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Assessment of the physical and chemical qualities of brine and the application of nano zerovalent iron for the treatment of brine effluent

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ABSTRACT

The arbitrary discharge of brine effluent from reverse osmosis treatment plants impacts negatively to the environment due to its high salinity. In the present study, brine effluent obtained from eMalahleni treatment plant, South Africa, was analysed by pH, electrical conductivity and total dissolved solids measurements. The ion chromatography and the inductively coupled plasma optical emission spectroscopy were also used to examine the anion and cation content of the brine effluent. The analysis of major cations and anions indicated that the brine water quality was above the target water quality range for potable water. Geochemical modelling of the brine effluent classified the brine as a type 2 brine solution containing sodium sulphate salt. Furthermore, nano zerovalent iron (nZVI) produced from acid mine drainage or commercial ferric chloride was used to treat samples of the brine effluent. The treatment showed that the optimum nZVI dosage and contact time for the treatment of 50 mL of brine effluent having a pH of 6.06 at 25°C is 0.02 g and 60 min, respectively. The nZVI was able to remove about 70% of most of the elements contained in the brine effluent except for Na, Ca and K.

Keywords: Brine effluent; Acid mine drainage; Nano zerovalent iron; Ferric chloride; Geochemical modelling; eMalahleni treatment plant

1. Introduction

Brine effluent is a waste from the treatment of mine water using reverse osmosis. When brine is disposed to the environment, it impacts negatively upon the environment by polluting natural water bodies. Brine is defined as water that is saturated or nearly saturated with salt and is more concentrated in dissolved materials than sea water. It could also be referred to as a saline effluent generated from the water desalination process. The chemical composition of brine is made up of cations such as K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+; anions such as Cl^-, NO^-, SO_4^{2-}, HCO_3^- [1] and dissolved solids greater than 1,500 mg/L [2,3]. Brine is characterised by high total dissolved solids (TDS) containing organics, calcium and sulphates, which makes it prone to scaling and fouling membrane systems used in water purification [4]. Brine can be classified into type 1 and type 2 brine solution. The type 1 solution is composed of sodium chloride while type 2 is composed of sodium sulphate [5–7]. Brine solutions contain cations and anions irrespective of the origin. The constituents of the brine produced from desalination plants depend on the technology used, the quality of feed water available, the cleaning and flushing methods used, the quality of water to

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be generated, etc. Brine generated from desalination of water creates an environmental problem associated with its disposal. The brine obtained from the desalination process contains about 20%–50% of the treated wastewater depending on the raw water quality. Brine effluent obtained after the treatment of mine water is a concentrate of highly saline nature.

High salinity impairs soil and reduces plant growth characterised by scorching of plant shoots and darkening of leaf colour [8]. Brine reduces growth and crop yield due to the increase in osmotic pressure of salts in the contaminated soil and water. Mohamed and Antia [9] reported that the seepage of brine in India resulted in groundwater contamination of the source well thereby increasing the groundwater hardness. A high concentration of sodium chloride can change the soil electrical conductivity (EC), soil aeration, impair the soil permeability, induce specific ion toxicity, alter sodium absorption ratio (an index used to classify waters used for irrigation), etc. [10]. Water with high salinity containing calcium and magnesium salts forms precipitates that hinder water movement in the soil structure.

The disposal of the brine produced after inland desalination processes has been a serious problem in South Africa because of the stringent environmental legislation on waste disposal [11]. Common disposal of brine effluent includes surface water discharge, land application (irrigation), deep well injection, sewer discharge, dust control, de-icing agent and evaporation pond. However, Turek [12] stated that the best way of disposing brine is to effectively reuse the solution to prevent environmental pollution. Studies have shown that about 3 million litres of brine effluent per day are currently generated by power stations in South Africa [13]. Research has been conducted on the effluent waste stream from eMalahleni water desalination treatment plant which uses reverse osmosis (RO) technology. Its feed source water emanates from large volumes of excess underground mine water. The quality of water generated from mining is associated with Mg^{2+}, Ca^{2+}, SO_4^{2-} ions (a neutral type of water), and the acidic type is associated with Mn^{2+}, Fe^{2+} and Al^{3+}. Underground mine acidic waters have properties of pH < 3, TDS of about 4,000 mg/L, EC in the range of 2,000–6,500 μS/cm and the acidity can be associated with the presence of Fe, Al and Mn concentrations [14]. A cost-effective and environmentally friendly brine treatment is required before its disposal. Many methods have been used such as RO [15–17], microfiltration (MF), ultrafiltration (UF), MF/UF-RO, ultraviolet technologies, etc. Ng et al. [18] proposed a brine treatment consisting of a biological activated carbon column followed by capacitive deionisation process. The authors reported that the technique demonstrated about 20% total organic carbon (TOC) removal efficiency using the biological activated carbon for 40 min, while the capacitive deionisation process removed more than 90% cations and anions. It was opined in their study that the capacitive deionisation process resulted in 78% TOC removal, 91% total nitrogen removal and about 90% water was recovered. Qurie et al. [19] treated brine by the use of an epuvalisation system (an activated sludge unit, two consecutive UF membrane filters followed by an activated carbon filter and an RO membrane). They reported that the treatment technique showed a remarkable decrease of the EC, PO_4^{3-}, chemical oxygen demand and K^+ with a reduction of 60%, 74%, 70% and 60%, respectively. Liu et al. [20] demonstrated the application of a Re–Pd bimetallic catalyst for the treatment of perchlorate in waste ion-exchange regenerant brine. The authors suggested that sequential catalytic treatment may be a promising strategy for enabling reuse of waste ion-exchange brine containing NO_3^- and ClO_4^-. Li et al. [21] presented the direct contact membrane distillation as an attractive technology for high salinity brine treatment.

Nano zerovalent iron (nZVI) has been successfully used in water and wastewater treatment. Owing to its reduced size, nZVI has a higher reactivity towards a broad range of water contaminants. It has been successfully applied for the remediation of surface water, groundwater and wastewater contaminated with organic compounds, heavy metals, nitrate, dyes, etc. The catalytic activity of nZVI for the degradation of major organic components of fracking wastewater and simultaneous recovery/removal of metals and potential toxic elements was reported by Abass et al. [22]. Sun et al. [23] reported the application of nZVI for metal/metalloid removal from model hydraulic fracturing wastewater. The authors demonstrated that the nZVI effectively removed Cu(II), Zn(II), Cr(VI)and As(V) from the high-salinity fracturing wastewater. Li et al. [24] stated that nZVI is able to perform fast and simultaneous removal of different heavy metal ions, and that the fast separation and seeding effect of nZVI facilitate its application in wastewater treatment process. nZVI could be combined with other technologies such as ultrasound, microwave, Fenton and the advanced Fenton processes to remove contaminants. An evident synergistic effect was usually observed in these integrated processes [25].

Therefore, the aim of this study is to assess the physical and chemical characteristics of brine effluent from eMalahleni treatment plant, Mpumalanga Province, South Africa, with the purpose of treating the brine effluent with nZVI synthesised from acid mine drainage or ferric chloride.

2. Materials and methods

2.1. Brine collection and analysis

Fresh brine was collected from eMalahleni water treatment plant in Mpumalanga province, South Africa. The brine effluent was collected in an airtight plastic container to prevent ingress of air. The brine effluent was filtered with 0.45 μm pore size membrane filter paper using a vacuum pump device. The physical methods involved the determination of pH, EC and TDS using HI 9828 pH meter (Hanna, Chelmsford, UK) with portable pH/EC/TDS/DO/temperature probe, while the chemical methods involved the determination of cations and anions by inductively coupled plasma optical emission spectroscopy (ICP-OES; Variance Liberty II) and ion chromatography (IC; Dionex ICS-1600 ion chromatograph), respectively. The brine reserved for cation analysis was preserved by adding three drops of concentrated HNO_3 to approximately 100 mL of brine sample. The brine sample was preserved at 4°C until the time of analysis. Geochemical modelling of the brine was carried out using the Geochemical Work Bench (GWB) software SpecE8 program.

2.2. Synthesis of nano zerovalent iron

The nZVI used for the treatment of the brine effluent in this study was synthesised by the sodium borohydride ($NaBH_4$) reduction of iron contained in Navigation coal mine Toeseep acid mine drainage (AMD) or ferric chloride solution (Rxn. (i)):

$$4Fe^{3+} + 3BH_{4^-} + 9H_2O \rightarrow 4Fe^0 + 3H_2BO_{3^-} + 12H^+ + 6H_2 \quad \text{(i)}$$

Hydrogen peroxide solution was used for the oxidisation of the ferrous iron present in the mine water to ferric iron prior to synthesis.

2.3. Treatment of brine effluent

nZVI synthesised from AMD (BAI) or commercial ferric chloride reagent (BFCl) was used for the treatment of some major elements (Ca, Na, Mg, Fe and K) and SO_4^{2-} in the brine effluent. Samples of 0.01 – 0.04 g of nZVI were weighed and transferred into 100 mL Erlenmeyer flasks. A volume of 50 mL of brine effluent was added to each flask and covered with a plastic stopper. A blank sample was also prepared by adding 50 mL of brine into empty flasks without iron nanoparticles. The flasks were placed in a shaker operated at a speed of 250 rpm at room temperature (25°C) for 10–120 min. The samples were removed from the shaker after the reaction contact time had been completed. The mixture was filtered with a 0.45 µm membrane filter, and the supernatant was analysed for elemental composition using ICP and IC. The metal uptake capacity and the percentage brine treatment were calculated using Eqs. (1) and (2), respectively:

$$q_e = \frac{(C_i - C_f)V}{m} \quad (1)$$

$$\% \text{ Removal} = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where q_e is the uptake capacity, m is the mass of the nZVI, V is the volume of brine effluent, C_i and C_f are the initial and final concentration of elements contained in the brine effluent, respectively.

3. Results and discussion

3.1. Physical and chemical qualities of the brine effluent

The physical and chemical characterisation of the brine helped to assess the quality of the brine effluent as received before its treatment commenced. Table 1 presents the results obtained for the measurement of pH, EC and TDS of the eMalahleni brine effluent on-site.

Table 1
pH, EC and TDS of brine effluent collected from eMalahleni water reclamation treatment plant

Parameter	eMalahleni brine effluent
pH	6.06 ± 0.25
EC	2.8 ± 0.09 mS/cm
TDS	1.54 ± 0.04 mg/L

The pH is a parameter that is used to assess the water quality of the brine effluent and it also determines if the brine effluent is acidic, basic or neutral. The pH value of the brine effluent as received from the sampling site was 6.06. The pH of the brine effluent falls within the range of pH values obtained in the literature [26,27], and falls within the target water quality range (TWQR) of the World Health Organisation (WHO) potable water limit. The EC is used to assess the concentration of the free mobile ions present in the waste brine effluent. The measured EC for the eMalahleni water treatment brine as received from the sample collection site was 2.8 ± 0.09 mS/cm and TDS was 1.54 ± 0.04 mg/L. Conductivity has a strong relationship with the TDS and it implies that the higher the EC the higher the TDS and the reverse is the case if the EC is low. The TDS value of the brine was low which indicated a low concentration of the dissolved solids, evidence of a dilute brine.

The chemical composition of the eMalahleni brine effluent (Table 2) was carried out using ICP-OES for a range of elements including cations, and IC was used for the anions.

The elemental composition of brine effluent collected from eMalahleni water treatment plant consists of Na, K, Mg, Ca, Fe, Al and Mn. The concentrations of these elements in the as-received brine effluent was Na (3,000.72 ± 72.53 mg/L), K (145.95 ± 8.44 mg/L), Mg (346.64 ± 14.04 mg/L), Ca (681.7 ± 30.5 mg/L), Fe (30.59 ± 1.6 mg/L), Al (20.93 ± 1.49 mg/L) and Mn (8.37 ± 0.01 mg/L). The type of cations found in a brine solution depends on their origin and the results obtained from the elemental analysis of eMalahleni brine effluent is similar to what has been reported in the literature [1,3]. The concentrations of these elements Al, Ca, Fe, Mg, Mn, K and Na present in the brine effluent were higher than TWQR for potable water limit [27,28]. The concentration of Al, Mn and Fe elements in the brine effluent was very low because at pH > 6 Al and Fe precipitate out of the solution as hydroxide while manganese only precipitates out at pH > 9 [29,30]. Ca in its free ionic state is soluble in solution and can be precipitated out as a carbonate or in combination with sulphate as gypsum from the brine effluent. The Ca is an essential component and a strong indicator that the brine effluent is a hard water because of its high concentration. The high concentration of Ca in the water makes it difficult to use brine for laundry. The presence of any Fe ions in the brine solution will cause the brine to be converted to an acidic solution by the oxidation of any trace of pyrite found in the solution. Higher concentrations of iron can cause serious problems such as orange colour stains on laundry or fixtures, undesirable taste and colour in drinking water. The Mg is a minor component of the brine effluent and a strong indicator of water hardness due to its relatively high concentration in the solution. The K is an important element and minor component of brine effluent, also an indicator of low-quality brine solution. The Na is the major component and indicator of the saline quality of the brine solution. The eMalahleni brine solution analysed was classified as type 2 salt solution containing sodium sulphate salt based on the results obtained from the geochemical modelling of the brine solution using the GWB software SpecE8 program (Fig. 1).

Three different anions (Cl^-, NO_3^- and SO_4^{2-}) were analysed in the brine effluent. The results presented in Table 3 revealed the high concentration of the sulphate anions present in the brine effluent, therefore, the brine effluent solution

Table 2
Elemental analysis of eMalahleni brine solution

Element	Concentration (mg/L)
Al	20.93 ± 1.49
As	BDL
B	BDL
Ba	0.11 ± 0.001
Be	0.01 ± 0.006
Ca	681.73 ± 30.5
Cd	0.06 ± 0.004
Ce	0.12 ± 0.002
Co	0.03 ± 0.003
Cu	BDL
Cr	0.9 ± 0.01
Fe	30.59 ± 1.6
Hg	BDL
K	145.95 ± 8.44
Li	0.54 ± 0.04
Mg	346.64 ± 14.04
Mn	8.37 ± 0.01
Mo	0.04 ± 0.01
Na	3,000.72 ± 72.53
Nb	BDL
Ni	1.11 ± 0.01
P	BDL
Pb	0.17 ± 0.01
Rb	BDL
Se	0.51 ± 0.01
Si	BDL
Sr	2.99 ± 0.04
Th	BDL
Ti	BDL
U	BDL
V	BDL
Y	0.09 ± 0.01
Zn	0.88 ± 0.002
Zr	0.70 ± 0.01

BDL, below detection limit.

required to be treated before disposal or use. The results of the cation and anion analysis indicated that the brine effluent has a high degree of salinity which agrees with some results obtained in the literature [31]. The disposal of this type of brine effluent will be harmful to the environment.

The modelling of this water using GWB subprogram SpecE8 helps to speciate the type of ions/elements and the various forms in which they may be distributed in aqueous effluent solution and also aids to predict the mineral phases that may be formed in the solution. The distribution of species of ions/elements in the aqueous solution of eMalahleni brine effluent sample is presented in Fig. 1.

Fig. 1(a) shows the SpecE8 program of GWB software prediction of sulphate ion distribution in the brine effluent. The program predicted that the sulphate existed mainly as free sulphate ions while the remaining sulphate existed in combined form as salts such as $NaSO_4$. The total concentration of sulphate in the brine effluent was 0.107 molal (mg/kg) and the GWB software SpecE8 program predicted sulphate distribution in the brine effluent solution as free SO_4^{2-} (0.07591 mg/kg, 70.94%), $NaSO_4^-$ (0.01208 mg/kg, 11.29%), $CaSO_4$ (0.009188 mg/kg, 8.59%), $MgSO_4$ (0.008527 mg/kg, 7.97%) and the remaining species KSO_4^-, $AlSO_4^-$, $Al(SO_4)_4^{2-}$, $MnSO_4^-$, HSO_4^-, $CaHSO_4^+$, $FeSO_4^+$, $FeSO_4^{2-}$, $AlHSO_4^{2+}$ and $FeHSO_4^{2+}$ account for 0.001% of the total sulphate concentration. The free sulphate is the most abundant species present in the brine effluent and the high concentration of the sulphate ions will cause the water to have a taste, and the taste varies with the type of metal ions associated with the sulphate ions. Studies have shown that the taste threshold of water containing sulphate associated with Na ions is 250 mg/L. The taste threshold of sulphate associated with Ca is about 1,000 mg/L and if this type of water contains more than 1,000 mg/L, it can cause a laxative effect to those who have not adapted to the water [27]. The speciation of the brine effluent analysed using specE8 of GWB software has shown the brine effluent to be a $NaSO_4$ type of water and the charge imbalance was –9.978% error which is still with the acceptable limit of ±10%. This implies that there are more anions present in the eMalahleni brine effluent solution than cations. Sulphate is usually the dominant anion species present in most brine wastewater.

The distribution of the chloride ions (Fig. 1(b)) shows that it remained in the solution as Cl^- ions (0.001505 mg/kg, > 99.98%) while less than 0.02% Cl^- ion was in the brine effluent as salts in their combined state. This confirms that Cl^- is a very conservative anion that is unlikely to precipitate out in any mineral or salt form at the conditions of the eMalahleni effluent solution. The results generated from the GWB software prediction for chloride ion (Cl^-) distribution in the eMalahleni brine effluent showed that chloride existed mainly as free chloride ions and very little or none of the remaining chloride ions was present in the salt form. The concentration of the Cl^- (53.35 mg/L) in the brine effluent obtained from the IC analysis is very low, but it is slightly higher than the TWQR for potable water.

The results for Na^+ obtained using the GWB specE8 program predicted the sodium ion distribution in the eMalahleni brine effluent. Fig. 1(c) shows that most sodium existed in the brine effluent mainly as free sodium ions (0.1184 mg/kg, 91.08%) and only a small amount existed in a combined form as $NaSO_4^-$ (0.01208 mg/kg, 9.29%). This shows that most of the Na^+ were not associated with sulphate, thus mainly existed in the free form without association with any other species. The Na is a conservative metal because it exists as free Na^+ ions in the brine solution. The eMalahleni brine effluent is classified mainly as type 2 brine because it contained $NaSO_4^-$ but very little salt [32]. The pH of the brine is within the TWQR for potable water but the concentration of the Na^+ is far above the TWQR for potable water and the modelled brine effluent has shown that the solution was composed mainly of free Na ions and sulphate ions.

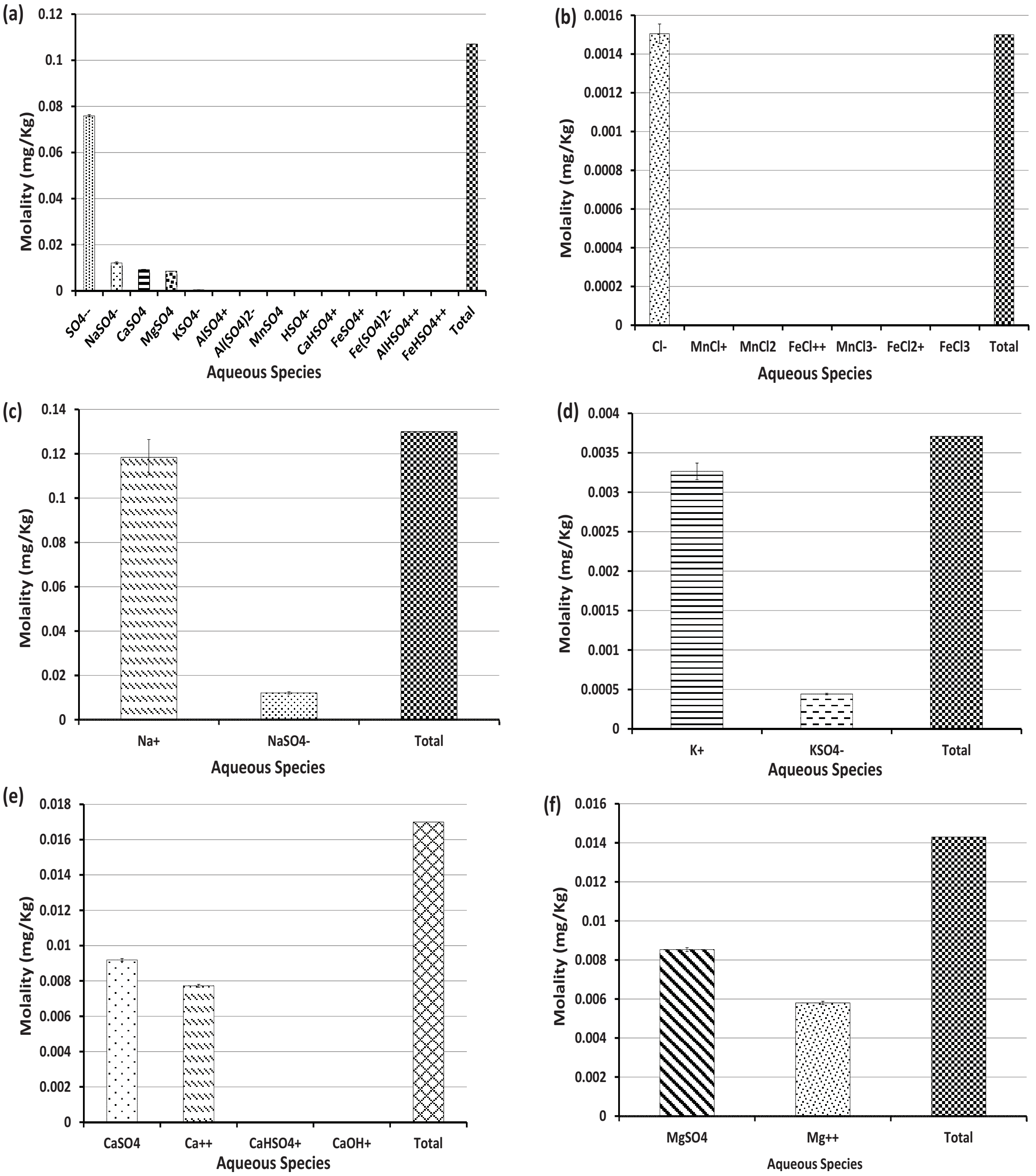

Fig. 1. Distribution of sulphate (a), chloride (b), sodium (c), potassium (d), calcium (e) and magnesium (f) species in eMalahleni brine effluent.

Fig. 1(d) shows that the potassium existed in the effluent solution mainly as free potassium ions (0.0033 mg/kg, 88.05%) and in a combined form as KSO_4^- (0.000443 mg/kg, 11.95%). Potassium thus existed mainly in the free ionic form without interacting with any other species except sulphate to a small extent. Similar to Na, the K also is a conservative metal and it existed mainly as free K^+ ions in the brine effluent. Fig. 1(e) shows that the calcium existed in the brine effluent mainly as calcium sulphate (0.0092 mg/kg, 54.05%), and in combined form as free Ca^{++} (0.0078 mg/kg, 46.01%), $CaHSO_4^-$ (6.72×10^{-8} mg/kg, 0.0004%) and $CaOH^+$ (6.110×10^{-10} mg/kg, 0.0000036%). The calcium in the effluent thus existed mainly in association with sulphate or as free Ca cations. The concentration of Ca in the brine effluent is far above the TWQR for potable water which makes the brine water hard [27]. Fig. 1(f) shows that the magnesium cations existed in the effluent solution mainly as $MgSO_4$ (0.00853 mg/kg, 59.63%), and free form as Mg^{++} (0.00573 mg/kg, 40.06%). Magnesium in solution thus existed mainly in association with sulphate which accounted for about 60% of the total amount of Mg or as the free cation.

3.2. Characteristics of nano zerovalent iron

Fig. 2 presents the scanning electron micrograph (SEM) and transmission electron micrograph (TEM) of the nZVI particles. The BAI and BFCl produced spherical bead-like structures attached to one another in a thread called nano-necklace. The average crystal size of BAI was 31.8 ± 5.5 nm and BFCl was 28.05 ± 3.8 nm.

The X-ray diffraction pattern of BAI and BFCI is presented in Fig. 3. Similar diffraction patterns were obtained for both samples. The spectral peaks indexed at angle 2θ of 44.5° and 35.1° or 65.2° for the BAI or BFCI indicate the presence of both zerovalent iron and iron oxide crystalline mineral phases, respectively.

3.3. Treatment of brine effluent with nano zerovalent iron

The treatment of the brine effluent with nZVI was conducted by optimising the dosage and the contact time of the treatment process.

3.3.1. Nano zerovalent iron dosage optimisation

Fig. 4 presents the uptake capacity of Fe and Mg from 50 mL brine effluent treated with different dosages of synthesised nZVI. The initial concentrations of Fe and Mg in the brine effluent were 30.59 and 346.64 mg/L, respectively.

Table 3
Anions content of brine effluent collected from eMalahleni water reclamation treatment plant

Parameter	Concentration (mg/L)
Cl^-	53.35 ± 4.92
NO_3^-	294.43 ± 9.09
SO_4^{2-}	10,265.43 ± 832.06

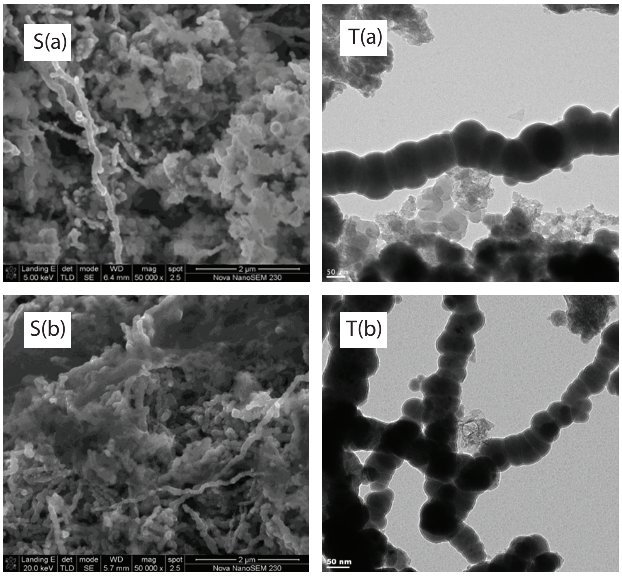

Fig. 2. SEM (S) and TEM (T) analysis of nano zerovalent iron synthesised from (a) AMD and (b) ferric chloride.

The uptake capacity of Fe from 50 mL brine effluent by BAI and BFCI was 20.6 and 21 mg/g, respectively and for soluble Mg, it was 185.89 and 189.16 mg/g, respectively. The maximum percentage removal of Fe from the brine effluent was average (54.4% and 55.7%, respectively), Mg was less than average (43.3% and 44.3%, respectively) which shows a low efficiency of the nZVI for the treatment of Mg. A 0.02 g of

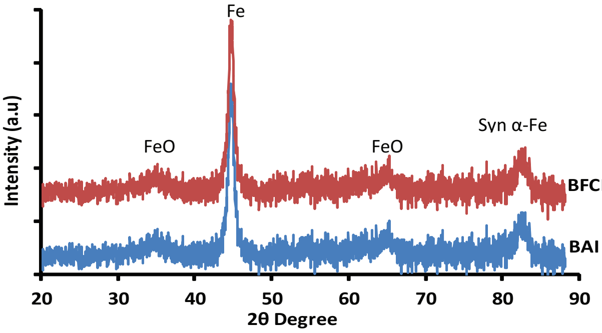

Fig. 3. X-ray diffractogram of BAI and BFCI.

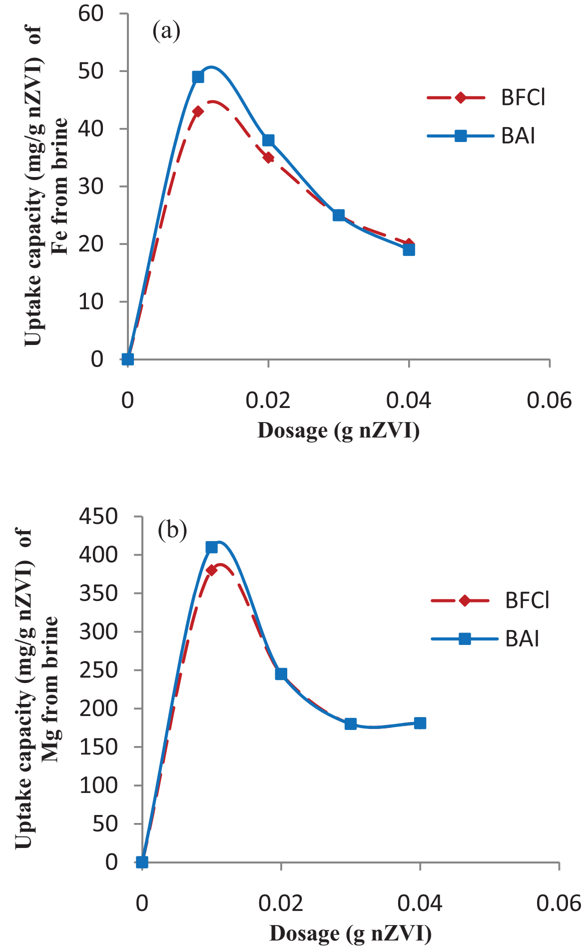

Fig. 4. Uptake capacity of Fe (a) and Mg (b) from brine effluent using synthesised nano zerovalent iron from AMD (BAI) or ferric chloride (BFCI). Experimental conditions: time = 24 h, temperature = 25°C, pH of AMD = 6.06, volume of AMD = 50 mL.

the nZVI was considered to be the optimum dosage required to remove Fe and Mg from the brine effluent.

Fig. 5 presents the result of the uptake capacity of Na and K from 50 mL brine effluent treated with different dosages of synthesised nZVI. The initial concentrations of Na and K in the brine effluent were 3,000.72 and 145.95 mg/L, respectively.

The nZVI optimum uptake capacity for Na was 1,201.22 and 1,229.1 mg/g and for K was 53.53 and 51.83 mg/g for BAI or BFCI, respectively. The percentage removal for Na was 32.4% and 33.26% and for K was 29.63% and 28.84%, respectively, for BAI and BFCI. The removal of Na and K by the nZVI from the 50 mL brine effluent showed similarity in their uptake capacity and percentage removal. A 0.02 g of the nZVI was considered to be the optimum dosage required to remove Na and K from the brine effluent. The Na and K cations are usually difficult to remove in most wastewater, which is why an ion-exchange technique is usually used to treat these elements (Na and K). The result agrees with the report by Feng et al. [33]. Nevertheless, considering the very high level of Na in solution, a considerable amount of Na could be adsorbed out of the brine by the nZVI.

Fig. 6 presents the result of the uptake capacity of Ca from 50 mL brine effluent treated with the synthesised nZVI. The initial concentration of Ca in the brine effluent was 681.72 mg/L.

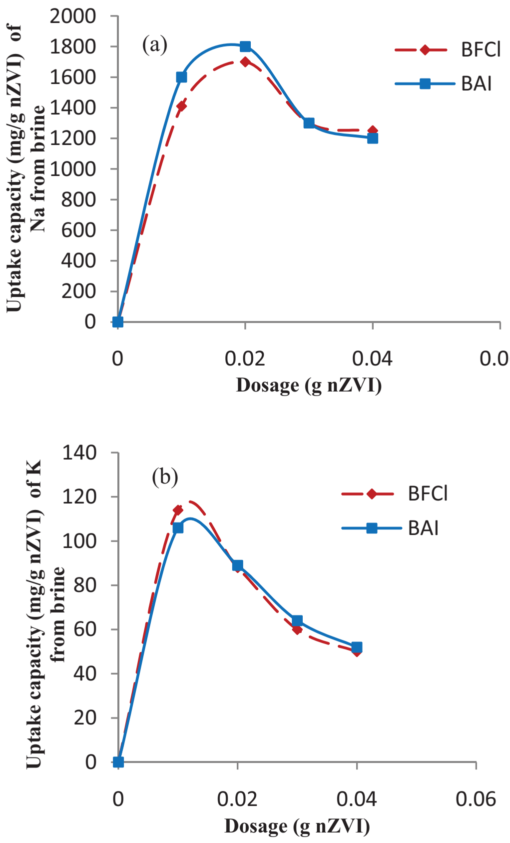

Fig. 5. Uptake capacity of Na (a) and K (b) from brine effluent using synthesised nano zerovalent iron from AMD (BAI) or ferric chloride (BFCI). Experimental conditions: time = 24 h, temperature = 25°C, pH of AMD = 6.06, volume of AMD = 50 mL.

The uptake capacity of soluble Ca from 50 mL brine effluent by BAI and BFCI was 198.39 and 191.56 mg/g, respectively, and the maximum percentage removal of the soluble Ca in the brine effluent was 23.51% and 22.82%, respectively. A dosage of 0.02 g of nZVI was considered to be the optimum required to remove Ca from the brine effluent. The removal of Ca from the brine effluent with the synthesised nZVI was very low which shows poor efficiency, and this is why Ca is usually removed by flocculation. The presence of Ca in the brine solution makes the water hard which can make its use for laundry difficult.

3.3.2. Contact time optimisation

Fig. 7 presents the results of contact time in the treatment of 50 mL brine effluent with the synthesised nZVI. The initial concentrations of Fe and Mg in the brine solution were 30.59 and 346.64 mg/L, respectively.

The concentration of Fe and Mg removed in 50 mL of brine effluent by BAI and BFCI at an optimum contact time of 60 min for Fe was 28.26 and 27.11 mg/L, respectively, and Mg was 297.26 and 246.54 mg/L, respectively. The maximum percentage removal of Fe was 92.38% and 88.64%, respectively, and for Mg removal, it was 85.76% and 71.12%, respectively. The results showed that the nZVI made from AMD removes more of these pollutants than the nZVI made from ferric chloride. The maximum percentage removal of Fe and Mg by nZVI (BAI or BFCI) was greater than 70% which indicated the high efficiency of the nZVI. The optimum contact time for the removal of Fe and Mg from the brine effluent was 60 min. The concentration of Fe and Mg decreased in the brine solution with an increase in the contact time during agitation and consequently increased the percentage removal of the elements by the nZVI over time.

Fig. 8 presents the effect of contact time on the Na and K removal in the treatment of 50 mL of brine effluent with the synthesised nZVI. The initial concentrations of Na and K in the brine effluent were 3,000.72 and 145.95 mg/L.

The maximum concentration of Na and K removed from 50 mL of brine effluent by nZVI for Na was 1,647.1 and 1,604.9 mg/L, respectively, and K was 69.57 and 72.38 mg/L, respectively, for BAI and BFCl. The maximum percentage

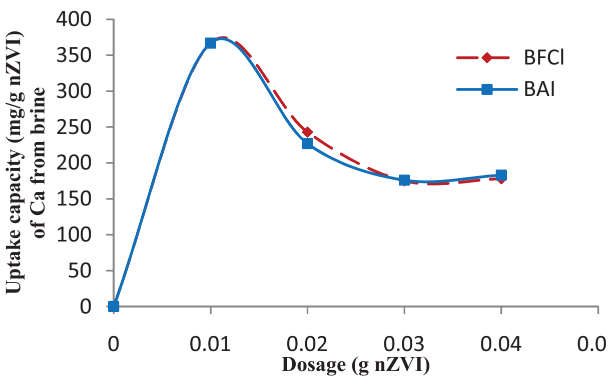

Fig. 6. Uptake capacity of Ca from brine effluent using synthesised nano zerovalent iron from AMD (BAI) and ferric chloride (BFCI). Experimental conditions: time = 24 h, temperature = 25°C, pH of AMD = 6.06, volume of AMD = 50 mL.

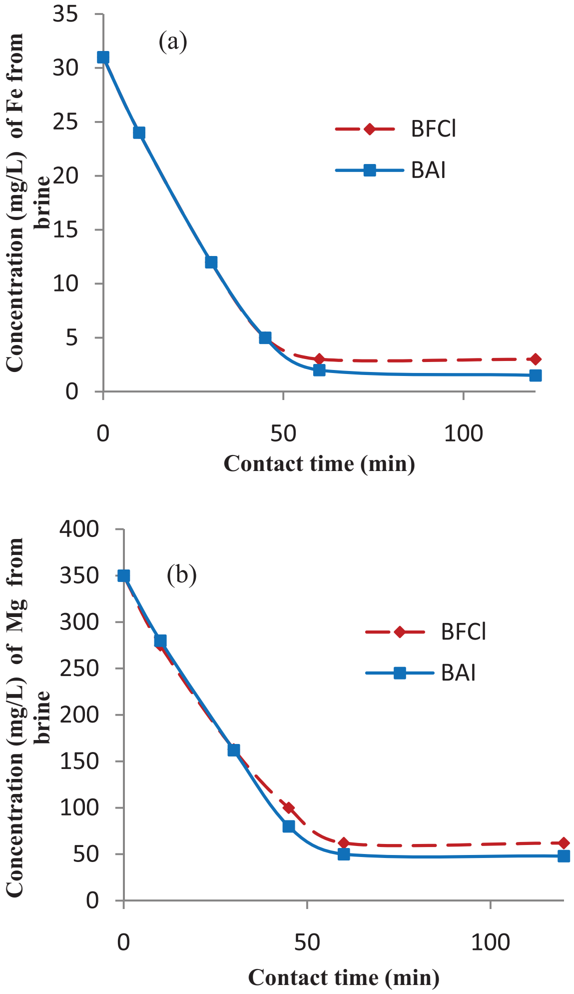

Fig. 7. Concentration of Fe (a) and Mg (b) from brine effluent at different contact time with the synthesised nano zerovalent iron from AMD (BAI) and ferric chloride (BFCl). Experimental conditions: dosage = 0.02 g, temperature = 25°C, pH of brine = 6.06, volume of brine = 50 mL.

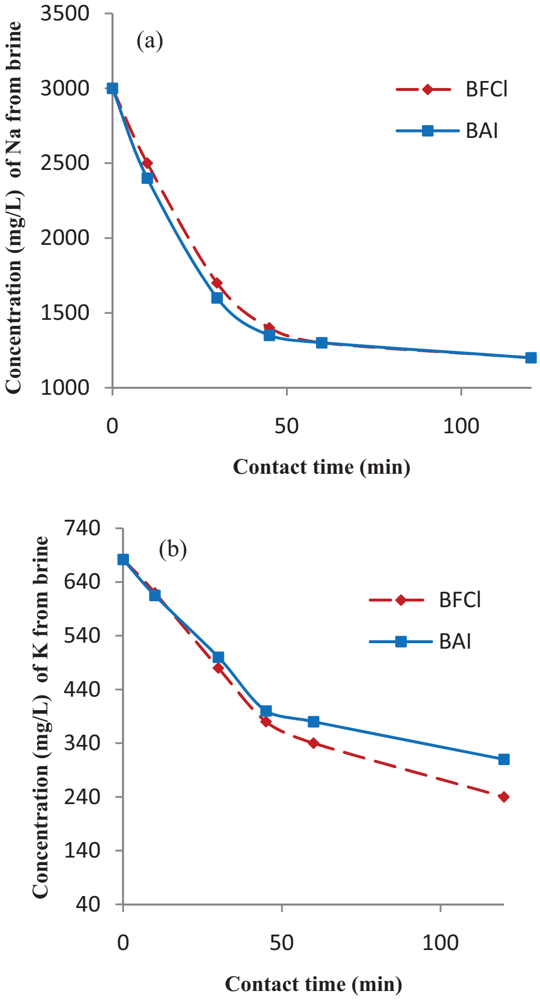

Fig. 8. Concentration of Na (a) and K (b) from brine effluent at different contact time with the synthesised nano zerovalent iron from AMD (BAI) and ferric chloride (BFCl). Experimental conditions: dosage = 0.02 g, temperature = 25°C, pH of brine = 6.06, volume of brine = 50 mL.

removal for Na was 54.89% and 53.48% and for K it was 47.67% and 49.59%, respectively, by BAI or BFCl. The optimum contact time required for the removal of Na and K from the brine effluent by the nZVI was considered to be 60 min. The BAI removed more of the Na and K pollutants in the brine effluent than the BFCl. The graphs in Fig. 8 show that the concentrations of the cations were decreased with increasing contact time, which means that the treatment depends largely on contact time. The nZVI removed almost half of the Na and K species in the brine effluent. The maximum percentage removal of Na and K in the 50 mL brine effluent by nZVI was greater than 50% for Na and 49% for K.

Fig. 9(a) presents the results of contact time on the removal of Ca in 50 mL brine effluent with BAI or BFCl. The initial concentration of Ca in the brine solution was 681.72 mg/L.

The maximum concentration of Ca removed by the BAI or BFCl from the brine solution was 305.73 and 339.73 mg/L, respectively, while the maximum percentage removal was 44.85% and 49.83%, respectively, at an optimum contact time of 60 min. The nZVI obtained from AMD removed less Ca than the nZVI obtained from ferric chloride. The percentage removal of Ca with the nZVI was close to 50% which indicates the efficiency of the nZVI. The concentration of Ca decreased in the brine solution with an increase in the contact time of agitation.

Fig. 9(b) presents the results of contact time in the removal of SO_4 during the treatment of 50 mL brine effluent with the synthesised nZVI. The initial concentration of SO_4 in the brine effluent was 10,265.43 mg/L. The initial concentration of sulphate in the brine effluent decreased with increasing contact time during treatment of the brine effluent with the nZVI. The remaining sulphate concentration after treatment of the 50 mL brine effluent with BAI and BFCl was 5,337.15 and 5,406.77 mg/L, respectively, after a contact time of 60 min. The percentage removal of sulphate from the brine effluent with nZVI made from AMD and ferric chloride at the optimum contact time was 48.01% and 47.33%, respectively. The result shows that the concentration of the sulphate decreased with the contact time. It is very true that sulphate is the most abundant anion in most mine and wastewaters

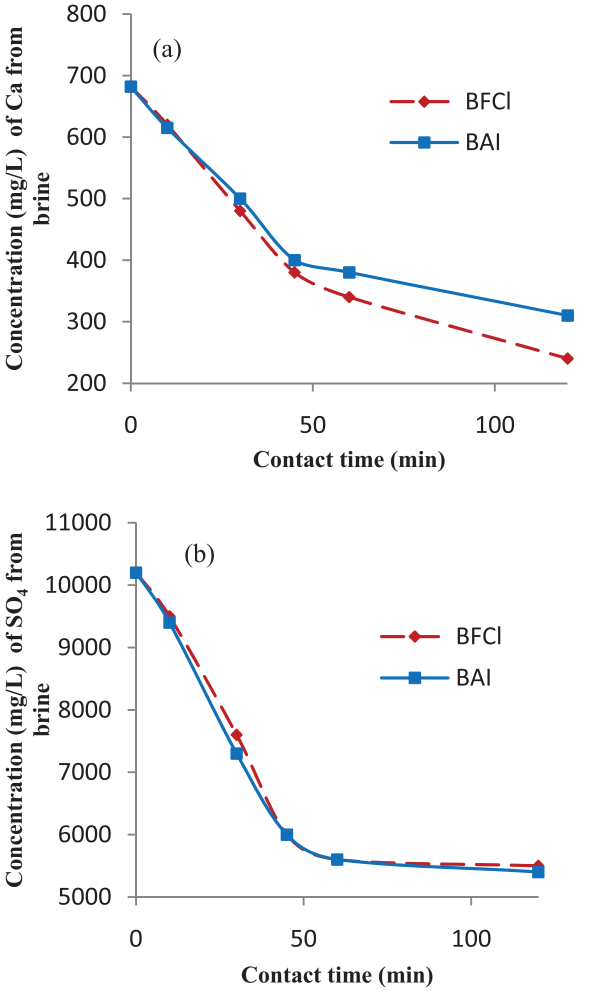

Fig. 9. Concentration of Ca (a) and SO_4 (b) from brine effluent at different contact time with the synthesised nano zerovalent iron from AMD (BAI) and ferric chloride (BFCI). Experimental conditions: dosage = 0.02 g, temperature = 25°C, pH of brine = 6.06, volume of brine = 50 mL.

[34,35]. Nevertheless, considering the very high SO_4^{2-} starting concentration, a very significant amount of anion was removed by the nZVI.

According to Klimkova et al. [36], Crane and Scott [37] and Wan Yaacob et al. [38], sorption, chemical reduction, ionic exchange and co-precipitation are the likely mechanisms for the removal of these toxic elements from the brine effluent. Most importantly, the nZVI can easily get oxidized to +2 and +3 oxidation states and in the process reduce the toxic inorganic elements.

4. Conclusion

Brine effluent collected from eMalahleni water treatment plant was analysed for its elemental composition, and it was found to contain some major elements such as Na, K, Ca, Fe and Mg. The results of the metal and non-metal composition present in the brine effluent showed that the predominant cation and anion were Na and SO_4, respectively. The pH of the brine effluent was about 6.06 ± 0.25 which is within the limit of TWQR for potable water, and it contained a high amount of ions such as SO_4^{2-}, Ca^{2+}, Mg^{2+} and Na^+ with concentrations higher than WHO or DWA standards for potable water. The high concentration of Ca and Mg present in the brine effluent is an indication that the water is hard. The brine was modelled using the GWB software Spec E8 and the outcome gave the cation–anion balance to be –9.978% errors which is within the acceptable limit of ±10%. The modelling and analysis showed that the brine effluent is a type 2 brine solution which contains mainly Na_2SO_4. The optimum nZVI dosage and contact time for the treatment of brine effluent were determined to be 0.02 g and 60 min, respectively. The nZVI was able to remove about 70% of most of the elements contained in the brine effluent. Na and SO_4^{2-} were present in a very high concentration, yet were relatively well removed by the nZVI. The BAI and BFCl samples of nZVI worked equally well showing that the iron sourced from AMD was of sufficient quality to utilise for brine treatment and offers a low-cost route to immobilise and remove conservative cations and anions from water. nZVI is known to rapidly transform to other types of iron oxides or oxy hydroxides in aerobic condition, therefore, future investigations on the chemical stability of nZVI and bio-toxicity assessment of the treated brine effluent are needed to be performed to further validate the applicability and compatibility of nZVI treatment.

References

[1] D.G. Randall, J. Nathoo, A.E. Lewis, A case study for treating a reverse osmosis brine using eutectic freeze crystallization—approaching a zero waste process, Desalination, 266 (2011) 256–262.
[2] M.R. Al-Agha, R.S. Mortaja, Desalination in the Gaza Strip: drinking water supply and environmental impact, Desalination, 173 (2005) 157–171.
[3] S. El-Manharawy, A. Hafez, A new chemical classification system of natural waters for desalination and other industrial uses, Desalination, 156 (2003) 1–3.
[4] P. Dama-Fakir, A. Toerien, Evaporation Rates on Brine Produced during Membrane Treatment of Mine Water, Paper Presented at the International Mine Water Conference, Pretoria, South Africa, 2009.
[5] V.N. Rumyantsev, Selection of mineralizers in the hydrothermal synthesis and growth of crystals, Soviet Physics-Crystallography, 22 (1977) 610–613.
[6] M. Schubert, J.W. Regler, F. Vogel, Continuous salt precipitation and separation from supercritical water. Part 1: Type 1 salts, J. Supercrit. Fluids, 52 (2010) 99–112.
[7] V. Valyashko, D. Palmer, R. Fernandez-Prini, A. Harvey, Aqueous Systems at Elevated Temperatures and Pressures, Physical Chemistry in Water, Steam and Hydrothermal Solutions, 2004, 597 p.
[8] M. Svensson, Desalination and the Environment: Options and Considerations for Brine Disposal in Inland and Coastal Locations, SLU for Yara International and Aqualyng, 2005.
[9] A.M.O. Mohamed, H.E. Antia, Geoenvironmental Engineering, Elsevier, 1998.
[10] M. Mickley, R. Hamilton, L. Gallegos, J. Truesdall, Membrane concentration disposal, American Water Works Association Research Foundation, Denver, Colorado, 1993.
[11] J. Schoeman, A. Steyn, Nitrate removal with reverse osmosis in a rural area in South Africa, Desalination, 155 (2003) 15–26.
[12] M. Turek, Electrodialytic desalination and concentration of coal-mine brine, Desalination, 162 (2004) 355–359.
[13] CSIR, Acid mine drainage in South Africa, CSIR Natural Resources and the Environment, Briefing Note 2009/02 (2009) 28–33.

[14] F. Buhrmann, M. van der Waldt, D. Hanekom, F. Finlayson, Treatment of industrial wastewater for reuse, Desalination, 124 (1999) 263–269.

[15] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, Desalination, 216 (2007) 1–76.

[16] L. Malaeb, G.M. Ayoub, Reverse osmosis technology for water treatment: state of the art review, Desalination, 267 (2011) 1–8.

[17] C.R. Martinetti, A.E. Childress, T.Y. Cath, High recovery of concentrated RO brines using forward osmosis and membrane distillation, J. Membr. Sci., 331 (2009) 31–39.

[18] H.Y. Ng, L.Y. Lee, S.L. Ong, G. Tao, B. Viawanath, K. Kekre, W. Lay, H. Seah, Treatment of RO brine-towards sustainable water reclamation practice, Water Sci. Technol., 58 (2008) 931–936.

[19] M. Qurie, J. Abbadi, L. Scrano, G. Mecca, S.A. Bufo, M. Khamis, R. Karaman, Inland treatment of the brine generated from reverse osmosis advanced membrane wastewater treatment plant using epuvalisation system, Int. J. Mol. Sci., 14 (2013) 13808–13825.

[20] J. Liu, J.K. Choe, Z. Sasnow, C.J. Werth, T.J. Strathmann, Application of a Re–Pd bimetallic catalyst for treatment of perchlorate in waste ion-exchange regenerant brine, Water Res., 47 (2013) 91–101.

[21] J. Li, Y. Guan, F. Cheng, Y. Liu, Treatment of high salinity brines by direct contact membrane distillation: effect of membrane characteristics and salinity, Chemosphere, 140 (2015) 143–149.

[22] O.K. Abass, M. Zhuo, K. Zhang, Concomitant degradation of complex organics and metals recovery from fracking wastewater: roles of nano zerovalent iron initiated oxidation and adsorption, Chem. Eng. J., 328 (2017) 159–171.

[23] Y. Sun, C. Lei, E. Khan, S.S. Chen, D.C. Tsang, Y.S. Ok, D. Lin, Y. Feng, X.D. Li, Nanoscale zero-valent iron for metal/metalloid removal from model hydraulic fracturing wastewater, Chemosphere, 176 (2017) 315–323.

[24] S. Li, W. Wang, F. Liang, W.X. Zhang, Heavy metal removal using nanoscale zero-valent iron (nZVI): theory and application, J. Hazard. Mater., 322 (2017) 163–171.

[25] F. Fu, D.D. Dionysiou, H. Liu, The use of zero-valent iron for groundwater remediation and wastewater treatment: a review, J. Hazard. Mater., 267 (2014) 194–205.

[26] M. Ahmed, W.H. Shayya, D. Hoey, A. Mahendran, R. Morris, J. Al-Handaly, Use of evaporation ponds for brine disposal in desalination plants, Desalination, 130 (2000) 155–168.

[27] WHO, Guidelines for Drinking-water Quality, 4th ed., World Health Organization, 2011.

[28] DWAF, Agricultural Water Use: Irrigation, South African Water Quality Guidelines, 2nd ed., 4 (1996) 1–5.

[29] W. Gitari, L. Petrik, O. Etchebers, D. Key, C. Okujeni, Utilization of fly ash for treatment of coal mines wastewater: solubility controls on major inorganic contaminants, Fuel, 87 (2008) 2450–2462.

[30] G. Madzivire, L.F. Petrik, W.M. Gitari, T.V. Ojumu, G. Balfour, Application of coal fly ash to circumneutral mine waters for the removal of sulphates as gypsum and ettringite, Miner. Eng., 23 (2010) 252–257.

[31] N. Afrasiabi, E. Shahbazali, RO brine treatment and disposal methods, Desal. Wat. Treat., 35 (2011) 39–53.

[32] M. Schubert, J.W. Regler, F. Vogel, Continuous salt precipitation and separation from supercritical water. Part 2. Type 2 salts and mixtures of two salts, J. Supercrit. Fluids, 52 (2010) 113–124.

[33] D. Feng, C. Aldrich, H. Tan, Treatment of acid mine water by use of heavy metal precipitation and ion exchange, Miner. Eng., 13 (2000) 623–642.

[34] T.E. Shokes, G. Möller, Removal of dissolved heavy metals from acid rock drainage using iron metal, Environ. Sci. Technol., 33 (1999) 282–287.

[35] R.T. Wilkin, M.S. Mcneil, Laboratory evaluation of zero-valent iron to treat water impacted by acid mine drainage, Chemosphere, 53 (2003) 715–725.

[36] S. Klimkova, M. Cernik, L. Lacinova, J. Filip, D. Jancik, R. Zboril, Zero-valent iron nanoparticles in treatment of acid mine water from in situ uranium leaching, Chemosphere, 82 (2011) 1178–1184.

[37] R. Crane, T. Scott, Nanoscale zero-valent iron: future prospects for an emerging water treatment technology, J. Hazard. Mater., 211 (2012) 112–125.

[38] W.Z. Wan Yaacob, N. Kamaruzaman, A.R. Samsudin, Development of nano-zero valent iron for the remediation of contaminated water, Chem. Eng. Trans., 28 (2012) 25–30.