Vanadium(V) removal from aqueous solution and real wastewater using quaternized pine sawdust
T. Leiviskä, A. Keränen, N. Vainionpää, J. Al Amir, O. Hormi and J. Tanskanen

ABSTRACT
Cross-linked and quaternized pine sawdust was tested for vanadium removal from a synthetic aqueous solution as well as from real industrial wastewater which had a considerable amount of vanadium and other ions such as sulphate, ammonium and nickel. The maximum vanadium sorption capacity of the modified pine sawdust was found to be 130 mg/g in synthetic solution and 103 mg/g in real wastewater. Modified pine sawdust worked well over a wide range of pH. Column studies with real wastewater proved that vanadium was efficiently desorbed from the material with 2 M NaOH and that the material could be reused.

Key words | biomaterial, chemical modification, strong anion exchanger, vanadate

INTRODUCTION
Vanadium is widely distributed in the Earth’s crust and can exist in the environment in oxidation states III, IV, and V. Vanadium(V) is the most common form in the aquatic environment in contact with atmospheric oxygen. Many different vanadium species can coexist in solution (Guzmán et al. 2002). At very low pH (<2-3), vanadium (V) occurs mostly as a cation (VO₂⁺), whereas the anionic forms dominate at higher pH values (>3): monovanadate species (VO₂(OH)₂⁻, VO₃(OH)²⁻, VO₄³⁻) polyvanadate species (V₂O₅(OH)³⁻, V₃O₉⁻, V₄O₁₂⁻) and decavanadate species (V₁₀O₂₆(OH)₂⁴⁻, V₁₀O₂₇(OH)⁵⁻, V₁₀O₃₈⁻). Vanadium and its compounds have multiple applications in industry, such as in alloys to increase strength and as a catalyst. Vanadium is released into the environment mainly by the combustion of oil and coal.

The concern about vanadium toxicity in humans has encouraged the study of vanadium removal from water. For example, vanadium pentoxide has been classified as possibly carcinogenic to humans (ATSDR 2012). Several techniques have been proposed for vanadium removal, e.g., ion exchange (Yeom et al. 2009; Keränen et al. 2015), adsorption (Namasi-vayam & Sangeetha 2006), nanofiltration (Lazadiris et al. 2003) and coagulation-floculation (Roccaro & Vagliasindi 2008). In particular, intensive research has been carried out with different natural or waste materials. For example, high sorption capacities for vanadium have been achieved with the use of chitosan (440 mg/g, Navarro et al. 2003) and metal oxides (65–165 mg/g, Naeem et al. 2007).

Recently, we demonstrated the high nitrate capacities of anion exchangers produced from pine sawdust (Keränen et al. 2015). In addition, the sorption of nitrate was found to be very rapid and reversible, and the sorption efficiency was maintained well over a wide pH range (3–10). The present study extends the previous research by examining vanadium sorption both from synthetic aqueous solutions and real industrial wastewater (IW) using modified pine sawdust. IWs are typically a complex mixture of cations, anions, inorganic and organic components, all of which may have an effect on sorbent efficiency. Thus, research on real wastewater should be performed on potential materials since that would confirm their functionality and possibly reveal some other benefits and drawbacks in use.

MATERIAL AND METHODS
Sawdust modification
Scots pine (Pinus sylvestris) sawdust was obtained from Stora Enso Veitsiluoto pulp mill in Kemi, Finland. The modification of pine sawdust was described in detail in our previous article and is referred to as the ETM method (Keränen et al. 2015).
2013), originally based on the method reported by Wang et al. (2010). In brief, the sawdust was dried (80°C, 24 h), ground and sieved. A size fraction of 90–250 μm was used in the study. 2 g of pine sawdust was weighed into a round-bottom flask, and 16 ml of N,N-dimethylformamide (≥99.5%, Merck, Darmstadt, Germany) and 13 ml of epichlorohydrin (≥99%, Merck) were added. The mixture was stirred at 60–70°C for 45 min. Next, 2.5 ml of ethylenediamine (≥99%, Merck) was added and the stirring was continued for 45 min at 60–70°C, after which 13 ml of triethylamine (≥99%, Merck, Hohenbrunn, Germany) was added. The mixture was then left to stir at 60–70°C for 120 min. The modified pine sawdust (MPSD) was washed with water and dried at 105°C for 12–24 h.

Vanadium solutions

The synthetic vanadium solution was made by dissolving sodium metavanadate (NaVO₃, Sigma Aldrich, St Louis, MO, USA) in ultrapure Milli-Q water (Merck Millipore, Darmstadt, Germany). In pH experiments, ionic strength was adjusted by sodium perchlorate (NaClO₄, Fluka, Milwaukee, WI, USA). The IW was taken from a synthesis gas scrubber from a European chemical plant and had the following characteristics: 50.4 mg/l of V (presumably in V(V) oxidation stage), <100 μg/l of NO₂-N, 180 μg/l of NO₃-N, 490 mg/l of NO₃-N, 3.2 mS/cm of conductivity and a pH of 5.1.

Batch and column tests

The test conditions in the batch and column experiments are listed in Table 1. The batch experiments were conducted by shaking MPSD (in the form of Cl⁻) with 50 ml of synthetic solution (SS) or IW in a plastic bottle in a shaker for 24 h, after which the sample was centrifuged (Jouan (Saint Nazaire, France) C4.12, 10 min at 800 g). First, 10 ml was taken from the top of the supernatant for metal analyses. Then, 25 ml was taken for pH analysis (referred to as the final pH).

Prior to the column test, the wastewater was filtered (11 μm) in order to prevent resin fouling. The activation of resin was done by mixing it in 2M NaOH (BDH Prolabo, Leuven, Germany) for 1 h and then rinsing with water (this changed the resin into OH⁻ form). The procedure was repeated three times. The activated resin was kept under water until the next day to prevent it from drying. The wet activated resin (≈2 g of dry resin) was wet packed into the column (a 50 ml burette with an 11 mm inner diameter). The bed volume was 7 ml. During each ion exchange cycle, 1,000 ml of wastewater was run through the resin bed at a flow rate of 3 ml/min (≈26 BV/h, bed volumes per hour). The effluent water was collected in fractions of 40 ml for analysis. Finally, the resin was rinsed concurrently with 40 ml of water. In regeneration, 800 ml of 2 M NaOH was run through the bed (3 ml/min) and the effluent regenerant was collected in fractions of 40 ml. After regeneration, the bed was rinsed concurrently with 40 ml of water. Three ion exchange and two regeneration stages were conducted. After the third ion exchange stage, the resin was rinsed with water and air-dried for field emission scanning electron microscopy-energy dispersive X-ray spectroscopy (FESEM-EDS) analysis.

Chemical resistance

The chemical resistance of MPSD to HCl (Merck, Darmstadt, Germany) and H₂O₂ (BDH Prolabo, Briare, France) was studied as follows: (1) 0.7 g of material was weighed and immersed in the chemical for a certain time, (2) the material was carefully rinsed with water, (3) the material was regenerated twice with 100 ml of 0.1 M NaCl (Merck) for 1 h and rinsed with water (this stage only in the case of H₂O₂), (4) the material was dried at 105°C for 24 h, re-weighed and

Table 1 | Experimental conditions for SS and IW (n – number of replicates). Temperature 23 ± 2°C. The resin was in OH⁻ form in the column study, otherwise in Cl⁻ form

<table>
<thead>
<tr>
<th>Effect of pH</th>
<th>SS: resin dosage 1.5 g/l, initial vanadium concentration 27 mg/l, contact time 24 h, pH 2–10, with and without 0.01 M NaClO₄, n = 2</th>
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<tr>
<td></td>
<td>IW: resin dosage 3 g/l, initial vanadium concentration 50.4 mg/l, contact time 24 h, pH 5, pH 7 and pH 9, n = 2</td>
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<tr>
<td>Isotherm</td>
<td>SS: resin dosage 1.5 g/l, initial vanadium concentrations 35–580 mg/l, contact time 24 h, pH 7, n = 3</td>
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<tr>
<td></td>
<td>IW: resin dosage 0.3–6 g/l, initial vanadium concentration 50.4 mg/l, contact time 24 h, pH 5, n = 2</td>
</tr>
<tr>
<td>Effect of resin amount</td>
<td>IW: resin dosage 2 g, bed volume 7 ml. Ion exchange: initial vanadium concentration 50.4 mg/l, pH 5, wastewater 1,000 ml, flow rate 3 ml/min. Regeneration: 2 M NaOH 800 ml, flow rate 3 ml/min</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>SS: resin dosage 1.5 g/l, initial vanadium concentration 94 mg/l, pH 6.5, n = 3</td>
</tr>
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</table>

*Conductivities without NaClO₄: 3.7 mS/cm (pH 2.1) and 0.1–0.4 mS/cm (pH 3.2–10.2). With NaClO₄: 4.2 mS/cm (pH 2.1) and 1.2–1.4 mS/cm (pH 3.2–10.2).
the yield was calculated, and (5) a batch test with vanadium solution was conducted (see Table 1). The contact times and concentration of chemicals were chosen according to the Dowex manual (Dowex 2014). With HCl, the pre-exposing was done first with 50 mL of 5% HCl for 0.5 h and then with 50 mL of 10% HCl for 1 h. With H2O2, the pre-exposing was done with 50 mL of 2% H2O2 for 1 h.

**RESULTS AND DISCUSSION**

**Analyses**

Samples (10 mL) for metal analysis were preserved with 30% HCl (Suprapur, 50 μL/10 mL; Merck, Darmstadt, Germany). Vanadium was analysed by graphite furnace atomic absorption spectrophotometry (Perkin Elmer Analyst 600, Überlingen, Germany) with argon (SFS 5074 1990). Nickel was analysed by flame atomic absorption spectrophotometry (Perkin Elmer Analyst 400, Shelton, CT, USA) with an air-acetylene mixture (SFS 5047 1980). Conductivity and pH were measured with a VWR PC5000H (Leuven, Belgium) and a Metrohm 744 pH meter (Herisau, Switzerland).

Total organic carbon (TOC) was measured with a Sievers 900 Portable TOC Analyzer (GE Analytical Instruments, Boulder, CO, USA). The wastewater was filtered with 11 and 0.2 μm filters prior to the analysis and the result is expressed as DOC; NH4-N, NO3-N and NO2-N were measured with a Seal AutoAnalyzer3 (Seal Analytical GmbH, Norderstedt, Germany) (SFS-EN ISO 13395 2003). Sulphate was analysed using a Dionex ICS-2000 ion chromatography system (Dionex Corp., Sunnyvale CA, USA; SFS-EN ISO 10304-1 2009). Conductivity and pH were measured with a WVR PC5000H (Leuven, Belgium) and a Metrohm 744 pH meter (Herisau, Switzerland).

The morphology of the fresh MPSD and MPSD loaded with components of the IW were studied at 5 kV, using FESEM (Zeiss Ultra Plus, Oberkochen, Germany). The samples were mounted on an aluminium disc and coated with carbon (15 nm, Jeol Vacuum Evaporator JEE-420, Jeol, Tokyo, Japan). EDS (Inca x-act, Oxford Instruments, Abingdon, UK) was used to investigate the elemental composition of samples. The EDS areal analyses were run in quadruplicate, and the elemental distribution data were normalized. Carbon was left out due to carbon coating.

**RESULTS AND DISCUSSION**

**Batch sorption studies**

It was confirmed that modified pine sawdust worked well in a wide pH range both with an SS and real wastewater (Figure S1, available online at http://www.iwaponline.com/wst/072/227.pdf). The same conclusion has also been drawn by other authors for these ETM-modified materials (e.g., Xu et al. 2010; Keränen et al. 2013). For the SS with a dosage of 1.5 g/l, a reduction of vanadium of >99% was achieved at pH 3–10 and 87% at pH 2 (initial vanadium concentration 27 mg/l, without NaClO4). The lower efficiency at pH 2 is probably due to the increased amount of the cationic form of vanadium (Guzmán et al. 2002) as well as the higher Cl– concentration (originating from pH adjustment with HCl).

The added ionic strength weakened the performance of the resin (0.7–16% points) and the effect was more pronounced at low pH. Weaker performance may also result from the competition between vanadate and perchlorate (ClO4–) for active resin sites (Xu et al. 2013). For wastewater with a dosage of 3 g/l, a reduction of >99% was achieved at all the pH values studied (Table S1, available online at http://www.iwaponline.com/wst/072/227.pdf). Nickel was also removed well at pH 7 and pH 9 (92 and 97%) and somewhat poorly at pH 5 (56%). Nickel was assumed to be present as a cationic nickel ammonia complex in the wastewater (Min et al. 2009; Keränen et al. 2013).

Figure 1(a) shows the isotherm for the SS. The maximum capacity achieved was as high as 150 mg/g. For IW, the maximum capacity achieved was slightly lower: 103 mg/g. A dosage of 2 g/l was able to remove 99% of vanadium at pH 5 (Figure 1(b)). The capacities achieved are at the same level as for metal oxides (Naeem et al. 2013). Sulphate is a common contaminant in IWs, especially wastewaters originating from mining and mineral processing. Thus, it is important to study the effect of sulphate on vanadium removal. Vanadium removal was high even at high sulphate concentrations. The removal of vanadium decreased from 99.8% (±0.07) to 97.8% (±0.09) as the SO4– concentration increased from 0 to 5,000 mg/l (initial vanadium concentration 22–28 mg/l). Sulphate reduction was not measured from these samples.

**Column studies**

In the column study with IW, the vanadium sorption efficiency of the resin seemed to be even better after the first and second cycles (Figure 2). During the first loading, vanadium appeared in the effluent after about 400 mL of wastewater had passed through the column. During the second and third loading, vanadium appeared in the effluent considerably later. For nickel, it was the opposite. Nickel appeared in the effluent very early and subsequent cycles...
did not improve the affinity. Sulphate was also attached to the material but after treating 600 ml of wastewater (equal to 86 bed volumes), the sulphate concentration reached the original value. In addition, an uptake of DOC and NH₄-N was detected at the beginning of the ion exchange cycle.

In regeneration, vanadium was efficiently eluted from the resin with 2 M NaOH. In the column study, the OH⁻ form of the resin was preferred, since vanadium did not desorb efficiently from the resin in Cl⁻ form. The elution of nickel was unsuccessful. In our previous studies with the same wastewater and a commercial strong anion exchanger, nickel fouling was also observed (Keränen et al. 2015). At that time, an acid rinse with 1M H₂SO₄ released nickel from the resin.

Figure 3 displays the FESEM images of fresh MPSD and loaded MPSD. As seen, compared with fresh MPSD, the appearance of loaded MPSD was similar: smooth and porous. The EDS analysis (Figure S2, available online at http://www.iwaponline.com/wst/072/227.pdf) of the fresh MPSD showed only the presence of oxygen (68.8 w-%) and chlorine (31.2 w-%). Carbon was left out of the analysis due to the coating method. Nitrogen was not detected by EDS, probably due to the limitations of the technique in detecting light elements (Ro et al. 1999). The high nitrogen content (9.4%) has been confirmed earlier by the flash combustion method (Keränen et al. 2013). The fresh resin was in a Cl⁻ form, i.e., Cl⁻ is the counter ion that is replaced by the contaminant ion in the ion exchange reaction. Therefore, chlorine was detected in the fresh MPSD.

The composition of loaded MPSD was confirmed by the presence of only oxygen, sulphur, vanadium and nickel. Chlorine was not detected in the loaded MPSD since, prior to the column study, the resin had been changed to OH⁻ form. The weight content (%) was as follows: 66.6 for O, 21.6 for S, 10.8 for V and 2.1 for Ni (Figure S2).

As the column studies showed, uptake of other components was detected to some extent. In ion exchange applications, accumulation of species in resin can occur when they are not removed by normal regeneration (Dowex 2014). This may result in resin fouling and the problem has to be resolved so that the resin lifetime can be extended. For example, iron and manganese in raw water tend to precipitate in the column. These precipitates can be dissolved by an acid. In addition, biological growth can exist on some occasions, e.g., during storage of resin. To remove microorganisms, oxidative treatment with peracetic acid or hydrogen peroxide has been recommended by Dowex (2014). It is thus important to study the chemical resistance of bio-based anion exchangers towards different cleaning solutions in order to be able to use them in a wide variety of applications.

**Chemical resistance**

Table 2 shows the yield and vanadium removal efficiency when the material was immersed in an acid or oxidizer. It is clearly evident that the H₂O₂-treated material had a higher weight loss. The removal of vanadium was also slightly lower than with untreated or HCl-treated material, although still very high. There was also a visible difference in particle size with the H₂O₂-treated material. The material did not settle as fast as the original MPSD or HCl-treated.

Figure 1 (a) Isotherm for synthetic vanadium solution (resin dosage 1.5 g/l, initial pH 7, temperature 23 ± 2 °C). Final pH 4.5–7.4. (b) Effect of material dosage on metal concentrations with industrial wastewater (initial pH 5). Final pH 5.0–5.4. Both figures show all repetitions.
material. Oxidative damage to the resin might have happened during the \( \text{H}_2\text{O}_2 \) treatment. Nevertheless, further studies on the chemical and physical stability of the material are necessary.

### CONCLUSIONS

The present study shows that ETM-modified pine sawdust can be used for the removal of vanadium from aqueous solutions at a wide pH range. The efficiency was confirmed with a challenging real IW containing a high amount of vanadium as well as other ions. The detailed study of the chemical resistance remains a challenge for the future.

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