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Coprecipitation of vanadium with iron(III) in drinking water: a pilot-scale study

Paolo Roccaro*, Federico G.A. Vagliasindi

Department of Civil Engineering and Architecture, University of Catania, Viale A. Doria 6, 95125 Catania, Italy, Tel. +39 095 7382716; Fax: +39 095 7382748; emails: proccaro@dica.unict.it (P. Roccaro), fvaglias@dica.unict.it (F.G.A. Vagliasindi)

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ABSTRACT

Vanadium concentrations higher than the Maximum Contaminant Level (MCL) of 50 µg/L set by the Italian Regulation were found in the groundwater of Mount Etna (Italy). Vanadium removal from this natural water by coprecipitation with iron(III) has been investigated in this study. Preliminary experiments were carried out at bench scale, while a large part of the study was conducted using a continuous flow pilot plant, operated in both in-line filtration (in-line iron(III) dosage followed by sand filtration with two sand filters in series) and direct filtration (iron(III) dosage in a flash mixed reactor, flocculation, sand filtration with two sand filters in series). Vanadium was effectively removed below the MCL by coprecipitation with iron (hydr) oxides produced by dosing ferric chloride. The pre-oxidation with chlorine has improved the vanadium removal by more than 25%, possibly due to the change in vanadium speciation. The breakthrough of iron micro-precipitates, with coprecipitated vanadium, has limited the duration of the process cycle because it resulted in iron concentration in the effluent higher than its MCL (0.2 mg/L). The addition of a cationic polyelectrolyte as flocculant aid has improved the flocs removal and therefore both iron and vanadium were removed well below their respective MCLs. The operating conditions were also optimized at pilot scale to minimize the sludge production while achieving the target vanadium effectiveness. Overall, the optimal condition to remove vanadium below its MCL (removal effectiveness >85%) requires a direct filtration scheme, a pre-oxidation with NaOCl = 0.3 mg/L, a $FeCl_3$ dose of 5 mg/L, a flocculation time of 20 min, and the addition of 0.3 mg/L of a cationic polyelectrolyte as flocculant aid.

Keywords: Adsorption; Cationic polyelectrolyte; Direct filtration; Emerging inorganic contaminant; Oxidation; Sludge production

1. Introduction

Vanadium, atomic number 23 and atomic weight 50.94 g/mol, is a transition metal that can form numerous compounds in its different oxidation states (−1, 0, +2, +3, +4, +5). In aqueous solutions it can be present in different species depending on the pH and redox potential of the solution. The dominant oxidation states are +3, +4, and +5, but the prevalent form under normal environmental condition is the +5 form [1].

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*Corresponding author.

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Vanadium can be found both in groundwater and in surface water and its concentration depend on environmental parameters and on the geological characteristics of the soil and rocks. The concentration of vanadium in fresh water varies usually from undetectable to few hundred μg/L. Values of 200–250 μg/L were observed in thermal acid water and in volcanic aquifers [2].

Groundwater of Mount Etna (Italy), the highest active volcano in Europe and the biggest hydrogeological reservoir of Sicily, widely used by the local population for potable purposes, contains several metals. For instance, concentrations up to 200, 5,100, 1,810 μg/L have been measured for vanadium, iron, and manganese [3,4]. In some case, the removal of such contaminants requires advanced treatment processes and higher cost than that usually required to treat groundwater for human consumption [5–7]. High levels of vanadium with peak values over 200 μg/L has been found in Ciapparazzo drainage gallery, that supplies 1,440 m^3/h of water for potable purpose [3]. The occurrence of vanadium in this water is possibly due to: (1) the abundant vanadium presence in volcanic rocks due to the ability of the vanadium(III) to replace itself to iron(III) present in magnetites and pyroxenes; (2) the CO_2 present in the groundwater (related to volcanic activities) lowers its pH, causing the water to be aggressive against volcanic rocks determining the dissolution of vanadium [4].

Due to the limited epidemiological evidence, at present there is not sufficient knowledge to establish the human toxicity of vanadium. However, several toxicological studies reported that decreased fertility, embriolethality, and fetotoxicity occur in rats, mice, and hamsters following vanadium exposure [8]. The tests *in vitro* had shown that vanadium(IV) and vanadium(V) can also produce DNA/chromosome damage [2]. Studies conducted on north-east Thailand's population that ingested water with high vanadium concentration, showed that the chronic vanadium ingestion can cause metabolic disorders [9]. However, most recent studies demonstrate that vanadium(V) does not induce geno-toxic effects in mice with reference to the concentrations found in Etna basin waters [10]. Nevertheless the effects due to ingestion of vanadium(IV) are not still well known. Both vanadium(IV) and vanadium(V) were found in the groundwater of the Etna area [11,12]. In Italy, the current regulation on drinking water quality [13], which transposed the European Directive 98/83/CE [14], has set a MCL of 50 μg/L for vanadium which has been recently updated with a MCL of 140 ug/L. It is noteworthy that the European regulation on drinking water [14] does not include vanadium in the standards. On the other hand, the United States Environmental Protection Agency (USEPA) lists vanadium in the "3rd Drinking Water Contaminant Candidate List" [15] and in the short list of contaminants being considered and evaluated further for regulatory determinations.

Due to the rare occurrence in natural water and partial toxicity results, few data are available on vanadium removal from drinking water [16]. Most studies have investigated vanadium removal from waters not intended for human consumption [17] or using synthetic water [18–21].

The objective of this study is to assess the efficiency of vanadium removal by coprecipitation with iron(III) at bench and pilot scale. Specifically, the influence of iron(III), flocculant, and pre-oxidant doses were investigated together with the sludge production. In this study the MCL of 50 ug/L for vanadium is considered as target value instead of the new standard (140 ug/L) in order to verify the possibility to fulfil such a low vanadium concentration already set by the italian regulation.

2. Materials and methods

2.1. Water used and materials

All chemicals used were of reagent grade (Carlo Erba Reagenti, Milan) and were employed without further purification. All solutions were prepared using ultrapure water (MilliQ system). The glassware was carefully cleaned with deionized water and then rinsed with ultrapure water. Anhydrous ferric chloride (Sicania Chimica, Catania, Italy) was used. A cationic polyelectrolyte (SNF, Italy) was used as flocculation aid. NaOCl was used as pre-oxidant agent (Carlo Erba, Reagents, Milan). All experiments were conducted using Ciapparazzo's water whose water quality parameters are reported in Table 1. The sample used for the bench-scale experiment had the same water quality parameters but a higher vanadium concentration (170 μg/L).

2.2. Analytical methods

An inductively coupled plasma optical emission spectroscopy, ICP-OES (Perkin Elmer Optima 4300 DVTM) was used for the analysis of metals. Samples where acidified with nitric acid in order to dissolve metals in the solution and refrigerated before to be analyzed. Concentrations of relevant ions were determined by ion chromatography (Dionex, DX-600). A portable digital pH-meter was used (mod. 340/SET-1,

Table 1
Main water quality parameters of the used water

Parameter	Value	Parameter	Value	Parameter	Value (mg/L)
pH	7.25	Ni	3 μg/L	SO_4	290
Al	4 μg/L	Pb	13 μg/L	NO_3	4
Cd	1 μg/L	Cu	2 μg/L	F	0.5
Cr	2 μg/L	V	125 μg/L	S	81
Fe	9 μg/L	Zn	1 μg/L	Ca	77
Mn	1 μg/L	Cl	112 mg/L	K	20

Table 2
Pilot plant treatment units, design and operating parameters

Treatment unit	Design and operating parameters
Raw water storage and pre-oxidation	2,000 L, 1.9 m high, 1.2 m inner diameter; 20 min residence time
Flash mixing	1 min of flash mixing at 120 rpm
Flocculation	10–20 min of slow mixing at 30 rpm
I Filter and II Filter	1.60 m high, 50 cm inner diameter; 33 cm coarse sand support; 75 cm packed bed with medium-fine sand; hydraulic load: 500 m^3/m^2 d (Runs 1 and 2), 240 m^3/m^2 d (all other Runs)
Thickening	1,000 L, 0.9 m high, 1.2 m inner diameter
Dewatering units (2 drying beds)	Length 1.5 m; width 1 m; depth 0.6 m; filled for 0.3 m with gravel (60–80 mm) and for 0.3 m with medium-fine sand

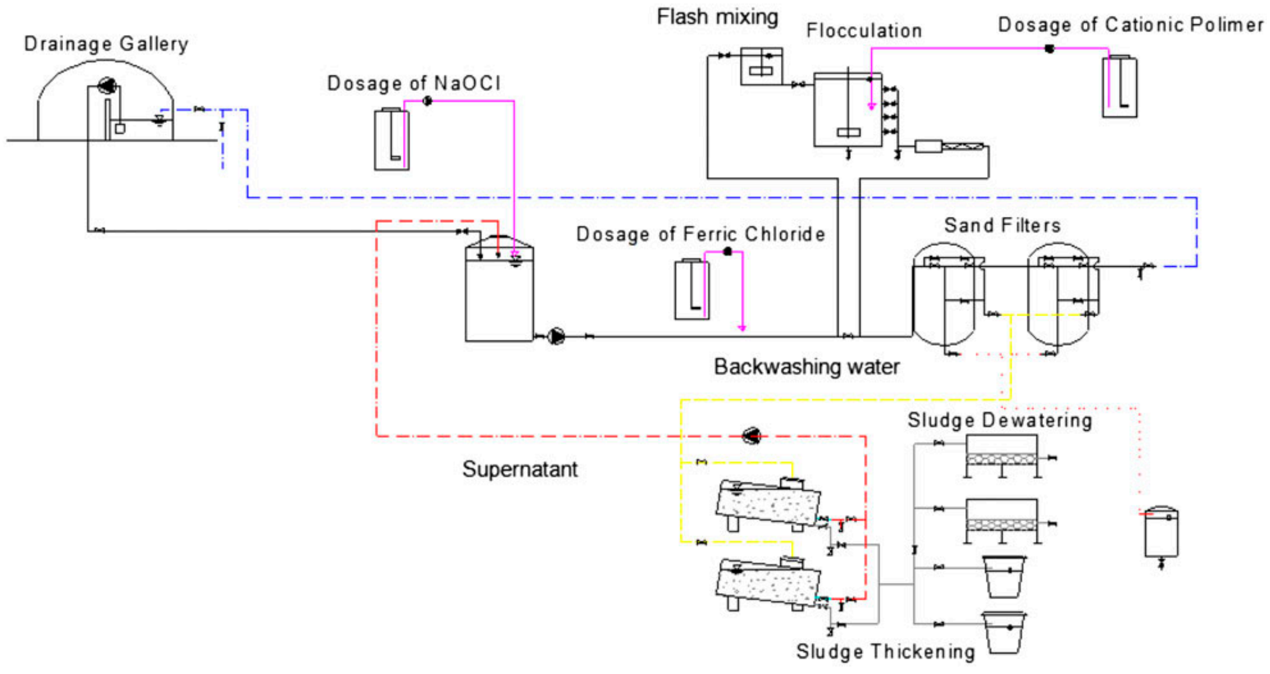

Fig. 1. Scheme of the pilot-scale treatment plant.

WTW). For the calibration of analytical instruments standard solutions were used (Carlo Erba Reagents, Italy).

2.3. Experimental methods

Preliminary tests were carried out using a bench-scale direct filtration plant which included the

Table 3
Pilot plant runs: experimental conditions

Experiments	$FeCl_3$ (mg Fe/L)	NaOCl (mg/L)	Flocculation (min)	Cationic polyelectrolyte (mg/L)
Run 1	5.0	0	0	0
Run 2	15.0	0	0	0
Run 3	5.0	0	0	0
Run 4	7.5	0	0	0
Run 5	7.5	0.3	0	0
Run 6	5.0	0.3	0	0
Run 7	2.5	0.3	0	0
Run 8	5.0	0.3	10	0
Run 9	5.0	0.3	20	0
Run 10	10.0	0.3	20	0
Run 11	2.5	0.3	20	0.4
Run 12	5.0	0.3	20	0.3

following units: flash mixing, flocculation, and sand filtration. A large part of the experiments were conducted using a continuous flow pilot plant. Treatment units included in the pilot plant are listed in Table 2, as well as their design and operating parameters. A scheme of the pilot plant treatment train is shown in Fig. 1. The pilot plant can be operated with or without pre-oxidation by chlorine addition and employing two different treatment schemes, in-line filtration (in-line ferric chloride dosage followed by sand filtration with two filters in series), direct filtration (flash mixing with ferric chloride addition, flocculation, sand filtration with two filters in series).

Conducted experiments and operational conditions are summarized in Table 3. Raw water was pumped as necessary from the drainage gallery to the pilot plant influent storage tank. Dosing units and filters were pre-assembled (Culligan Italy, HI FLO 9, model MF 20). Flash mixing and flocculation reactors were built in house.

During the experimental runs, two samples were collected every hour from the effluent of each filter operated in series; one was filtered by 0.45 μm cellulose membranes in order to remove vanadium adsorbed on particulate iron (this will be referred as "microfiltered" effluent).

3. Results and discussion

3.1. Bench-scale vanadium removal

Results obtained from the bench-scale experiments show that the removal efficiency of vanadium was constant for the duration of the test for both the ferric chloride doses employed (2.5 and 5.0 mg/L of $FeCl_3$ as Fe), as shown in Fig. 2. In particular, the test with a ferric chloride dose of 2.5 mg/L not allowed to comply with the vanadium MCL and showed an average removal efficiency of 45%. On the other hand, the test conducted with a ferric chloride dose of 5 mg/L has resulted in an average vanadium removal of 85%. In the latter case the concentration of vanadium in the treated water was always below the MCL.

Obtained results indicate that vanadium can be effectively removed by coprecipitation with iron(III). The removal mechanism of vanadium could be due to a formal coprecipitation intended as the incorporation of vanadium in the iron particles formed by the addition of iron(III) and/or adsorption of vanadium on the iron (hydr)oxides surface. Both these mechanisms have been elucidated in prior research that addressed the removal of other metals from water by sorption. For instance, previous studies have demonstrated the coprecipitation of cations [22,23] and anions [24] with iron (hydr)oxides. However, distinguishing metals coprecipitation from adsorption is a very complex task [25–28]. In this study, the term coprecipitation is used in order to indicate that the iron(III) is dosed in water already containing vanadium and that vanadium will precipitate together with iron (hydr)oxides regardless of the removal mechanism, according with prior research [23].

The obtained result is in agreement with prior research which reported an efficient removal of vanadium by adsorption/coprecipitation with iron (hydr) oxides [18] or by adsorption onto goethite [21]. However, these studies were carried out using synthetic water containing vanadium(V), while in the present work vanadium was present as both vanadium(IV) and vanadium(V) [12]. Prior research has also demonstrated that vanadium(IV) can be removed from aqueous solution by using calcium hydroxypatite and that the mechanism of removal is adsorption by the

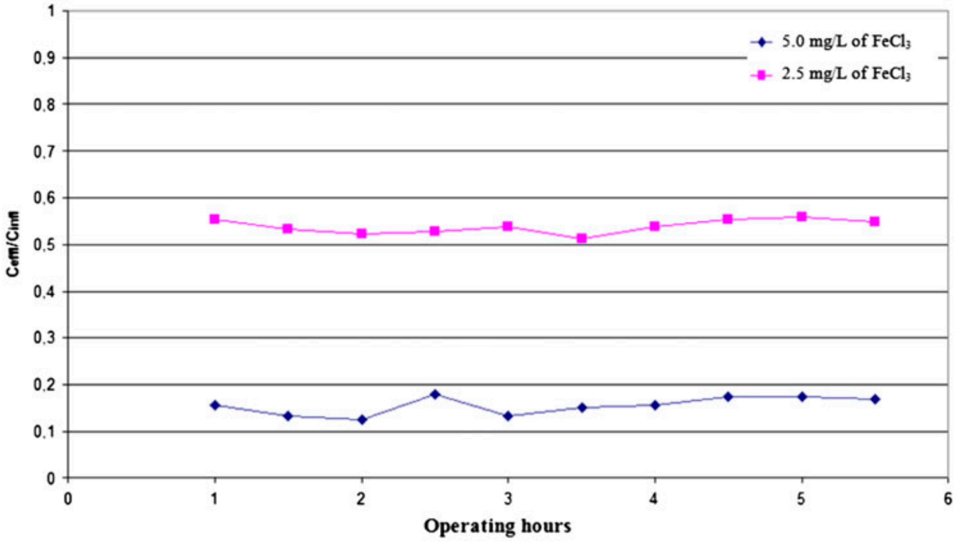

Fig. 2. Removal of vanadium at the bench-scale direct filtration plant. $FeCl_3$ dose 2.5 and 5.0 mg/L as Fe.

formation of a inner-sphere surface complex [20]. It can be speculated that the same mechanism of vanadium removal has occurred in this study, i.e. inner-sphere bonding between the surface of iron (hydr)oxides groups and vanadium ions, but further research is needed to demonstrate this hypothesis.

3.2. Pilot-scale vanadium removal

3.2.1. Effect of sand filtration and microfiltration

The results obtained from the pilot plant study have confirmed that vanadium can be removed by coprecipitation with iron(III). However, the effectiveness of vanadium removal was strongly affected by the type of filtration as shown in Fig. 3 for a selected ferric chloride dose. Indeed, it is notable that the concentrations of both vanadium and iron in the effluent from the first filter at varying operation hours with a $FeCl_3$ dose of 15.0 mg/L are higher than their relative MCLs, 50 and 200 μg/L for vanadium and iron, respectively (Fig. 3(a)). This is due to fact that most iron (hydr)oxides particles are not removed by sand filtration. On the other hand, the vanadium level in the microfiltered effluent was always lower than its MCL, highlighting that microfiltration can effectively remove the iron (hydr)oxides particles containing the vanadium removed from water. However, the concentration of iron in the microfiltered samples is still higher than its MCL (Fig. 3(b)).

The fact that the pattern of vanadium concentration in the effluent is similar to that of iron, regardless of the type of filtration, can be explained as the presence of vanadium coprecipitated with iron (hydr)oxides particles. Overall, this result demonstrates that vanadium is removed with iron (hydr)oxides which are very small particles and escape the sand filter but can be very well removed by microfiltration. As a consequence, the breakthrough of iron was the main limiting factor for the application of the proposed treatment process.

3.2.2. Effect of pre-oxidation with NaOCl

Pre-oxidation with 0.3 mg/L of NaOCl has strongly improved the vanadium removal, as shown in Fig. 4 for the results obtained with Runs 3 and 6. The addition of NaOCl has enhanced the vanadium removal of about 25%. This result could be explained as a change in vanadium speciation due to its oxidation by chlorine. For instance, oxidation of vanadium(IV) could result in vanadium(V) which may be better coprecipitated with iron(III). This is in agreement with prior research on vanadium(V) coprecipitation with iron (hydr)oxides [18]. Furthermore, in natural water, vanadium(IV) is positively charged [29], while vanadium(V) is negatively charged [21], therefore the oxidation by chlorine can enhance the presence of negatively charged vanadium species in water. As a result, the adsorption of vanadium(V) on iron (hydr) oxides, which are positively charged at the investigated pH, can occur by charge neutralization because the point of zero charge (PZC) of iron (hydr)oxides is ca 8.5 [30,31]. However, Veschetti et al. [12] reported for the same water investigated in his study that a dose of 0.2 mg/L of chlorine resulted in only about 20% of transformation of vanadium(IV) in

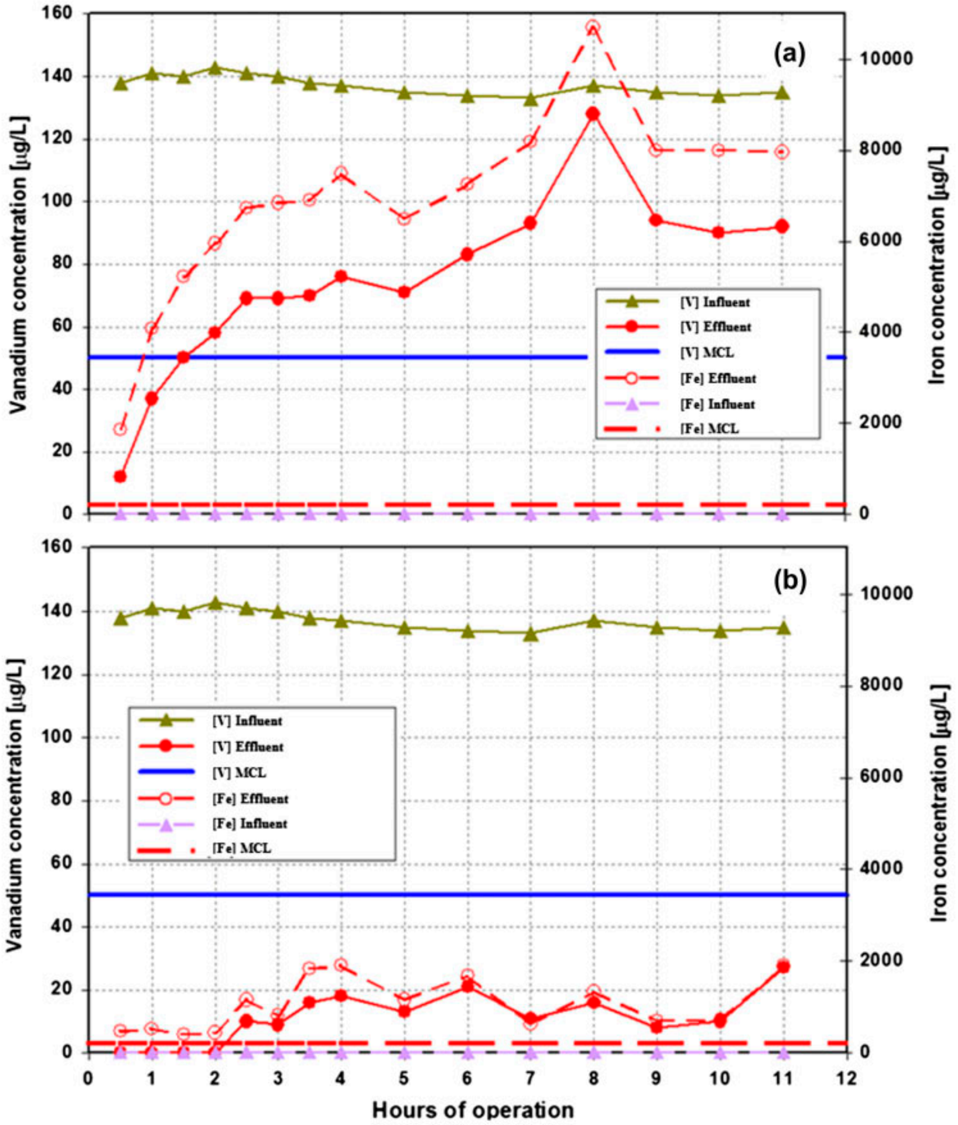

Fig. 3. Concentrations of vanadium and iron in the effluent of the first filter. $FeCl_3 = 15$ mg/L as Fe. (a) samples not microfiltered, (b) samples microfiltered.

vanadium(V). Therefore, more research is needed to elucidate the mechanism of vanadium removal.

3.2.3. Effect of ferric chloride dose

In order to optimize the operating conditions, the pilot plant was operated employing doses of $FeCl_3$ from 2.5 to 15.0 mg/L (Table 3). Obtained data confirms the results observed at bench scale. Indeed, a $FeCl_3$ dose of 5.0 mg/L was sufficient to remove the vanadium well below the MCL, as shown in Fig. 5. The average vanadium removal was always higher than 85%. On the other hand, a lower dose (2.5 mg/L of $FeCl_3$) was not enough to remove vanadium under its MCL. Again the effect of microfiltration is remarkable since the microfiltered samples had a much lower vanadium concentration, highlighting that the vanadium is coprecipitated with iron micro-particles which are not well removed by sand filtration.

At increasing $FeCl_3$ doses the iron particles breakthrough was more significant as shown in Fig. 6. Therefore, the optimal dose of iron(III) for vanadium removal was selected as 5.0 mg/L of $FeCl_3$. However, the iron level in the effluent of the filters was higher than its MCL. This issue was overcome by the identification of the appropriate treatment scheme and operating conditions which are addressed in the following sections.

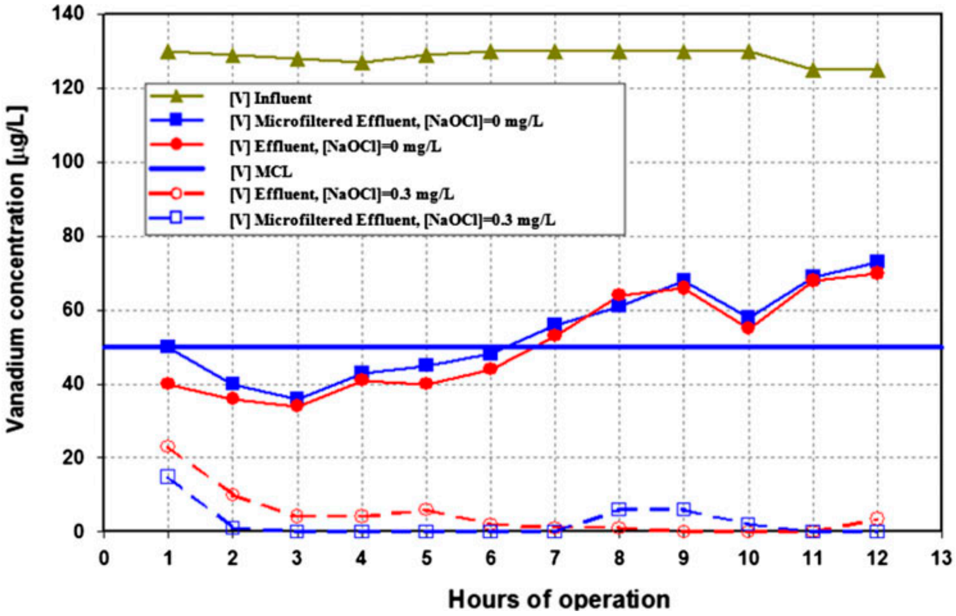

Fig. 4. Effect of pre-oxidation with chlorine (NaOCl = 0.3 mg/L) on the concentration of vanadium. Effluent from the second filter with $FeCl_3$ = 5 mg/L as Fe. Runs 3 and 6.

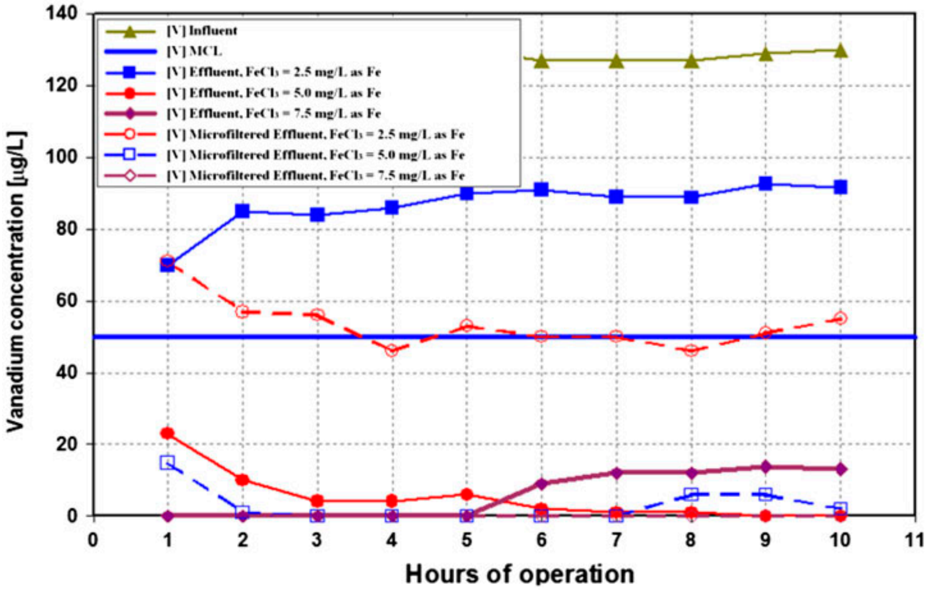

Fig. 5. Effect of iron(III) dose on the concentration of vanadium. Effluent of the second filter with pre-oxidation (NaOCl = 0.3 mg/L). Runs 5, 6, 7.

3.2.4. *Effect of flocculation (direct filtration plant)*

Since most vanadium was coprecipitated with iron micro-particles but these flocs were very difficult to be removed by employing the in-line filtration scheme, the pilot plant was operated as a direct filtration plant.

The addition of a flocculation reactor has improved the vanadium removal by coprecipitation with iron (hydr)oxides. The flocculation time has slightly affected the vanadium removal, as shown in Fig. 7, where results from Runs 8 and 9 are compared. Both

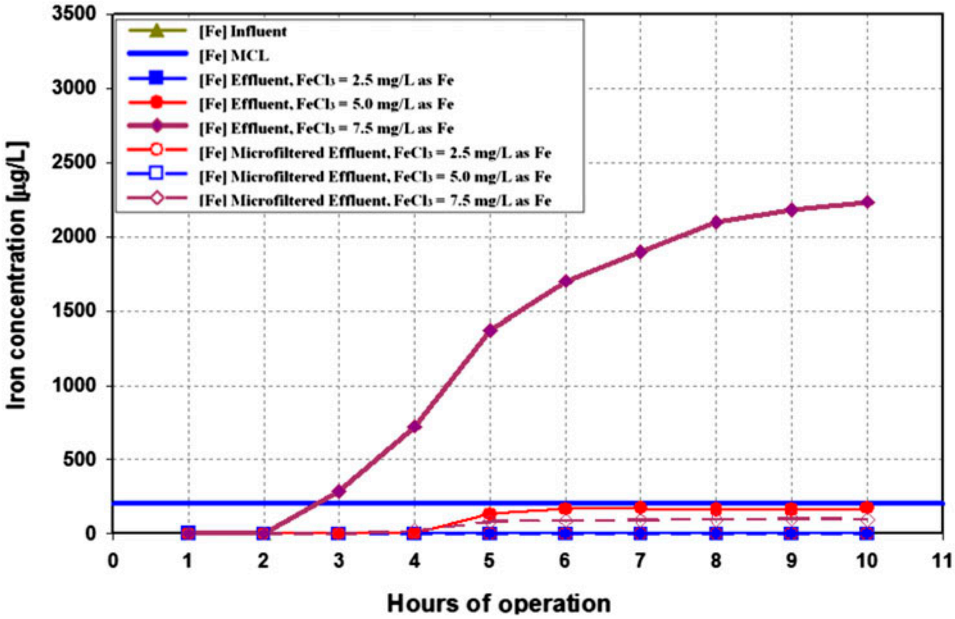

Fig. 6. Effect of iron(III) dose on the concentration of iron. Effluent from the second filter with pre-oxidation (NaOCl = 0.3 mg/L). Runs 5, 6, 7.

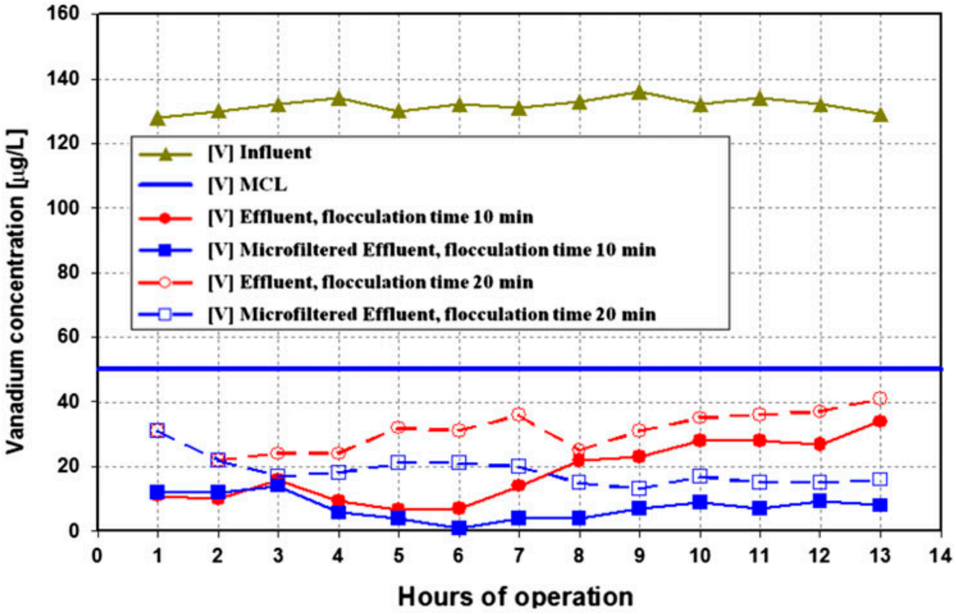

Fig. 7. Effect of flocculation time on the vanadium concentration. Effluent from the second filter with $FeCl_3 = 5$ mg/L as Fe. Runs 8 and 9.

10 and 20 min of flocculation time showed an effective removal of vanadium well below its MCL. This result is possibly due to the bigger and stronger iron particles flocs formed during flocculation compared with those formed by the in-line filtration plant.

Although the obtained results allowed the identification of the operating conditions to maximize the vanadium removal by coprecipitation with iron(III), still the iron concentration in the effluent was higher than its MCL.

3.2.5. Effect of polyelectrolyte addition as flocculant

In order to lower the iron concentration in the effluent of the sand filters, the size of the flocs formed during the flocculation process was increased by the addition of a cationic polyelectrolyte as flocculant aid. The use of the cationic polyelectrolyte has resulted in a better removal of iron micro-particles. Indeed, as shown in Fig. 8(b), the iron concentration in the effluent of the second filter was well below its MCL only when the polyelectrolyte was added while was higher than the MCL after only two operating hours when the polyelectrolyte was absent. It is noteworthy that the addition of the polyelectrolyte has resulted in a lower removal of vanadium as shown in Fig. 8(a), possibly due to the negative impact of the flocculant on the sorption mechanism of vanadium.

3.2.6. Sludge production from the pilot plant

As expected the sludge production was higher with increasing $FeCl_3$ dose, as shown in Table 4 which presents the specific sludge production (L/m^3 of treated water) as both thickened and dewatered sludge obtained for Runs from 4 to 12. The addition of the

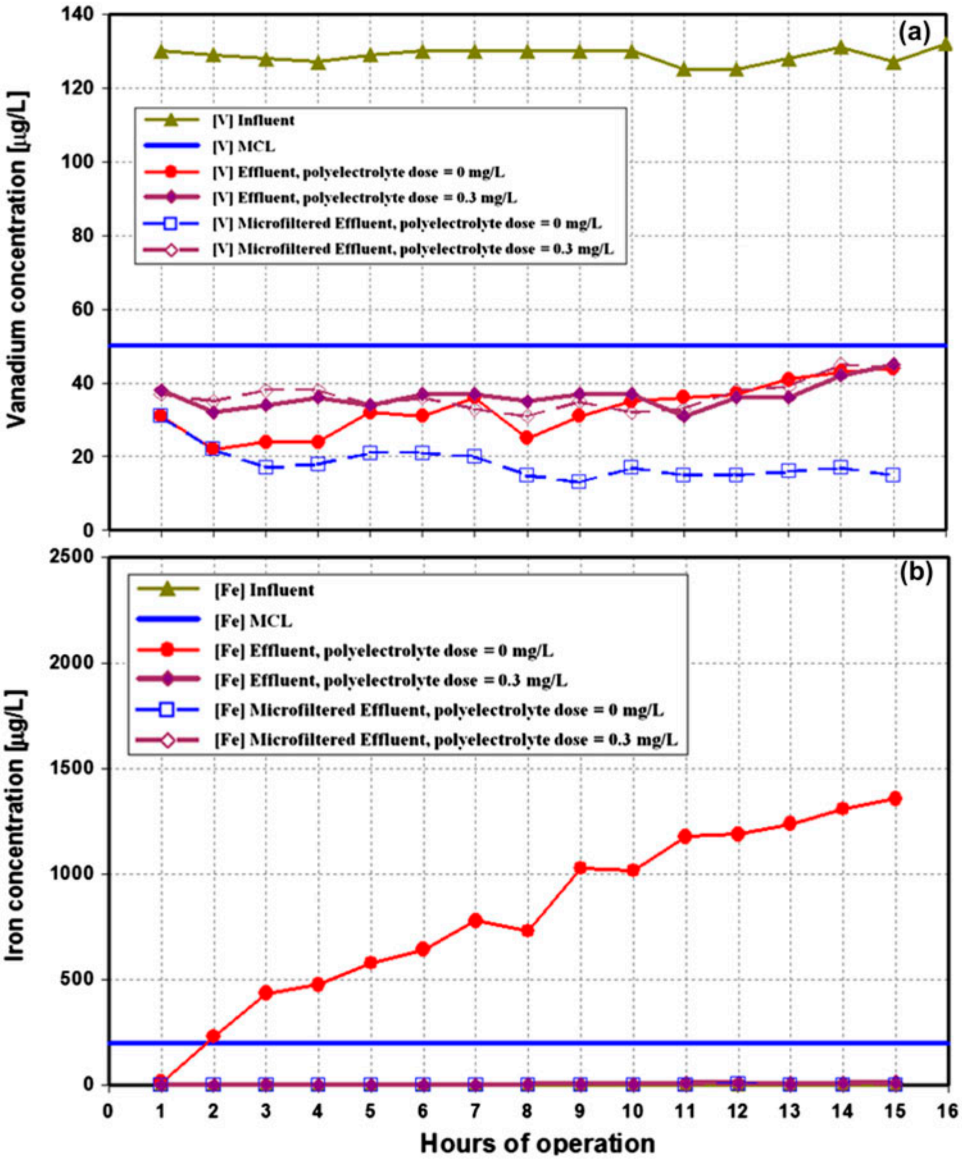

Fig. 8. Effect of polyelectrolyte addition on the concentration of vanadium (a) and iron (b). Effluent from the second filter with $FeCl_3 = 5$ mg/L as Fe, NaOCl = 0.3 mg/L, flocculation time of 20 min. Runs 9 and 12.

Table 4
Specific sludge production (L of sludge/m^3 of treated water)

Experiments	Thickened sludge	Dewatered sludge
Run 4	1.36	0.049
Run 5	1.85	0.055
Run 6	1.59	0.060
Run 7	0.98	0.035
Run 8	1.55	0.053
Run 9	1.46	0.046
Run 10	2.16	0.067
Run 11	0.90	0.026
Run 12	1.67	0.054

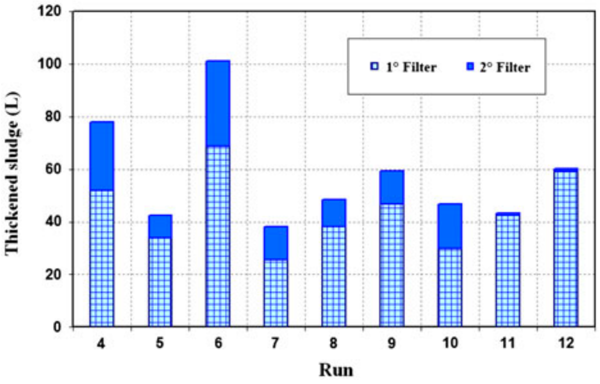

Fig. 9. Volume of sludge produced during the different experimental runs from the first and second filter.

cationic polyelectrolyte also increased the sludge production as can be observed comparing the results from the Runs 8 and 12.

Overall, the production of both thickened and dewatered sludge was larger when higher iron(III) doses were used or the polyelectrolyte was added at fixed iron(III) dose. However, the amount of sludge produced in the optimized condition (Run 12) was not significantly higher than that observed for the same condition without the addition of polyelectrolyte (Run 9). This result can be interpreted as the better dewaterability of the sludge when the cationic polyelectrolyte is added. This is not surprising since often cationic polymers are used as chemical conditioning of sludge before the dewatering process.

Fig. 9 shows the volume of sludge produced during the different experimental runs from the backwashing of the first and second filter. It is noteworthy that the amount of sludge coming from the second filter is significantly reduced compared to that of the first filter when the cationic polyelectrolyte was added (Run 11 and 12). This result confirms that the addition of the flocculant produced larger flocs which were mainly removed by the first filter, leaving the second filter as a further barrier for the attenuation of effects of a possible process failure.

4. Conclusions

In this study, bench-scale and pilot-scale experiments have demonstrated that vanadium, naturally occurring in groundwater as both vanadium(IV) and vanadium(V), can be successfully removed by coprecipitation with iron(III). In particular, the following conclusions can be drawn:

- the pre-oxidation with chlorine (NaOCl = 0.3 mg/L) has improved the vanadium coprecipitation of about 25%, probably due to the shift of vanadium(IV) to vanadium(V);
- a dose of 5 mg/L of $FeCl_3$ as Fe together with the pre-oxidation by chlorine was sufficient to coprecipitate the vanadium with iron(III)—the resulting vanadium removal efficiency was always > 85%;
- the granular sand filtration was not effective for the removal of the iron precipitates and this resulted in a significant iron level in the effluent;
- the presence of a flocculation reactor has improved the vanadium removal and to some extent the iron breakthrough;
- the addition of a cationic polyelectrolyte (0.3 mg/L) has resulted in successful removal of iron (hydr)oxides particles by the sand filters, resulting in vanadium and iron concentrations lower than their respective MCLs;
- the sludge production has increased with increasing $FeCl_3$ dose;
- the addition of the cationic polyelectrolyte has also increased the sludge production but this raise was not significant. On the other hand, the cationic polyelectrolyte addition generates larger flocs which were mainly removed by the first filter, leaving the second filter as a further barrier.

In conclusion the best plant configuration to remove vanadium below its MCL (removal effectiveness >85%) and minimize both the iron breakthrough and the sludge production is a direct filtration scheme, with a dose of NaOCl = 0.3 mg/L, a $FeCl_3$ dose of 5 mg/L, a flocculation time of 20 min, and a dose of 0.3 mg/L of a cationic polyelectrolyte as flocculant aid.

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