

Adsorption of iron(II) onto filter media

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ABSTRACT: An experimental method was developed to measure the capacity of filter media to adsorb iron(II) ions. In addition to virgin sand, sand sampled from two water treatment plants and other filter materials namely anthracite, basalt, pumice, limestone and magnetite were tested. Used filter sands from treatment plants indicated the influence of time in use on the extent of surface coverage with the iron oxide coat. Compared to virgin filter media, used sand from groundwater treatment plants had a much higher capacity for iron(II). The effect of pH on the adsorption capacity of virgin sand and used sand was evaluated. It was observed that the adsorption capacity of filter materials increases with increases in pH and that the used sand has 20–25-fold higher adsorption capacity for iron(II) than virgin sand. Experimental data fitted the Freundlich isotherm model. The adsorption capacity of used filter sand was found to vary with water quality.

INTRODUCTION

Iron is an objectionable constituent of water for a variety of aesthetic reasons. These include discoloration, bad taste and the staining of laundry and plumbing fixtures. Iron deposited in the distribution system may promote the growth of microorganisms, leading to high turbidity. It may cause a reduction in the carrying capacity of the pipes, eventually blocking them unless frequent cleaning is undertaken. The EC standard [1] recommends that the iron concentration in drinking water should be less than 0.2 mg/L. In the Netherlands, the guideline level of iron in drinking water is less than 0.05 mg/L [2], and the desirable level is 0.03 mg/L. The lower level is desirable in order to avoid problems and increased costs in the maintenance of the distribution system.

In anaerobic ground water, iron is present in the soluble iron(II) form. The removal of this iron(II) is very often the only step in the treatment of ground water which is hygienically reliable. Conventional iron removal from ground water is generally achieved by aeration followed by filtration [3,4]. In this method, soluble iron(II) is oxidised to insoluble iron(III) and removed as flocs in the filters. The limitation of this floc formation mechanism is that formed colloidal iron can pass the filter. Organic molecules can form a complex with the iron again allowing it to pass through the filter. Furthermore, the floc formation reduces the run time of the filters and produces a sludge which must be disposed. Different mechanisms of iron removal exist, namely oxidation–floc formation, adsorption–oxidation and biological oxidation. They can all contribute to iron removal in filters. The dominant mechanism depends on the properties of the raw water and the operation of the process.

An alternative method to conventional treatment is to

remove the iron via the adsorption of iron(II). In this mechanism, the iron(II) is adsorbed on to the filter media. After adsorption it is oxidised, forming an iron oxide. In this way the process continues. The iron oxide builds up to form a coating. This coating is capable of adsorbing more iron(II) from the water than the original filter media surface. It is believed that this is the removal mechanism in conventional filters for the iron entering the filter in the form of iron(II). For the adsorption mechanism to dominate, the oxidation of iron before filtration must not occur to any great extent. The oxidation can be slowed down by reducing the pH, the oxidant concentration or the time available for the reaction [5]. Adsorption of iron(II), however, is a function of pH; adsorption increases with increases in pH. The subsequent oxidation of the adsorbed iron(II) may also be a function of the oxidant concentration. The requirement for lowering the pH to maintain the iron(II) form and then to adsorb and oxidise the ions is conflicting.

Several authors have reported that iron removal efficiency in conventional treatment has been improved following the development of an iron oxide coating on the filter media [3,6,7]. Cox [6] found that filters may serve as contact beds following aeration where the catalytic action of previously precipitated iron oxides will facilitate the oxidation of iron. Ghosh *et al.* [8], in their study of iron removal concluded that a fraction of the iron(II) may be adsorbed on the iron(III) hydrate precipitates. O'Connor [3] reported that the rate of oxidation may be increased by the oxide coat. In addition, he surmised that deposited precipitates of hydrous oxides of iron(III) formed after oxidation serve as sorption media for the iron that is still in solution. The hydrous precipitates have a high sorption capacity for iron(II), and this accounts for their improved removal during the filter run. These results of pilot plant

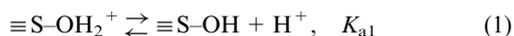
experiments and studies of iron removal plants [3,6–8] clearly indicate that the iron oxide coating can play an important role in the oxidation and removal of iron. The efficiency of iron removal in a filter can be improved by maximising the adsorption of iron(II) on to iron oxide-coated media.

Compared to conventional chemical precipitation, adsorption-based processes can achieve a higher level of removal over a wider range of solution conditions and can generally reduce the quantity of sludge produced [9,10]. In addition to offering a more reliable and more efficient removal of uncomplexed cationic metals, adsorption processes can often remove inorganically and organically complexed metals that would not be removed by conventional treatment methodology [11,12]. Iron oxide coated sand has been successfully employed in fixed beds to treat metal bearing water and wastewaters [9,10,12,13].

The exploitation of the adsorption capability of iron oxide coatings on the surface of the sand grains in the filtration unit may require some modification of the design parameters and process conditions (pH, detention time, bed depth). No information is available on the effectiveness of this mechanism when it is used as the only mechanism. In order to understand and optimise this process of iron removal in filters, an accurate method for quantifying the adsorption capacity on the filter media is required. To achieve this, a method for the measurement of the adsorption capacity of filter media for iron(II) was developed. It was used to determine the adsorption capacity of commonly used filter media at various pH.

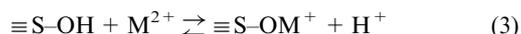
Theoretical background

The adsorption of metal cations onto iron oxide has been well studied [14–16]. Davis & Leckie [15] proposed a mechanism involving surface ionisation and complexation of trace metal ions with hydrous iron oxide surfaces. In aqueous systems the surfaces of oxides are covered with surface hydroxyl group. The acid base equilibrium of a hydroxylated oxide surface is commonly represented as:

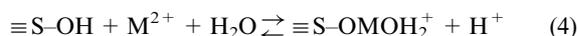


where $\equiv\text{S-OH}_2^+$, $\equiv\text{S-OH}$ and $\equiv\text{S-O}^-$ represent positively charged, neutral and negatively charged surface hydroxyl groups, K_{a1} and K_{a2} are the acidity constants. This diprotic acid representation is widely accepted because it is simple and provides a convenient means of describing zero proton charge at the surface [14].

The adsorption of a metal ion on an oxide surface involves the formation of bonds of the metal ion with the surface oxygen atoms and the release of protons from the surface.



or equivalently



where M^{2+} represents a divalent cation.

Consistent with eqn 3 or 4, the adsorption of cations on to the hydrous oxide surface increases with the increase in pH. However, it has been found that there is a narrow pH range, usually one or two units, over which the percentage adsorption of cation on hydrous oxides increases from 0 to 100%, giving typical adsorption ‘pH edges’ [14,16].

MATERIALS AND METHODS

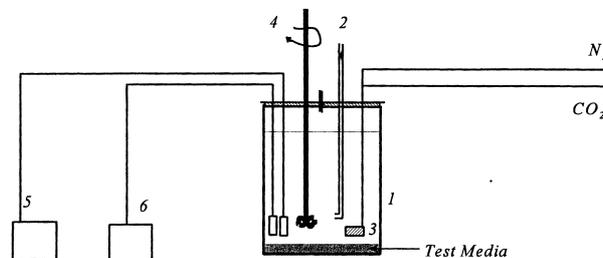
Experimental set up

A laboratory batch experiment, as shown in Fig. 1, was developed to measure the adsorption of iron(II) on to filter media. The experimental apparatus consisted of a sealed 2 L glass reactor. The vessel cover had ports to allow solution feeding and sampling, oxygen, temperature and pH measurement, gas supply and for mechanical stirring. The experiments were conducted at room temperature (18–20 °C). The pH and oxygen concentration were monitored continuously.

A model ground water, prepared by mixing iron(II) sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) with demineralised water, was used for the experiments. The pH of the water could be adjusted using the $\text{CO}_2/\text{HCO}_3^-$ buffer system. 1.2 g/L of NaHCO_3 was dosed in the water for this purpose. A controlled amount of CO_2 was passed through the solution via diffusers. All the chemicals used were of reagent grade. Nitrogen gas was passed through the water to strip out the oxygen. This continued throughout the experiment to control the oxygen concentration and pH. The gas provided the positive pressure against the inflow of air. Through the removal of oxygen, iron is maintained in the iron(II) form. The adsorbed iron will not be oxidised and the adsorption sites will not be recreated.

Experimental procedure

Initially 1.5 L of water was deoxygenated by bubbling nitrogen gas through the solution. The pH was adjusted to the desired



1. Reactor 2. Solution Feeder & Sampler 3. Diffuser 4. Stirrer 5. pH meter 6. Oximeter

Fig. 1 Experimental setup for batch study.

level with CO₂. Iron(II) solution was dosed into the reactor containing a known amount of filter material. An initial pH drop of up to 0.2 units was observed on addition of the acidified iron(II) stock solution. The pH returned to the required value within 15–25 min. The pH during the experiment was controlled to within 0.05 units.

The solution in the reactor was mixed using a mechanical stirrer. The media remained settled on the bottom of the vessel. This avoided scouring any of the surface coating. The system attained equilibrium with respect to iron(II) adsorption. Then the total iron and iron(II) concentrations were measured. The amount of iron(II) adsorbed on to the filter media was calculated by a mass balance of iron. Duplicate experiments were carried out for different pH values and for different types of media. Experiments without filter media revealed that the loss of iron(II) on to the glass reactor was less than 1% of that dosed.

The equilibration time for each filter media was determined by measuring the hourly variation in iron(II) concentration. It was found that most of the adsorption (about 80%) takes place in the first 2 h. Equilibrium was considered as being reached when no measurable difference could be detected in the iron(II) concentrations. The weight of the filter material used in the experiments was varied to so as to reduce the time that each

experiment took to reach equilibrium. The weights of the media tested and corresponding equilibration times are presented in Table 1.

A sieve analysis of the media was used to determine the grain size distribution. The equivalent spherical diameter for the grains on each sieve was computed by multiplying the geometric mean of the passing and retaining sieve sizes with the shape factor. The geometric surface area of the fractions retained on each sieve were calculated separately and the average geometric surface area per unit weight of the material determined. The amount of iron(II) adsorbed per unit surface area at different equilibrium concentrations were plotted on a log–log graph. The Freundlich isotherm model constants were calculated by linear regression.

Filter materials

Virgin sand, anthracite, basalt, pumice, limestone and magnetite were tested for their adsorption capacity. Additionally, sand taken from two groundwater treatment plants were tested (WZHO Ridderkerk and WNWB Gilze). These sands are naturally coated with iron oxide. Table 2 presents a size characterisation of the media tested.

The virgin sand was washed with demineralised water, soaked in concentrated hydrochloric acid (pH = 1) for 24 h and again rinsed with demineralised water and dried at 40 °C. The other virgin media were washed with demineralised water and dried at 40 °C. The sands from the two water treatment plants were washed gently to remove any deposits and dried at room temperature.

Table 1 Equilibration time of the filter materials

Filter media	Equilibration time (h)	Weight of the media tested (g)
1 Virgin sand	4	100
2 Used sand (Ridderkerk)	4	100
3 Used sand (Gilze)	6	50
4 Anthracite	7	25
5 Basalt	6	75
6 Limestone	5	50
7 Pumice	5	25
8 Magnetite	5	40

RESULTS

Adsorption isotherms

The Freundlich isotherm model is mathematically represented as:

$$q = kC_e^{1/n} \quad (5)$$

where q = iron(II) adsorbed in g/m² surface area of filter

Filter media	Grain size (mm)	Effective size d_{10} (mm)	Uniformity coefficient d_{60}/d_{10}	Geometric surface area (m ² /g)
1 Virgin sand	0.7–1.25	0.81	1.17	2.78×10^{-3}
2 Used sand (Ridderkerk)	2.7–5.2	2.86	1.34	7.58×10^{-4}
3 Used sand (Gilze)	0.7–1.25	0.77	1.23	2.82×10^{-3}
4 Anthracite	1.4–2.5	1.48	1.38	4.09×10^{-3}
5 Basalt	0.8–1.6	2.04	1.21	3.49×10^{-3}
6 Limestone	0.8–1.6	0.93	1.35	3.39×10^{-3}
7 Pumice	2–3.15	0.95	1.39	4.36×10^{-3}
8 Magnetite	0.5–0.8	0.53	1.25	3.17×10^{-3}

Table 2 Size characterisation of the filter media analysed

Table 3 Freundlich isotherm constants for iron(II) adsorption on to filter media

Filter material	pH	k [g/m ² /(g/m ³) ^{1/n}]	1/n	r^2
Virgin sand	6.0	2.32×10^{-3}	0.54	0.95
	6.5	2.48×10^{-3}	0.73	0.98
	7.0	3.85×10^{-3}	0.70	0.98
	7.5	1.16×10^{-2}	0.45	0.94
Used sand (Ridderkerk)	6.5	4.80×10^{-2}	0.60	0.99
Used sand (Gilze)	6.0	4.27×10^{-2}	0.49	0.96
	6.5	6.11×10^{-2}	0.54	0.99
	7.0	11.7×10^{-2}	0.43	0.98
	6.5*	5.74×10^{-2}	0.48	0.98
Anthracite	6.5	7.90×10^{-3}	0.78	0.97
Basalt	6.5	1.81×10^{-2}	0.38	0.99
Limestone	6.5	5.44×10^{-4}	0.60	0.90
Pumice	6.5	1.54×10^{-3}	0.94	0.92
Magnetite	6.5	2.88×10^{-3}	0.63	0.92

* Experiment conducted in the final effluent of the Gilze groundwater treatment plant.

material, C_e = equilibrium iron(II) concentration in g/m³, k , n = isotherm constants.

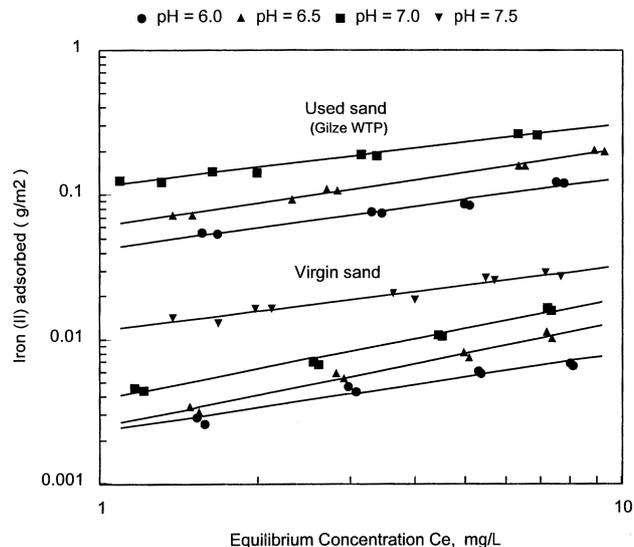
The experimental adsorption data fitted the Freundlich isotherm model, corresponding to straight lines with slopes of less than 1.0 on log-log graphs. This is in agreement with the observations of other researchers studying the adsorption of cations on to hydrous oxide surfaces [14,16].

The adsorption capacities of the filter media for iron(II) were measured in the batch experiment. Table 3 presents the isotherm constants derived.

Effect of pH on iron(II) adsorption

Figure 2 presents the adsorption isotherms for virgin sand and used sand from the Gilze water treatment plant (WTP), respectively. The isotherms were derived for pH 6.0, 6.5, 7.0 and 7.5 of virgin sand and for pH 6.0, 6.5 and 7.0 of used sand from Gilze WTP. For both media, the adsorption capacity increases with increases in pH. The point of zero charge (p.z.c.) for silica is approximately 2.0 [17]. In the pH range we investigated, the silica surface is negatively charged, and therefore has a high affinity for positively charged ions. As the pH increases, the surface charge becomes more negative, and therefore its adsorption capacity increases. For both media, the slopes of the isotherms at different pHs are approximately identical. This indicates that the increase in adsorption capacity with the increase in equilibrium concentration is nearly the same in the pH range we investigated.

The sand from the Gilze WTP had developed an iron oxide coating on its surface. This surface had developed over the normal operation of the iron-removal process. The point of

**Fig. 2** Adsorption isotherms of iron(II) on to virgin and used sand in demineralised water.

zero charge for hydrous ferric oxides (HFO) lies between 7.8 and 8.2, depending on the ionic concentration [10]. In the pH range 6.0–7.0, the iron oxide coating on the sand is positively charged, and hence the adsorption of iron(II) is taking place against electrostatic repulsion. As the pH increases the hydrated oxide surface becomes less positively charged. There are more sites available for iron(II) adsorption, hence its adsorption capacity increases [14,17]. The increase in adsorption with pH is consistent with the acid–base equilibria of hydrated oxide surfaces, as represented by eqns 1–4. The isotherm equations show that the isotherm constant k (adsorption capacity) for used sand (from Gilze) is 25-fold higher than that of virgin sand. Adsorption on to used sand is also less sensitive to changes in equilibrium concentration. This may be due to differences in the number and types of adsorption sites.

The variation of the isotherm constant k with pH for virgin sand and used sand are illustrated in Figures 3a and b. For both media, there is an increase in k between pH 6 and 6.5. A sharp increase in k is seen as the pH changes from 6.5 to 7. With an increase in pH from 6 to 6.5, k increases by 55% for virgin sand and 91% for the coated sand. The increases are 66% and 174%, respectively, following an increase in pH to 7. At pH = 7.0, the k for used sand seems to be more sensitive to pH change.

Development of the iron oxide coating

The effectiveness of the iron oxide coating at adsorbing iron(II) is clearly shown. Little is known about the development process of such coatings. The sand from the Gilze WTP was in use for three and a half years. The average influent iron concentration was 1.7 mg/L and the pH 7.6. The sand from the Ridderkerk plant was used in a trickling filter for two years. The average

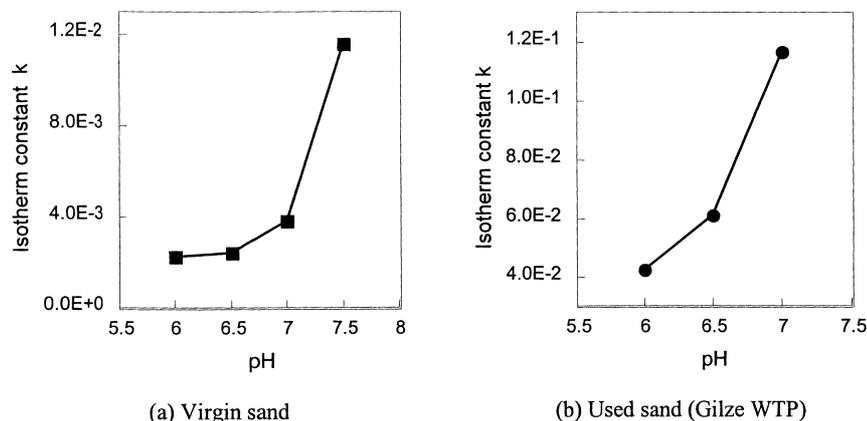


Fig. 3 Variation of isotherm constant k with pH.

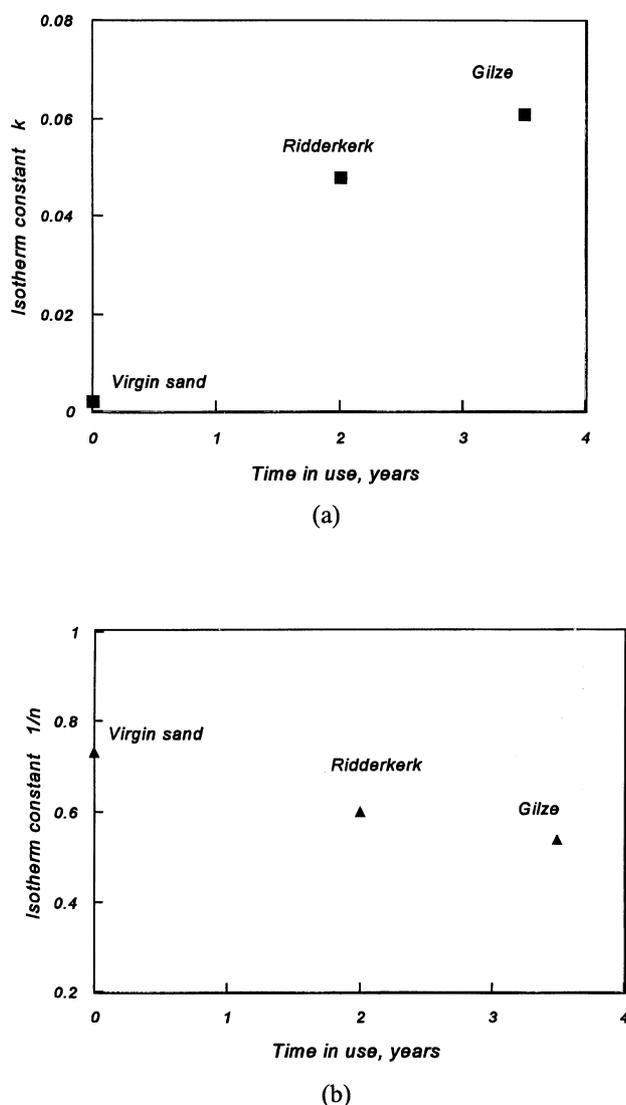


Fig. 4 Variation of isotherm constant k and $1/n$ with time in use as a filter media.

influent iron concentration was 7 mg/L and the pH 7.1. The sand from the Gilze WTP was fully coated with a dark brown iron oxide. The sand from the Ridderkerk WTP was less coloured than the Gilze sand, and was only partially covered with iron oxide. Figure 4a and b shows the variation of the isotherm constant k and $1/n$ of the sands at a pH of 6.5. The isotherm constant k for sand from Gilze WTP is about 24-fold that of virgin sand and 1.3-fold that of sand from Ridderkerk WTP. Figure 4 indicates that the filter sand becomes coated with iron oxide (ripened) over time and that the k -value may increase to a maximum value.

Benjamin *et al.* [12] reported that the method of coating influences its surface characteristics and adsorption capacity. Stenkamp & Benjamin [18] concluded that the nature of the underlying media can influence the adsorption characteristics of the media coat, particularly when the coating is thin. The difference in k -values of the sand from the two water treatment plants is due to differences in the extent of the iron oxide coating surface coverage and the composition and mineralogy of this coating. Factors affecting these properties include the time that it is in use, the grain size and the influent water quality (iron concentration, pH, alkalinity, organic matter content). The constant $1/n$ apparently decreases over time with use. In comparison to virgin sand, the adsorption capacity of iron oxide coated sand is less influenced by the iron(II) concentration.

Adsorption capacity of different materials

Figure 5 compares the adsorption capacities for iron(II) of different materials tested at pH 6.5. Among the media tested, the used sand from the Gilze WTP had the highest and limestone the lowest capacity for iron(II) adsorption. The variations in adsorption capacity are due to the surface charge, the density of adsorption sites, the crystal structure and the mineralogy of the media surface.

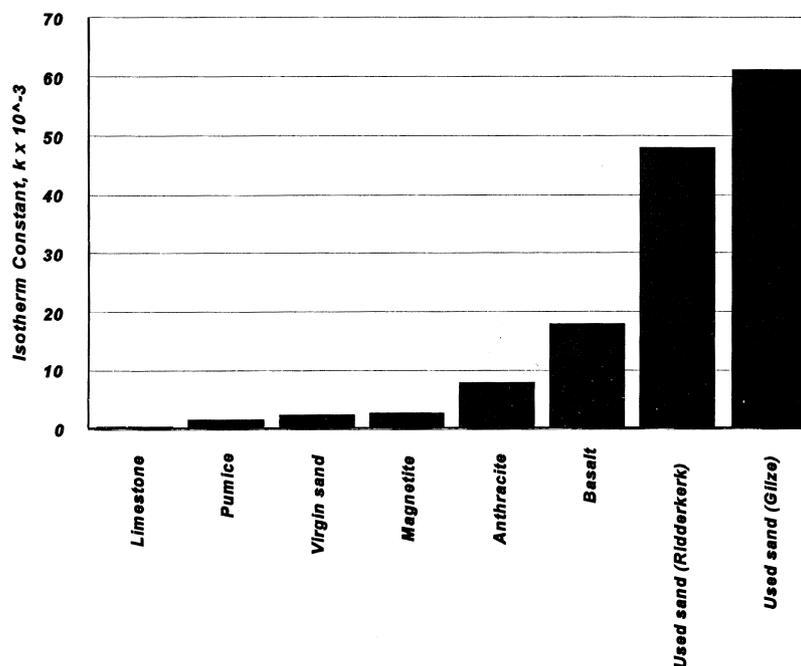


Fig. 5 Isotherm constant k for iron(II) on filter materials, pH = 6.5 in demineralised water.

Effect of water quality on adsorption capacity

The adsorption capacity of the sand from the Gilze WTP was measured in the final treated water. The adsorption capacities obtained with the model ground water and the actual ground water could be compared. The final treated water from Gilze contained 0.01 mg/L of iron(III) and < 0.01 mg/L of manganese. It was dosed with iron(II) sulphate to recreate the raw water. Experiments were conducted as before at pH 6.5 ± 0.05 but without adding NaHCO_3 . The pH was controlled using the natural buffering capacity of the water.

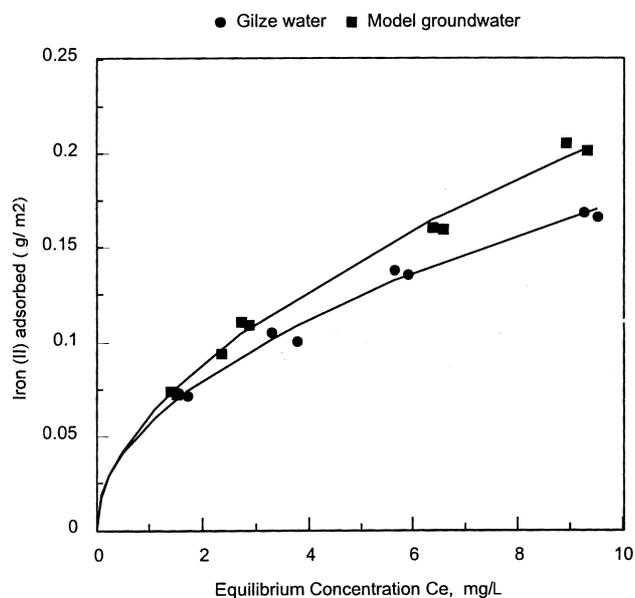


Fig. 6 Adsorption of iron(II) on Gilze sand in different water.

Figure 6 shows the adsorption capacity in the actual ground water to be lower than that in the model ground water. This may be because of the presence of different ions and compounds in actual ground water. The TOC content of the Gilze water (1.5 mg/L) is higher than that of the model ground water (0.4 mg/L). Organic matter forms complexes with iron(II) and iron(III) [19] and can adsorb on the iron oxide, masking the properties of the underlying surface [15,20]. The ground water also contains calcium (52 mg/L), chloride (15 mg/L) and sulphate (13 mg/L) ions which may mutually enhance, act relatively independently or may interfere with adsorption [11,20]. The ions present in the water might alter the surface charge density and the thickness of the double layer. In this case the overall effect of these ions and compounds was to lower the adsorption capacity of the media.

DISCUSSION

Experimental results have shown that the filter media can adsorb iron(II) on its surface. This capacity increases with pH and varies between media. The capacity is greatly increased with the development of an iron oxide coating on the media.

The adsorption capacity of the media can be used to remove iron(II) in groundwater. Since adsorption depends on the influent iron(II) concentration, adsorption and hence removal is greater at the top of the filter. As the water passes through the filter, the iron(II) concentration decreases. As the capacity of the upper bed is exhausted, adsorption will take place lower down in the bed. The bed may become exhausted if the rate of adsorption is greater than the rate of site recreation. If, however, the adsorption sites in the bed are renewed (via the

oxidation of adsorbed iron(II) faster than the rate of exhaustion, breakthrough will never occur. The experimental results illustrate that a filter bed can have very high capacity for iron(II) adsorption; however, maintenance of the proper process conditions is necessary to exploit this capacity. The effect of ionic concentration, alkalinity and organic matter content on iron(II) adsorption on to filter media and the physical stability of the media coating is not known.

A filter could be operated under anaerobic conditions until its capacity is exhausted. When this occurs, the filter media is supplied with oxygen-rich water to oxidise the iron(II) adsorbed and to recreate the adsorption sites. The same treatment cycle can then be repeated. Another alternative would be to maintain a very low oxygen concentration in the filter influent. The oxygen present should be sufficient for the oxidation of adsorbed iron without a significant oxidation of the iron(II) in the bulk solution. It should be noted that the filter media may have high adsorption capacity; however, the adsorbed iron(II) needs to be oxidised quickly to regain the catalytic or adsorption capacity. The rate of oxidation of adsorbed iron(II) is likely to be different from that of iron(II) in water. This may also be influenced by the water quality and the process conditions. Hence, understanding the rate and factors affecting the recreation of adsorption sites is equally important.

The adsorption oxidation mechanism creates a very low head loss, as the iron forms a coating rather than a floc. The filtration run is longer and the backwash water requirement and sludge is reduced. There could be considerable savings in the capital, operation and maintenance costs of iron removal.

CONCLUSIONS

A batch study of adsorption capacities of different filter media showed that iron oxide coated sand has a higher capacity for iron(II) adsorption compared to new filter media. It was found that the adsorption capacity of both virgin and iron oxide coated sand increases with increasing pH. Adsorption on coated sand is more sensitive to pH change than is new sand. The adsorption of iron(II) on to filter media fits the Freundlich Isotherm model, with a slope of less than 1.0 on a log-log graph.

Among the different media tested, sand which had been in use the longest in an iron removal plant had the highest capacity. Of the virgin materials, the order of decreasing adsorption capacity is basalt, anthracite, magnetite, sand, pumice and limestone. The adsorption capacities of used media from different water treatment plants were not the same. The extent of iron oxide coating, the time in use, the water quality and the treatment processes employed may all be factors which influence the capacity of the coating. The adsorption capacity of the coated media was found to vary with water quality.

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BIBLIOGRAPHY

- EEC. *Official Journal of the European Communities* 30 August 1980; **23**: Official Directive, L229/11–L229/23.
- VEWIN Aanbevelingen 1993 (a. de hoedanigheid van het water = waterkwaliteit). VEWIN, the Netherlands, 1993.
- O'Connor JT. *Iron and Manganese; Water Quality and Treatment—A Handbook of Public Water Supplies*. Chap. 11, pp. 378–396. McGraw-Hill, New York, 1971.
- JM Montgomery Consulting Engineers. *Water Treatment, Principles and Design*. John Wiley & Sons Inc., USA, 1985.
- Stumm W, Lee GF. Oxygenation of ferrous iron. *Indust Engng Chem* 1961; **53**(2): 143–146.
- Cox CR. *Operation and Control of Water Treatment Processes*: WHO, 1964: 209–218.
- Anderson DR, Row DD, Sindelar GE. Iron and manganese studies of Nebraska water supplies. *JAWWA* 1973; **65**: 637–641.
- Ghosh MM, O'Connor JT, Engelbrecht RS. Removal of iron from ground water by filtration. *JAWWA* 1967; **59**(7): 878–896.
- Edwards M, Benjamin MM. Adsorptive filtration using coated sand: a new approach for the treatment of metal bearing wastes. *JWPCF* 1989; **61**(9): 1523–1533.
- Bailey RP, Bennett T, Benjamin MM. Sorption onto and recovery of Cr(VI) using iron oxide coated sand. *Water Sci Technol* 1992; **26**(5–6): 1239–1244.
- Benjamin MM. Adsorption and surface precipitation of metals on amorphous iron oxyhydroxides. *Environ Sci Technol* 1983; **17**(11): 686–691.
- Benjamin MM, Sletten RS, Bailey RP, Bennett T. Sorption and filtration of metals using iron oxide coated sand. *Water Res* 1996; **30**(11): 2609–2620.
- Joshi A, Chaudhuri M. Removal of Arsenic from groundwater by iron oxide coated sand. *J Environ Engng—ASCE* 1996; **August**: 769–771.
- Dzombak DA, Morel FMM. *Surface Complexation Modeling—Hydrous Ferric Oxides*. John Wiley & Sons, USA, 1990.
- Davis JA, Leckie JO. Surface ionization and complexation at the oxide/water interface: surface properties of amorphous iron oxyhydroxide and adsorption of metal ions. *J Colloid Interface Sci* 1978; **67**(1): 90–107.
- Benjamin MM, Leckie JO. Multiple site adsorption of Cd, Cu, Zn and Pb on iron oxyhydroxide. *J Colloid Interface Sci* 1981; **79**(1): 209–221.
- Stumm W, Morgan JJ. *Aquatic Chemistry*. 3rd edn, John Wiley & Sons Inc., USA, 1996.

- 18 Stenkamp VS, Benjamin MM. Effect of iron oxide coatings on sand filtration. *JAWWA* 1994; **86**(8): 37–50.
- 19 Theis TL, Singer PC. Complexation of iron(II) by organic matter and its effect on iron(II) oxygenation. *Environ Sci Technol* 1974; **8**(6): 569–573.
- 20 Gu B, Schmitt J, Chen Z, Liang L, McCarthy JF. Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environ Sci Technol* 1994; **28**(1): 38–46.