L and Fe(II) = 2.5 mg/L).

as well [22]. Similar results were also obtained when using water samples with initial Cr(VI) concentration equal to 50 and 250 µg /L.

3.1.2. pH dependence of reaction kinetics

The observed rate coefficient was strongly depended upon the pH of the solution. The increase in reaction rates at pH values above 4 was explained by the increase in the concentration of highly reactive hydroxylated [$Fe(OH)^+$ and $Fe(OH)_2$] species of Fe(II) [22]. Fig. 3 shows Cr(VI) reduction experiments at pH values between 6 and 8, at 25°C. The reduction rate progressively rises above pH 6, as also described by Buerge and Hug [19], resulting in maximum Cr(VI) reduction in 5 min at pH 7 and in less than 2 min at higher pH values. At pH = 6 ($k_{obs}[Cr(VI)] = 6.5\times10^2\ M^{-1}s^{-1}$) and pH = 6.5 ($k_{obs}[Cr(VI)] = 3.4\times10^3\ M^{-1}s^{-1}$) reduction of Cr(VI) was almost complete (Cr(VI) ≤ 2 µg/L) in 240 min (data not shown) and 60 min (Fig. 1), respectively. At pH 7 a value of $k_{obs}[Cr(VI)]$ on the order of 1×10^4 was calculated, while at higher pH significantly greater $k_{obs}[Cr(VI)]$ values were estimated. Plotting $\log k_{obs}$ of the above mentioned values against pH a slope close to one (1.15) was calculated (data not shown). These results indicate that $Fe(OH)^+$ is the most important iron species (reductant) contributing to the observed reaction rate, in agreement to the results of Sedlak and Chan [22]. The higher values of $k_{obs}[Cr(VI)]$ calculated in the present work in comparison to those of Buerge and Hug [19], were attributed to the higher non stoichiometric concentrations of Fe(II) dose, as well as to the components of the natural water used, such as suspended solids, SiO_2 (H_2SiO_3-$HSiO_3^-$) and TOC (Table 1), since solid phases surface, H_2SiO_3-$HSiO_3^-$ and organic ligands have strong positive influence on the kinetics of Cr(VI) reduction by Fe(II) [23]. These results also disagree with the findings of Fendorf and Li [18], who observed a pH-independent empirical rate law:

$$-d[\mathrm{Cr(VI)}]/dt = k\,[\mathrm{Fe(II)}]^{0.6}\,[\mathrm{Cr(VI)}] \qquad (3)$$

at a pH range between 6 and 8.2, where $k = 56.3\pm 3.7\ mmol^{-0.6}min^{-1}L^{0.6}$. Moreover, in experiments by Eary and Rai [17], initial concentrations of 96 µM Cr(VI) and 192 µM Fe(II) at pH 2–13 resulted in a complete (stoichiometric) transformation within 1–2 min. In contrast, our kinetic data predicts that such a fast reaction is only possible above pH 7. In addition, our findings were substantiated by kinetic studies [17] which postulated that the rate-limiting step for the aqueous reduction of Cr(VI) by Fe(II) was controlled by an inner-sphere reaction, which in turn can generally be expected to increase the rate of reduction as pH increases, because hydrolysis of the reactants promotes the transfer of electrons through bridging hydroxyl ions.

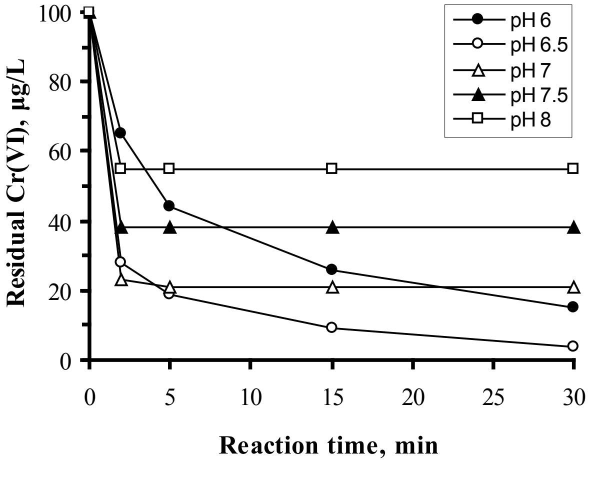

Fig. 3. Influence of pH on Cr(VI) removal, (Cr(VI) = 100 µg/L and Fe(II) = 0.5 mg/L, T = 25°C).

3.1.3. Influence of dissolved oxygen

However, as pH increases the oxidation rate of the aqueous Fe(II) to Fe(III) by dissolved oxygen increases as well [Eq. (4)]. The self-evident high dissolved oxygen concentration in all natural waters, which is necessary for Cr(III) oxidation to Cr(VI) must be underlined.

$$-d[\mathrm{Fe(II)}]/dt = k_{Fe}[\mathrm{Fe(II)}][\mathrm{OH}^-]\ 2p\ \mathrm{O}_2 \qquad (4)$$

Data of Fig. 3 show that the Cr(VI) residual concentrations, after 30 min reaction time, at pH 6.5, 7, 7.5 and 8 were 4, 21, 38 and 55 µg/L, respectively, proving that dissolved oxygen strongly competes with Cr(VI) in Fe(II) oxidation at a pH higher than 6.5. In contrast, at a pH range between 6 and 6.5 a stoichiometric value of reaction ratio [Fe(II)]/[Cr(VI)] = 3.1±0.1 was observed, confirming the negligible participation of dissolved oxygen in Fe(II) oxidation. However, at this pH range the oxidation rate of the residual Fe(II) by dissolved oxygen was so slow as to result in a residual total iron concentration higher than the maximum contaminant level 200 µg Fe/L and low Cr(III) separation (Fig.4 – compare Cr(VI) and Cr_{total} concentrations). Concerning the coefficient of the second-order rate equation:

$$-d[\mathrm{Fe(II)}]/dt = k_{obs[Fe(II)]}\,[\mathrm{Fe(II)}][\mathrm{O}_2] \qquad (5)$$

for oxygen oxidation reaction of the excess of Fe(II) dose at dissolved oxygen concentration 7.9 ±0.2 mg/L and at constant pH value, the follows remarks can be made:

- At 25°C the value $k_{obs}[Fe(II)] = 2\pm1\ M^{-1}s^{-1}$ at pH 6.5 increased to $14\pm3\ M^{-1}s^{-1}$ at pH 7 (Fig. 2) and to significantly greater than 2×10^2 at pH 7.5. These values at pH 6.5 and 7 are lower by almost three orders of magnitude than that of Cr(VI) reduction by Fe(II) (see section 3.1.1). However, these values are close to that observed by Sung and Morgan, 1980 [24] for Fe(II) heterogeneous oxidation by dissolved oxygen.

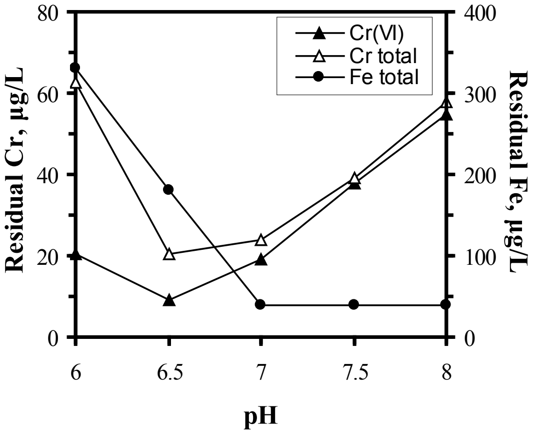

Fig. 4. Residual Cr(VI), Cr_{total} and Fe_{total} as a function of pH, (Cr(VI) = 100 μg/L and Fe(II) = 0.5 mg/L, T = 25°C).

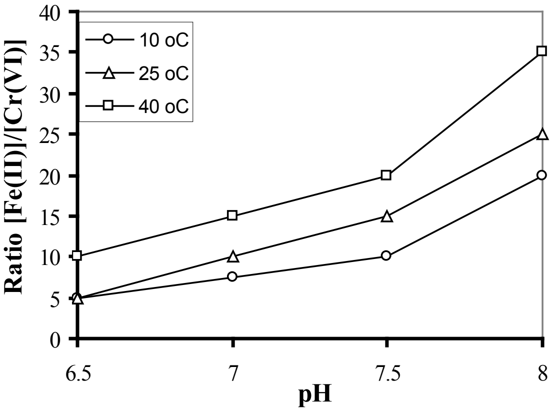

Fig. 5. Optimum [Fe(II)]/[Cr(VI)] ratio for Cr(VI) removal at sub-ppb level as a function of pH and temperature.

- Fig. 2 verifies the endothermic character of oxygen oxidation of Fe(II) and also reveal the higher rate increase of k_{obs}[Fe(II)] with temperature in comparison of Cr(VI) reduction; compare the slope of Cr(VI) reduction by Fe(II) with that of excess Fe(II) oxidation by dissolved oxygen of the water. This influence of temperature on the excess Fe(II) oxidation by oxygen resulted in a higher demand for Fe(II) dose with the increase of temperature; e.g. for lowering Cr(VI) at sub-ppb level at pH 7, a molar ratio [Fe(II)]/[Cr(VI)] of 7.5, 10 and 15 at temperatures 10, 25 and 40°C was respectively calculated (Fig. 5).
- The rate limiting step in the process of Cr(VI) removal seems to be the oxidation of the excess of Fe(II) dose.

The technological significance of these observations concerning potable water treatment — Cr(VI) < 1 μg/L, Cr_{total} < 5 μg/L and Fe_{total} < 50 μg/L — were as follows:

- pH values higher than 7 resulted in fast and complete Cr(VI) reduction and Fe(II) oxidation (Fig. 4) as well as in an efficient precipitates removal.
- The required molar ratios [Fe(II)]/[Cr(VI)] for complete Cr(VI) removal were increased with pH and temperature for all initial Cr(VI) concentrations (Fig. 5). A complete Cr(VI) removal was ensured at 25°C and 5 min reaction time using molar ratio of 10, 15, 20 at pH 7, 7.5 and 8, respectively. These molar ratios were increased by almost 50% at 40°C (Fig. 5). The lower molar ratio at 10°C must be accompanied with a 30 min reaction time for a complete reduction of Cr(VI).

3.1.4. *ζ-potential*

The isoelectric point (IEP) of the particles of natural water used in this study was calculated to be 4.6 at 25°C.

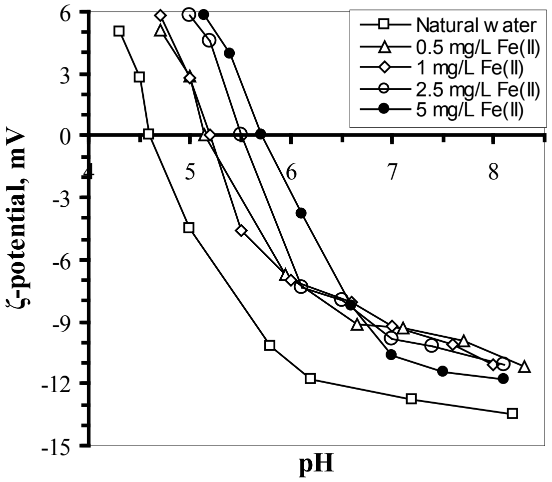

Fig. 6. Influence of Fe(II) dose on ζ-potential of the natural water.

The ζ-potential in the pH range 6.5–8.5, concerning water treatment technology, was determined to be between –12 and –14 mV (Fig. 6). The IEP was increased step-wise from 5.15 to 5.7 as Fe(II) dose increased from 0.5 mg/L to 5 mg/L, respectively. However, in the pH range 6.5–8.5 a 0.5 mg/L Fe(II) resulted in "lower absolute" ζ-potential values which gradually increased as Fe(II) dose increased. At pH 7.5, for example, the natural water's ζ-potential value –13 mV "decreased" to –9.7 mV through the addition of 0.5 mg Fe(II)/L, which in turn "increased" to –11.4 mV at 5 mg/L Fe(II) dose (Fig. 6). The latter increase of ζ-potential value seems numerically to be low, while on the contrary it strongly influenced the particles removal efficiency (see Table 2 line 16, column 5). In the end, a shift of –1mV and +1mV from the ζ-potential curve of the

Table2
Pilot scale data concerning the Cr(VI) removal from a natural water[a] using Fe(II)

Initial concentration		Residual concentration, μg/L			Particles/mL	Molar ratio [Fe(II)]/[Cr(VI)]
mg Fe(II)/L	μg Cr(VI)/L	Cr(VI)	$Cr_{(total)}$	$Fe_{(total)}$		
pH 7						
0	33	33	35	BDL[b]	2.1×10^3	0
0.5	33	BDL	2±1	9±2	80±20	14
1	33	BDL	BDL	9±2	60±20	28
2.5	33	BDL	BDL	3±2	100±20	70
2.5	33 + 200[c]	BDL	BDL	3±2	100±20	10
pH 7.5						
0	33	33	35	BDL	2.1×10^3	0
0.5	33	2±1	4±1	5±2	110±50	14
1	33	BDL	3±1	7±2	200±40	28
2.5	33	BDL	BDL	10±3	100±50	70
2.5	33 + 100[c]	BDL	2±1	5±2	100±50	17.5
5	33	BDL	BDL	150±50	10^3±500	140
Detection limit		1.4	0.8	1.5	20	—

[a] The physicochemical analysis presented in Table 1; [b] BDL: below detection limit; [c] Added Cr(VI) concentration.

Table 3
Full scale data concerning the Cr(VI) removal from a natural water using Fe(II)

Fe(II) dose (mg/L)	Residual concentration (μg/L)				Molar ratio [Fe(II)]/[Cr(VI)]
	Cr(VI)	$Cr_{(total)}$	Fe(II)[a]	$Fe_{(total)}$	
pH 7.05±0.05					
0.2	4±1	4±1	BDL	19±5	6.5
0.4	BDL	BDL	45±5	55±10	13
0.8	BDL	BDL	75±10	85±20	26
pH 7.25±0.05					
0.2	5±1	5±1	BDL	15±5	6.5
0.4	BDL	BDL	BDL	10±5	13
0.8	BDL	BDL	7±2	12±5	26
pH 7.5±0.05					
0.2	7±1	8±1	BDL	8±4	6.5
0.4	BDL	BDL	BDL	10±3	13
0.8	BDL	BDL	BDL	14±6	26
Detection limit	1.4	0.8	1.5	1.5	-

[a] Measured by GFAAS at effluent filtered through a 0.45 μm pore-size membrane filter.

natural water at 25°C was respectively observed at 10°C and 40°C, indicating an influence of minor importance on ζ-potential within the temperature range studied.

3.2. Pilot scale experiments

The main objective of these experiments was to examine the efficiency of a sand filter to remove the precipitates formed due to the reaction of Cr(VI) with Fe(II), since the sand filter is the most frequently practiced water treatment process for suspended solids separation. The significantly low particle counts (< 250 particles/mL) of treated water substantiate the efficiency of the sand filter process in the precipitate's removal for a Fe(II) dose lower than 2.5 mg/L. In contrast, our feeling was that a dose of 5 mg Fe(II)/L at pH 7.5 resulted in an unstable process, since a higher variation and lower particles' removal were observed (Table 2 line 16, column 6). Similar deterioration of sand filters efficiency, which influence in turn total chromium removal, was also observed by McGuire et al. [10].

The experimental results confirmed the batch experiments data (Fig. 5), since a reactants [Fe(II)]/[Cr(VI)] ratio equal to 10 at pH = 7 and equal to 17.5 at pH = 7.5 resulted in residual Cr(VI) BDL (1.4 μg/L, Table 2). A significant contribution of the sand filter to Fe(II) oxidation was also observed, since residual total iron concentrations lower than 50 μg/L were determined (data not shown) even for Fe(II) dose of 2.5 mg/L at pH 7, improving in turn the removal of chromium precipitates. This residual total iron concentrations achieved were significantly lower than the maximum contaminant level of 200 μg Fe/L for potable water. This was attributed to ferric oxy-hydroxides retained on the sand bed, whose surface hydroxyl groups coordinated with Fe(II) increasing its oxidation rate and removal. It must be stressed that during batch experiments with 100 μg Cr(VI)/L, using Fe(II) dose of 2.5 mg/L at pH 7, 25°C and 30 min reaction time, poor iron removal efficiencies were observed, since a residual total iron concentration of 0.25 mg/L was determined.

3.3. Full scale experiments

Evaluating the experimental results of section 3.1 as well as of section 3.2 it was concluded that for Cr(VI) removal, at sub ppb level, from the natural water (Table 1) along with efficient iron removal:

- the optimum pH ranged between 7 and 7.5,
- the key-parameter for fast Cr(VI) reduction is the Fe(II) hydrolysis-precipitation, since hydrolysis products promotes the transfer of electrons through bridging hydroxyl ions,
- a reaction time greater than 5 min, due to waters' temperature (17.5°C), should be selected, and
- the selected value of the molar ratio [Fe(II)]/[Cr(VI)] should range between 7 and 14.

The full scale experimental results of Table 3 show that a molar ratio 6.5 (<7) at pH 7 resulted in a residual Cr(VI) concentration of 4±1 μg/L and a molar ratio of 13 at pH 7.5 resulted in residual Cr(VI) concentration below method's detection limit (1.4 μg/L) verifying the results shown in Fig. 5. Total chromium and iron concentration before (sand-filter's effluent) and after micro-filtration were determined to be not significantly different, verifying the optimum efficiency of the sand filtration. The significantly better efficiency of iron removal achieved during pilot scale experiments (Table 2, column 5) should be attributed to the greater reaction time (45.6 min) and to the lower filtration rate (5 m^3/m^2h) practiced, in comparison with the 9.6 min and 10 m^3/m^2h, respectively, of full scale experiments (Table 3, column 5).

Applying the data of Table 3 in equation (5); Cr(VI) removal 33 μg/L (0.635 μM/L), dissolved oxygen 8.4 mg/L (263 μM/L) and time 540 s (9 min) the following k_{obs}[Fe(II)] values were obtained:

- At pH 7 for Fe(II) dose 0.4 mg/L(7.15 μM/L), excess Fe(II) dose removed by oxygen 7.15 – 3×0.635 = 5.245 μM/L and residual Fe(II) concentration 0.804 μM/L (45 μg/L), a k_{obs}[Fe(II)] = 39 $M^{-1}s^{-1}$ is calculated
- At pH 7 for Fe(II) dose 0.8 mg/L(14.3 μM/L), excess Fe(II) dose removed by oxygen 14.3 – 3×0.635 = 12.395 μM/L and residual Fe(II) concentration 1.34 M/L (75 μg/L), a k_{obs}[Fe(II)] = 58 $M^{-1}s^{-1}$ is calculated
- At pH 7.25 for Fe(II) dose 0.8 mg/L(14.3 μM/L), excess Fe(II) dose removed by oxygen 12.395 μM/L and residual Fe(II) concentration 0.125 μM/L (7 μg/L) a k_{obs}[Fe(II)] = 6.9×10^2 $M^{-1}s^{-1}$ is calculated.

The value of k_{obs}[Fe(II)] equal to 49±10 $M^{-1}s^{-1}$ at pH 7 and temperature 17.5°C was almost 5 times greater than that observed in batch experiments — 7 $M^{-1}s^{-1}$ — as calculated from data of Fig. 2 at 17.5°C. This significantly greater oxidation rate of the excess Fe(II) dose should attributed to additional reaction time due to sand filtration process, deposition of iron oxy-hydroxides at sand bed [25] and plug flow reaction process ensured by the bed of sand.

The experience from almost one year running of the full scale treatment plant showed that the Cr(VI) removal using Fe(II) is a simple and effective method resulting in residual total chromium concentration in sub-ppb levels. In addition the process proved trouble free, trustworthy and without unexpected variations in residual chromium and iron concentration. The operation and maintenance cost for the plant's production capacity 600 m^3/d consists of:

- Supervision, preparation of $FeSO_4.H_2O$ solution and Cr(VI) determination using an appropriate test kit, which were estimated to be 2 working hours per day with the cost of 30 €/d.
- The $FeSO_4.H_2O$ consumption (~1 kg/d), the cost of which was estimated to be 0.5 €/d.
- The CO_2 consumption (~12 kg/d) for pH adjustment at 7.4±0.1, the cost of which was estimated to be 4.8 €/d.
- The energy consumption — including the microfiltration— which was estimated to be around 215 kWh/d with current cost 17.2 €/d.
- The spent water for backwash of sand filter was determined around 15 m^3/d (2.5% of treated water), which was disposed to the sewage.
- The maintenance cost, which was estimated to be around 7.000 €/y.

Consequently, the total operation and maintenance cost, which is the sum of all the above mentioned costs, was estimated to be around 0.12 €/m^3.

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