Decision support system for optimisation of iron removal from groundwater

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Abstract Floc filtration and adsorptive filtration are the two main physicochemical mechanisms of iron removal in filters. Under the commonly applied treatment conditions in iron removal plants, the floc filtration is commonly believed to be the dominant mechanism and the adsorptive filtration complimentary. Iron removal filters with iron oxide coated sand are expected to perform better in terms of filtrate quality, filter run time and costs, by switching the mode of operation from predominantly floc filtration to predominantly adsorptive filtration. A decision support system (DSS) is being developed to assess the applicability and to quantify the possible benefits associated with adsorptive iron removal for a given groundwater and a specific plant. This paper introduces the different independent and interconnected modules of the DSS and elaborates on one particular sub-module for the analysis of the extent of floc filtration and adsorptive filtration iron removal in a groundwater treatment plant under given conditions. This computer model would be helpful in optimising the plant performance under the existing mode of operation, formulating strategies for switching from floc filtration to adsorptive filtration, and designing new iron removal plants. Sensitivity analysis showed that pH, iron oxidation rate constant and pre-oxidation time (a function of depth of supernatant and filtration rate) are the main parameters determining the extent of floc filtration and adsorptive iron removal under given conditions. Predominantly adsorptive iron removal in filters can be achieved by reducing the depth of supernatant, increasing the rate of filtration and/or controlling the oxygen concentration in the feed water.
Keywords Adsorptive filtration; decision support system; groundwater; iron removal

Introduction

Groundwater is one of the main sources for drinking water worldwide. Approximately two billion people in the world rely on groundwater as the only source for drinking water (Sampat, 2000). Iron is a common constituent of groundwater worldwide. The presence of iron in drinking water is not harmful to human health (WHO, 1996), however, it is undesirable because of the associated aesthetic and operational problems, namely: bad taste, colour, stains on laundry and plumbing fixtures, and deposition and aftergrowth in the distribution system (O'Connor, 1971; Vigneswaran and Visvanathan, 1995). The World Health Organisation (WHO) and the European Commission (EC) guideline values of iron in drinking water are 0.3 mg/l and 0.2 mg/l, respectively (WHO, 1996; EC, 1998). Conventionally, iron is removed from groundwater by the processes of aeration (sometimes followed by sedimentation) and rapid sand filtration. Two main physico–chemical removal mechanisms namely oxidation–floc formation (floc filtration) and adsorption–oxidation (adsorptive filtration) play an important role in the removal process (Sharma *et al*., 2001).

In floc filtration, soluble iron(II) present in groundwater is oxidised to insoluble iron(III) and the flocs formed are removed in filters. In adsorptive filtration, the iron(II) present in anoxic groundwater is removed by adsorption onto the surface of the filter media. This adsorbed iron(II) subsequently undergoes oxidation in the presence of oxygen thus creating a new surface for adsorption. Under commonly applied treatment conditions, floc filtration mode is believed to predominate. Adsorptive filtration mode of iron removal,

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however, has several potential advantages over the floc filtration mode namely: longer filter run, better filtrate quality, shorter ripening time and less backwash water use, and strongly reduced sludge volumes produced.

There are strong indications that many plants with iron oxide coated sand will perform better in terms of filtrate quality and costs when the mode of operation is switched from predominantly floc filtration to predominantly adsorptive filtration (Sharma *et al.*, 1999, 2001, 2002). Applicability of the newly developed adsorptive iron removal process for particular groundwater is, however, a function of a complex matrix including groundwater composition, design parameters of the treatment plant and specific characteristics of the filter media. Therefore, a rational method to analyse the existing situation and to predict the performance and potential cost savings in adsorptive filtration mode could be very useful for the water supply companies using groundwater sources. Additionally, even in cases when adsorptive treatment is not suitable, such tools could be helpful in optimising the plant performance under the existing mode of operation. Hence, the objective of this study was to develop a decision support system (DSS) to assess the applicability and to quantify the possible benefits associated with the adsorptive iron removal for a given groundwater and a specific plant. This paper introduces the DSS under development and focuses on one of the DSS sub modules for the analysis of the extent of floc filtration and adsorptive filtration iron removal for a groundwater treatment plant under given conditions.

Decision support system components

The decision support system consists of four main sub modules. Each of these modules is being developed to operate as an independent module. Eventually, these modules will be combined in an integrated system for the optimisation of the iron removal process for the given water quality, process conditions, filtrate quality and treatment costs. In order to make this DSS easily accessible to potential users of the adsorptive groundwater treatment, the DSS modules will be deployed over the Internet.

- *Module 1*. Analysis of the dominant iron removal mechanism (extent of floc filtration and adsorptive filtration) under given raw water quality and process conditions.
- *Module 2*. Analysis of the suitability of the adsorptive iron removal for a given groundwater based on the effect of water quality parameters on iron(II) adsorption onto filter media, as well as the removal of other groundwater impurities.
- *Module 3*. Prediction of the filtrate quality and filter run time of the adsorptive iron removal filters.
- *Module 4*. Estimation of the operation and maintenance cost savings by switching the mode of operation from predominantly floc filtration to predominantly adsorptive filtration.

Further details of the first module of the DSS which calculates the contribution of floc filtration and the adsorptive filtration mode of iron removal under given conditions are presented below.

Assessment of dominant physico–chemical iron removal mechanism

In practice, both floc filtration, as well as adsorptive filtration, contribute to the iron removal in filters. In order to operate the iron removal filters predominantly in the adsorptive-filtration mode and to maximise the benefits, it is first necessary to determine the contribution of each of these two physico–chemical mechanisms in the iron removal process under given conditions. Therefore, a computer programme was developed to calculate the extent of floc filtration and adsorptive-filtration iron removal in a groundwater treatment plant under given conditions. Such a model is important to explore the available alternatives to switch from floc filtration to adsorptive filtration. Additionally,

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this model could also be helpful in optimising the plant performance under the existing mode of operation and in designing new iron removal plants. The assessment procedure is as follows.

Assessment procedure

- Analysis of groundwater quality:
  (i) analysis of groundwater quality (measure temperature, oxygen, iron(II), total iron, pH and alkalinity of the raw water);
  (ii) analysis of the extent of iron(II) oxidation after aeration (measure oxygen, iron(II), total iron and pH after aerators);
  (iii) determination of iron(II) oxidation rate constant k for the given groundwater (the rate constant k can be determined experimentally in the laboratory or the standard values from the literatures, available in the model, can be used).
- Data input to the model:
  (i) input (measured or assumed) the iron(II) concentrations in the feed water and in the filtrate, and other relevant feed water quality parameters including temperature, pH, O_2, and HCO_3^- into the computer program;
  (ii) input filtration system parameters (filtration rate, depth of supernatant, bed depth and porosity) into the model.
- Model calculations:
  (i) determination of the theoretical iron(II) oxidation in the supernatant and in the filter bed based on the Stumm and Lee equation (Stumm and Lee, 1961) (in calculating the iron(II) oxidation it is assumed that there is no adsorption of the iron(II) in the filter bed, which gives an overestimation of iron oxidation in the filter bed);
  (ii) calculations of the changes in pH and alkalinity based on CO_2-HCO_3^--CO_3^{2-} equilibria equations;
  (iii) calculation of iron removal in floc filtration mode (sum of iron oxidised in the supernatant and iron oxidised in the filter bed);
  (iv) calculation of iron removal in the adsorptive filtration mode (iron(II) removed by adsorption is the difference between the total iron removed in the filter system and the iron removed in the oxidation-floc filtration mode);
  (v) calculation of the %iron removed in floc-filtration and adsorptive-filtration mode.

The equations used in these calculations are included in the Appendix. Typical inputs and outputs of this model are presented in Figure 1.

### Sensitivity analysis of model predictions

The sensitivity of the model predictions with the change in the values of the model parameters (specifically, depth of supernatant, filtration rate, feed water oxygen concentration, oxidation rate constant, pH and alkalinity) were analysed to determine their relative importance. While analysing the sensitivity of one parameter, the other parameters were kept constant.

Effect of depth of supernatant and filtration rate. Figure 2 presents the effect of depth of supernatant and filtration rate on iron removal mechanisms. As expected, floc filtration is the dominant iron removal mechanism when the pre-oxidation time is longer (lower filtration rate and/or higher depth of supernatant). When the depth of supernatant is decreased or the filtration rate is increased, the contribution of adsorptive filtration on iron removal becomes more pronounced. When the depth of supernatant was decreased from 1.0 m to 0.5 m (at the filtration rate of 5 m/h), the percentage iron removed by floc filtration decreased from 49% to 38%, whereas when the filtration rate was increased from 5 m/h to

Figure 1 Inputs and outputs of the computer program for the assessment of the extent of the floc-filtration and adsorptive-filtration mode of iron removal under given conditions
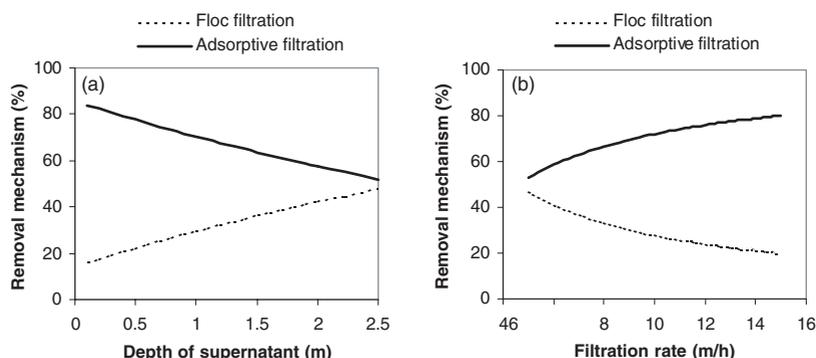
Figure 2 Effect of: (a) depth of supernatant, and (b) filtration rate on the dominant iron removal mechanism (pH = 7.7, Fe = 1.72 mg/l, O_2 = 8.62 mg/l, oxidation rate constant $k = 6.78 \times 10^{15}$ l^3 mol^{-3} min^{-1})

10 m/h (with the depth of supernatant of 1.0 m), the percentage iron removed by floc filtration decreased from 49% to 30%. This indicates that the iron removal mechanism is likely more sensitive to the change in the filtration rate than the change in depth of supernatant.

Effect of feed water oxygen concentration and oxidation rate constant. The effect of feed water oxygen concentration and oxidation rate constant k on the dominant iron removal mechanism is presented in Figure 3. It shows that adsorptive filtration is the dominant removal mechanism when the feed water oxygen concentration and/or iron oxidation rate constant k are low. With increasing oxygen concentration in the feed water and/or higher oxidation rate constant k, the iron(II) oxidation in the filter is much faster and hence the floc filtration becomes the dominant iron removal mechanism. Figure 3b also shows that the dominant iron removal mechanism under given conditions is highly dependent on the iron oxidation rate constant k of that groundwater which depends on water quality (Stumm and
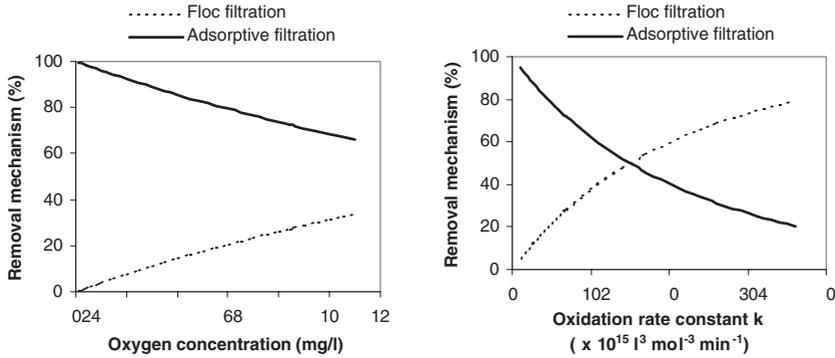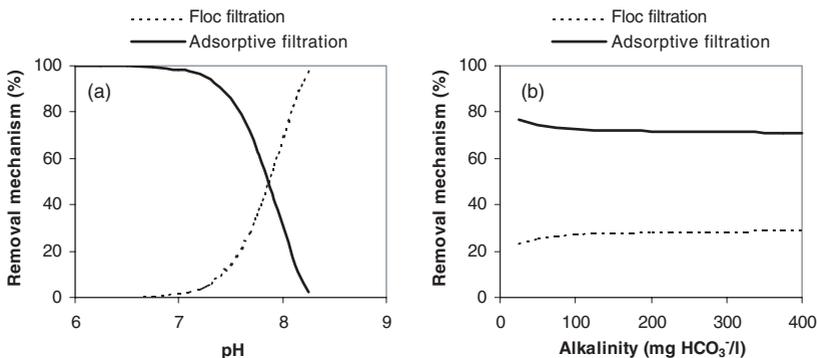
Figure 3 Effect of: (a) oxygen concentration, and (b) oxidation rate constant *k* on the dominant iron removal mechanism (pH = 7.7, Fe = 1.72 mg/l, depth of supernatant = 0.9 m, filtration rate = 10 m/h)

Lee, 1961; Sung and Morgan, 1980). This implies that the precise determination of oxidation rate constant *k* for a given groundwater is very important for an accurate prediction of the percentages of iron removed by floc filtration and adsorptive filtration.

Effect of pH and alkalinity. Figure 4 presents the effect of pH and alkalinity on the percentage of iron removed by floc filtration and adsorptive filtration iron removal mechanism. It is clear from Figure 4a that pH has a pronounced effect of dominant iron removal mechanism and in the presence of oxygen floc filtration is dominant at higher pH and adsorptive filtration is dominant at lower pH. An increase in pH from 7.7 to 8.2 increases the percentage of iron removed by floc filtration from 28% to 94%. This is because the rate of iron(II) oxidation is proportional to the square of the hydroxyl ion (OH^-) concentration (Stumm and Lee, 1961). Figure 4b shows that an increase in alkalinity from 25 mg HCO_3^-/l to 400 mg HCO_3^-/l has no significant effect on the dominant iron removal mechanism for given groundwater. However, when the alkalinity or the buffer capacity of the water is very low, the pH may decrease with iron(II) oxidation consequently influencing the removal mechanism.

Discussion

Calculation of the amount of iron removed by either of these two mechanisms gives an indication of the dominant iron removal mechanism. The model calculations and sensitivity analysis also suggest the possible actions which could be carried out to maximise the adsorptive iron removal. For this, the majority of the iron entering filter in the

Figure 4 Effect of: (a) pH, and (b) alkalinity on the dominant iron removal mechanism (Fe = 1.72 mg/l, O_2 = 8.62 mg/l, oxidation rate constant $k = 6.78 \times 10^{15}$ l^3 mol^{-3} min^{-1}, depth of supernatant = 0.9 m, filtration rate = 10 m/h)

filter should be maintained in the iron(II) form. This can be achieved by one or combination of the following measures.

- Reducing the depth of supernatant.
- Increasing the rate of filtration.
- Reducing the oxygen concentration in the feed water by: (i) partial aeration (aerating all the feed water to lower oxygen concentration), or (ii) split aeration (aerating only the part of the feed water and mixing it with the unaerated raw feed water to obtain the influent of desired oxygen concentration). With limited aeration, CO_2 removal and pH increase is low and consequently pre-oxidation of iron(II) is low.

Model calculations showed that even under conditions that are favourable for floc filtration iron removal (high pH, high O_2 and higher depth of supernatant), adsorptive filtration contributes considerably to the total iron removal. It is also important to note that this model assumes no adsorption of onto filter media while calculating the contribution of floc filtration. However in reality, part of the iron(II) entering the filter bed is removed by adsorption onto the filter media and consequently less iron(II) is available for oxidation. Hence, it is likely that the actual contribution of floc filtration in overall removal is smaller than that predicted by the model. Further development of the model should take this aspect into account.

Conclusions

- Decision support system (DSS) for iron removal from groundwater could be an useful tool in: (i) analysis and optimisation of the iron removal in existing groundwater treatment plants; (ii) formulation of strategies for switching from the floc-filtration mode to the adsorptive-filtration mode of iron removal; and (iii) design of new iron removal plants.
- The feed water pH, iron(II) oxidation rate constant k and pre-oxidation time (a function of depth of supernatant and filtration rate) are the main parameters which determine the extent of floc filtration and adsorptive filtration under given conditions.
- Predominantly adsorptive iron removal in filters can be achieved by reducing the depth of supernatant, increasing the rate of filtration and/or controlling the oxygen concentration in the feed water.

Acknowledgements

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Appendix: equations used in calculations

Iron oxidation kinetics:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+ \tag{1}$$

$$\frac{-d[Fe(II)]}{dt} = k\,[O_2]\,[Fe(II)]\,[OH^-]^2 \tag{2}$$

where $d[Fe(II)]/dt$ is the rate of iron(II) oxidation (mol l^{-1} min^{-1}), k is the oxidation rate constant (l^3 mol^{-3} min^{-1}), $[O_2]$ is the actual concentration of oxygen in water (mol/l), $[Fe(II)]$ is the concentration of iron(II) (mol/l), and $[OH^-]$ is the concentration of hydroxyl ions (mol/l).

Assuming that pH and O_2 concentration are constants and on integrating Eq. (2), we have:

$$Fe(II)_t = Fe(II)_0 e^{-k[O_2][OH^-]^2 t} \tag{3}$$

Change in pH and alkalinity:

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \tag{4}$$

$$H^+ + CO_3^- \rightarrow HCO_3^- \tag{5}$$

For CO_2-HCO_3^- system:
$$pH = pK_1 + \log\left(\frac{[HCO_3^-]}{[CO_2]}\right) \tag{6}$$

For CO_3^{2-}-HCO_3^- system:
$$pH = pK_1 + \log\left(\frac{[HCO_3^-]}{[CO_2]}\right) \tag{7}$$

$$pK_w = pH + pOH \tag{8}$$

where $pH = -\log[H^+]$ and $pOH = -\log[OH^-]$.

All concentrations are expressed in moles per litre. Constants pK_1, pK_2 and pK_w are temperature dependent. At 10°C their values are 6.46, 10.49 and 14.54, respectively (Snoeyink and Jenkins, 1980; Stumm and Morgan, 1996).