

## Sorption of Ni(II) on surface of bed grains used in iron and manganese removal filters

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### ABSTRACT

This paper reports the results of determinations of crystalline phase type, specific surface area, point of zero charge pH ( $pH_{pzc}$ ), and Ni(II) sorption capacities of beds for groundwater treatment. Bed materials from iron and manganese removal filters (FeRF, MnRF) as well as a catalytic bed (G1) were investigated. The reference material was MnO<sub>2</sub>-coated quartz sand (MnQS). The efficiency of Ni(II) sorption was investigated as a function of pH. It was found that the naturally formed coating on FeRF was characterised by the highest sorption efficiency (80–88%) in the wide pH range (4–9) of the solution. Sorption on MnRF was weaker (35–45%). G1 and MnQS, which contained only manganese oxides, were characterised by a very low sorption efficiency of 0–6% and 3–8%, respectively. A lower Ni(II) removal efficiency was observed at an initial pH close to the  $pH_{pzc}$  values. During Ni(II) sorption, the pH of the solution was not constant and tended towards the value of  $pH_{pzc}$  for all tested materials. The slightly pH-dependent sorption of Ni(II) indicates that its removal depends more on the chemical composition and the specific surface area of the oxide coatings covering the bed materials.

**Key words** | iron oxides, manganese dioxide,  $pH_{pzc}$ , surface properties

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### INTRODUCTION

The term ‘heavy metals’ is often used as a collective name for metals and metalloids that have been associated with contamination and potential toxicity or ecotoxicity (Duffus 2002). These elements can occur in excessive amounts in groundwater as a result of local pollution, release of sewage or expired plant protection agents from waste storage facilities, and metal leaching from rocks (Kowal & Świdarska-Bróź 2007). The presence of mobile forms of heavy metals in groundwater makes using it as a source of high quality water difficult. Research done in the area of the Ntem watershed in West Africa shows that the occurrence of higher than permissible levels of heavy metals (Pb, Cd, Cr, and Ni) in groundwater poses a potential threat to public health (Defo *et al.* 2017). The form and concentration of heavy metals which occur in natural sources of water depend on the physical and chemical composition of the water and the various processes which take place in water

and ground environments. Heavy metals can accumulate in living organisms causing pathological changes (Duffus 2002). For example, nickel, a heavy metal which is the focus of this present study, may cause disturbances in the development of living organisms and exert carcinogenic effects (El-Dars *et al.* 2015). That is why the permissible content of nickel in water intended for human consumption is very low at  $20 \mu\text{g dm}^{-3}$  (Council Directive 98/83/EC).

To prevent the detrimental effects of heavy metals, including nickel, on consumers’ health, they must be removed from water intended for human consumption. Even amounts that only slightly exceed the permissible concentration require measures to be taken in the production of potable water (Siwiec *et al.* 2016) and can cause problems in its distribution.

The processes which enable removal of heavy metal elements from groundwater include adsorption, chemical precipitation, and ion exchange. These processes often

accompany filtration and contribute to the removal of heavy metals in filter beds in which grains of filter material are covered by iron oxide and manganese dioxide (Jeon *et al.* 2004; Han *et al.* 2006). Such types of oxides cover grains of beds in the filters removing iron and manganese in groundwater treatment plants. Thus, these types of beds can reveal properties for nickel sorption. In iron removal beds, precipitated iron hydroxide forms a natural coating on filter material. Sorption of nickel on the surface of this material depends on pH and follows from Coulomb's interaction, that is the load located on the surface of the oxide (Jeon *et al.* 2004; Juang & Chung 2004). The situation is different in the case of manganese removal filters, in which the filling material becomes naturally coated with manganese dioxide. The form of the coating, crystalline or amorphous, shows heterogeneous affinity for ions of nickel during removal from water (Vol'Khin *et al.* 2002; Boonfueng *et al.* 2005). Hence, the type of oxide covering the grains of a filtration bed is an important factor influencing nickel sorption.

The aim of this study was to determine the influence of oxide type on the effectiveness of nickel sorption in beds used in iron and manganese removal filters over a common environmental pH range. In this work the results obtained on the surface properties of beds commonly used at groundwater treatment plants were reported. The influence of the material's properties, such as crystalline composition, specific surface area and point of zero charge pH value on the efficiency of nickel removal at various pH from dilute aqueous solutions were investigated.

## MATERIALS AND METHODS

### Characteristics of research materials

The following materials were used in the study: (1) FeRF – bed from an iron removal filter, (2) MnRF – bed from a manganese removal filter, (3) G1 – catalytic bed, and (4) MnQS – manganese-dioxide-coated quartz sand. FeRF and MnRF were natural coatings accumulated after many years of exploitation at a groundwater treatment plant. G1 was a commercial product whose main component was pyrolusite, a manganese dioxide mineral which can be used to remove manganese compounds dissolved in water and

oxidise them in the presence of oxygen to manganese dioxide (Catalog materials). MnQS was obtained by coating quartz sand with manganese dioxide in accordance with the method described by Michel & Kiedryńska (2011).

### Characteristics of the surface properties of materials

In order to characterise the surfaces of the tested beds, the crystalline phases of each material were identified and the specific surface area and point of zero charge pH ( $pH_{pzc}$ ) were measured. The identification of the crystalline phases was performed using a PANalytical X'Pert MPD device equipped with a Cu lamp (40 kV and 40 mA). The samples obtained in the form of powder from the coatings covering each of the beds were analysed using the Greasing Incidence Diffraction (GID) method.

The specific surface area was determined using the BET method. Prior to the measurements, the samples were heated for 8 hours at 403 K in vacuum. The end pressure during the heating was below 0.001 mmHg. The BET measurements were carried out at 77 K on a Micrometrics ASAP2010 device using the method of low-temperature nitrogen adsorption.

The  $pH_{pzc}$  value for each of the materials was determined using the immersion method as described by Babić *et al.* (1999). Samples of the test material with a constant weight of 1 g were agitated at 100 rpm<sup>-1</sup> in 50 ml of a 0.03 KNO<sub>3</sub> solution with a variable initial pH ( $pH_i$ ) in the range 3–12, at 283 K. The pH was adjusted with 0.1 N KOH and 0.1 N HNO<sub>3</sub>. The final pH ( $pH_f$ ) of the solutions after 24 h of agitation was measured by the potentiometric method. For each of the materials, a  $pH_f = f(pH_i)$  curve was drawn. The  $pH_{pzc}$  value was read as a point of inflection of the obtained curve from the convex to the concave function.

### Sorption tests

Batch sorption tests were carried out by agitating 1 g of bed material in 0.15 L of a sorptive solution prepared by dissolving Ni(NO<sub>3</sub>)<sub>2</sub> in double distilled water. The initial concentration of nickel was 5 mg Ni L<sup>-1</sup>. Sorption was measured as a function of pH (4, 5, 6, 7, 8, 9), and pH was adjusted using 0.1 N KOH and 0.1 N HNO<sub>3</sub>. The ionic strength of Ni(NO<sub>3</sub>)<sub>2</sub> solution was low and its value equaled 0.00025 mol L<sup>-1</sup>. The pH adjustment insignificantly

increased the ionic strength to values  $0.00028 \text{ mol L}^{-1}$  and  $0.00039 \text{ mol L}^{-1}$  for solutions with pH 4 and pH 9 respectively. The samples were placed in a thermostatic shaker and agitated at  $150 \text{ rpm}^{-1}$  and  $283 \text{ K}$ ; the time of contact was 24 hours. The pH of the solutions and Ni(II) concentration were determined before and after the sorption. The pH and Eh measurements were carried out using the potentiometric method. Ni(II) concentration was determined by the flame atomic absorption method using a PGI Instruments spectrophotometer at a wavelength of  $232.0 \text{ nm}$ . The equilibrium sorption capacity  $q_e$  ( $\text{mg L}^{-1}$ ) was calculated according to Equation (1) (Juang & Chung 2004; Reczek et al. 2017):

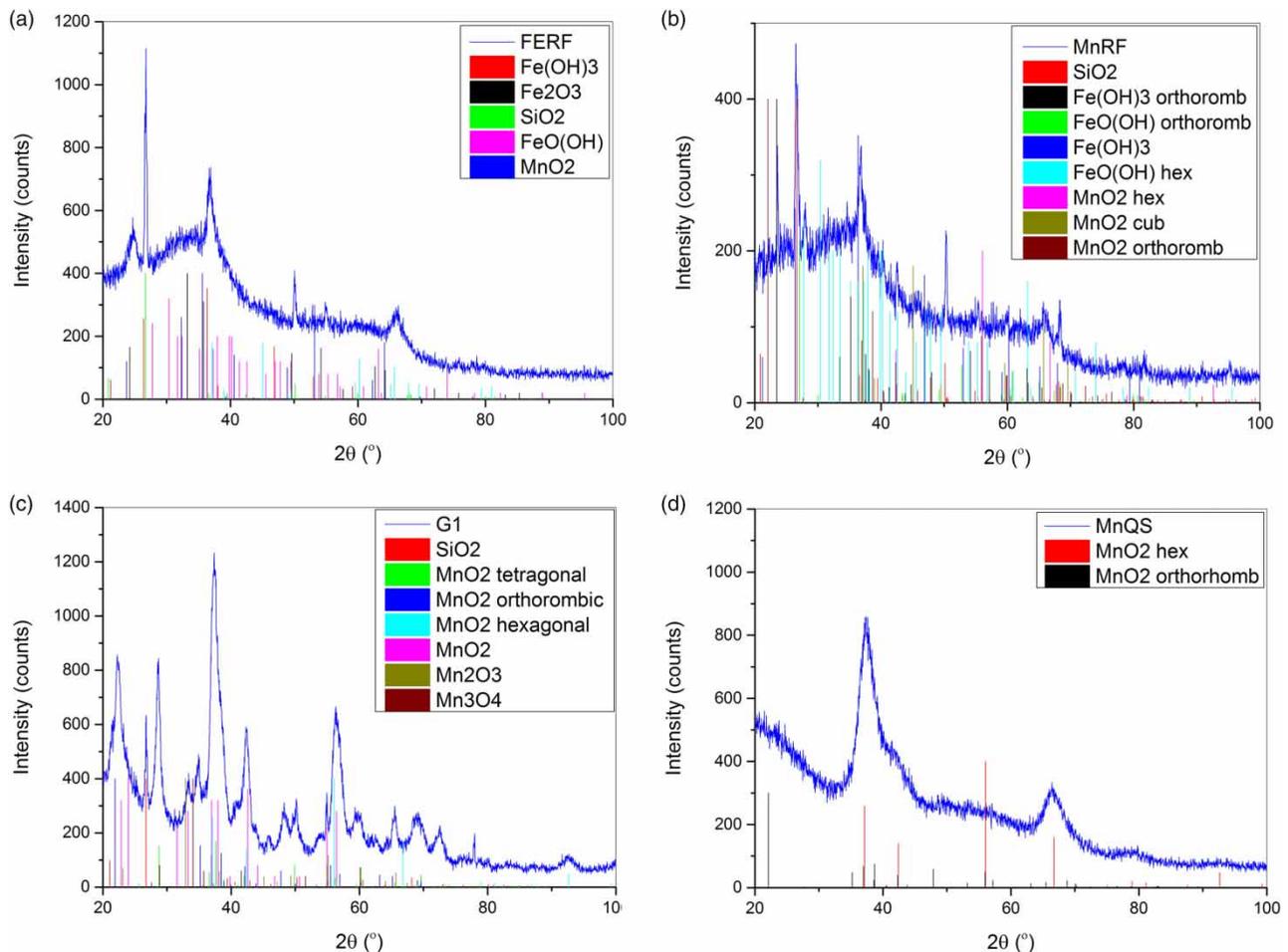
$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where  $C_0$  is the initial Ni(II) concentration in the sorptive solution ( $\text{mg L}^{-1}$ );  $C_e$  is Ni(II) concentration in the sorptive solution at equilibrium ( $\text{mg L}^{-1}$ );  $m$  is the mass of the material tested (g);  $V$  is the volume of the sorptive solution (L).

## RESULTS AND DISCUSSION

### Surface properties of bed materials

The diffractograms showing the crystalline phases of the surfaces of the bed materials tested are compared in Figure 1. In the beds taken from the iron and manganese removal filters, crystalline phases of iron oxides, iron hydroxides, and manganese dioxide were identified. A large number of crystalline phases were observed on the surfaces of both these beds.



**Figure 1** | Diffractograms of FeRF, MnRF, G1 and MnQS.

This was a consequence of the fact that each of the filters had been in operation for many years before the time of the study, which resulted in a rich set of crystalline phases on the surface of FeRF and MnRF. By contrast, the surfaces of the G1 bed (pyrolusite, crystalline form  $\beta$ -MnO<sub>2</sub>) and the modified sand of the MnQS bed contained only crystalline phases of manganese oxides. Comparing the diffractograms of G1 and MnQS, one can notice a diversity of crystalline phases on the surface of G1 accounting for the presence of manganese oxides. Similarly to the case of FeRF and MnRF, this is a consequence of a long period of crystallisation, because G1 is a fossil material. By contrast, the MnO<sub>2</sub> coated sand has only two crystalline phases, a number that is very low in comparison with the other materials. The coating of MnQS was produced in a laboratory, not during a natural process, which probably explains why a large part of the manganese dioxide in this material was in an amorphous form, which cannot be determined by X-ray diffraction (XRD). A similar conclusion was drawn by Bruins *et al.* (2015), who interpreted a lack of signals from the crystalline phase as confirmation of the presence of amorphous manganese dioxide.

The specific surface areas of the tested materials were: FeRF – 39.6 m<sup>2</sup> g<sup>-1</sup>, MnRF – 8.3 m<sup>2</sup> g<sup>-1</sup>, G1 – 16.5 m<sup>2</sup> g<sup>-1</sup>, and MnQS – 0.2 m<sup>2</sup> g<sup>-1</sup>. In the work of Lai *et al.* (2000), the specific surface area of sand modified with iron in laboratory conditions was 2.76 m<sup>2</sup> g<sup>-1</sup>. This value is almost 15 times smaller than the value for FeRF obtained in our study. This difference results from the way the coating had been formed on FeRF over an extended period of exploitation in the iron removal filter. In a study by Han *et al.* (2006), the specific surface area of manganese-coated sand was 0.712 m<sup>2</sup> g<sup>-1</sup>. A higher value of 1.99 m<sup>2</sup> g<sup>-1</sup> was obtained by Hu *et al.* (2004). MnQS, which was characterised by the smallest specific surface area among the tested beds, reveals similar development of the surface as in the given examples. Perreault *et al.* (2016) reported that the specific surface area for pyrolusite was 15 m<sup>2</sup> g<sup>-1</sup>, a value that is very close to the result we obtained for G1.

The point of zero charge ( $pH_{pzc}$ ) is the pH of a solution at which the total charge of the surface of a material is zero. This parameter has a specific value for each particular sorbent. The results of the  $pH_{pzc}$  measurements are presented in Figure 2. The  $pH_{pzc}$  values obtained for FeRF and MnRF were very similar: 7.54 and 7.41, respectively. Such

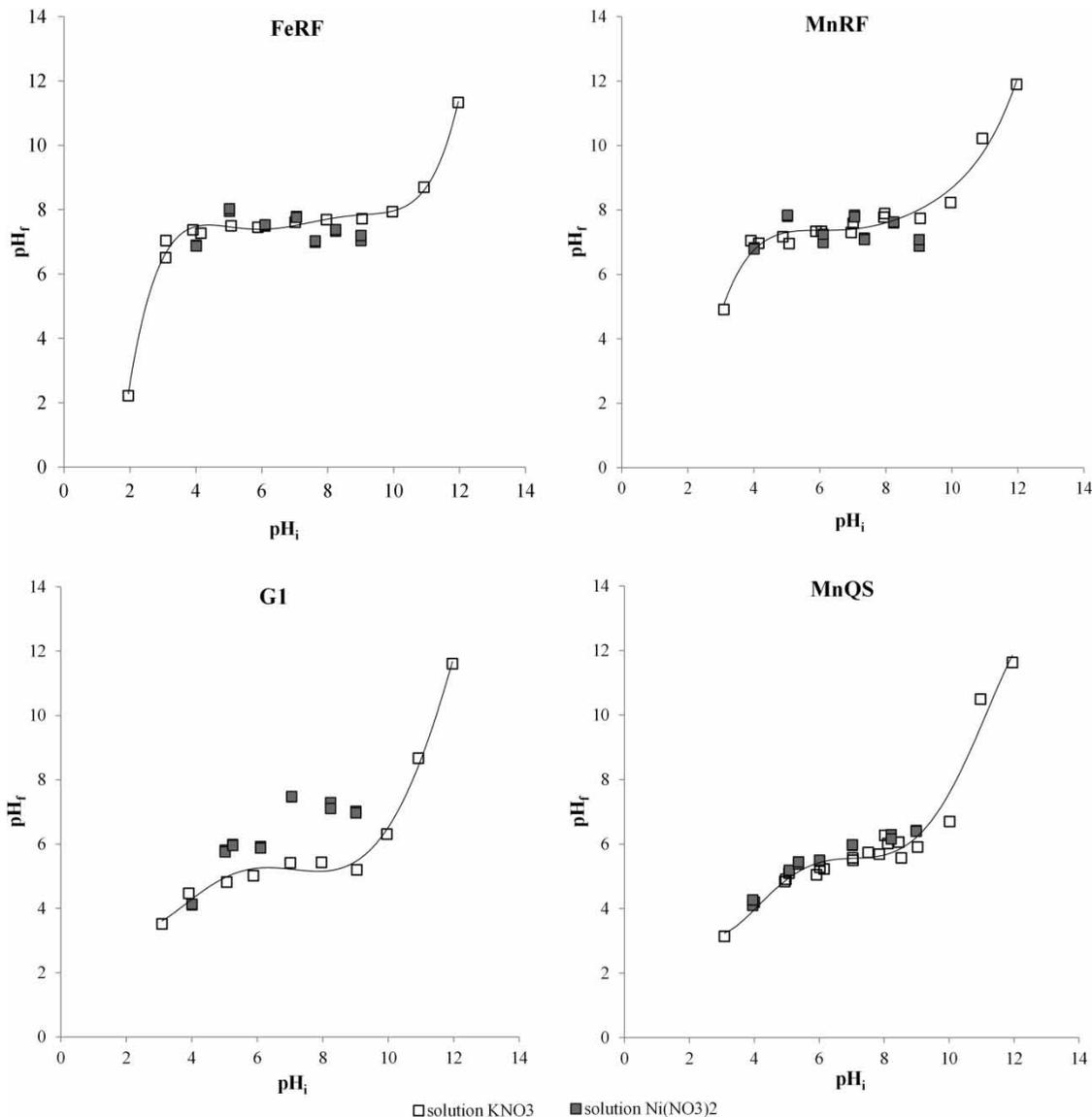
a result follows from the similar chemical composition of the surfaces of these beds. The values obtained in our study are in agreement with the results reported for iron hydroxides in the work of Juang & Chung (2004), in which the  $pH_{pzc}$  determined for goethite was 7.85. In our study, the  $pH_{pzc}$  of G1 was 5.27; a similar value was obtained for MnQS (5.44). According to Murray (1974), these values are typical of manganese oxides whose  $pH_{pzc}$  is within the range of 1.5–5. The  $pH_{pzc}$  value of bed materials for groundwater treatment significantly depends on the oxides covering the grains of the bed.

### pH changes during Ni(II) sorption

Sorption of Ni(II) was tested at different values of initial pH of the Ni(NO<sub>3</sub>)<sub>2</sub> solution. When a sorption equilibrium was reached, the final pH was measured. The dependencies are presented in Figure 2. The measuring points were compared with the points obtained in the  $pH_{pzc}$  tests performed in KNO<sub>3</sub> solutions. The measuring points concerning the pH change during the sorption of Ni(II) on the tested materials locate around the ‘plateau’ of the function for the measuring points determined by the immersion technique. During Ni(II) sorption on the tested beds, the pH changed and obtained a value similar to the  $pH_{pzc}$  value. This was a result of the state of equilibrium between OH<sup>-</sup> and H<sup>+</sup>, which also explains why zero charge was observed on the surface of the beds during Ni(II) sorption. These results show that the pH of the solution during sorption was not constant, but changed in a way closely dependent on the  $pH_{pzc}$  value for each of the tested materials.

### Ni(II) sorption

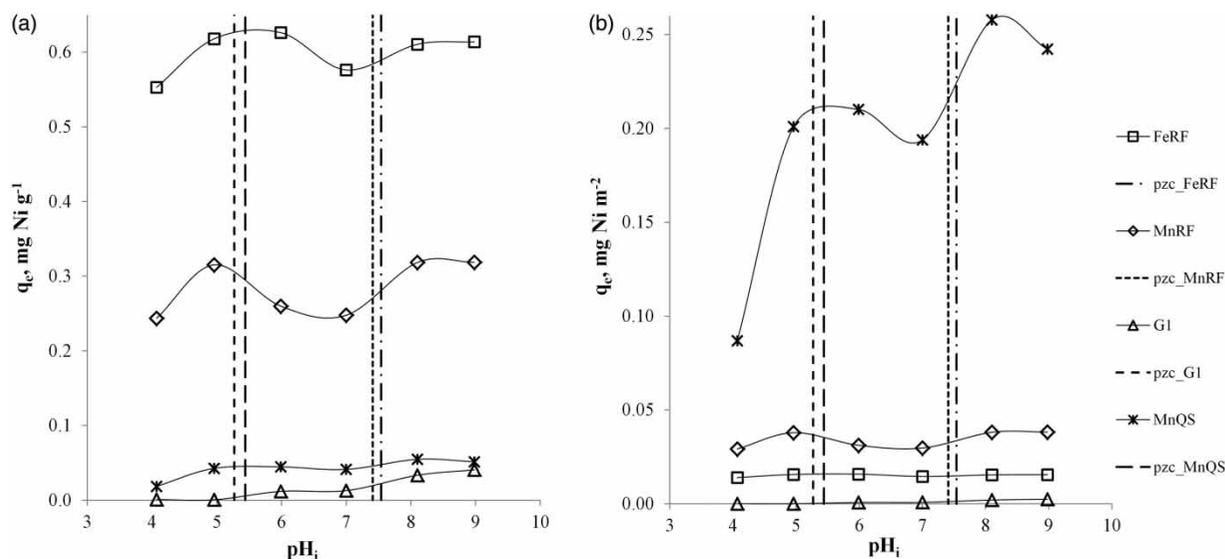
A graph showing Ni(II) sorption as a function of pH is given in Figure 3(a). The sorptive solutions used in the experiment were characterised by an activity of dissolved nickel of 7.6 10<sup>-5</sup> mol L<sup>-1</sup>, pH 4–9, and Eh 0.5–0.6 V. Eh–pH diagrams for nickel species in solutions (Brookins 1988) and the parameters of the sorptives given above indicate that the most abundant form of nickel was the divalent nickel cation. This assumption can also be adopted for sorptives after sorption. Considering the distribution of nickel species in aqueous systems as a function of pH (Kul *et al.* 2011), the



**Figure 2** | Relationship between the initial ( $pH_i$ ) and the final ( $pH_r$ ) pH of the filter bed materials: □ – determination of  $pH_{pzc}$  in  $KNO_3$  solution; ■ – sorption experiment in  $Ni(NO_3)_2$  solution.

hydrated divalent cation occurs predominantly between pH 2 and 8.5. At higher pH values, first and second hydrolysis products start to appear. This means that specific sorption of nickel hydroxy complexes could be partially present only in experimental samples with initial pH 9, while in the remaining samples, electrostatic attraction of hydrated cations predominated. The highest sorption was observed for naturally coated beds. The FeRF bed removed Ni(II) ions the most intensively when the initial pH was slightly acidic: maximum  $q_e$   $0.60 \text{ mg Ni g}^{-1}$  was observed at pH 5–6. Similarly, the highest sorption value on the bed from

the manganese removal filter was  $q_e$   $0.30 \text{ mg Ni g}^{-1}$  at initial pH 5. Strong sorption reactions of Pb(II) and Cu(II) ions on  $Fe(OH)_3$  were typically observed at  $pH \leq pH_{pzc}$  (Sposito 2008). The chemical compositions of the coatings on the FeRF and MnRF materials were similar, and so were the dependencies presented in Figure 3(a). The sorption capacity of FeRF and MnRF decreased slightly in the samples of the sorptives with an initial pH close to  $pH_{pzc}$ . G1 and MnQS were characterised by very low Ni(II) sorption capacities of  $q_e < 0.03$  and  $< 0.05 \text{ mg Ni g}^{-1}$  respectively. To generalise, in the tested pH range 4–9, the highest efficiency of Ni(II)



**Figure 3** | The volume of sorption of Ni(II): (a) mg Ni g<sup>-1</sup>, (b) mg Ni m<sup>-2</sup> as a function of the initial pH of the sorptive.

sorption (80–88%) was observed for naturally coated bed material obtained from an iron removal filter. The efficiency of the bed material naturally coated with manganese was lower (35–45%). G1 and MnQS were characterised by the lowest efficiencies of 0–6% and 3–8% respectively. The following sequence of efficiencies was obtained: FeRF >> MnRF >> MnQS > G1.

Generally speaking, our results show that the sorption of Ni(II) is only slightly dependent on pH, and rather relies on the surface area of oxide coating. Sorption of nickel is closely connected not only with the weight of the sorbent but also with its surface area. For this reason, the quantity of sorbed Ni(II) was related to the specific surface area of the tested materials, as presented in Figure 3(b). In accordance with this approach, quartz sand modified with manganese dioxide (MnQS) was characterised by the highest sorption capacity, which was several times higher than that of the other materials. The amount of manganese dioxide in the coating of the MnQS material was very small, and, therefore, its specific surface area was also small in comparison with the very well-developed coating of FeRF. Only by determining sorption capacity as mg m<sup>-2</sup> units were we able to show that amorphous manganese dioxide was characterised by the highest Ni(II) sorption. In this sense, MnRF was characterised by a higher sorption capacity counted on unit specific surface area in comparison with FeRF.

G1 mainly consisted of pyrolusite, and in both cases the capacity of this material to adsorb Ni(II) was residual. When Ni(II) sorption capacity was considered in reference to the specific surface area of the bed materials, the following sequence was established: MnQS >> MnRF > FeRF > G1. MnQS was covered by an amorphous form of MnO<sub>2</sub>, which has been reported to have better sorption properties than crystalline forms of manganese dioxide (Boonfueng et al. 2005; Bruins et al. 2015). Amorphous MnO<sub>2</sub> applied to the surface of a silica medium using the same method as the one we employed in preparing MnQS was characterised by an efficient sorption of lead and manganese from water (Michel & Kiedryńska 2012; Reczek et al. 2014).

## CONCLUSIONS

The bed materials obtained from iron and manganese removal filters (FeRF and MnRF) exhibited very similar properties. They were characterised by the presence of iron and manganese, a large number of crystalline phases found in the coatings covering the grains of sand, a similarity of those phases, as well as similar  $pH_{pzc}$  values (7.54 and 7.41). The G1 and MnQS bed materials were characterised by similar  $pH_{pzc}$  values (5.27 and 5.44) typical of MnO<sub>2</sub>. However, while G1 was crystalline-form pyrolusite, the

coating of modified sand was mainly amorphous. The  $pH_{pzc}$  values for G1 and MnQS were significantly lower in comparison with those obtained for FeRF and MnRF, which follows from the predominance of  $MnO_2$  on the surface of the former. FeRF, MnRF, and G1 had a larger specific surface area in comparison with MnQS.

During the sorption of Ni(II) on the tested beds, significant changes in the final pH in relation to the initial pH of the sorptives were observed. The direction of the changes indicated that the pH of the sorptives tended toward the  $pH_{pzc}$  of each of the materials tested. Hence, the initial pH did not have a very substantial influence on sorption capacity.

The bed material naturally coated in iron oxides (FeRF) at the groundwater treatment station was characterised by the highest efficiency of Ni(II) sorption (80–88%). The naturally coated bed material from the manganese removing filter had a lower efficiency of Ni(II) removal of 35–45%. A much lower efficiency was obtained for the catalytic, manganese removing bed (G1) and quartz sand chemically modified with  $MnO_2$  (0–6% and 3–8% respectively).

When sorption capacity was expressed as a quantity of Ni(II) per unit mass of the bed the following sequence was obtained: FeRF > MnRF > MnQS > G1. The sequence was different when sorption capacity was considered in reference to the material's specific surface area: MnQS > MnRF > FeRF > G1. The results showed that amorphous  $MnO_2$  had very strong sorptive properties in comparison with the crystalline forms of this compound and that pyrolusite (G1) was the poorest adsorbent of nickel.

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