

Effect of Fulvic Acid on Adsorptive Removal of Cr(VI) and As(V) from Groundwater by Iron Oxide-Based Adsorbents

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Abstract Natural contamination has become a challenging problem in drinking water production due to metal contamination of groundwater throughout the world, and arsenic and chromium are well-known toxic elements. In this study, iron oxide-coated sand (IOCS) and granular ferric hydroxide (GFH) were used to study the effects of fulvic acid (FA) on the adsorptive removal of Cr(VI) and As(V) from synthetic groundwater. IOCS and GFH were characterized by SEM/EDS, and experiments were performed at different pH levels (6, 7, and 8). The surface of IOCS and GFH showed a high content of Fe and O (75 and 60 % of the atomic composition, respectively), suggesting that they can highly effectively adsorb Cr(VI) and As(V). Adsorption tests with the simultaneous presence of As(V) and FA, on the one hand, and Cr(VI) with FA, on the other hand, revealed that the role of FA on chromate and arsenate adsorption was insignificant at almost all pH values

investigated with both adsorbents. A small influence as a result of FA was only observed for the removal of As(V) by IOCS at pH 6 with a decrease of 13 and 23 % when 2 and 5 mg/l were added to the synthetic water, respectively. It was also found that organic matter (OM) was leached from the IOCS during batch adsorption experiments. The use of FEEM revealed that humic-like, fulvic-like, and protein-like organic matter fractions are present on the IOCS surface.

Keywords Adsorption · Iron oxide-based adsorbents · Groundwater · As(V) · Cr(VI) · Fulvic acid

1 Introduction

Groundwater is considered as a major source of drinking water in many countries because of its general advantages such as constant and good quality, and accessibility (Vrba and Gun 2004). However, this source is vulnerable to contamination by several substances. Impurities in groundwater originate from natural activities (non-human), e.g., rainwater, rock, and soils in the earth crust, seawater intrusion, biological activities in the soil, and animal activities. Natural contamination has become a challenging problem in drinking water production due to metal contamination of groundwater throughout the world, and arsenic and chromium are well-known toxic trace elements. The World Health Organization (WHO 2011) set a standard value for a maximum contaminant level (MCL) for arsenic and

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total chromium in drinking water at 10 and 50 $\mu\text{g/l}$, respectively.

Arsenic occurs in groundwater predominantly in inorganic forms, with speciation and valence depending on the oxidation-reduction conditions in the aquifer and the pH of the water (Smedley and Kinniburgh 2002; Wang et al. 2002). Naturally occurring chromium concentrations in groundwater are generally very low (less than 2 $\mu\text{g/l}$), although concentrations as high as 120 $\mu\text{g/l}$ have been reported (Sharma et al. 2008). The concentration of naturally occurring organic matter is low, and cannot be considered as a contaminant of natural water (Zaporożec 2004).

Aquatic natural organic matter (NOM) is present in groundwater around the world, the concentration being between 0.5 and 10 mg/l of organic carbon. In general, NOM can be classified into two categories, the humic and non-humic fractions. The humic fraction is more hydrophobic and comprises humic and fulvic acids (Owen et al. 1995). Fulvic acid (FA) is the part of the humic substances that is soluble in water under all pH conditions, remaining in solution after the precipitation of humic acid by acidification (<http://www.ar.wroc.pl/~weber/humic.htm>, 2013). Basically, NOM is considered non-toxic, but its presence in groundwater imparts an unwelcome color. Elevated color levels in groundwater can have an effect on taste and odor, and can cause several problems during groundwater treatment and distribution. Another indirect but very important effect is the formation of potentially harmful disinfection by-products and/or biological re-growth in the distribution systems (Genz et al. 2008).

It has been shown that metal (hydr)oxides play an important role in the adsorption of heavy metals (Khaodhiar et al. 2000; Petrusevski et al. 2002; Amy et al. 2005), as well as in the adsorption of organic substances (Ali and Dzombak 1996; Filius et al. 1997; Gu et al. 1994, 1995; Wershaw et al. 1995). Different factors including the nature and characteristics of the adsorbate, the ionic concentration, the presence of organic matter, the pH, and the temperature can affect the effectiveness of the metal adsorption (Sharma et al. 2002; Abdu-Salam and Adekola 2005).

The main goal of this research was to assess the effect of FA on the adsorptive removal of arsenate—As(V)—and chromate—Cr(VI)—by iron oxide-coated sand (IOCS) and granular ferric hydroxide (GFH) at different pH values. The research focused on As(V) and Cr(VI) due to their toxicity and their behavior during the

adsorption process such as their solubility and charge. FA was chosen as a model compound for NOM because FA is the most significant NOM acid component, is highly soluble, and exhibits a (pH-dependent) negative charge. As several studies have found that the negative charge of fulvic acid increases with increasing pH (Filius et al. 1997), fulvic acid is expected to compete with As(V) and Cr(VI) for adsorption surface sites of IOCS and GFH.

2 Methods

2.1 Adsorbents

GFH was obtained from the manufacturer GEH Wasserchemie in Osnabruck (Germany). IOCS was obtained from the Dutch water company Vitens, from the water treatment plant Brucht that treats groundwater with high iron content. For the screening and batch adsorption experiments, pulverized coatings of IOCS and pulverized GFH grains were used. After grinding, the bulk adsorbent was sieved through a 63- μm sieve to obtain the required size fraction. The physical properties of the GFH and IOCS adsorbents are given in Table 1.

2.2 Solutions Preparation

A stock solution containing 100 mg/l of Cr(VI) was prepared from analytical grade potassium chromate (K_2CrO_4), while the stock solution of As(V) was prepared from a standard As(V) solution (1,000 mg/l in 2 % HNO_3) from Sigma-Aldrich. The stock solution of FA was prepared from powdered Suwannee River fulvic acid from the International Humic Substances Society (IHSS). The required amount of sodium bicarbonate (NaHCO_3) was added to achieve the targeted concentration of 100 mg/l HCO_3^- in the synthetic water.

2.3 Batch Adsorption Experiments

Several batch adsorption experiments were carried out to investigate the effect of FA on As(V) and Cr(VI) removal. The FA concentration varied between 0 and 5 mg/l, and the concentration of As(V) and Cr(VI) was 0.2 mg/l. The adsorption tests were performed at pH 6, 7, and 8, and the adsorbent dosage was 0.2 g/l. Acid-cleaned and closed 500-ml plastic bottles, fitted with tubes for periodic sampling, were filled with synthetic

Table 1 Physical characteristics of GFH and IOCS

	Grain size (mm)	Surface area (m ² /g)	pH _{ZPC}	Porosity (%)	Moisture content (%)	Bulk density (g/cm ³)
GFH	0.2–2.0	555	7.5–8.0	0.75–0.80	43–48	1.32
IOCS	1.4–5.6	261	6.9	0.53	13.3	1.05

water, and the required amount of pulverized IOCS or GFH was added. Subsequently, the pH was adjusted to the required values using 1 M HNO₃ or NaOH solutions. Bottles were placed on an Innova 2100 rotary shaker at 100 rpm and kept at 20 °C for 24 h. Blank tests were carried out without adsorbent addition. All the water samples were filtered through a 0.45- μ m membrane filter using a polypropylene syringe filter.

2.4 Analytical Methods

As(V) and Cr(VI) were analyzed with an atomic absorption spectrometer (Thermo Elemental Solaar MQZe-GF 95) with an auto-sampler and a graphite furnace (AAS-GF). For dilution, acidified demineralized water was used. Five percent Ni in 1 wt% HNO₃ was used as the matrix modifier. Water samples were passed through a 45- μ m cellulose acetate membrane filter and acidified with HCl to a pH below 2. IOCS and GFH were characterized by SEM/EDS methods (Modgi et al. 2006). Scanning electron microscopy (SEM) images and electron dispersive spectroscopy (EDS) spectra were collected with a Quanta 200D SEM machine (FEI, Netherlands) equipped with an EDAX (Ametek, UK) EDS instrument.

For NOM analysis, the total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were measured by a SHIMADZU TOC-VCPN analyzer. A fluorescence excitation-emission matrix (EEM) was developed using a Horiba Jobin Yvon FluoroMax-3 spectrofluorometer with a xenon lamp as the excitation source. Samples were filtered through a 0.45- μ m cellulose acetate membrane filter. The filters were soaked in Milli-Q water for 24 h before use, because the membrane filters could influence the reading by leaching DOC. Samples with concentrations of organic carbon above 20 mg/l were always diluted before analysis. The EEM contours were plotted in MATLAB. The EEM spectra, representing a three-dimensional plot of fluorescence intensity versus excitation and emission wavelengths, were used to reveal changes in protein-

like organic matter (corresponding to an EEM peak at lower excitation/emission wavelengths) and humic-like organic matter (corresponding to an EEM peak at higher excitation/emission wavelengths).

The ultraviolet absorbance (UVA) was performed using a UV-2501 PC spectrophotometer, and the specific ultraviolet absorbance (SUVA) was calculated. Since water samples absorb UV light at wavelengths ranging from 200 to 300 nm, measurements of UV absorbance (UVA) were carried out at a wavelength of 254 nm. Specific UVA (SUVA) was then calculated by dividing a particular UVA₂₅₄ by its corresponding DOC value. SUVA is an indicator of the relative aromaticity of organic components.

3 Results

3.1 SEM/EDS Analysis of IOCS and GFH

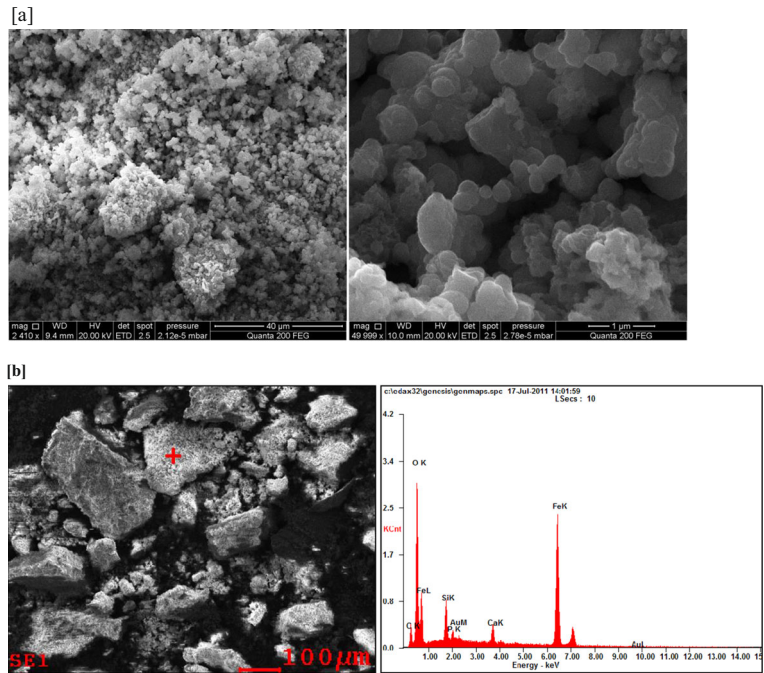
SEM/EDS results (Fig. 1a and b) showed that the surface of the virgin IOCS exhibits an accumulation of sub-micron sponge-like grain formations. The presence of C, O, Si, P, Ca, and Fe was identified in the IOCS coating. EDS analysis suggested that iron and oxygen represent about 75 % of the atomic IOCS coating composition in addition to about 10 % carbon. Si, P, and Ca were detected as trace elements. The EDS surface analysis of the GFH (Fig. 2) showed that Fe and O represent about 32 and 28 % of its chemical composition, respectively. Spot analyses indicate that the relative abundance of these elements on the surface varies considerably. These spot analyses also revealed traces of Na, Si, S, Cl, K, and Ca.

3.2 Batch Experiments

3.2.1 Stability of Cr(VI)

The stability of Cr(VI) in synthetic water was assessed in order to ensure that no precipitation takes place under the conditions applied. The stability of Cr(VI) was

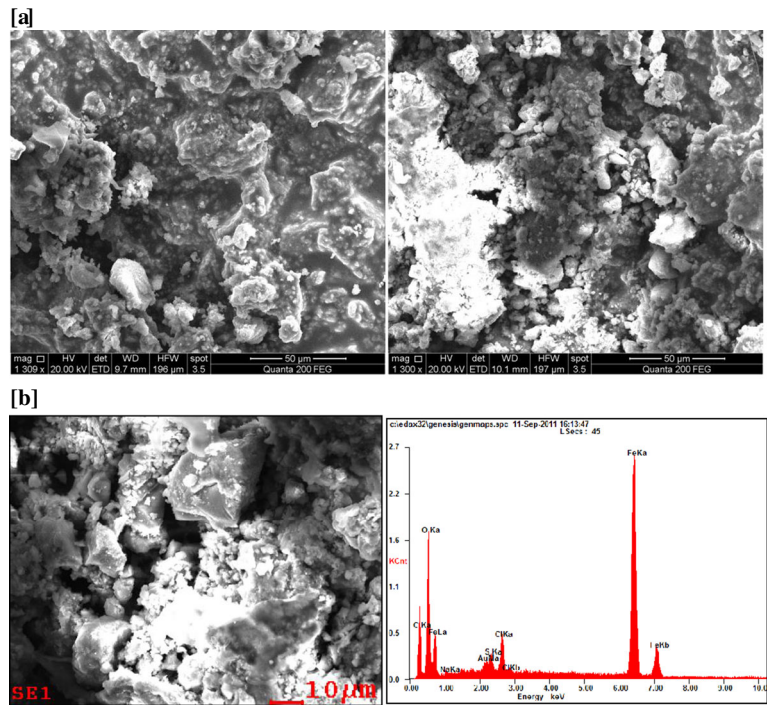
Fig. 1 SEM view (a) and EDS results (b) of the virgin IOCS



examined in the absence and presence of FA, at pH 6, 7, and 8 for a period of 24 h. The initial concentrations of Cr(VI) and FA were 0.2 and 2 mg/l, respectively. It was found that Cr(VI) was stable under both conditions

(with and without FA). Only a very slight reduction of 1 % (in synthetic water without FA) and 2 % (in model water with FA) in concentration of Cr(VI) was observed at pH 6. The stability of As(V) was not tested because it

Fig. 2 SEM view (a) and EDS results (b) of the virgin GFH



is known that arsenic does not precipitate easily (Masscheleyn et al. 1991; Langmuir et al. 2006).

3.2.2 Screening Tests on Adsorption of As(V), Cr(VI), and FA by IOCS and GFH

Adsorption tests with single-system synthetic waters containing either As(V), Cr(VI), or FA were performed at pH 6, 7, and 8. The efficiencies of As(V) and Cr(VI) adsorption on IOCS and GFH are shown in Fig. 3. Under the conditions applied, IOCS appears to be less effective in As(V) removal as compared to GFH. At pH 6, the adsorption of As(V) was 57 % by IOCS versus 93 % by GFH. GFH was also more effective for As(V) removal at other pH values tested. Besides, As(V) adsorption with GFH was considerably faster with 74, 57, and 54 % of As(V) removal at pH 6, 7, and 8, respectively, after only 2 h. Unlike the results of adsorption of As(V), Cr(VI) was adsorbed less effectively by both IOCS and GFH. GFH was confirmed to be much more effective than IOCS at pH 6 (Cr(VI) removal of 39 and 8 %, respectively). At higher pH values, both adsorbents were ineffective for Cr(VI) removal.

The removal of FA with IOCS and GFH was also assessed at the same pH values (6, 7, and 8). Figure 4 shows that FA is poorly removed by both adsorbents. As for As(V) and Cr(VI), FA was better adsorbed on GFH achieving 21, 13, and 8 % removal at pH 6, 7, and 8, respectively. In contrast, FA concentration in synthetic water with IOCS increased by 5, 12, and 6 % at pH 6, 7, and 8, respectively.

3.2.3 Screening Tests on the Effect of FA on Adsorption of As(V) and Cr(VI) by IOCS and GFH

The effect of FA on As(V) adsorption at pH 6 was assessed using synthetic waters containing three concentrations of FA (0, 2, and 5 mg/l). A slight decrease in the removal efficiency of As(V) with IOCS was observed at increasing FA concentrations (e.g., 63, 50, and 40 % As(V) removal from synthetic water with 0, 2, and 5 mg/l of FA, respectively, after 24 h of contact time). However, the presence of FA did not affect the removal of As(V) by GFH (Fig. 5).

In the absence of FA, only 11 % of the Cr(VI) was removed by the IOCS. The adsorption efficiency slightly decreased to 10 % when 5 mg/l of FA was added to the model water (Fig. 5). Thus, under the conditions applied, FA did not appear to be a competitive species that can further reduce the poor performance of IOCS for Cr(VI) adsorption. GFH showed much better removal of Cr(VI). In the absence of FA, 82 % of Cr(VI) was removed, while the removal efficiency was reduced to 77 and 75 % when 2 and 5 mg/l of FA were added to the model water, respectively (Fig. 5). Thus, under the conditions applied, the influence of FA on the adsorption of Cr(VI) by IOCS and GFH was rather limited.

3.3 Removal of FA by IOCS

Additional batch adsorption tests were performed to study the removal of FA (present in the model water at a concentration of 2 mg/l) by different dosages of IOCS

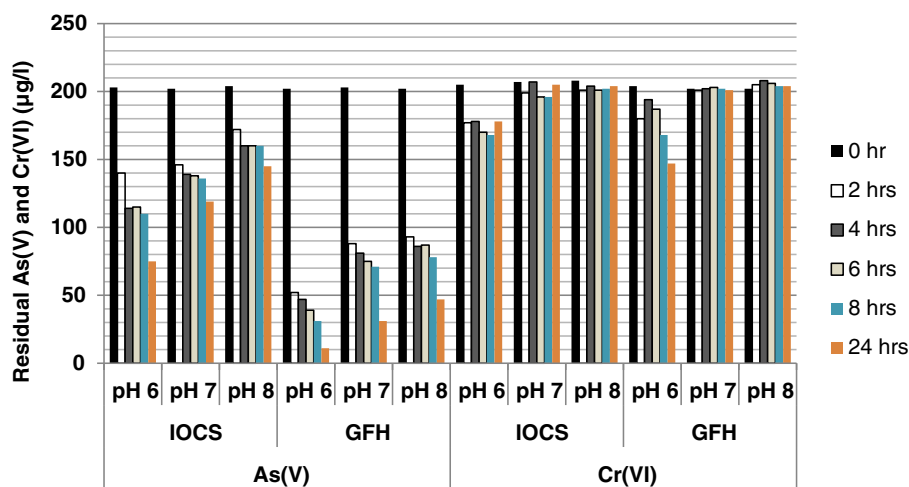


Fig. 3 Adsorption of As(V) and Cr(VI) by IOCS and GFH. Model water composition [As(V)] or [Cr(VI)]=0.2 mg/l, [HCO₃⁻]=100 mg/l, pH 6, 7, and 8; dosage of adsorbent=0.2 g/l

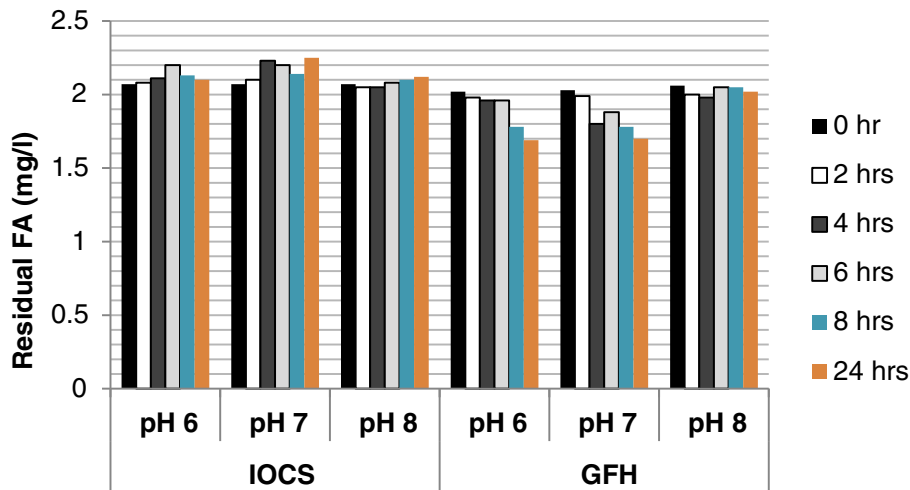


Fig. 4 Adsorption of FA by IOCS and GFH at pH 6, 7, and 8. Model water composition: [FA]=2 mg/l, [HCO₃⁻]=100 mg/l and dosage of adsorbent=0.2 g/l

(blank, 0.2, 0.5, 1, 2, 5, and 10 g/l) at pH 6 (Fig. 6). As expected, the results from the blank samples showed that FA remained relatively stable over the 10 days of the experiment. It was also observed that the concentration of FA in the model water increased with increasing IOCS dosage and contact time. With prolonged contact time (10 days), the concentration of FA increased by 59, 122, 238, and 443 % at IOCS dosages of 1, 2, 5, and 10 g/l, respectively. The results obtained strongly suggest that IOCS releases some OM into the model water (Fig. 6).

The hypothesis of the release of organic matter from the IOCS was verified by submerging different amounts of IOCS (2, 5, and 10 g/l) into the demi water, which were then shaken at 100 rpm for 24 h at different pH values (6, 7, and 8). The values of total organic carbon (TOC) and dissolved organic carbon (DOC) increase as the amount of IOCS increases.

With an increase of synthetic water pH and IOCS dosage, the concentration of organic matter measured as DOC increases as well (Table 2); however, the portion of leached amount of organic matter decreased. Results

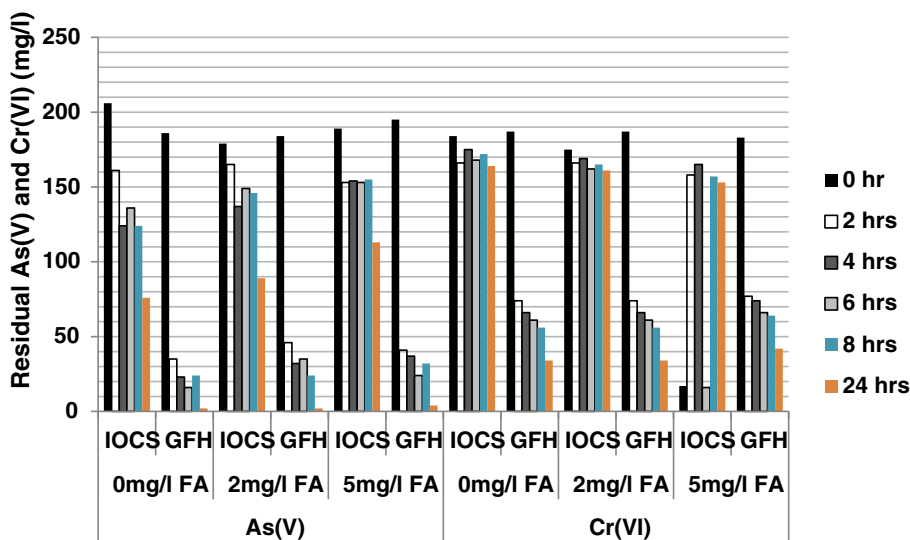


Fig. 5 Removal of As(V) and Cr(VI) at pH 6 as a function of fulvic acid concentration. Model water composition: As(V) and Cr(VI)=0.2 mg/l, HCO₃⁻=100 mg/l, dosage of adsorbent=0.2 g/l, concentration of FA=0, 2, and 5 mg/l

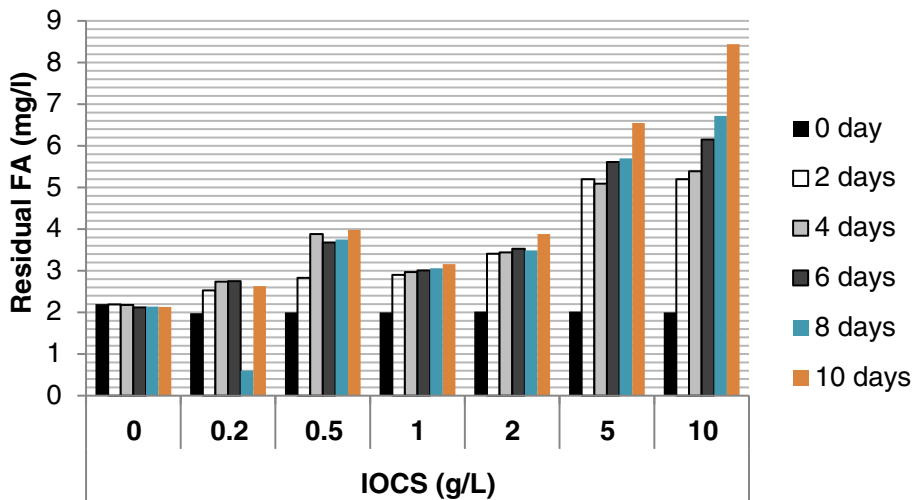


Fig. 6 Leaching of FA as a function of IOCS dosage and contact time. Model water composition: FA=2 mg/l, [HCO₃⁻]=100 mg/l, pH=7.0, and IOCS dosage 0–10 g/l

obtained indicated that the portion of OM leaching from IOCS was not linearly correlated with the total amount of OM introduced in synthetic water with increasing IOCS dosage.

Different fractions of the organic matter leached from IOCS were analyzed by the fluorescence excitation-emission matrix (FEEM) as shown in Fig. 7. Table 3 shows the excitation and emission of different fractions of OM. The excitation was observed at 240 and 300 nm and at 270 nm for humic-like, fulvic-like, and protein-like organic matter fractions, respectively. The emission was observed at around 430 and 420 nm for humic-like and fulvic-like organic matter fractions, respectively, and at 310 nm for protein-like organic matter fractions. Table 3 also shows that the amount of OM leached from IOCS increased with prolonged contact time. From 0 to 96 h of contact time, the intensity increased by 46, 80, and 19 % for humic-like, fulvic-like, and protein-like

organic matter fractions, respectively. The increase in the intensity of the fulvic-like organic matter fraction of 80 % clearly confirms the leaching of FA in significant amounts from IOCS.

3.4 Removal of NOM and Arsenic from Serbian Groundwater by IOCS

In order to verify the effect of NOM on arsenic adsorption with IOCS, a batch adsorption test was performed with groundwater from Zrenjanin (Serbia) that contains a very high DOC of about 7.55 mg/l, and total As concentration of about 80 µg/l. Batch experiments with a contact time of 24 h were performed at pH 6, 7, and 8. In addition to arsenic removal, the concentrations of DOC and UV were monitored during adsorption tests, and related SUVA values were calculated. Figure 8 shows that As contained in the Serbian groundwater is

Table 2 Leaching of organic matter (OM) from IOCS in demineralized water

IOCS dosage (g/l)	Total amount of OM in the bottle (mg/l)	OM leached (mg/l)			OM leached (%)		
		pH 6	pH 7	pH 8	pH 6	pH 7	pH 8
0.2	34	0.3	0.7	1.4	0.9	2.1	4.1
0.5	86	0.8	1.2	2.0	0.9	1.4	2.3
1	171	1.2	1.8	3.8	0.7	1.1	2.2
2	342	1.9	3.0	5.6	0.6	0.9	1.6
5	855	3.8	5.5	9.8	0.4	0.6	1.1
10	1,710	4.6	8.0	13.0	0.3	0.5	0.8

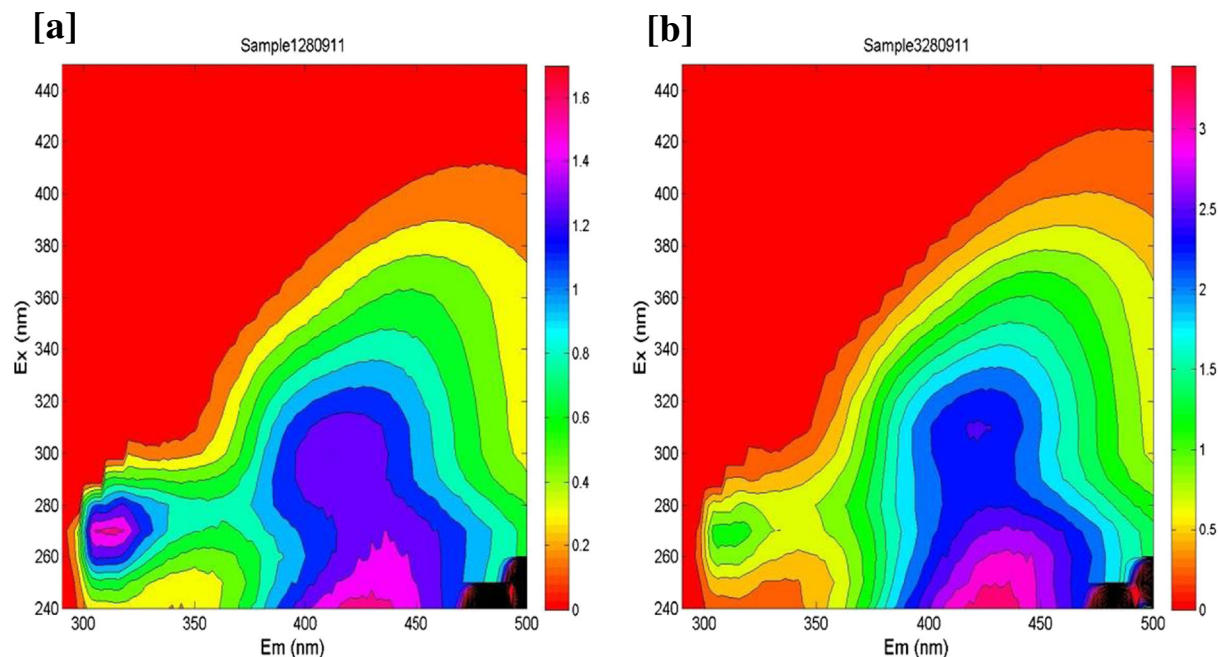


Fig. 7 FEEM spectra of OM that leached from IOCS in demineralized water. **a** After 24 h of contact time. **b** After 96 h of contact time

well adsorbed by IOCS, with a removal efficiency of 78, 65, and 37 % at pH 6, 7, and 8, respectively.

It was also found that the DOC concentration significantly increased, in line with results obtained in the experiments with model water and IOCS as adsorbent. UVA values were almost constant, while SUVA values decreased from 0.49 to 0.45 L/mg m at pH 6, and from 0.54 to 0.48 L/mg m at pH 7, indicating that OM was released from IOCS. However, the SUVA value changed only slightly at pH 8 after 24 h of contact time (Fig. 9).

An EEM of the Serbian groundwater was done to characterize the different fractions of OM present. The groundwater was found to contain humic-like and fulvic-like organic matter fractions with high intensity compared to the ones leaching from the IOCS, 10.5 and 5.7 Int/mg C for humic and fulvic fractions, respectively (Fig. 10).

4 Discussion

4.1 Screening Tests on Adsorption of As(V), Cr(VI), and FA by IOCS and GFH

This study showed that IOCS and GFH can remove both As(V) and Cr(VI). Their capability to remove As(V) and Cr(VI) can be related to the high amounts of iron and oxygen revealed by SEM/EDS analyses. However, the screening tests have shown that IOCS was less effective for As(V) adsorption as compared to GFH. This can be explained by the higher porosity and larger surface area of GFH, as shown in Table 1. Screening tests also showed that there was more effective adsorption of both As(V) and Cr(VI) by GFH and IOCS at pH 6. This is probably related to the point of zero charge (pH_{pzc}) of the IOCS and GFH (Table 1). As pH 6 is less than the

Table 3 FEEM analyses of OM leaching from IOCS in demineralized water at 100 rpm

	After 24 h (Fig. 7a)			After 96 h (Fig. 7b)		
	Humic	Fulvic	Protein	Humic	Fulvic	Protein
Excitation	240	300	270	240	310	270
Emission	428	416	312	430	422	310
Intensity	1.608	1.397	1.062	2.352	2.515	1.26

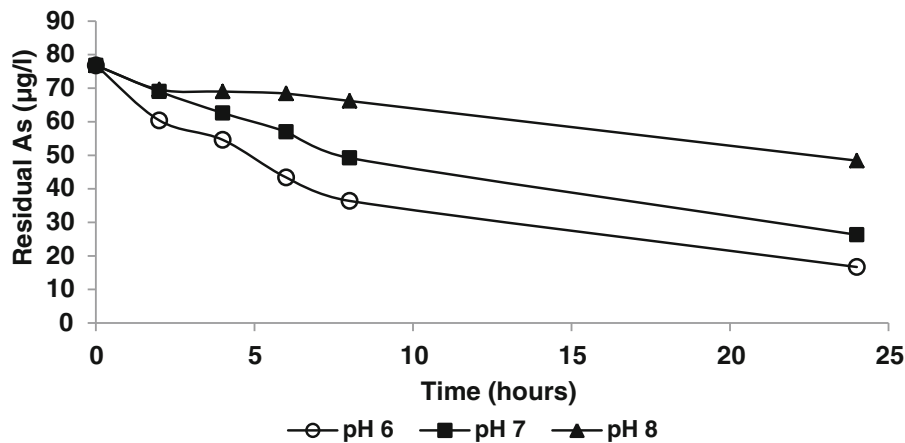


Fig. 8 Effect of pH on adsorptive removal of As from groundwater from a water production well in Zrenjanin (Serbia) with 7.6 mg DOC/l. IOCS dosage 0.2 g/l

pH_{pzc}, the surface of IOCS and GFH was positively charged and attracted negatively charged species such as Cr(VI) and As(V) (e.g., CrO₄²⁻ and H₂AsO₄⁻).

The results from this study showed that FA was not adsorbed at all by IOCS at all pH values tested, as is the case with GFH, at the higher pH value of 8. Only limited FA removal with GFH was observed at pH 6 and 7 with 16 % of FA adsorbed. This is in contrast with the results obtained by Gu et al. (1995) and Kaiser et al. (1997) that reported that both carboxylic and hydroxylic groups are involved in the binding of NOM by hematite and goethite. However, a limited FA removal at low pH is in agreement with the results obtained by Evanko and Dzombak (1998) who found that organic acids containing carboxylic groups have a maximum adsorption at low pH,

whereas compounds containing phenolic groups show a maximum adsorption at high pH. Yoon et al. (2004) also studied the adsorption of FA by boehmite (aluminum hydroxide) and reported that the adsorption of FA was better at lower pH and decreased as the pH was increased.

The variety of interactions taking place on mineral surfaces is largely determined by the differences in the amount and reactive ability of functional groups (Li et al. 2008). This could explain the low adsorption efficiency of FA by IOCS and GFH. In fact, the structure of FA contains not only a large proportion of aromatic moieties with OH⁻, HCOO⁻, and other oxygen rich groups but also contains a portion of aliphatic groups. All these functional groups may result in different hydrophobicity, aromaticity, and polarity of fulvic acid.

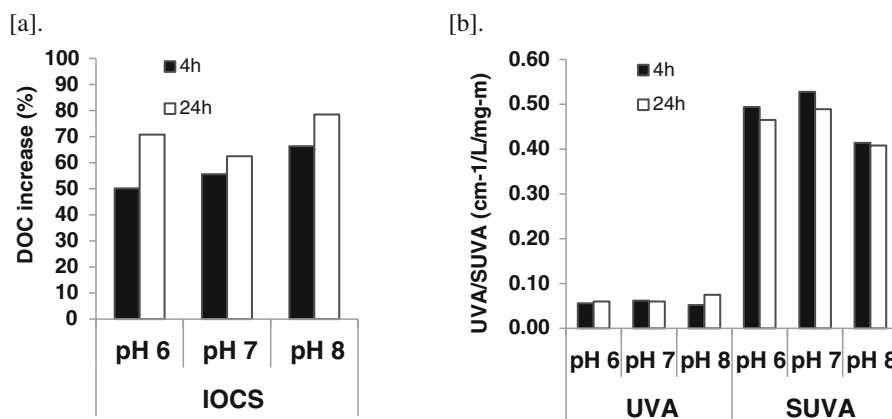


Fig. 9 Effect of pH and contact time on DOC concentration (a), UV254 absorbance and SUVA (b) during adsorptive arsenic removal with IOCS: groundwater from Zrenjanin, Serbia (DOC=7.55 mg/l). IOCS dosage 0.2 g/l

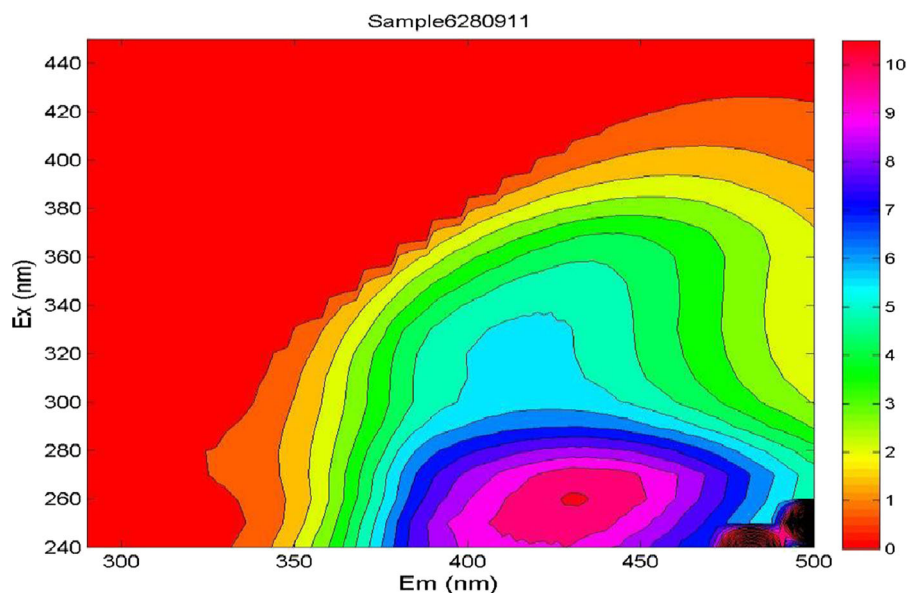


Fig. 10 FEEM spectra of OM contained in groundwater from Zrenjanin (Serbia)

4.2 Screening of Adsorption of As(V) and Cr(VI) in the Presence of FA by IOCS and GFH

The results from the present study showed a slight decrease in the removal efficiency of As(V) at increasing FA concentration (Fig. 5) and almost no effect on the removal efficiency of Cr(VI) by IOCS. The results also showed only very limited effect of FA on the removal efficiency of As(V) and Cr(VI) by GFH. In previous studies, the effects of several substances, commonly found in natural water, on arsenic sorption by hydrous ferric oxide (HFO) have been tested. These substances include bicarbonate (Appelo et al. 2002), silica (Swendlund and Webster 1999), phosphate (Manning and Goldberg 1996), and natural organic matter (NOM) (Redman et al. 2002). Redman et al. (2002) showed that NOM dramatically delayed the attainment of sorption equilibrium and diminished the extent of sorption for both arsenate and arsenite. Humic acid (HA) was found to exert an obvious inhibitory effect on Cr(VI) removal by zero valent iron (Fe^0) nanoparticles. HA adsorbed on the surface of Fe^0 nanoparticles and occupied the active surface sites, leading to a decrease in Cr(VI) reduction rates (Wang et al. 2011).

Thus, FA is expected to act as a competitive ion for As(V) and Cr(VI) adsorption on IOCS and/or GFH, and can consequently reduce the adsorption capacity of the adsorbent. Alternatively, the presence of FA might create complexes and change the behavior of the species in

the solution. Furthermore, negatively charged FA might influence the natural charge of the IOCS and GFH. Consequently, with the increasing concentration of FA species in the solution, negatively charged metals are expected to be less strongly attracted to more negatively charged adsorbents. However, under the conditions applied in this study, the effect of FA on Cr(VI) and As(V) adsorption on iron oxide based adsorbents was negligible.

4.3 Removal of FA by IOCS

The results from batch adsorption tests conducted with different dosages of IOCS revealed that organic matter was released from the adsorbent into the model water instead of being adsorbed (Figs. 6 and 7). The release of OM into the model water by IOCS suggests that FA will probably not affect the removal of As(V) and Cr(VI) through competition for adsorption sites on IOCS. With an increase of IOCS dosage and related total concentration of organic matter present in synthetic water, an increase of pH was observed (Table 2), together with a decrease of leaching rate. This coincides with the observation made by Grybos et al. (2009) who found that any chemical process that increases the pH might play a role in the solubilization of the organic matter. This can be linked with the results with natural groundwater (Fig. 10). IOCS being a by-product, the release of OM from IOCS probably indicates that the treated water at

the Brucht water treatment plant (Dutch water company Vitens) has a high amount of OM.

The observed absence of any adsorption of organic matter by IOCS is probably due to the conditions applied in this study, such as pH. According to previous studies (Weng et al. 2009; Chi and Amy 2004), adsorption of natural organic matter was well observed at low pH and decreased as the pH was increased. Thus, the pH range of natural groundwater (6.5–8.5) might not be favorable to the adsorption of FA and therefore will probably not affect the adsorption of As(V) and Cr(V).

5 Conclusions

- SEM/EDS analyses of IOCS and GFH showed a high iron and oxygen content, which together with the high surface area and porosity suggest that IOCS and GFH can adsorb Cr(VI), As(V), and FA.
- The screening batch tests showed that IOCS was less effective in adsorption of As(V) and Cr(VI) as compared to GFH, probably due to differences in surface area and porosity of both adsorbents. FA was poorly adsorbed by both IOCS and GFH, especially at higher pH values of 7 and 8.
- FA was expected to act as a competitive ion of As(V) and Cr(VI) and can consequently reduce the adsorption capacity of the adsorbent. However, the influence of FA on the adsorption of As(V) and Cr(VI) by IOCS and GFH under the conditions applied was very limited.
- Batch adsorption experiments with real groundwater demonstrated that effective removal of arsenic with IOCS can be obtained in the presence of a high concentration of natural organic matter.

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References

- Abdu-Salam, N., & Adekola, F. A. (2005). The influence of pH and adsorbent concentration on adsorption of lead, and cadmium on natural goethite. *African Journal of Science and Technology (AJST) Science and Engineering Series*, 6, 55–66.
- Ali, M. A., & Dzombak, D. A. (1996). Competitive sorption of simple organic acids and sulfate on goethite. *Environmental Science and Technology*, 30, 1061–1071.
- Amy, G., Chen, H. W., Dinzo, A., Gunten, U., Brandhuber, P., Hund, R., et al. (2005). *Adsorbent treatment technologies for arsenic removal*. USA: AWWA Research Foundation.
- Appelo, C. A. J., Van der Weiden, M. J. J., Tournassat, C., & Charlet, L. (2002). Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. *Environmental Science and Technology*, 36, 3096–3103.
- Chi, F. H., & Amy, G. L. (2004). Kinetic study on the sorption of dissolved natural organic matter onto different aquifer materials: the effects of hydrophobicity and functional groups. *Journal of Colloid and Interface Science*, 274(2), 380–391.
- Evanko, C. R., & Dzombak, D. A. (1998). Influence of structural features on sorption of NOM-analogue organic acids to goethite. *Environmental Science and Technology*, 32, 2846–2855.
- Filius, J. D., Hiemstra, T., & Van Riemsdijk, W. H. (1997). Adsorption of small weak organic acids on goethite: modeling of mechanisms. *Journal of Colloid and Interface Science*, 195, 368–380.
- Genz, A., Baumgarten, B., Goernitz, M., & Jekel, M. (2008). NOM removal by adsorption onto granular ferric hydroxide: equilibrium, kinetics, filter and regeneration studies. *Water Research*, 42, 238–248.
- Grybos, M., Davranche, M., Gruau, G., Petitjean, P., & Pédrot, M. (2009). Increasing pH drives organic matter solubilization from wetland soils under reducing conditions. *Geoderma*, 154, 13–19.
- Gu, B., Schmitt, J., Chem, Z., Liang, L., & McCarthy, J. F. (1994). Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environmental Science and Technology*, 28, 38–46.
- Gu, B., Schmitt, J., Chem, Z., Liang, L., & McCarthy, J. F. (1995). Adsorption and desorption of different organic matter fractions on iron oxide. *Geochimica et Cosmochimica Acta*, 59, 219–229.
- <http://www.ar.wroc.pl/~weber/humic.htm>. Accessed 28 June 2013.
- Kaiser, K., Guggenberger, G., Haumaier, L., & Zech, W. (1997). Dissolved organic matter sorption on subsoils and minerals studied by ¹³C-NMR and DRIFT spectroscopy. *European Journal of Soil Science*, 48, 301–310.
- Khaodhiar, S., Azizian, M. F., Osathaphan, K., & Nelson, P. O. (2000). Copper, chromium, and arsenic adsorption and equilibrium modelling on iron-oxide-coated sand, background electrolyte system. *Water, Air, and Soil Pollution*, 119, 105–120.
- Langmuir, D., Mahoney, J., & Rowson, J. (2006). Solubility products of amorphous ferric arsenate and crystalline scorodite (FeAsO₄·2H₂O) and their application to arsenic behavior in buried mine tailings. *Geochimica et Cosmochimica Acta*, 70, 2942–2956.
- Li, A., Xu, M., Li, W., Wang, X., & Dai, J. (2008). Adsorption characterizations of fulvic acid fractions onto kaolinite. *Journal of Environmental Sciences*, 20, 528–535.
- Manning, B. A., & Goldberg, S. (1996). Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. *Soil Science Society of America Journal*, 60, 121–131.

- Masscheleyn, P. H., Delaune, R. D., & Patrick, W. H. (1991). Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environmental Science and Technology*, 25(8), 1414–1419.
- Modgi, S., McQuaid, M. E., & Englezos, P. (2006). SEM/EDX analysis of Z-direction distribution of mineral content in paper along the cross-direction. *Pulp and Paper Canada*, 107(5), 124–127.
- Owen, D. M., Amy, G. L., Chowdhury, Z. K., Paode, R., McCoy, G., & Viscosil, K. (1995). NOM characterization and treatability. *Journal of the American Water Works Association*, 87, 46–56.
- Petrusevski, B., Boere, J., Shahidullah, S. M., Sharma, S. K., & Schippers, J. C. (2002). Adsorbent-based point-of-use system for arsenic removal in rural areas. *Journal of Water Supply: Research and Technology-Aqua*, 51, 135–144.
- Redman, A. D., Macalady, D. L., & Ahmann, D. (2002). Natural organic matter affects arsenic speciation and sorption onto hematite. *Environmental Science and Technology*, 36, 2889–2896.
- Sharma, S. K., Petrusevski, B., & Schippers, J. C. (2002). Characterization of coated sand from iron removal plants. *Journal of Water Science and Technology: Water Supply*, 2, 247–257.
- Sharma, S. K., Petrusevski, B., & Gary, A. (2008). Chromium removal from water: a review. *Journal of Water Supply: Research and Technology*, 57, 541–553.
- Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517–568.
- Swendlund, P. J., & Webster, J. G. (1999). Adsorption and polymerisation of salicylic acid on ferrihydrite, and its effect on arsenic adsorption. *Water Research*, 33, 3414–3422.
- Vrba, J., & Gun, J. (2004). The world's groundwater resources: contribution to chapter 4 of WWDR-2, International Groundwater Resources Assessments Centre, Report Nr IP-1.
- Wang, J., Zhao, F. J., Meharg, A. A., Raab, A., Feldmann, J., & McGrath, S. P. (2002). Mechanisms of arsenic hyperaccumulation in *Pteris vittata*. Uptake kinetics, interactions with phosphate, and arsenic speciation. *Plant Physiology*, 130, 1552–1561.
- Wang, Q., Cissoko, N., Zhou, M., & Xu, X. (2011). Effects and mechanism of humic acid on chromium (VI) removal by zero-valent iron (Fe⁰) nanoparticles. *Journal of Physics and Chemistry of the Earth*, 36, 442–446.
- Weng, L., Van Riemsdijk, W. H., & Hiemstra, T. (2009). Effects of fulvic and humic acids on arsenate adsorption to goethite: experiments and modeling. *Environmental Science and Technology*, 43(19), 7198–7204.
- Wershaw, R. L., Leenheer, J. A., Sperline, R. P., Song, Y., Noll, L. A., Melvin, R. L., et al. (1995). Mechanisms of formation of humus coatings on mineral surfaces 3. Composition of adsorbed organic acids from compost leachate on alumina. *Colloids and Surfaces*, 96, 93–104.
- WHO. (2011). *Guidelines for drinking water quality: health criteria and other supporting information* (2nd ed., Vol. 2). Geneva: World Health Organization.
- Yoon, T. H., Johnson, S. B., & Brown, G. E. (2004). Adsorption of Suwannee River fulvic acid on aluminum oxyhydroxide surfaces: an in situ ATR-FTIR study. *Langmuir*, 20, 5655–5658.
- Zaporozec, A. (2004). Groundwater contamination inventory, UNESCO IHP-VI, Series on Groundwater 2.