Properties of vanadium-loaded iron sorbent after alkali regeneration

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ABSTRACT

The aim of this research was to investigate the regeneration and reuse of a commercial granular iron sorbent (mainly goethite) when used in vanadium removal. A regeneration rate of 3 M NaOH was the highest (85%) achieved, followed by 2 M NaOH (79%) and 1 M NaOH (68%). The breakthrough curves show that the regenerated material can be reused. The BET (Brunauer–Emmett–Teller) surface area increased by 35–38% and the total pore volume increased by 123–130% as a consequence of NaOH treatment. The results indicated that sodium hydroxide could be used for the regeneration of iron sorbent although the regeneration was incomplete. This may be explained by the fact that vanadium diffusion into pores is a significant sorption mechanism in addition to complex formation with surface functional groups. As a consequence, vanadium desorbability from pores is not as effective as the regeneration of surface sites. X-ray photoelectron spectroscopy analyses confirmed a very low vanadium content on the surface of the NaOH-treated iron sorbent.

INTRODUCTION

Vanadium and its compounds have multiple applications in industry, such as in the production of high-strength low-alloy steels and special steels. It has been predicted that the demand for vanadium will markedly increase in the coming years due to new applications (e.g. in batteries) (Perles 2014). The ever-increasing consumption of vanadium will increase the risk of vanadium pollution. The toxicity of vanadium varies depending on its oxidation state; V(V) being more toxic and stable in an aqueous environment among its oxidation states. The release of hazardous compounds containing V(V) causes serious environmental degradation in soil and water (Zhao et al. 2014). For the reasons mentioned above, the development of techniques to recover vanadium from liquid waste streams is important from both environmental and economic points of view.

Sorption is one of the metal removal and recovery methods from waste streams which is easy to implement in field conditions. Among commercially available sorbents, iron sorbents are prime candidates due to their large specific surface area and high affinity to form surface complexes with anions like vanadates (Naeem et al. 2007; Gillenwater et al. 2011; Leiviskä et al. 2017). Cost-efficiency can be increased with a regeneration step and reuse of sorbent since the media replacement cost forms the majority of the total cost (Wang & Chen 2011). This also enables the recovery of valuable components from the spent regenerant.

Anion sorption onto iron materials is favoured at pH values lower than the pH_{PZC} (the pH of the point of zero charge) of materials due to electrostatic attraction and, thus, a higher pH can be utilized for the desorption. Regeneration of commercial iron sorbents in the case of arsenic removal from ground water has been carried out with success using sodium hydroxide (Chen et al. 2015). About 80% of arsenic could be desorbed from the exhausted iron sorbents with a 4% NaOH solution, thus allowing the iron sorbent reuse. Chaudhary & Farrell (2015) also reported that a small part of the arsenate was resistant to desorption with NaOH. They investigated NaOH regeneration with ferric hydroxide loaded support materials. Although these studies confirm the possibility of regenerating iron sorbents, the desorption of vanadium from iron materials has not yet been adequately addressed. In addition, there is limited information on the textural and chemical properties of regenerated iron materials, which would reveal why the efficiency of regenerated material is different than that of fresh media.
Previously, we have shown that granulated amorphous ferric oxyhydroxide (CFH-12) performed well for vanadium sorption from concentrated industrial wastewater at high temperature (80 °C) with fluctuating water quality (vanadium concentration varied from 51 to 83 mg/L, pH about 9 (at 25 °C) (Leviski et al. 2017). This study continues the investigation of the regeneration of the same iron sorbent using a synthetic vanadium solution. The specific objectives of this study were (i) to determine the optimal NaOH concentration for vanadium desorption and (ii) to investigate the characteristics of the iron sorbent after regeneration by using the following analytical techniques: FTIR, XRD, XPS, surface area and pore size distribution.

**MATERIALS AND METHODS**

The CFH-12 material comprises ferric oxyhydroxide granules, which have an iron content of 39–48% and a diameter D50 of 0.9 mm, according to the supplier (Kemira). Sodium metavanadate (NaVO3, Sigma-Aldrich) was used for the preparation of synthetic vanadium solution (50 mg/L V). Solid pellets of NaOH (Sigma-Aldrich) were used for the preparation of regenerant solutions.

Two sorption-regeneration cycles were performed. The CFH-12 (5 g) was wet-packed in a glass column with an inner diameter of approximately 19 mm. The vanadium solution (50 mg/L, 1,500 mL per sorption cycle) was pumped down-flow through the CFH-12 bed using a peristaltic pump. A flow rate of 4.1 mL/min was used. The effluent water was collected in 150 mL fractions. After the sorption cycle, the CFH-12 was rinsed by pumping 150 mL of Milli-Q water through the resin bed. At the beginning of the regeneration stage, the rinsing water left in the column was purged before the collection of fractions began. During desorption, 850 mL of NaOH solution was pumped down-flow through the resin bed at a flow rate of 4.1 mL/min. The spent regenerant solution was collected in 50 mL fractions. After regeneration, the CFH-12 was rinsed overnight with water. The second cycle was performed similarly to the first one. The effluent samples were preserved with 30% HCl. The spent regenerant samples were diluted before acidification. Vanadium concentration was analysed using graphite furnace atomic absorption spectroscopy (GFAAS, Perkin Elmer AAnalyst 600) with argon, following standard method SFS 5074:1990.

The total amount of the sorbed and desorbed vanadium (Vanadiumsorbed and Vanadiumdesorbed, mg), as well as the regeneration rate (%), were calculated using the following equations:

\[
\text{Vanadium}_{\text{breakthrough}}(\text{mg}) = \sum_{i=1}^{n} C_{\text{eff\_fraction}_i} \times \frac{V_{\text{eff\_fraction}_i}}{1000}
\]

\[
\text{Vanadium}_{\text{sorbed}}(\text{mg}) = \text{Vanadium}_{\text{influent}}(\text{mg}) - \text{Vanadium}_{\text{breakthrough}}(\text{mg})
\]

\[
\text{Vanadium}_{\text{desorbed}}(\text{mg}) = \sum_{j=1}^{k} C_{\text{des\_fraction}_j} \times \frac{V_{\text{des\_fraction}_j}}{1000}
\]

\[
\text{Regeneration rate(\%) = } \frac{\text{Vanadium}_{\text{desorbed}}}{\text{Vanadium}_{\text{sorbed}}} \times 100\%
\]

where Vanadium_{breakthrough} is the total amount of vanadium in effluent fractions (mg), \( C_{\text{eff\_fraction}_i} \) is the amount of vanadium in the effluent fraction i (mg/L), n is the amount of effluent fractions in sorption stage, \( V_{\text{eff\_fraction}_i} \) is the volume of effluent fraction i (mL), Vanadium_{influent} is the total amount of vanadium in the influent solution passed through the column (mg), \( C_{\text{des\_fraction}_j} \) is the amount of vanadium in the desorption fraction j (mg/L), k is the amount of desorption fractions in regeneration stage and \( V_{\text{des\_fraction}_j} \) is the volume of desorption fraction j (mL).

After the second desorption, the CFH-12 materials (referred to as NaOH-treated) were thoroughly rinsed and then dried at 60 °C for 24 h. Loss in material was calculated by comparing the oven-dried weight of the CFH-12 used with the weight of fresh CFH-12.

Fresh, washed (performed separately), vanadium-treated (after the first cycle, performed separately) and NaOH-treated CFH-12 samples were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD) after grinding using a mortar and pestle. FTIR analyses were performed using a Bruker Vertex V80 vacuum FTIR spectrometer with Harrick Praying Mantis™ DRIFT equipment. Samples were analysed in solid state for FTIR spectra and all measurements were recorded within the range of 400–4,000 cm\(^{-1}\). The XRD analyses were performed using a Rigaku Smartlab rotating anode diffractometer using Co Kα radiation. Samples were measured at room temperature in the 2-theta range from 15° to 90° with a step size of 0.01. The diffraction patterns were analysed using PDXL2 (Rigaku) analysis software with an ICDD PDF-4 database and Rietveld analysis was performed to measure the proportion of crystalline compounds.
RESULTS AND DISCUSSION

Column studies

The aim of the sorption stage was to provide exhausted iron material for the desorption studies and not to optimize the sorption stage (e.g. flow rate). By comparing the two sorption stages with fresh and regenerated media (Figure 1), the breakthrough curves show that the regenerated material (3 M NaOH was used) can be reused for vanadium sorption. In total, the first sorption stage retained 16.9 ± 1.2 mg of vanadium and the second sorption retained 23.0 ± 0.2 mg of vanadium. Although the present study did not aim to measure the maximum capacity, the obtained capacities (3.4 and 4.6 mg/g in the first and second sorption stage, respectively) were compared to previous studies. The obtained capacities were lower than that was obtained in the removal of vanadium from real industrial wastewater by using the same iron sorbent (Leiviskä et al. 2017). In batch test, the capacity was 7.4 mg/g and much higher capacity was obtained in the pilot study at high temperature (according to X-ray fluorescence measurement). Higher vanadium removal capacities have also been reported for similar iron sorbents (Naeem et al. 2007). The removal capacity is affected greatly by the particle size and process conditions.

A lower uptake would have been expected with the regenerated material due to the incomplete desorption of vanadium in regeneration (discussed below) and slightly different pH conditions in the sorption stages. The pH was between 3.4 and 6.1 in the first sorption stage (low due to leaching of impurities, discussed below), while for the
second sorption stage it varied between 7.2 and 7.8. The surfaces of iron oxides generally have a net positive surface charge at acidic-neutral pH values. The main mechanism for vanadium removal with iron oxides is that vanadium forms an inner-sphere complex with surface hydroxyl groups (\(>\text{Fe-OH}_2^+\)) (Peacock & Sherman 2004). Naeem et al. (2011) reported that pH 3–4 was the optimal range for vanadium removal (50 mg/l V) with a commercial iron sorbent using a dosage of 0.34 g/l, whereas a higher dosage (1.4 g/l) resulted in good removal efficiency at a wide pH range. Higher efficiency in the second sorption stage is probably related to the change in surface area, pore volume and pore width, which are discussed below.

Chen et al. (2011) also reported that the arsenic removal capacity was higher with the regenerated medium than with the virgin medium (ferric oxyhydroxide), when they conducted a full scale regeneration study. These findings indicates that the alkali treatment has an effect on the properties of the iron sorbents.

Vanadium desorbed fast initially (Figure 2) and then the desorption rate decreased gradually. The results indicated an increase of cumulative vanadium recovery with an increasing volume of NaOH. In addition, increasing NaOH concentration resulted in increasing vanadium release rates. A regeneration rate of 3 M NaOH was the highest (85%) recorded, followed by 2 M NaOH (79%) and 1 M NaOH (68%). The majority of the vanadium was recovered when 260 ml NaOH was passed through the column. Slower rate in regeneration might improve the vanadium release and minimize the volume of spent regen- erant. The results confirmed that vanadium sorption on CFH-12 was reversible, but complete desorption was not achieved. The amount of desorption-resistant fraction was the highest with the lowest NaOH concentration. The second regeneration rate for 3 M NaOH was worse (only 3 M was studied). The low regeneration rate was affected by the desorption-resistant fraction both from the first and second desorption. It is likely that barely any desorption from pores occurs.

After the column experiment, the total material loss was approximately 1.2 g, which was 24% of the initial CFH-12 material. This decrease in the amount of CFH-12 was mostly related to the leaching of impurities, such as jarosite (which is discussed below). Leaching of primary iron material cannot be excluded but it is presumably low. Chen et al. (2015) reported a small amount of leaching of iron (\(<2.5\%\)) from various commercial iron sorbents when subjected to NaOH regeneration (1–6%).

Characterization of sorbent

CFH-12 is mainly composed of amorphous (non-crystalline) iron oxyhydroxide. However, XRD data showed some variations in crystallinity and composition between different batches obtained from the manufacturer. In our earlier study (Leiviskä et al. 2017), the only mineral phase identified in the first batch used was gypsum, whereas the batch used in the pilot study also contained goethite. In the present study, fresh CFH-12 contained goethite and hydronium jarosite ((H₃O)Fe₃(SO₄)₂(OH)₆) (Figure 3). The relative abundance of hydronium jarosite determined through Rietveld calculations was low (\(<4\%\) of crystalline mineral
phases). According to the manufacturer, CFH-12 is prepared by neutralizing ferric sulphate with magnesium oxide. Different reaction conditions (e.g. pH, temperature, rate of hydrolysis, concentration of Fe$^{3+}$ and the nature of anion present) can cause slight variations in the composition of the product (Adegoke et al. 2013). A small amount of hydronium jarosite might result from the lower pH of the process (Yue et al. 2016). Gypsum is only an impurity in the CFH-12 product and may exist in some batches.

The vanadium-treated CFH-12 also contained hydronium jarosite in addition to goethite (Figure 3). In all the NaOH-treated CFH-12 samples, the absence of hydronium jarosite was evident. The peaks relating to hydronium jarosite at 20.2°, 33.3° and 33.7° disappeared, and thus goethite was the only phase detected. No transformation into hematite occurred in the present experimental conditions (1–3 M NaOH, room temperature), which was the case in our earlier study (Leiviskä et al. 2017). During the pilot experiment under alkaline and hot process conditions (80°C), the amorphous iron material of CFH-12 (different batch than in this study) was crystallized into a hematite-like phase (Fe$_{1.67}$H$_{0.99}$O$_3$) and goethite (FeO(OH)).

All the FTIR spectra were dominated by an OH stretching band at 3,185 cm$^{-1}$ confirming the presence of structural hydroxide, and by the bands at around 3,400 and 1,645–1,654 cm$^{-1}$ confirming adsorbed water (Figure 4). The band at 1,150 cm$^{-1}$ with fresh, washed and V-treated CFH-12 samples may be associated with sulphate (Gotíc & Musíc 2007) originating from the hydronium jarosite. The absence of a sulphate band in the spectra of NaOH-treated CFH-12 confirmed the leaching of jarosite from the material. By comparing the spectra of V-treated CFH-12 with fresh and washed CFH-12, it can be concluded that vanadium treatment did not contribute to any clear visible changes in FTIR spectra.

The bands in the 700–950 cm$^{-1}$ range are due to OH bending vibrations and the bands at a frequency lower than

![Figure 3](https://iwaponline.com/wst/article-pdf/76/10/2672/241644/wst076102672.pdf)  
**Figure 3** | XRD patterns for fresh CFH-12, vanadium-treated CFH-12 collected after the first sorption and NaOH-treated CFH-12 after the second desorption stage. The arrows show the position of the most important hydronium jarosite peaks, which could clearly be distinguished from the goethite peaks.

![Figure 4](https://iwaponline.com/wst/article-pdf/76/10/2672/241644/wst076102672.pdf)  
**Figure 4** | FTIR of fresh, washed, V-treated and 3 M NaOH-treated CFH-12 samples.
700 cm\(^{-1}\) are related to Fe-O vibrations in the lattice structure (Cambier 1986; Cornell & Schwertmann 2006). The intensity of these bands increased especially with 3 M NaOH-treated samples. The appearance of new bands at 1,507 cm\(^{-1}\) and 1,340 cm\(^{-1}\) with NaOH-treated samples are likely to correspond to the asymmetric O–C–O stretch vibration and the symmetric stretch of carbonates (Villalobos & Leckie 2001). The carbonates may have originated from the water that was used for rinsing the CFH-12 material.

As Table 1 depicts, the wide-scan XPS spectra of fresh and treated CFH-12 indicated the presence of Fe, O, C, Si and Na in the surface of all samples (at a depth of ∼5 nm). Fresh, washed and V-treated CFH-12 had clear S 2p and N 1 s peaks, whereas Ca 2p peaks were detected only for the fresh samples. With all the NaOH-treated samples, an F 1 s peak appeared in the wide-scan XPS spectra. Moreover, the 3 M NaOH-treated CFH-12 contained a small amount of magnesium. The binding of vanadium onto the surface of CFH-12 was evident (1.9 at.% with the vanadium-treated sample. The V 2p\(_{3/2}\) peak existed at 517.2 eV and a V 2p\(_{1/2}\) signal was observed at 524.7–524.8 eV. For NaOH-treated samples, only a minor indication of a V 2p\(_{3/2}\) signal was observed (<0.18 at.%). This might imply that the reverse reaction of surface complex formation was the main mechanism for vanadium desorption in this case.

The proportion of iron increased on the surface as a consequence of treatment (Table 1). Figure 5 shows the Fe 2p spectra of fresh and treated CFH-12. The Fe 2p\(_{3/2}\) existed at 711.0–712.0 eV. The peak at 724.7–725.4 eV is assigned to Fe 2p\(_{1/2}\). The Fe 2p\(_{3/2}\) shifted to lower binding energy as a consequence of treatment (Figure 5). Fresh CFH-12 had an Fe 2p\(_{3/2}\) peak at 711.9–712.0 eV, washed CFH-12 at 711.5–711.6 eV, V-treated 711.5–711.6 eV, and NaOH-treated CFH-12 at 711.1 eV. The shift probably originated from the jarosite leaching and more pronounced effect of goethite on the peak position. Jarosites have an Fe 2p\(_{3/2}\) peak at binding energies of around 712 eV (Parker 2008; Khoshkhoo 2014), whereas goethite has an Fe 2p\(_{3/2}\) peak of around 711 eV (Harvey & Linton 1983; Echigo et al. 2012).

In previous sorption studies, the shift of Fe 2p to higher binding energy has been explained as resulting from bond formation between iron oxide and the adsorbate. Mallet et al. (2013) studied phosphate sorption on ferricydrate and found a shift in Fe 2p\(_{3/2}\) toward higher binding energy and explained it as originating from the Fe–O–P bond. Fan et al. (2016) found that the shift in Fe 2p\(_{3/2}\) occurred after Sb sorption on goethite and that it was due to the formation of an Fe–O–Sb bond. In the present study, the shift that might result from the formation of an Fe–O–V bond is difficult to analyse since the fresh, washed and V-treated CFH-12 samples contained a small amount of hydronium jarosite, which affects the Fe 2p\(_{3/2}\) position. In contrast, the NaOH-treated samples still contained a small amount of vanadium (a minor indication of V 2p\(_{3/2}\) signal was observed). However, comparing V-treated CFH-12 to NaOH-treated CFH-12 with very low impurity content, the Fe 2p\(_{3/2}\) of V-treated CFH-12 had ~0.5 eV higher binding energy. The reason that the Fe 2p\(_{3/2}\) peak of washed and V-treated CFH-12 existed at the same binding energy might relate to the decreasing concentration of hydronium jarosite (fresh > washed > V-treated), which resulted in the shift to lower binding energy, whereas the formation of a V–O bond with V-treated CFH-12 may cause the shift to higher binding energy.

The O 1 s spectra show two components, which are two different kinds of oxygen species (Figure 6). The peak at lower binding energy (529.6–530.3 eV) is related to oxygen (O\(^{2−}\)) bound to metal cations (O 1s–oxide) whereas the peak at higher binding energy (530.9–531.8 eV) is related to surface oxygen (O 1s–hydroxide), being mainly oxygen of the hydroxyl group (OH\(^{−}\)) (Brundle et al. 1977). The presence of physically adsorbed water was not considered during the curve fitting, which would exist on the high BE side (Harvey & Linton 1983; Echigo et al. 2012). The V–O bonding in the V-treated sample may be included in the O 1s–hydroxide component (531.5 eV).

The proportion of the O 1s–oxide component increased along with treatment and the NaOH-treated samples consisted of two O 1s peaks of approximately equal intensity (1 M NaOH-treated only shown in Figure 6), which is consistent with the goethite structure (McIntyre & Zetaruk 1977). Moreover, treatment shifted the oxygen peaks to

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**Figure 5** The XPS spectra of Fe 2p for fresh, washed and treated CFH-12 samples.
lower binding energy as compared to fresh CFH-12. For NaOH-treated samples, the O 1s oxide existed at 529.6–529.7 eV and the O 1s hydroxide at 530.9–531.0 eV, which is in good agreement with the reported values for goethite (Harvey & Linton 1981; Echigo et al. 2002).

As reviewed by Adegoke et al. (2013), it was stated that the level of interaction of oxyanions with iron oxide materials was strongly influenced by the surface area and preparation method of iron oxide materials as well as pH. Iron oxide materials have a relatively high surface area (Adegoke et al. 2013). Regeneration with NaOH had a clear influence on the surface area and pore size distribution (Table 2). The BET surface area increased by 35–38%, the total pore volume more than doubled, and the average pore width increased from 4.0 nm to 4.4–4.5 nm as a consequence of NaOH treatment. The nitrogen adsorption isotherm of fresh CFH-12 confirmed that the isotherm is a type IV with a type H4 hysteresis loop (data not shown) according to IUPAC classification (Thommes et al. 2005), indicating a mesoporous structure. An H4 hysteresis loop is often associated with narrow slit-like pores.

Goethite particles with lower surface area (and higher crystallinity) have shown a higher concentration of surface hydroxyls (Echigo et al. 2002). As the NaOH treatment decreased the proportion of surface hydroxyls and increased the surface area of CFH-12, it is likely that the high sorption capacity of CFH-12 material after regeneration was due to an increase in vanadium diffusion into pores. The smaller surface area of fresh CFH-12 most likely resulted from the impurities that occupied the iron oxyhydroxide pores. As the material was free of impurities after regeneration, the accessibility of N₂ increased. Likewise, organic matter sorption on material will result in a smaller surface area due to clogging of pores, as demonstrated by Kaiser & Guggenberger (2007) with goethite. The composition of wastewater may also significantly change the available pore area. For a pure goethite sorbent, the optimal surface area and pore size in terms of efficient sorption and desorption should be determined.

### CONCLUSIONS

These results indicate that sodium hydroxide can be used for the regeneration of granular goethite materials (CFH-12) after vanadium sorption and that the reuse of CFH-12 is possible. The very low vanadium content on the surface of the NaOH-treated iron sorbent (according to XPS data) revealed that the reverse reaction of surface complex formation was the main mechanism for the vanadium desorption. However, CFH-12 was not completely regenerated under the studied conditions, probably due to the low desorbability of vanadium from pores. In addition, the NaOH treatment had a clear influence on the surface area and pore size distribution. These changes in textural characteristics may explain the higher vanadium removal capacity of the regenerated medium than the virgin medium. Future studies should aim to optimise the regeneration process by studying the kinetics of regeneration as well as the optimal pore size in order to reduce the desorption-resistant fraction.

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