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Removal of nickel and vanadium from ammoniacal industrial wastewater by ion exchange and adsorption on activated carbon

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ABSTRACT

Nickel and vanadium were removed from real ammoniacal industrial wastewater (Ni 2–4, V 40–50 mg/L) obtained from a synthesis gas scrubber. The aim of the study was to develop an industrial application for simultaneous removal of nickel and vanadium. The studied methods were adsorption (activated carbon (AC), AquaSorb 2000), anion exchange (Amberjet™ 4200 Cl) and cation exchange (Amberjet™ 1200 H). AC removed > 95% of nickel at pH 5.5–9 (dose > 2 g/L) but the vanadium uptake remained poor. In batch cation exchange, all nickel was removed (optimum pH 4–7) and 70–75% of vanadium was removed at pH 7 (5–10 g/L). All nickel was removed in batch anion exchange (optimum pH 5.5–9, 2–10 g/L). Over 89% of vanadium was removed in batch anion exchange at pH 7 (1–10 g/L). Adsorption capacities of 4.36 and 48.9 mg/g were obtained for nickel and vanadium in anion exchange at pH 7. In column anion exchange, all nickel and 92–98% of vanadium were removed in all three ion exchange cycles at pH 7–9. In regeneration, 72–96% of vanadium was eluted from the resin with 2.5 M NaOH. However, the elution of nickel with 2.5 M NaOH was not successful. An acid rinse (1 M H_2SO_4) enhanced nickel recovery up to 94%. Anion exchange proved to be the most effective method for simultaneous removal of nickel and vanadium from industrial wastewater.

Keywords: Nickel; Vanadium; Industrial wastewater; Adsorption; Ion exchange; Regeneration

1. Introduction

Nickel is a common impurity in wastewaters from the metallurgical industry, e.g. electroplating, smelting, metal plating, mining operations and alloy industries, and also tanneries, radiator manufacture and storage batteries manufacture [1]. Vanadium is an important alloying element used in ferrous and non-ferrous alloys due to its high tensile strength, hardness and fatigue resistance. It is also widely used in catalytic applications in automobiles and

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industries [2]. The main sources of vanadium as an environmental pollutant are the combustion of crude oil, coal and peat, oil refinery and catalytic applications [3,4].

Nickel exists in water solutions in cationic form, mostly as Ni(II). Nickel can form many kinds of complexes with various anions (monodentate, bidentate and polydentate) and neutral ligands, e.g. hexaquonickel, $[Ni(H_2O)_6]^{2+}$, nickel hexammine, $[Ni(NH_3)_6]^{2+}$ [5], tetracyanonickelate, $[Ni(CN)_4]^{2-}$, nickel(II)-ethylenediamine, $[Ni(en)_3]^{2+}$ and the nickel–EDTA complex, $[Ni(EDTA)]^{2-}$ [6,7]. The most common oxidation stages of vanadium in aqueous systems are III, IV and V [4]. In water, vanadium is bound with oxygen in *oxoanion* form, e.g. $V_3O_9^{3-}$. Depending on the pH, several different oxoanionic, or *(oxo)vanadate*, forms might be present in water. At low pH, vanadium exists as a cation [8,9]. When vanadates are strongly acidified, *cis*-$[VO_2(H_2O)_4]^+$ is formed [8]. It can form complexes with EDTA, oxalic acid and chlorine, for example, by displacement of water molecules in its structure as follows: $[VO_2(EDTA)]^{3-}$, $[VO_2(ox)_2]^{3-}$ and $[VO_2(Cl)_4]^{3-}$, respectively [8]. Vanadium (V) complexes with lactate and other anions are also known [8].

Nickel can be removed by chemical precipitation [10–12], filtration [13–15], adsorption onto various materials [16–19] and ion exchange [20,21]. Vanadium can be removed by coagulation–flocculation [22,23], nanofiltration [24], adsorption onto various materials [25–28] and ion exchange [29,30]. Adsorption and ion exchange are commonly used in industrial applications because of their easy operation.

Activated carbon (AC) has an extremely large surface area. Almost any carbon-containing material, for example coal, nutshells, tree bark, straw, or wood can be used as a raw material. Today, there is great emphasis on the study and the utilization of agricultural wastes in AC manufacture. Promising results on nickel removal by AC prepared from agro-based waste materials have been reported in the literature. Erdoğan et al. [16] reported a 100% reduction (for 10 mg Ni/L, AC dose 0.7 g/10 mL, pH 5) by using AC prepared from waste apricot. Hasar [17] achieved a nickel sorption capacity of 34.3 mg/g by using AC prepared from almond husk.

Several studies have been conducted on nickel and vanadium removal by ion exchange in recent years. The kinetics of nickel(II) removal has been studied by using Lewatit MonoPlus SP 112 cation exchange resin [21]. A maximum nickel uptake of 100% was achieved at pH 6.0 [21]. Nickel reductions of 98% (for 100 mg Ni/L, resin dose 2 g/L, pH 2–8) have been achieved with a commercial Dowex HCR S/S cation exchange resin [20]. The efficiency of the anion exchange resin D314 in the recovery of vanadium from acid leach solutions (pH 4, 2.06 mg V/L as V_2O_5) of coal has also been studied [30]. At pH 4.0, 99% of vanadium was recovered in a 1 h contact time [30]. Chelating resins have also been applied in the removal of nickel from fly ash solution using iminodiacetic acid resins [31] and vanadium from ammonium molybdate solutions [32].

The aim of this study was to investigate adsorption and ion exchange for the removal of nickel and vanadium from a particular ammoniacal industrial wastewater. Nickel and vanadium must be removed from the wastewater before conveying it to the communal wastewater treatment plant, and therefore, a feasible simultaneous removal method must be developed. In the ammoniacal industrial wastewater studied, nickel was probably bound as an inorganic ammine complex, e.g. $Ni(NH_3)_2^{2+}$, $Ni(NH_3)_3^{2+}$ and $Ni(NH_3)_4^{2+}$ [5,33], which are formed in the presence of ammonia [5]. According to Min et al. [33], the aforementioned forms appear at pH 8 and above. The exact form of the complex in the wastewater has still not been fully identified. We have previously analysed the wastewater by gas chromatography and mass spectrometry in order to reveal the composition of the organic matter. The amount of organic matter was very low and no organic compounds capable of forming a complex with nickel were found (unpublished data). All this indicates the presence of an inorganic nickel complex. According to Min et al. [33] ammonia and nickel can be removed simultaneously. They studied a nickel–ammonia complex containing wastewater and applied air stripping for the removal of ammonia. It was enabled by raising the pH of the wastewater to 11 in the presence of air, which lead to simultaneous precipitation of nickel as $Ni(OH)_2$ [33]. However, we also discovered in our preliminary lime precipitation studies on this wastewater that nickel did not precipitate as a hydroxide (unpublished data). The possible complex form may have contributed to this. We also found that the coagulation–flocculation of vanadium using ferric sulphate was possible but the doses of coagulant were very high (about 1,500 mg/L) (unpublished data). In addition, the chemical plant already had facilities for the application of adsorption and ion exchange. Hence, these technologies were chosen. Only very few studies on the treatment of nickel-ammonia complex containing wastewaters and real wastewaters are available [33]. Therefore, this study is seen as being of great importance to the scientific field of wastewater treatment and pollution control and to the fields of industry dealing with ammoniacal wastewaters.

2. Experimental

2.1. Materials

The wastewater was obtained for the experiments from a European chemical plant between November 2011 and February 2012. In each test series, wastewater from the same batch was used (each figure caption contains the initial concentrations of the corresponding sample batch). The wastewater was obtained from a synthesis gas scrubber and was sampled from the process stream in 10–15 L grab samples under normal process operating conditions. The wastewater was clear in appearance and had a pH of around 9. The temperature of the water in the process was about 70–80°C but the laboratory experiments were conducted at room temperature (20–23°C). The raw water samples were stored under refrigeration in polyethylene canisters. The treated water samples from the batch tests were stored under refrigeration in small polyethylene bottles. Samples from the column tests were stored under refrigeration in polypropylene tubes. The chemical properties of the water (during 2009–2012) are presented in Table 1 (gathered during a longer period). Nitrogen is found mostly in ammonium form because the concentrations of nitrite and nitrate in the wastewater were very minor. Metal reductions are calculated based on the original metal concentrations of the wastewater.

The ion exchange resins Amberjet™ 1200 H and Amberjet™ 4200 Cl were provided by Rohm & Haas, USA. Their ion exchange properties are based on a styrene-divinyl benzene structure in which the functional groups ($-SO_3^-$ for Amberjet™ 1200 H and $-N^+(CH_3)_3$ for Amberjet™ 4200 Cl) are attached [34,35]. The AC AquaSorb 2000 was provided by Jacobi Carbons AB, Sweden. Hydrochloric acid (1 M, Merck), sulphuric acid (1 M, Merck) and sodium hydroxide (2–2.5 M, BDH Prolabo, max. 1 ppm Ni) were used in the experiments. Ultra-pure Milli-Q water (Merck Millipore) was used in the preparation of acid and base solutions and reagents.

Table 1
Chemical properties of raw industrial wastewater during 2009–2012

Parameter	Value	*n*
pH	8.6–9.3	20
Conductivity [mS/cm]	1.36–2.70	20
Ni [mg/L]	0.5–4.4	13
V(V) [mg/L]	25.5–51.9	13
SO_4^{2-} [mg/L]	334–660	2
NH_4^+ [mg/L]	215–460	7
NO_3^- [mg/L]	0.3	1
NO_2^- [mg/L]	18	1
TOC [mg/L]	115–230	8
Total suspended solids [mg/L]	2–20	6

n = number of analysed samples.

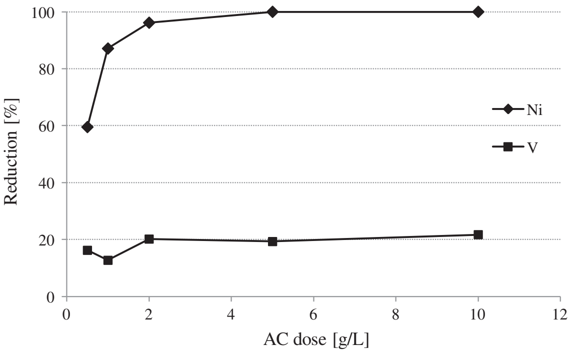

Fig. 1. Nickel and vanadium reductions vs. AC dosage at the original pH of wastewater (9.0). Contact time 24 h. Initial metal concentrations: Ni 2.44 and V 45.6 mg/L.

2.2. Analyses

Conductivity and pH were measured with VWR PC5000H and a Metrohm 744 pH meter, respectively. All aqueous samples (10 mL) for the metal analyses were preserved with 30% HCl (Suprapur, 0.5 mL/100 mL). Nickel was analysed by flame atomic absorption spectrophotometry (Perkin–Elmer AAnalyst 400) with an air acetylene mixture [36,37]. The slit width was 0.2 nm and the wavelength was 232.0 nm. Vanadium was analysed by graphite furnace atomic absorption spectrophotometry (Perkin–Elmer AAnalyst 600) with argon [38]. The slit width was 0.7 nm and the wavelength was 318.4 nm. Nonlinear calibration (0.1–5 ppm, $r^2 > 0.999000$) was used for nickel and linear five-point (100–500 ppb) calibration ($r^2 > 0.999000$) for vanadium. Total organic carbon (TOC) was analysed using a Shimadzu TOC-5000A with an ASI-5000A autosampler and ammonium (NH_4^+) using Dionex ion chromatography equipment with an LC20 chromatography enclosure, a GP40 gradient pump, a CD20 conductivity detector and an AS40 automated sampler. Nitrate (NO_3^-), nitrite (NO_2^-) and sulphate (SO_4^{2-}) were analysed using a Dionex ICS-2000 ion chromatography system. Total suspended solids were determined by filtration through a GF/A filter (1.6 μm) [39].

2.3. Adsorption on AC

Three adsorption tests were performed with AC. Adsorption of nickel and vanadium was first studied at the original pH of the wastewater (pH 9) with varying amounts of adsorbent (0.5–10 g/L). One repetition of each test sample was performed. The desired amounts of AC were measured into 250 mL polyethylene bottles and 100 mL of wastewater was added to each. The bottles were shaken in a horizontal shaker (Edmund Bühler SM-30) for 24 h at a frequency of 125 motions per minute and subsequently centrifuged (Jouan C4.12, 10 min at 800 × *g*) in order to improve clarification. Samples (about 40 mL) were taken from the supernatants for nickel, vanadium and pH analyses.

The effect of pH on adsorption was tested in two separate tests. Constant AC doses of 2 g/L and 5 g/L were tested at a pH range of 4–9. The dose of 2 g/L was chosen based on the results of the optimum dose test: a dose small enough would not remove metals entirely and thus, variations in the residual concentrations would be more easily detected. The 5 g/L dose was chosen for the removal of vanadium since the reduction at 2 g/L was low. The pH of the wastewater was adjusted using HCl. The test was repeated twice and the deviations of the results are shown as error bars. The procedure was otherwise identical to the first adsorption test. Samples were taken from the supernatants for nickel, vanadium and pH analyses.

2.4. Ion exchange

The cation exchange resin Amberjet™ 1200 H and the anion exchange resin Amberjet™ 4200 Cl were investigated in batches. Anion exchange was also tested in column in order to simulate a real process environment. The resins were activated prior to the tests with an appropriate regeneration solution (1 M H_2SO_4 for the cation exchange resin and 2 M NaOH for the anion exchange resin), which were selected based on the technical data sheets of the resins [34,35]. Thus, the ionic form was H^+ for the cation exchange resin and OH^- for the anion exchange resin. Hence, successful metal sorption would cause clear changes in the effluent pH. It was decided to perform the activation in batch in a decanter, thus making the procedure easier to control. The activation was done a day before the ion exchange experiments. An abundant amount (about 5 g) of resin was measured out into a decanter and covered with Milli-Q water. The resin was left to soak for at least 24 h. Just before the activation the resin was drained. Activation solution, (1 M H_2SO_4 or 2 M NaOH) was poured onto the drained resin covering it completely and the mixture was then let to mix slowly on a magnetic stirrer for 1 h. The spent regenerant was decanted and the resin was rinsed with Milli-Q water a couple of times. The rinsing water was decanted and a new batch of activation solution was added. The procedure was repeated three times and the final rinse was done thoroughly so that the pH of the effluent was near neutral. The finished resin was kept under Milli-Q water until the next day to prevent it from drying.

2.4.1. Batch ion exchange experiments

The first batch experiments were performed using a fixed pH 7 and varying amounts of resin in order to find the optimum resin dose. One repetition of each test sample was performed. Predetermined doses (0.5–10 g/L) of the drained, wet and activated resin were measured into plastic bottles. In order to measure the resin accurately, the moisture content of the wet, drained resin compared to air-dry resin was determined by drying samples of wet and air-dry resin in a drying oven for 24 h. The moisture content of the wet resin was found to be 40% and was uniform for all resin samples. The intention was to study the ion exchange phenomena at a lower pH as well so the pH was set to 7. This choice was supported by some related literature [20,21]. One hundred millilitres of wastewater was then pipetted into the bottles. The bottles were placed in a horizontal shaker (Edmund Bühler SM-30) and shaken for 24 h at 125 motions per minute. Small samples were separated and centrifuged (Jouan C4.12, 10 min at 800 × *g*). Samples of 40 mL were taken from the supernatant for metal and pH analyses.

The second batch experiments were performed as a function of pH with a fixed amount of resin similarly to the adsorption tests with AC. The pH of the wastewater was set to 4, 5.5, 7 and 9. The resin dose selected was 3 g/L for the cation exchange resin and 1 g/L for the anion exchange resin based on the results of the first batch experiments. Fairly good removal rates were achieved with these doses and therefore variations in the residual metal concentrations would be easily detected. The test was repeated twice and the deviations of the results are shown as error bars. The experiment was otherwise carried out as described earlier.

2.4.2. Column experiments with anion exchange resin

The anion exchange resin was also tested in a packed bed column in order to simulate a real process environment. The resin was also regenerated in the column. For the column tests, larger particles were removed by filtration in order to prevent resin fouling.

Filtration was done under vacuum using 11 μm filter paper (Whatman 1, Cat. No 1001-070), a Büchner funnel and a filter flask. The experiments were performed at the original pH of the wastewater, which was around 8.7–9.0, and at pH 7. Using Milli-Q water, 2.8 g of wet activated resin (equal to about 2 g of dry resin) was wet packed into the column. The volume of the bed was about 2.5–3 mL depending on how compactly it had collapsed. A 50 mL burette with an 11 mm inner diameter was used as a column. A flow rate of 48 BV/h (bed volumes per hour) was used. During each ion exchange cycle, 800–850 mL of wastewater was run through the resin bed at the target flow rate. Three ion exchange cycles were conducted. The effluent water was collected in fractions of appropriate size (10–40 mL) for metal analyses. Finally, the resin was rinsed concurrently with 30 mL of Milli-Q water and the rinse water was collected. The resin was left under a small amount of Milli-Q water until the regeneration on the following day. Metal reductions of ion exchange and resin regeneration were determined by mass balance of each cycle.

2.4.3. Resin regeneration

The regeneration of the resin bed was done in a column. A flow rate of 8 BV/h was used in regeneration. Four hundred and eighty millilitres of 2.5 M NaOH was run through the bed and the effluent regenerant was collected in fractions of appropriate size (10–40 mL). Three regeneration cycles were conducted. Each regeneration cycle was performed during a 3d period in order to enhance nickel desorption. After regeneration, the bed was rinsed concurrently with 30 mL of Milli-Q water and the effluent was collected. The resin was left under a small amount of rinse water until the next ion exchange phase. The recovery of metals was determined by mass balance of each regeneration cycle.

In order to enhance nickel recovery, an acid rinse was conducted. Sixty millilitres of 1 M H_2SO_4 was run through both beds at the regeneration flow rate, about 8 BV/h. The effluent acid was collected in two fractions, 30 mL each. Finally, both beds were rinsed with 30 mL of Milli-Q water. Samples (10 mL) for nickel analyses were taken from the acid and rinse water fractions.

3. Results and discussion

3.1. Adsorption on AC

3.1.1. Effect of AC dose

In the first batch adsorption test with varying doses of adsorbent, AC worked well on nickel: a 100% reduction was achieved at doses of 5 g/L and above at pH 9 (Fig. 1). Vanadium, on the other hand, was not adsorbed on AC very well. A mere 20% vanadium reduction was achieved at pH 9 and the AC dose did not affect the removal. The results of the experiment represent the basic mechanism of adsorption well. With higher doses, 5 g/L and over, nickel was adsorbed completely. This suggests that there is an excess of adsorption sites and thus free adsorption sites are still available and the adsorbent could adsorb larger quantities of metals. Lower doses were unable to remove nickel entirely, which proves that the adsorbent was loaded by the metals with doses under 2 g/L. Adsorption capacities of 2.88 and 14.7 mg/g were achieved for nickel and vanadium at pH 9.

3.1.2. Effect of pH

The results of the second experiment in which AC was tested with a fixed dose at pH 4–9 are presented in Fig. 2. Nickel was removed best at initial pH 5.5 and higher. Similar behaviour has been observed by Erdoğan et al. and Hasar [16,17]: the optimum initial pH for nickel removal was 5 in synthetic solutions. For vanadium, a clear change was observed in adsorption efficiency as a function of pH. The best result was achieved at initial pH 4, although the residual concentration was as high as 15 mg/L (Fig. 2). An adsorption capacity of 15.4 mg/g was achieved for vanadium at pH 4. The test was repeated with a higher AC dose, 5 g/L, to see if the AC dosage had any impact on vanadium adsorption. Surprisingly, at initial pH 5.5–9, the vanadium uptake at a dose of 5 g/L was even lower than the uptake achieved at 2 g/L. This might be due to the nature of the real industrial wastewater, for

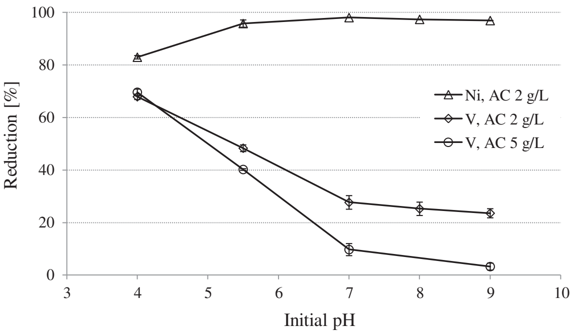

Fig. 2. Nickel and vanadium reductions vs. pH at AC doses of 2 and 5 g/L (V only). Contact time 24 h. Initial metal concentrations: Ni 2.44 and V 45.6 mg/L. The error bars represent deviation of two repetitions. The final pH values of the samples were 6.6, 7.3, 8.0, 8.0 and 8.7 at 2 g/L and 6.9, 7.5, 7.9 and 9.0 at 5 g/L for initial pH values of 4, 5.5, 7, 8 and 9, respectively.

example slightly varying amounts of suspended solids in the samples. The variety of contaminants in the wastewater may have caused unexpected phenomena. Higher AC doses may have induced adsorption of some other component instead of vanadium. This indicated that the residual vanadium concentration does not depend on the AC dose, at least with doses of 2 and 5 g/L.

3.2. Ion exchange

3.2.1. Effect of resin dose

The cation exchange resin Amberjet™ 1200 H removed nickel at pH 7 as expected. Nickel was removed completely with doses of over 5 g/L at initial pH 7 (Fig. 3). The final pH values of the batch samples were 7.9, 7.7, 7.8, 7.0, 2.6 and 2.1 for resin doses ranging from 0.5 to 10 g/L. This demonstrates the ion exchange reactions occurring in the system. With resin doses of 5 and 10 g/L, the final pH dropped dramatically to almost 2. This indicates the release of H^+ ions in the system through the ion exchange reactions ($R{-}H^+ + M^+ \rightarrow R{-}M^+ + H^+$). Surprisingly, vanadium levels were also decreased at high resin doses. This may have resulted from changes in vanadium speciation: initially anionic vanadium probably turned cationic at low pH as more and more protons were released into the system thus enabling vanadium sorption. At lower resin doses (0.5–2 g/L), the amount of metals attached to the resin was fairly minor because of the smaller number of ion exchange sites and thus the concentration of protons released was substantially lower. This resulted in a smaller change in the final pH of the samples. Adsorption capacities of 0.49 and 10.1 mg/g were achieved for nickel and vanadium in cation exchange at pH 7.

The removal efficiency of the anion exchange resin was excellent at initial pH 7 for both nickel and vanadium. With resin doses of 1 g/L and above, nearly 100% of nickel and 88.9–96.8% of vanadium were removed as shown in Fig. 3. The adhesion mechanism of nickel has not been identified and it may involve mechanisms other than ion exchange. The inorganic complex form of nickel may have contributed to the surprisingly high affinity of the anion exchange resin for nickel. Adsorption capacities of 4.36 and 48.9 mg/g were obtained for nickel and vanadium in anion exchange at pH 7.

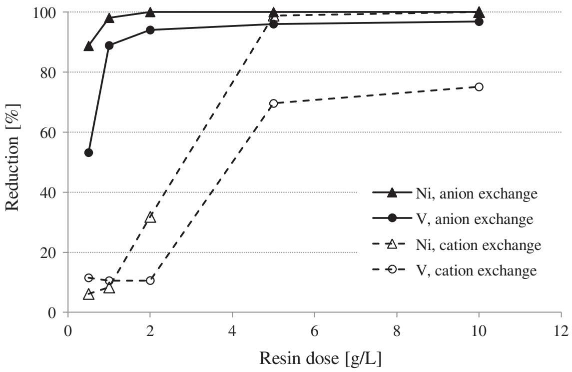

Fig. 3. Nickel and vanadium reductions vs. resin dosage at pH 7 in batch cation and anion exchange. Contact time 24 h. Initial metal concentrations: Ni 2.44 and V 45.6 mg/L. The final pH values of the batch samples were 7.9, 7.7, 7.8, 7.0, 2.6 and 2.1 for cation exchange and 7.9, 8.0, 8.0, 8.0, 8.4 and 8.8 in anion exchange for resin doses of 0.5–10 mg/L, respectively.

3.2.2. Effect of pH

A clear change in the ion exchange efficiency for nickel was observed in cation exchange with a resin dose of 3 g/L at the studied pH range of 4–9 (Fig. 4). At initial pH 7 and below, nickel was removed almost completely. Maximum nickel removal rates in cation exchange have been achieved at pH 6.0 [21]. Similar pH dependence has been observed with Dowex HCR S/S, a resin with the same functional groups as Amberjet™ 1200 H [20]. As presented in Fig. 4, at pH 9, the residual nickel concentration (3.77 mg/L) was only slightly lower than the original concentration. Based on these observations, pH adjustment seems to be required for successful nickel removal. The changes in

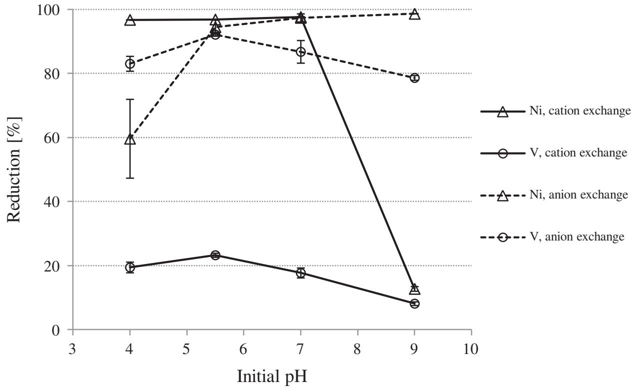

Fig. 4. Nickel and vanadium reductions vs. pH at resin doses of 3 g/L (cation exchange) and 1 g/L (anion exchange). Contact time 24 h. Initial metal concentrations: Ni 4.4 and V 51.9 mg/L. The error bars represent deviation of two repetitions. The final pH values of the batch samples were 2.4, 2.5, 2.8 and 7.3 in cation exchange and 6.0, 7.1, 7.7 and 8.6 in anion exchange for initial pH values of 4, 5.5, 7 and 9, respectively.

pH did not enhance vanadium removal much. The highest reduction of vanadium, about 23%, was observed at pH 5.5, which resulted in a residual vanadium concentration of about 40 mg/L. The resin dose of 3 g/L was not sufficient to initiate the release of protons and turn vanadium into cation form.

In anion exchange, maximum removal rates for nickel (98.7%) and vanadium (92.1%) were obtained at pH 9 and 5.5, respectively. However, nickel reduction was also good at pH 5.5 (Fig. 4), which means that both metals could be successfully removed at this pH. Lowering the pH from 9 to as low as 5.5 may, however, cause major expenses in terms of pH chemicals which affects the economic feasibility of this method.

3.2.3. Anion exchange in column

Three ion exchange and regeneration cycles were performed at the original pH of the wastewater, 8.7–9.0, and at pH 7 (Fig. 5). Proper s-shaped breakthrough curves were not obtained probably due to insufficient volume of wastewater (800–850 mL, 320–340 BV). The effluent vanadium concentrations did not reach the initial levels, which means that the resins did not reach saturation (exhaustion) in terms of vanadium. However, the reduction of nickel was outstanding in both experiments: practically all the nickel was removed in all three ion exchange cycles (data not presented). In addition, vanadium reduction was also very good. Vanadium reductions of 91.7–94.2% were achieved at the original pH (Fig. 5) for 320–340 BV of treated water. A slightly lower pH of wastewater seemed to have a positive effect on the removal rate: at pH 7 the vanadium reductions were 97.7–98.3%.

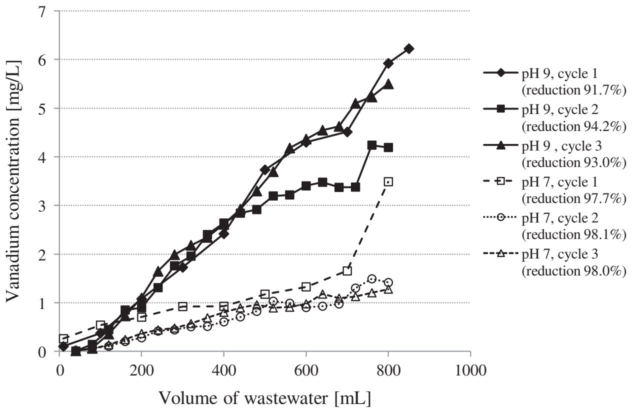

Fig. 5. Breakthrough of vanadium in anion exchange at the original pH of wastewater (8.7–9.0) and at pH 7. Bed volume 2.5 mL. Initial vanadium concentration 38.7–40.8 mg/L.

TOC, sulphates, nitrate and ammonium were also analysed for some of the fractions of the first anion exchange cycles in column at the original pH and at pH 7. Overall reduction trends were very similar at both pH values and no significant difference was observed. Uptake of other anions—sulphate and nitrate—as well as TOC was detected during the first fractions regardless of the initial pH, but the resins were quickly exhausted. After about 100 bed volumes, the sulphate concentration rose back to the initial level, 500–600 mg/L. TOC uptake remained minor for the whole cycle and slowly reached 150 mg/L in the end of the cycle (initially 170 mg/L). The nitrate content of the wastewater was initially very low, around 1 mg/L.

3.2.4. Resin regeneration in column

Vanadium was recovered well in regeneration: 75.6–84.7% of the vanadium was eluted at the original pH and 93.7–95.6% at pH 7 (Figs. 6 and 7). The pH of the wastewater in the ion exchange experiments seemed to have some impact on metal desorption as well, even though the molarity of the regenerant was the same for both resin beds. The variety of vanadate species present at pH 7 is different compared to the species at pH 9 [10]. It could be that these differing vanadate anions were not as tightly bonded to the resin at pH 7 compared to the test performed at the original pH. This may have resulted in a higher vanadium recovery.

In terms of nickel, the resin did not regenerate adequately. As Fig. 8 illustrates, only a small amount (3.5–10.6%) of the nickel was recovered at both pH values. The presumed nickel–ammonia complex may

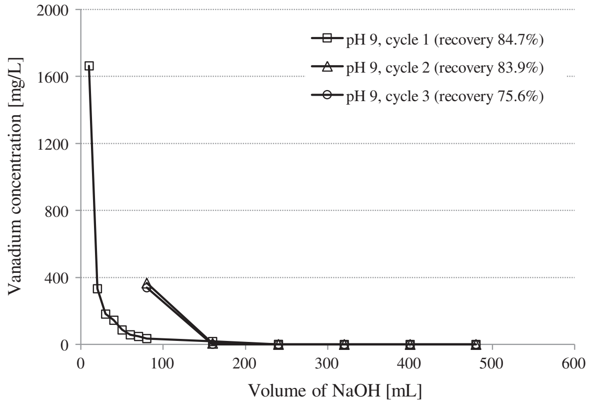

Fig. 6. Breakthrough of vanadium in regeneration with 2.5 M NaOH when the anion exchange tests were carried out at the original pH of wastewater (8.7–9.0). Bed volume 2.5 mL.

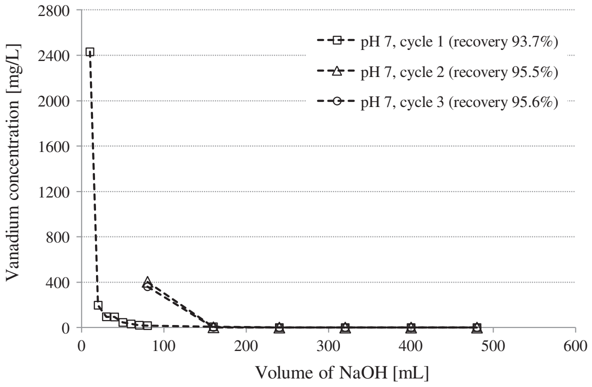

Fig. 7. Breakthrough of vanadium in regeneration with 2.5 M NaOH when the anion exchange tests were carried out at pH 7. Bed volume 2.5 mL.

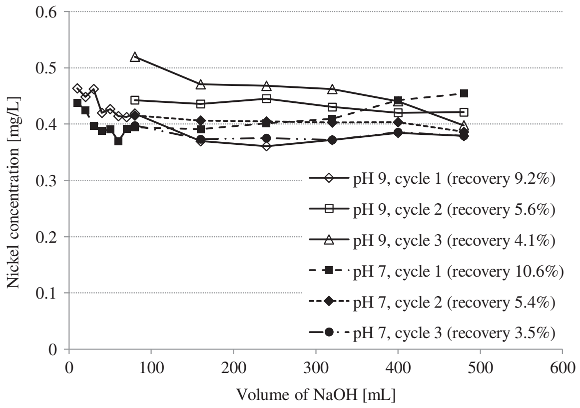

Fig. 8. Breakthrough of nickel in regeneration with 2.5 M NaOH when the anion exchange tests were carried out at the original pH of wastewater (pH 8.7–9.0) and at pH 7. Bed volume 2.5 mL.

have affected the nickel desorption significantly. These results prove that the resins—at both the pH values—will eventually be completely exhausted by nickel, and if no efficient method for nickel desorption is available, the resin must be replaced by fresh resin. Unfortunately, it was impossible to estimate how long the exchange capability of the resins could be sustained due to the limited number of ion exchange cycles.

According to the anion exchange batch experiment at different pH values (see Fig. 4), nickel reduction seemed to be the lowest at initial pH 4. This would indicate that nickel might be more easily removable at a low pH, and thus an acid rinse (1 M H_2SO_4) was applied to both resin beds in order to improve the nickel recovery. The technical data sheet of Amberjet™ 4200 Cl confirms that any pH (0–14) is suitable for the operation of the resin [35]. Hence, it is doubtful that an acidic medium would damage the anion exchange resin, even though it is not the recommended regenerant for such a resin.

The acid treatment was a success: 85.5% of nickel was eluted from the resin of the pH 7 tests and 94.3% from the resin bed of the tests carried out at the original pH of the wastewater (8.7–9.0). No further ion exchange experiments were conducted on the resins, and thus, the effect of an acid rinse on future ion exchange cycles was not studied. Chelating resins have also been successfully applied in the removal of nickel [31,32] and we will consider studying them in our future experiments.

4. Conclusions

Anion exchange proved to be the most effective method for simultaneous removal of nickel and vanadium. Both nickel and vanadium were removed well in anion exchange at the original pH of the wastewater (8.7–9.0) and at pH 7. In the column experiments, vanadium was successfully eluted from the anion exchange resin using 2.5 M NaOH but the elution of nickel was not possible. An acid rinse with 1 M H_2SO_4 removed nickel almost completely. According to the results, anion exchange can be recommended as a potential solution for simultaneous nickel and vanadium removal from ammoniacal wastewaters. The poor recovery of nickel may, however, affect the feasibility of anion exchange in terms of chemical demand and increased need for maintenance. AC removed nickel very efficiently but removal rates for vanadium remained moderate. The AC could be disposed of easily by incineration, but the low affinity for vanadium did not make it an attractive option. A combination of AC and anion exchange might offer a feasible solution to the problem. Further investigations are needed to find out detailed information about the behaviour of nickel in ammoniacal solutions.

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