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Removal of nickel and vanadium from desalination brines by ion-exchange resins

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ABSTRACT

This study determined Ni and V levels in brines produced by seawater desalination plants using the multi-stage flash distillation process and in the produced water generated at oil fields in Kuwait, and developed an ion-exchange system to remove such metals. Ni concentrations in brine blowdown varied from 0.558 to 1.167 mg L^{-1}, while V levels ranged between 0.181 and 0.923 mg L^{-1}, which are about two times higher than those of seawater feed since contaminants from corrosion of pipes and chemical inhibitors used to find their way in the brines. Produced water from oil fields has much higher Ni and V concentrations than seawater. Such concentrations greatly exceed the permissible levels set by environmental authorities. A cation-exchange resin with high sorption selectivity for Ni and V proved very effective as removal efficiencies up to 98% were obtained, and removals were consistently higher than 80% as the metal concentration increased 50 times. Design parameters and breakthrough curves were determined for the system used. The resin beads can be readily regenerated with 1 M NaOH and 1 M HNO_3 for repeated use without any significant capacity loss. The system used proved to be a viable alternative to other traditional treatment processes.

Keywords: Brine waters; Cationic exchange resin; Desalination plants; Sorption capacity; Toxic micro-pollutants

1. Introduction

Worldwide, the demand for freshwater is rising rapidly, especially in coastal areas. In arid zones where the Arabian Gulf countries are located, fresh water is scarce and people depend on the seawater desalination as a primary source of potable water supply. One example is the state of Kuwait where seven desalination plants with a total capacity of about 3 million m^3 d^{-1} provide the country with its fresh water supply. Kuwait is among the top 10 countries in the world in total desalination capacity. Five of desalination plants in Kuwait use the multi-stage flash (MSF) distillation method while one plant employs the reverse osmosis (RO) membrane method for desalination and another plant employs both methods.

Water desalination plants generate brine, which is a highly concentrated salt effluent that is also referred to as "brine-blowdown". The desalination plants discharge large quantities of brines into the sea thus progressively increasing the salinity of the seawater and contributing some heavy metals contained in the brine that poses serious environmental, ecological, and health problems [1]. The greatest adverse impacts have occurred around older MSF plants discharging to water bodies with little flushing. Chemical pretreatment and cleaning is a necessity in most desalination plants, which typically includes the treatment against biofouling (antifouling: biocides and their halogens' organic compounds of degradation), scaling (antiscaling: carbonic acids, polyphosphates), foaming (antifoaming: detergents), and

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corrosion (anticorrosive agents and others: sodium sulphite and sulphuric acid) in thermal plants, and against biofouling, suspended solids and scale deposits in membrane plants. The chemical residues and by-products used are typically washed into the sea along with the concentrate. Typical effluent properties of MSF and RO plants were reported by Lattemann and Höpner [1].

In desalination processes, seawater-borne metals are concentrated in the reject brine. Heavy metals may be present in the inhibitors as components or contaminants. Another source of metal input to reject effluent is the corrosion of permeation tubes and other utility pipes. There are several metal input sources to the effluent either from a desalination plant, or feed seawater (FSW) might be contaminated with heavy metals from different industrial sources, such as oil fields, factories and other human activities, and by process of desalination, which could be doubly concentrated in the brine discharged into the sea. Therefore, heavy metals content in brine discharged reflects the chemical characteristics of seawater. Among these heavy metals, nickel (Ni) and vanadium (V) are of major concern as toxic substances which are highly soluble in saline waters [2]. Moreover, in Kuwait, oil fields in particular generate waters (produced waters) which contain high concentrations of Ni and V, thus limit the possibility for water recycling unless the water is adequately treated to satisfy the water quality standards set by environmental authorities.

Desalination processes have always been limited by the disposal costs of the concentrated waste brines produced and the adverse impact of brine compositions on the environment, particularly in large-scale plants. The major environmental problem associated with a desalination plant is how to get rid of the surplus of concentrated brines, known as brine blowdown. In order to ensure the proper dispersion of brine discharge and minimize their adverse effects on the marine environment, it is necessary to select an appropriate technology for treatment of brine.

Removal of heavy metals from desalination brines and produced waters from oil fields has gained considerable interest [3–6]. Kumar et al. [7], suggested an ion exchanger, ceralite IR cation exchanger resin for the removal of nickel(II) from aqueous solutions, and they confirmed that the effluent from these desalination plants having nickel is known to be one of the major toxic pollutants. This necessitates the development of effective methods to remove heavy metals from the brine effluents. Elshazly and Konsowa [8] also used a cation-exchange resin for removal of nickel ions from wastewater. Effluent limits have become stricter in recent years causing the chemical process industries to upgrade their wastewater discharge standards. To meet strict effluent discharge limits, plants have to employ sophisticated chemical and physical processes because biological treatment alone is not adequate. A number of treatment methods for the efficient removal of Ni(II) and V(V) from brines have been studied which include chemical precipitation, chemical reduction, flocculation, filtration, evaporation, solvent extraction, biosorption, activated carbon, adsorption, ion exchange, RO, electrodialysis, membrane separation processes, and electrodeposition. New trends in removing heavy metals were described by different researchers [9,10]. Effective removal of undesirable metals from water systems is still a very important and challenging task for environmental engineers [11]. Although all the above techniques can be employed for the removal of heavy metal from wastewater, it is important to mention that selection of the most suitable treatment techniques depends on the initial metal concentration, the component of the wastewater, capital investment and operational cost, plant flexibility and reliability and environmental impact, etc. Ion-exchange processes have been widely used to remove heavy metals from wastewater due to their many advantages, such as high treatment capacity, high removal efficiency and fast kinetics [12]. Ion-exchange resin, either synthetic or natural solid resin, has the specific ability to exchange its cations with the metals in the wastewater. Among the materials used in ion-exchange processes, synthetic resins are commonly preferred as they are effective to nearly remove the heavy metals from the solution.

It is clear from literature that, although ion-exchange resins were studied for water softening, their applications in the treatment of brines were rather limited. In particular, the selective removal of nickel and vanadium as toxic substances by cationic ion-exchange resins was not tested. Therefore, this study was conducted to examine the performance of a novel synthetic ion-exchange resin (Lewatit TP 207), in an attempt to test its viability to remove Ni and V from desalination brines as to cope with water quality standards set by Kuwait Environment Public Authority (KEPA) calling for 0.2 ppm for Ni and 0.1 ppm for V in industrial brine effluents discharged into the sea [13]. The study focused on investigating (1) presence of nickel (Ni) and vanadium (V) as heavy metals in brines produced by desalination plants and in produced water generated at oil fields; and (2) feasibility of removing Ni and V from brines using a cationic ion-exchange treatment process.

2. Materials and methods

2.1. Collection of brines

The brine blowdown (BBD) samples were obtained from two large seawater desalination plants in Kuwait which employ MSF distillation process, namely the Doha West Desalination Plant (DWDP) with a capacity of 110 MIG d^{-1} (500,000 m^3 d^{-1}) and the Shuaiba South desalination plant (SHSDP) with a capacity of 30 MIG d^{-1} (136,000 m^3 d^{-1}), both are located along the sea coast. These plants receive seawater feed which have total dissolved solids (TDS) in the range of 45,000–50,000 mg L^{-1} depending on the intake location and generate a concentrated brine reject with TDS in the range of 60,000–65,000 mg L^{-1}.

Produced water samples were obtained from three major oil fields, namely the Borgan (1.7 M barrels/d = 0.27 Mm^3 d^{-1}) being the largest field located at the South of Kuwait, as well as the Rawdatain and Sabriya oil fields located at North of Kuwait.

2.2. Experimental methods

The samples were collected at a rate of twice a week during 6 months from July to December 2016. Specific water samples for Ni and V analyses were taken from four effluents of the two desalination plants: FSW, distilled water, brine recirculation, and brine blowdown. Sample volumes of 1,500–2,500 mL were collected in each case using polyethylene bottles and transported to the laboratory for chemical analysis at the day of collection for Ni and V contents, or stored under refrigeration with no additives at 4°C during weekends. The samples were filtered, then analyzed using an inductively coupled plasma (ICP) instrument (Shimatzu Corporation, Japan) and concentrations were further checked using flame atomic absorption instrument SensAA GBA flame/graphite furnace GF3000 with a spectrometer, equipped with single element hollow cathode lamps. Both instruments were operated at maximum sensitivity for working elements, according to the recommendations of the manufactures. Measurements by ICP–OES were preferred for determination of the lowest concentration values.

The pH of solution was measured with a pH meter using a combined glass electrode. To ensure quality control of metal analyses, the standard solutions for Ni and V were analyzed with each batch of samples. An appropriate blank was also analyzed with each batch of samples. No detectable amounts of any metal were found in the blanks. An average value of three replicates was accepted. Special precautions were taken to avoid contamination during sample preparation and analyses. Determination of other parameters (e.g., TDS, salinity) was carried out according to procedures outlined by the Water Environment Federation Standard Methods [14].

All the chemicals used were of analytical reagent (AR) grade. LANXESS Lewatit TP 207 is a Na^+ form weakly CXR (Sigma-Aldrich Company, UK). Synthetic solutions of nickel and vanadium were prepared by dissolving $NiCl_2.6H_2O$ and V_2O_5 in distilled water. The concentration range of nickel and vanadium prepared varied between 1, 10, 50, and 100 mg L^{-1}. Glassware, glass column (Outside Diameter (OD) 24 mm, Inside Diameter (ID) 19.4 mm), Teflon tubing, containers. Polyethylene bottles, Milli Q water, filtration set (Büchner flask, Büchner funnel, Whatman 150 mm filter paper) and N_2 gas cylinder were used. Standard solutions of Ni and V were prepared from 1,000 mg L^{-1} for calibration. 0.6 M NaOH and 0.5 M HNO_3 for washing and pH adjustment for the resin and 0.1 M HNO_3 as an eluent acid.

2.3. Ion-exchange treatment

Laboratory experiments were conducted using ion-exchange resin – Lewatit TP 207 (from Lanxess Pty Ltd., Marketing commercial name: Lewatit MonoPlus TP 207) is a weakly acidic, macroporous cation-exchange resin with chelating iminodiacetate groups for the selective extraction of heavy metal cations from weakly acidic to weakly basic solutions. Divalent cations are removed from neutralized waters in the following order: copper > vanadium (V) > uranium (UO^{2++}) > lead > nickel > zinc > cadmium > iron(II) > beryllium > manganese > calcium > magnesium > strontium > barium > sodium [15]. The resin was used to remove nickel and vanadium ions from the brine blowdown water samples because of its outstanding selectivity to nickel and vanadium. The resin's metal ion–exchange operation was at its fullest capacity at neutral pH of 7.0. It was conditioned following standard procedures of cyclic exhaustion with 0.1 M nitric acid and regeneration with 2 N sodium hydroxide.

Laboratory ion-exchange treatment studies were carried out at room temperature of 25°C using a glass column (30 cm length, 2.4 cm outer diameter, 1.94 cm internal diameter). A small amount of glass wool was placed at the bottom of the resin in order to prevent any loss of the resin beads during the sample loading. Weighed quantity of CXR was taken. The 35 g of Lewatit TP 207 resin beads were packed into the clean column to a particular height (10 cm). The resin is dried in oven at 50°C for 40 h. Before starting experiment, the resin was washed to remove all inorganic and organic impurities using water and 0.1 M HNO_3, then it was preconditioned using 0.6 M NaOH, 0.5 M HNO_3 and distilled water to pass thoroughly through the column until the effluent is neutral pH = 7. The Lewatit resin experimental set-up is shown in Fig. 1.

3. Results and discussion

3.1. Brine generated by desalination plants

Samples collected from DWDP and Shuaiba South Desalination Plant (SHSDP) were analyzed for nickel and vanadium concentrations during the period July to December 2016. Such period represents the maximum desalinated water production during the year. All water samples collected from the two aforementioned desalination plants were analyzed for the presence of two heavy metals, which are Ni and V. Table 1 presents the statistical analysis of the results obtained on concentrations of Ni and V from both desalination plants which exceed the limits (Table 2) set by Kuwait Environment Public Authority [13] and other international agencies [11] for seawater, thus it should not be allowed to discharge the brine into the seawater without further treatment for heavy metals. Chemical and physical analyses of the brines used in this study are shown in Table 3.

Table 4 shows that the desalination plants have led to the enrichment of reject brine with Ni and V ions as indicated from the calculated ratios (reject water:feed water). The Ni of BBD appears to be nearly two times higher than Ni in

Fig. 1. Experimental set-up for the ion-exchange treatment process.

Table 1
Summary of Ni and V concentrations in brine blowdown samples from Doha West and Shuaiba South Desalination Plants

Plant	Metal	Concentration (mg L^{-1} BBD[a] samples)			
		Mean[b]	S.D.	Minimum	Maximum
DWDP[c]	Nickel	1.1	0.037	1.046	1.167
	Vanadium	0.387	0.176	0.181	0.728
SHSDP[d]	Nickel	0.759	0.121	0.558	1.095
	Vanadium	0.633	0.149	0.387	0.923

[a] Brine blowdown.
[b] No. of observation = 45.
[c] Doha West Desalination Plant.
[d] Shuaiba South Desalination Plant.

FSW, and V of the BBD is two to three times higher than that of FSW. Nickel and vanadium concentrations found in this study are higher than those stated in the guidelines by KEPA [13]. Figs. 2 and 3 show that concentrations in brine blowdown (BBD) are largely related to their content in the FSW. However, BBD contains higher Ni and V concentrations than FSW. In desalination processes, seawater-borne metals are concentrated in the reject brine. Nickel is used as an alloy in pipes and heat exchangers in both plants studied. Moreover, heavy metals may be present in the corrosion and fouling inhibitors as components or contaminants. The corrosion of permeator tubes and other utility pipes may contribute to heavy metals. In brief, there are several metal input sources to the effluent either from a desalination plant, or feed seawater might be contaminated with heavy metals from different industrial sources, such as oil fields, factories and other human activities, and by process of desalination it will be doubly concentrated in the brine discharged into the sea. Therefore, heavy metals content in brine discharged reflects the chemical characteristics of seawater.

Discharge of brine effluents from desalination plants have the potential to elevate metal concentrations in outfall areas. In the Arabian Gulf region, many large desalination plants discharge effluent directly into the Arabian Gulf, a hypersaline water body that is constantly under environmental stress from oil spill. Each metal is a component of petroleum oils, and can be also contributed by highly contaminated sites affected by oil fields, produced water, sewage and industrial wastes discharged into the sea. Also, Ni–Cd batteries contribute to heavy metals. Meanwhile, it is evident that Ni and V concentrations can exceed levels at which toxic effects would be expected.

3.2. Produced water from oil fields

Extraction of oil and gas from underground reservoirs often is accompanied by water or brine, which is referred to as produced water (PW). Approximately, five barrels of water are generated for one barrel of oil produced. Water samples collected from three major oil fields that came from oil exploitation as usually discharged into the sea. In view of the increasingly stringent norms of disposal of effluent

Table 3
Chemical and physical analyses of the brines tested in this study

Parameter	Brine
Salinity	In the range of 60 psu
Temperature	5°C–15°C above ambient
Oxygen	Very low due to use of oxygen scavengers
Chlorine	Approximately 10%–25% of dosage
Sodium	5,200 mg L^{-1}
Potassium	170 mg L^{-1}
Magnesium	1,650 mg L^{-1}
Calcium	1,850 mg L^{-1}
Chloride	7,350 mg L^{-1}
Sulfate	8,210 mg L^{-1}
Halogenated organics	Varying composition and concentration
Antiscalants (e.g., polymaleic acid)	1–2 mg L^{-1}
Acid (H_2SO_4)	pH 6–7
Antifoaming agents (e.g., polyglycol)	0.1 mg L^{-1}
Heavy metals (in varying concentrations)	Copper, nickel (from heat exchangers), and vanadium
Cleaning chemicals	Acidic (pH 2) solution containing corrosion inhibitors such as benzotriazole derivatives

Table 2
Environmental standards for water from Kuwait EPA [13]

Parameter	Nickel (mg L^{-1})	Vanadium (mg L^{-1})	Supplement No.
Quality standards of seawater	0.0002	0.000094	12
Threshold levels of industrial brine in Kuwait's seawater	0.2	0.1	13
Standards of treated brine	0.2	NM	14
Standards of treated brine uses for irrigation	0.2	NM	15
Levels of inorganic contents for drinking water that affect health	0.02	NM	16

NM: Not mentioned in the reference.

Table 4
Ratio of Ni and V ions in FSW and BBD of the Doha West and Shuaiba South plants

Plant	Average concentrations (mg L^{-1})	
	Ni	V
DWDP[a]		
FSW[b]	0.606	0.242
BBD[c]	1.167	0.728
BBD/FSW ratio	1.92	3
SHSDP[d]		
FSW	0.605	0.458
BBD	1.095	0.923
BBD/FSW ratio	1.8	2

[a] Doha West Desalination Plant.
[b] Feed seawater.
[c] Brine blowdown.
[d] Shuaiba South Desalination Plant.

from petroleum activities and interest in water conservation, the treatment of the oilfield-produced water, which is the largest wastewater stream associated with oil and gas industry [16].

The Borgan oil field is located at the South of Kuwait, whereas the Rawdatain and Sabriya oil fields are located at North of Kuwait. The produced water is discharged into Kuwait Bay from these oil fields. Nickel and vanadium concentrations measured in unfiltered produced water samples are presented in Table 5. Such concentrations can be very high (as much as 300,000 times V, and 14,000 times Ni than in ambient seawater, and 30 times V, and 3 times Ni than in the industrial brine) and are very variable. It is clear that V is higher than Ni in these samples.

Nickel and vanadium are oil-related metals present mainly in organometallic form in crude oil and has been considered as a “marker” for petroleum hydrocarbon contamination from illegal discharges from tankers passing the Kuwait coast. In the desalination plant, where oil loading and storage activities are not far in place, Ni and V in samples

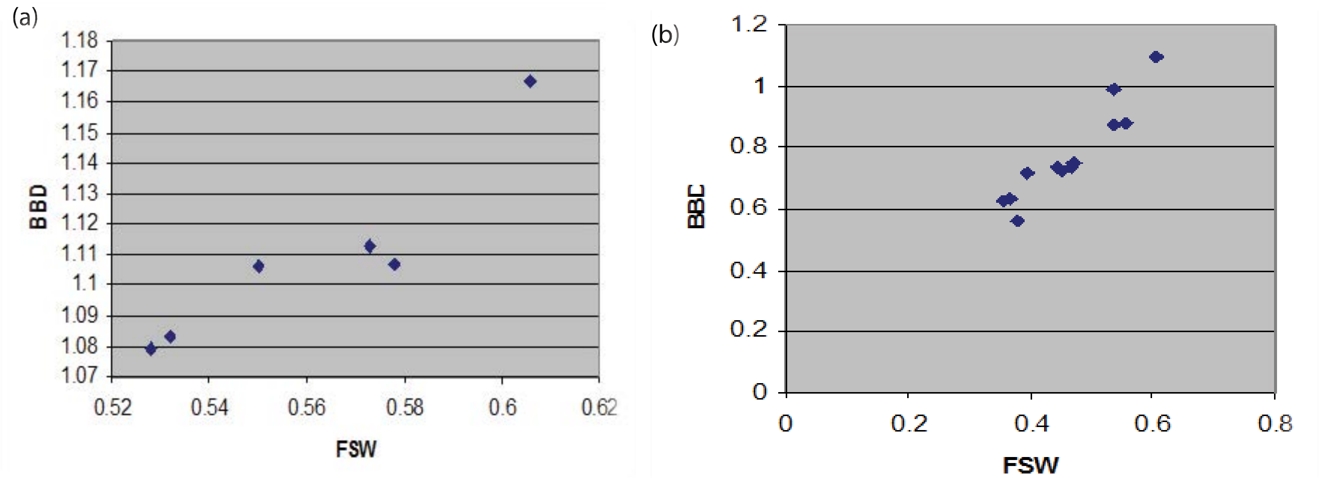


Fig. 2. Nickel concentration (mg L^{-1}) in brine blowdown (BBD) as related to feed seawater (FSW) at (a) Doha West and (b) Shuaiba South Desalination Plants.

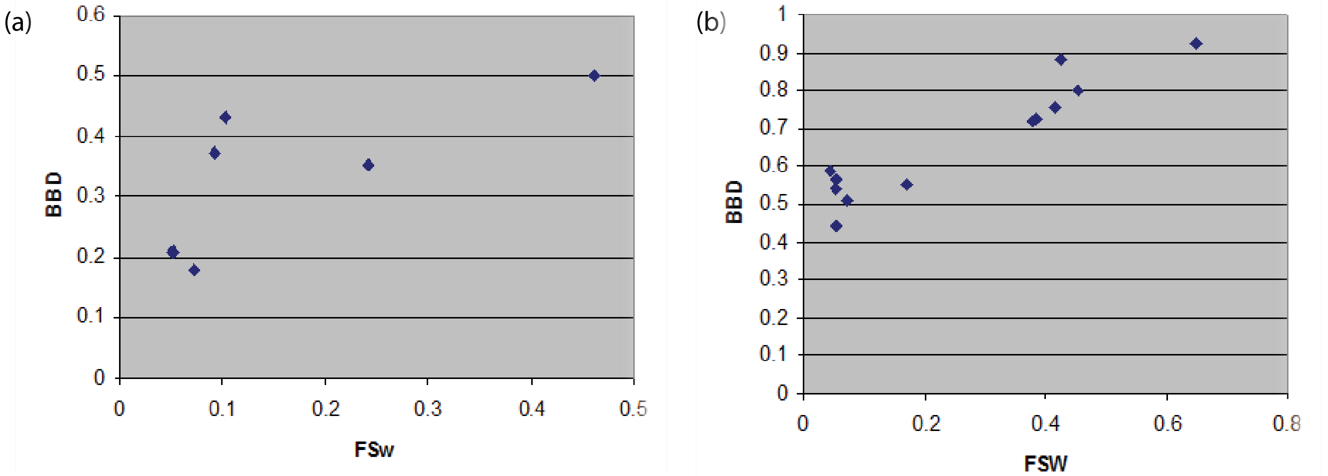


Fig. 3. Vanadium concentration (mg L^{-1}) in brine blowdown (BBD) as related to feed seawater (FSW) at (a) Doha West and (b) Shuaiba South Desalination Plants.

of feed seawater to desalination plants reached 0.606 mg L^{-1}, and 0.458 mg L^{-1}, respectively, during the same period of study.

The Ni and V concentrations displayed in Table 6 are comparable with those reported by Neff et al. [17], Azetsu-Scott et al. [18] and Zeng et al. [19], who presented produced water as it is comprised of naturally occurring formation water in the oil and/or gas reservoir and seawater injected to maintain reservoir pressure, Table 6 presents the average produced water characteristics from Wafra oil field as an example. It is usually hot, saline reduced water that contains high concentrations of heavy metals, radionuclides, hydrocarbons and ammonia compared with the receiving environment. In addition, produced water may also contain process chemicals such as demulsifies and corrosion inhibitors added during the operation of the oil well.

3.3. Ion-exchange treatment of brines

Nickel and vanadium are known to be major toxic pollutants, which necessitates the development of effective methods to remove these heavy metals from the brines of desalination plants. Results on ion-exchange treatment experiments on brine blowdown from the two desalination plants under study are shown in Table 7. This table presents the characteristics of brine blowdown from the two desalination plants before and after ion-exchange treatment. The brine blowdown from the two desalination plants is a basic solution (pH = 9.02–9.38). Flow rate for the ion-exchange resin column is 20–40 mL min^{-1}. The amount of samples passed through the column was 13 BV h^{-1} for 6 h, resin pH was 7–8 (neutral). In general, removal of Ni and V from Doha BBD was comparable with that of Shuaiba BBD, with continuous addition of the influent over the resin beads several times. This is true in spite of presence of slightly higher Cu concentration in Doha BBD compared with Shuaiba, knowing that Cu is considered as the first competitor for Ni and V. In comparison between the two metal ions, the removal of V was higher than that of Ni in both samples of synthetic and BBD. This is because of V has a higher selectivity order than Ni.

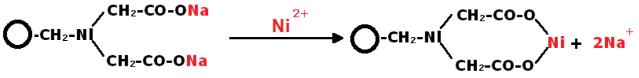
Table 5
Concentrations of nickel and vanadium in produced water from oil fields

Oil field	Average metal concentration	
	Ni (mg L^{-1})	V (mg L^{-1})
Borgan	0.18	1.74
Sabriya	0.28	0.491
Rawdatain	0.14	0.447
Wafra	0.20	0.45

Table 6
Characteristics of produced water from Wafra oil field in Kuwait

Constituent/parameter	Average value in the year 2011
Flow, m^3 h^{-1}	200
pH	6.5–8.5
Chemical oxygen demand (COD), mg L^{-1}	200
Oil and grease, mg L^{-1}	10
Total dissolved solids (TDS), mg L^{-1}	5,000
Phosphate, mg L^{-1}	2
Ammonia, mg L^{-1}	5.5
Nitrate–NO_3, mg L^{-1}	30
Total nitrogen, mg L^{-1}	35
Phenol, mg L^{-1}	1
Fluorides, mg L^{-1}	2
Sulphides, mg L^{-1}	0.5
Chlorine, mg L^{-1}	0.5
Turbidity, NTU	50

The mechanism of the two metal ions removal by Lewatit TP 207 resin is shown in the following scheme. However, resin may be considered as an acid as it possesses (CH_2COO^-) ion and hence would prefer to bind with base, most preferably with high electronegative and low polarizable Ni ion. The Ni saturated resin was regenerated with acid and base. All the regeneration experiments were carried out at room temperature. Desorption efficiency of the resin was studied using 0.1 M HNO_3 as eluent. It has been observed that 99%–100% desorption can successfully be made.



The breakthrough curves for an ion-exchange column and an adsorption column are similar, and the contacting techniques are almost identical. Consequently, the same procedures used for the design of adsorption columns may be used for ion-exchange columns. A laboratory- or pilot-scale breakthrough curve is required for both procedures. The breakthrough curve for a column shows the solute or ion concentration in the effluent on the y-axis vs. the

Table 7
Characteristics of raw and treated brine effluents from SHSDP and DWDP

Plant	SHSDP[a]		DWDP[b]	
Parameters	Raw BBD[c]	Treated BBD	Raw BBD	Treated BBD
Ni, mg L^{-1}	0.3–0.7	0–0.1	0.3–0.68	0
V, mg L^{-1}	0.38–0.7	0.01–0.02	0.37–0.7	0–0.01
Cu, mg L^{-1}	0.017–0.396	0.03	0.25–0.56	ND[d]
Pb, mg L^{-1}	0.024–0.56	0.01	1.82	ND
Hg, mg L^{-1}	0.02–0.046	0.009	3.96	ND
Mo, mg L^{-1}	0.001	<0.0001	0.0014	<0.0001
pH	9.02–9.08	6.9	9.38	6
Color	Pale Yellow	Clear	Pale yellow	Clear

[a] Shuaiba South Desalination Plant.
[b] Doha West Desalination Plant.
[c] Brine blowdown.
[d] Not determined.

effluent throughout volume on the *x*-axis. The area above the breakthrough curve represents the amount of solute or ions taken up by the column and is $\int(C_0-C)dV$ from $V = 0$ to $V =$ the allowable throughout volume under consideration. At the allowable breakthrough volume, V_B, the area above the breakthrough curve is equal to the amount of ions removed by the column. At complete exhaustion, $C = C_0$ and the area above the breakthrough curve is equal to the maximum amount of ions removed by the column. At complete exhaustion, the entire exchange column is in equilibrium with the influent and effluent flows. Also, the ion concentration in the influent is equal to the ion concentration in the effluent.

The effect of influent Ni concentration on removal efficiencies was examined using four different concentrations: 1, 10, 50, 100 mg L^{-1} with Lewatit TP 207, as illustrated in Fig. 4. The removal efficiency is decreased as the influent concentration is increased. At a constant flow rate of 25–35 mL min^{-1}, for an initial concentration of 1 mg L^{-1} the removal is almost 100%, but when the influent concentration is 10 mg L^{-1}, the removal is slightly decreased to reach 99%. Whereas, while the influent concentration is increased to 50 mg L^{-1}, the removal decreased a bit more to reach 96.5%, and when the concentration is doubled to become 100 mg L^{-1}, the removal efficiency sharply decreased reaching about 84.7%. Since the adsorption capacity of the resin mostly does not change, as long as the resin is not exhausted, what is apparently changing is the total amount of Ni adsorbed due to the increasing initial concentration.

The effect of initial Ni^{2+} ion concentration in the range of 1–100 mg L^{-1} on adsorption was also investigated. The results indicated that the percentage nickel removal decreased with increase in initial nickel concentration, in other words, the adsorption capacity increased from 0.26 to 149 mg g^{-1} as the metal concentration increased from 1 to 100 mg L^{-1}. This may be due to the progressive increase in the electrostatic interaction between the nickel ions and the adsorbent active sites. Moreover, this can be explained by the fact that more adsorbent sites were being covered as the nickel ions concentration increased.

A similar trend was observed in the case of vanadium removal (Fig. 5), as the percentages removal of V were, 99.58% at a flow rate of 1–5 mL min^{-1} for 1 mg L^{-1} V_2O_5, 99% for 10 mg L^{-1} at a flow rate of 3–10 mL min^{-1}, 88.3% at a flow rate of 27 mL min^{-1} for 50 mg L^{-1}, and 0% at a flow rate of 25 mL min^{-1} for 100 mg L^{-1}. This can be explained by the fact that as the concentration of vanadium ion increases so does the metal loading on the adsorbent. For example, a concentration of 100 mg L^{-1} will have higher surface loading as compared with concentration of 1 mg L^{-1}. Because it causes an increase in number of the metal ions coming in contact with the resin during same interval of time, while on the other hand, the number of sites available for adsorption is constant for all concentrations. So, when influent V concentration is higher, more ions will be competing for same adsorption sites and will go through without being adsorbed.

Results from the treatment experiments show that sorption of vanadium on the resins used occurs at acidic pH whereas for nickel it was at alkaline media that total recovery of the nickel and vanadium from the Lewatit TP 207 column can be achieved by use of nitric acid (0.1 M). The percentage of metal adsorbed on the column was calculated from the amounts of metal in the starting sample and the amounts of metal eluted from the column.

In general, the studied metals were recovered with high yield throughout the pH range from 6.8 to 7.8 for Ni solutions, and from 1 to 3 for V solutions. Controlling the valence of vanadium in aqueous solutions is a major problem. Under reducing conditions and the pH of seawater vanadium exists in such medium in the oxidation state (V), forming the complex $H_2VO_4^-$. Vanadium in seawater is mostly present according to the equilibrium equation as follows:

$$H_2VO_4^- + 2H^+ \rightarrow H_3VO_4 + H^+ \rightarrow VO_2^+ + 2H_2O \qquad \text{(I)}$$

In acidic media, this equilibrium will be displaced towards the formation of VO_2^+. For example, at pH 3.5, 58% of the total dissolved vanadium is present as a mixture of the two ions (VO_2^+ and $H_2VO_4^-$), and only 42% as in the form

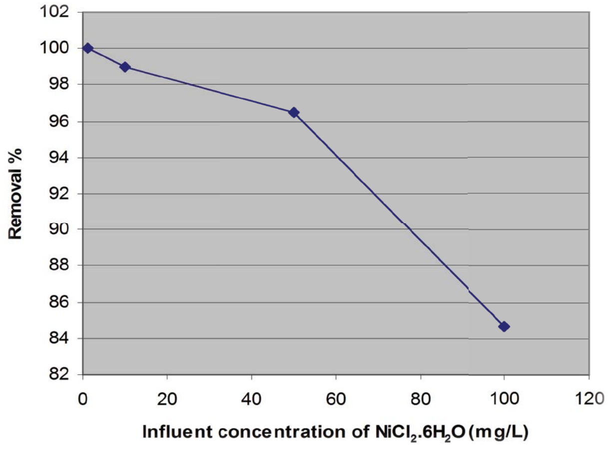


Fig. 4. Effect of influent concentration on the removal efficiency for four different concentrations of $NiCl_2.6H_2O$ at flow rate of 25–35 mL min^{-1} and a pH range 6.8–7.8.

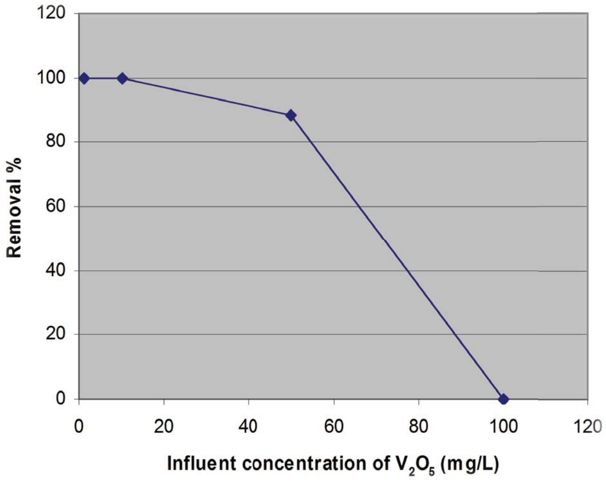


Fig. 5. Effect of influent concentration on the removal efficiency for four different concentrations of V_2O_5 at a flow rate of 1–27 mL L^{-1} and a pH range 1–3.

H_3VO_4. The cation (VO_2^+) is retained by the complexing agents used. So, total recoveries of vanadium are obtained at acidic pH. In alkaline media, the vanadium (IV) is oxidized to vanadium (V), which occurs as anionic complexes. The vanadium is completely retained by the resins used at acidic pH (recovery is ~100% in the pH range 1–5), then recovery decreases rapidly as pH moves to the alkaline side.

The extent by which the competing ion interfered with the uptake of Ni and V is important for the choice of resins that will selectively remove Ni and V contaminants from brine seawater. The feasibility of the proposed method was examined in the presence of possibility matrix ions of seawater samples. The series order below shows the matrix ions (interference elements) of Ni and V that may have an effect on their recoveries. Copper, lead, and mercury may affect the recovery of nickel when using Lewatit TP 207, and copper and uranium may affect the recovery of vanadium. The selectivity of ion-exchange resins is expressed via the so-called selectivity series for an International Desalination Association (IDA) resin. The heavy metal ions bind more strongly than the alkali earth ions and these bind more strongly than alkali metals.

3.4. Design considerations

In order to determine design parameters, loading of the resin was tested in a column (internal diameter 19.4 mm, resin height 10 cm) containing 35 g of resin. The influent containing 1 mg L^{-1} of nickel was fed to the column at 13 bed volumes (BV) per hour. The flow rate was 15 mL min^{-1}, at a pH = 6.23–6.3. The results displayed in Fig. 6 show the characteristic breakthrough curve for the resin at an influent Ni concentration of 1 mg L^{-1}. Similar trends were obtained at other influent concentrations studied. At the allowable breakthrough volume, V_B, the area above the breakthrough curve is equal to the amount of ions removed by the column. At complete exhaustion, $C = C_0$ and the area above the breakthrough curve is equal to the maximum amount of ions removed by the column. At complete exhaustion, the entire exchange column is in equilibrium with the influent and effluent flows. Also, the ion concentration in the influent is equal to the ion concentration in the effluent.

The adsorption capacity was calculated using the following formula [12]:

$$q_e = \frac{\left(C_0 - C_e\right)}{m} \times V \tag{1}$$

where q_e (mg g^{-1}) is the equilibrium adsorption capacity, C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of metal ions in solution, V (L) is the volume, and m (g) is the amount of the resin. By using this formula q_e values for different metal concentrations were calculated.

Based on the saturated adsorption capacity of the resin as shown in Fig. 6, the calculated adsorption capacity of the resin = 42.82 mg of nickel/g of resin. After resin adsorption, the resin becomes saturated with the nickel metal. This figure indicates the effect of initial concentration of the Ni in the solution on capacity sorption of Ni(II) by Lewatit TP 207. The capacity goes up with increasing initial concentration of the Ni in the solution. Also observed was a gradual breakthrough point for the initial nickel concentrations. In the first phase of the filtration, the residual concentrations are below 0.1 mg L^{-1}. This is usually in compliance with environmental legislation. After a certain point, the residual concentrations of metals suddenly increase.

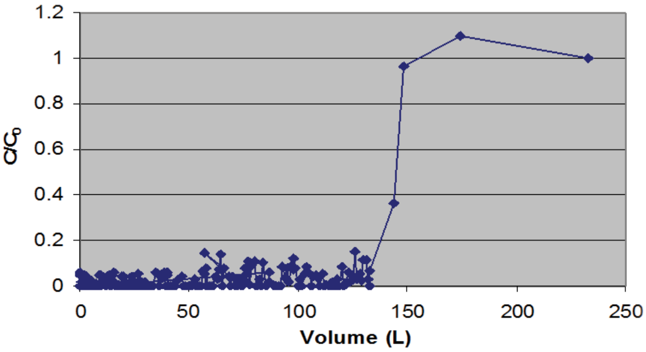


Fig. 6. Breakthrough curve of 1 mg L^{-1} $NiCl_2.6H_2O$ by Lewatit TP 207.

The Ni(II) was sorbed and desorbed on 35 g of the resin several times. It was found that sorption capacity of resin after 170 runs of its equilibration with Ni(II), changes less than 10%. Therefore, repeated use of the resin is feasible. The resin cartridge, after loading it with samples, can be readily regenerated with 1 M NaOH and 1 M HNO_3. The sorption capacity of the resin as stored for more than 6 months under ambient conditions has been found to be practically unchanged.

3.5. Process applications

Brine disposal causes many environmental problems, therefore, various technologies have been developed at different scales for its treatment and possible recovery of metals [20,21]. It is known that seawater withdrawn in the desalination plants usually contains 60 elements from the periodic table and some of them are scarce and expensive. Attention has long been oriented towards removing such elements appearing in the brine before discharging it back into the sea in order to eliminate their accumulation in the seawater, but recent trends call for recovering valuable metals from the rejected brine. Ion exchangers have been used in this regard but ion selectivity appears to be the critical issue. Although the Lewatit TP 208 resin, as a weakly-acidic cation-exchange resin, was studied by some researchers [21], it was not tested previously to prove its ability to selectively remove nickel and vanadium from concentrated brines. This study clearly demonstrated the potential applicability of Lewatit TP 207 resin for highly efficient removal and recovery of Ni and V metals from contaminated brines even at high concentrations and in the presence of substantial concentrations of other cations present in different brines collected in Kuwait. In other words, this study showed that if the brine is pre-concentrated, nickel at high concentrations of 100 mg L^{-1} can be recovered. However, calculations of separation factors will be studied in a future work in which scale-up analysis of the process will be also conducted.

4. Conclusions

High levels of Ni and V were observed in feed seawater, brine water from MSF desalination plants, and produced water from oilfields, and all exceed the permissible limits. Chemical analysis showed variations in the concentrations of Ni and V in water samples collected from the two desalination plants (DWDP and SHSDP), especially, in feed seawater and brine water samples. Although the Ni and V concentrations in the brine blowdown from each desalination plant are closely related to those of the feed seawater to the plant, the Ni of BBD appeared to be nearly two times higher than Ni in FSW, and V of the BBD was two to three times higher than that of FSW. The increase in these heavy metals in desalinated water brine is apparently due to the concentration of such heavy metals in the feed seawater within the desalination plant. Contaminants due to corrosion of pipes and chemical inhibitors used find their way in the brines. Effluents discharged into the marine environment can have adverse effects on the seawater and poses a significant ecological and health risks to the marine environment. Nickel and vanadium are oil-related metals, thus produced water discharged from oil fields contains high levels of Ni and V. Therefore, the produced water could be a major source of Ni and V in the seawater, as these two heavy metals are not considered to be among the major components of seawater. Cation-exchange resin Lewatit TP 207 was found to be an efficient technique for nickel (II) and vanadium (V) removal from brines with efficiencies up to 98%, and remained above 80% even though the metal concentration increased 50 times. The cationic ion exchange process is likely to become a very viable alternative to other traditional treatment processes.

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