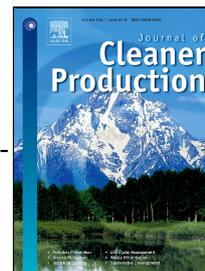


Accepted Manuscript

Efficient removal of arsenate from oxic contaminated water by colloidal humic acid-coated goethite: batch and column experiments



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PII: S0959-6526(18)31074-6
DOI: 10.1016/j.jclepro.2018.04.055
Reference: JCLP 12636
To appear in: *Journal of Cleaner Production*
Received Date: 24 October 2017
Revised Date: 05 April 2018
Accepted Date: 06 April 2018

Please cite this article as: Daniela Montalvo, Ruth Vanderschueren, Andreas Fritzsche, Rainer U. Meckenstock, Erik Smolders, Efficient removal of arsenate from oxic contaminated water by colloidal humic acid-coated goethite: batch and column experiments, *Journal of Cleaner Production* (2018), doi: 10.1016/j.jclepro.2018.04.055

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1 **Word count:7572**

2 **Efficient removal of arsenate from oxidized contaminated water by colloidal humic acid-**
3 **coated goethite: batch and column experiments**

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12

13 **Abstract**

14 Arsenic (As) contamination of groundwater frequently occurs and there is a need for cost-
15 effective *in situ* remediation techniques. The injection of iron oxide colloids coated with
16 humic substances has been proposed. This technology is based on injecting mobile humic
17 acid-coated goethite colloids that are subsequently deposited by aggregation in the
18 contaminated zone where the ionic strength is large, thereby creating an *in situ* reactive
19 barrier for As. While coagulation and deposition are desirable for colloid immobilization, its
20 effect on adsorption properties have been previously overlooked. This study was set up to
21 investigate if i) humic acid-coated goethite colloids retain their As(V) adsorption properties
22 after coagulation in quartz sand and ii) if batch As(V) adsorption data can predict As
23 immobilization in columns at variable flow conditions. Equilibrium batch adsorption
24 experiments showed that humic acid-coated goethite colloids coagulated and deposited on
25 quartz sand have equal As(V) adsorption capacity, but two-fold lower affinity than humic
26 acid-goethite colloids in suspension. This results indicated that there were some interactions
27 between the sand and colloids but the overall adsorption capacity was not affected. Column
28 experiments using sand coated with humic acid-goethite colloids (2.80 mg goethite g⁻¹ sand)
29 and stepwise injection of As(V) (1–4.9 mg As L⁻¹) showed a highly efficient As(V) removal
30 from the liquid phase as the outflow As(V) concentrations remained below the drinking water
31 limit (10 µg As L⁻¹) until about 45% of the sorbent capacity (30 mg As g⁻¹ goethite) was
32 reached. The flow rate dependent leachate As concentrations, including responses to stop-
33 flow events, illustrated non-equilibrium sorption. The equilibrium batch adsorption

34 parameters failed to predict the observed As(V) breakthrough curves, which were better fitted
35 with a chemical non-equilibrium consideration. This study confirms the feasibility of the
36 technology on lab-scale but suggests that safety factors must be embedded to account for
37 As(V) by-pass flow that could occur during field applications.

38

39 **Keywords**

40 iron oxide colloids, humic acids, reactive barrier, arsenic adsorption, transport, coagulation

41 1. Introduction

42 Arsenic (As) contamination of groundwater poses serious threat to the environment and
43 human health through use as drinking and irrigation water (Smedley and Kinniburgh, 2002).
44 It has been estimated that over 226 million people worldwide are exposed to As via the intake
45 of contaminated water and food (Murcott, 2012). Due to the high toxic nature of As and the
46 well documented negative health effects associated to its chronic exposure, the World Health
47 Organization (WHO) set a limit concentration of $10 \mu\text{g L}^{-1}$ for As in drinking water (WHO,
48 2011). This standard has been adopted in the legislation of many countries; however, in many
49 places the previous WHO limit of $50 \mu\text{g L}^{-1}$ is still in place mainly due to technical
50 difficulties and the lack of an effective remediation technology (Cundy et al., 2008).

51 Background As concentrations in natural water are mostly below the WHO guideline
52 value; however, elevated concentrations ($> 5000 \mu\text{g L}^{-1}$) have been reported in groundwater
53 linked to geogenic sources or anthropogenic activities (Smedley and Kinniburgh, 2002). In
54 aquatic environment the predominant forms of As are the inorganic species arsenite As(III)
55 and arsenate As(V). At circumneutral pH, As(V) as ($\text{H}_2\text{AsO}_4^{-1}$ and HAsO_4^{-2}) is the most stable
56 form of As in oxic water; whereas As(III) as (H_3AsO_3^0) is more prevalent in anoxic water
57 (Mohan and Pittman, 2007). Arsenite is more mobile and toxic than arsenate and both species
58 have strong affinity for iron oxides (*e.g.* ferrihydrite, goethite, hematite) (Dixit and Hering,
59 2003), also under natural conditions, where several competitors for association with iron
60 oxides coexist (Fritzsche et al., 2011). Hence, the use of iron oxides to adsorb and remove As
61 from groundwater have been widely investigated for remediation of contaminated sites
62 (Mohan and Pittman, 2007).

63 In recent years, nanoremediation has been proposed as a potential more cost effective
64 technology for *in situ* remediation of soil and groundwater (Karn et al., 2009).
65 Nanoremediation entails the use of colloidal particles, which are defined as material with at
66 least one dimension between 1–1000 nm (Christian et al., 2008). The large surface area and,
67 hence, high adsorption capacity make colloidal size particles very attractive for remediation
68 purposes compared to non-colloidal macro size aggregates. Additionally, small particles have
69 better mobility and can achieve a wider radius of influence after injection in the subsurface.
70 In this context, engineered goethite ($\alpha\text{-FeOOH}$) colloids, which have a very high affinity for
71 As(V), combine all desirable characteristics for *in situ* remediation of As contaminated
72 groundwater.

73 The application of goethite (Goe) colloids for *in situ* remediation of contaminated
74 groundwater consists of the injection of a suspension of colloids into the contaminated plume
75 and then deposition *in situ* by coagulation (*e.g.* particle aggregation) in the porous matrix of
76 the aquifer material due to the conditions of groundwater (high ionic strength, pH) (Tosco et
77 al., 2014). In this way, the colloidal Goe forms a *reactive zone* within the aquifer through
78 which contaminated water is filtered and decontaminated. The immobilization of the Goe
79 colloids after their injection into the aquifer is mandatory to prevent the export of Goe from
80 the reactive zone; however, coagulation may affect its sorption properties. Coagulation can
81 reduce the Goe reactive surface area and thus the adsorption properties for contaminants
82 (Hotze et al., 2010). While there has been substantial research on the adsorption of As onto
83 iron oxide minerals (Aredes et al., 2012; Mamindy-Pajany et al., 2011) and iron-coated sand
84 (Benjamin et al., 1996; Mähler and Persson, 2013) there are, to the best of our knowledge, no
85 studies that investigate the effect of aggregation and deposition of colloidal iron oxides onto a
86 substratum on their adsorption capacity of contaminants. This information is mandatory prior
87 to field applications and thus the relevance of this study.

88 A second aspect that needs investigation is to what extent the deposited particles form a
89 homogenous reactive barrier for instantaneous reaction with the contaminants. This translates
90 to the question if the reactive transport of the contaminant can be modelled assuming local
91 equilibrium *i.e.* if the resident solution concentration is locally at equilibrium with the
92 adsorbed concentration. In soils, the local equilibrium assumption (LEA) for the transport of
93 As is mostly violated, resulting in breakthrough curves featuring early breakthrough and
94 distinct tailing (Darland and Inskeep, 1997). Non-equilibrium transport of As has been
95 observed in studies that were conducted at large (32 cm h^{-1}) (Williams et al., 2003) or low
96 (0.34 cm h^{-1}) (Zhang and Selim, 2006) pore water velocities. For colloidal Goe deposition, it
97 is possible that homogenous thin layers of particles may yield a large contact area between
98 the mobile water and the sorbent, suggesting that the LEA may apply to a greater extent.

99 Against this background, a laboratory study was set up to investigate the feasibility of
100 applying Goe colloids as an adsorbent for the removal of As(V) in an aquifer. Previously,
101 humic acid-coated goethite (HA-Goe) colloids were synthesized showing sufficient colloidal
102 stability in water for subsurface injection. For these HA-Goe colloids, studies were set up to
103 address both questions described above, *i.e.* i) if the colloids retain their efficient As(V)
104 adsorption properties after deposition on an aquifer model substrate and ii) if the LEA is valid
105 during reactive transport. The column study addresses the question to what extent the WHO
106 drinking water limit can be met after passage of As-spiked solutions through a reactive zone,

107 where HA-Goe is present. It is hypothesized that there will be a reduction in As adsorption
108 capacity due to the aggregation and deposition of the HA-Goe colloids but that, overall, the
109 LEA during reactive transport is met. First, a range of batch As adsorption experiments with
110 colloidal HA-Goe and non-colloidal HA-Goe, which was deposited onto quartz sand, were
111 conducted. Second, a suite of column experiments were conducted at different As(V)
112 concentrations and different flow rates to determine its effects on the capacity and efficiency
113 of the reactive barrier for the removal of As(V). Additionally, flow interruption events were
114 included to gain better insights into possible kinetic limitations during the transport of As(V).
115 The LEA was tested by forward modelling the column data with the convection-dispersion
116 equation (CDE) using parameter values independently obtained from batch equilibrium
117 adsorption. This study did not address the adsorption of As(III) under anoxic conditions since
118 iron(III) oxides are not stable under such conditions, *i.e.* this study is addressing the potential
119 to remediate oxic groundwater.

120

121 **2. Materials and Methods**

122 2.1. Humic acid-coated goethite colloids

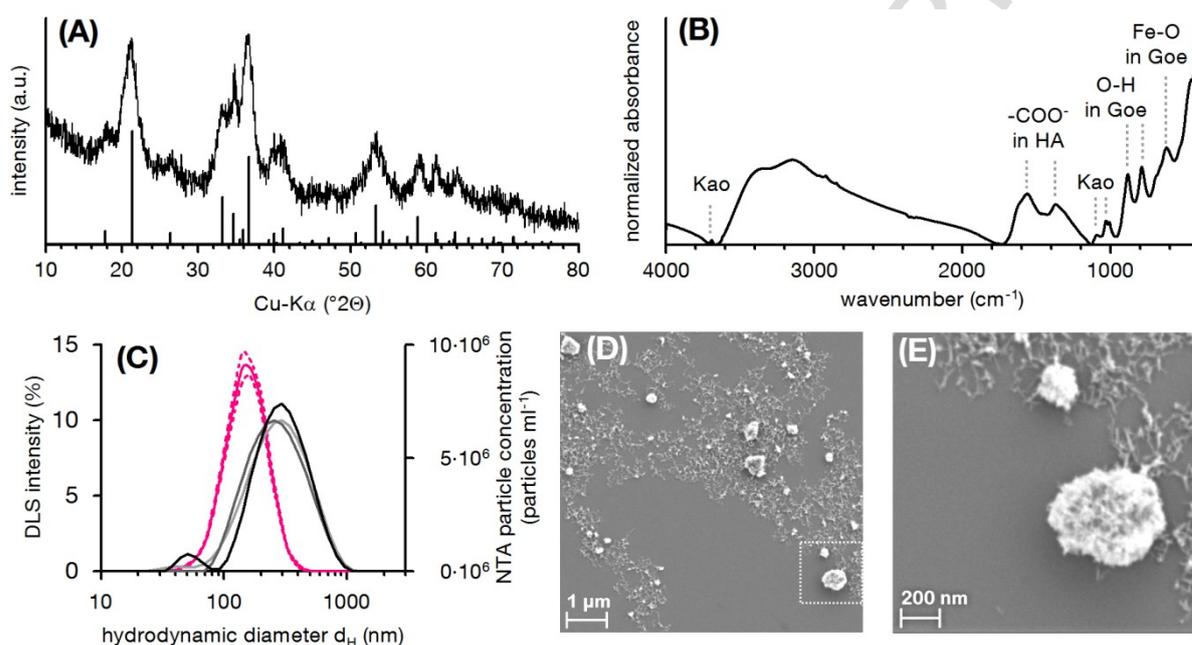
123 A stock suspension of goethite colloids coated with humic acids (HA-Goe) [66.4 g iron
124 (Fe) L⁻¹; 11.2 g organic carbon (OC) L⁻¹] was synthesized according to US patent 8921091B2
125 (Meckenstock and Bosch, 2014) and provided by the University of Duisburg-Essen.

126 Analysis with X-ray diffraction (XRD) and fourier-transform infrared (FTIR)
127 spectroscopy revealed that the desired HA-Goe colloids were obtained from synthesis (Figure
128 1A, B). The presence of humic acids (HA) was revealed by carboxyl-induced bands
129 (Socrates, 2004), which are commonly observed in mineral-associated natural organic matter
130 (Kleber et al., 2015) and by the negative net-surface charge of the HA-Goe colloids at pH 7.3
131 (Zeta potential -37 ± 4 mV), where goethite exhibits a net-positive surface charge
132 (Kosmulski, 2009). The observed traces of kaolinite were introduced due to impurities in HA
133 (Figure 1B; molar ratio goethite:kaolinite 283:1). Generally, HA-Goe used in this study had a
134 rather low long-range order compared to goethite that is commonly synthesized in the
135 laboratory. This was indicated by comparably broad reflexes in the diffractogram. This points
136 to comparably small-sized crystallites in HA-Goe, which was supported by a high specific
137 surface area (202.4 ± 0.3 m² g⁻¹; mean \pm min/max deviation from duplicate analysis) and by
138 the corresponding scanning electron microscopy (SEM) images (Figure 1D, E). The latter
139 showed nano-sized needles, which were assembled in aggregates of different size. The offset
140 in hydrodynamic diameters determined with dynamic light scattering (DLS; intensity-

141 weighted; 243 ± 125 nm) and nanoparticle tracking analysis (NTA; number-weighted; $186 \pm$
 142 69 nm; Figure 1C) indicate that the HA-Goe suspension contained colloids with a broad size
 143 distribution, while the number of smaller colloids (<200 nm) exceeded the number of larger
 144 colloids (>200 nm).

145 Unless otherwise indicated, the stock of HA-Goe colloids used in this study was diluted
 146 with Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) to the desired working concentration to perform the
 147 experiments.

148



149

150 Figure 1 Characterization of the initial humic acid-coated goethite (HA-Goe) colloids before
 151 exposition to 5 mM Ca^{2+} and/or deposition on quartz sand. (A) Powder X-ray diffractogram,
 152 (B) Fourier-transform infrared spectrum, (C) hydrodynamic diameter distributions as
 153 estimated with dynamic light scattering (DLS) analysis (triplicate; black/grey graphs) and
 154 nanoparticle tracking analysis (NTA; quintuplicate, solid pink graph: mean, dashed pink
 155 graphs: standard deviation), and (D,E) scanning electron images. (E) = region marked in (D).
 156 Bars in (A): goethite (Downs and Hall-Wallace, 2003). Kao: kaolinite, HA: humic acid, Goe:
 157 goethite.

158

159 2.2. Sand coated with humic acid-goethite colloids

160 Sand coated with humic acid-goethite colloids (HA-Goe-coated sand) was prepared by
 161 optimizing a procedure that favors the deposition of HA-Goe colloids on the substrate by
 162 adjusting the pH and ionic strength of the colloidal suspension (Scheidegger et al., 1993). As
 163 previously indicated, it was hypothesized that the as prepared HA-Goe-coated sand may have
 164 a much lower adsorption capacity compared to the HA-Goe colloids in suspension, since the
 165 reactive sites from deposited colloids may be hindered and not readily accessible for

166 adsorption. To prepare HA-Goe-coated sand, acid washed sand [Dorsilit 8, grain size 0.3–0.8
167 mm, silica (SiO₂) 97.9% by weight, 23 ± 4 μg Fe g⁻¹ sand] was mixed with 10 g L⁻¹ of HA-
168 Goe colloidal suspension diluted in 10 mM calcium chloride (CaCl₂) at pH 7. The high
169 calcium (Ca²⁺) concentration is likely the main factor causing aggregation by reducing the
170 negative potential at the humic acid coated surface through adsorption and/or forming Ca
171 bridges (Philippe and Schaumann, 2014). After the sand had settled, the supernatant
172 suspension was removed and the HA-Goe-coated sand was dried at room temperature. The Fe
173 content of the HA-Goe-coated sand (1.37 ± 0.10 mg Fe g⁻¹ sand) was determined by
174 inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific
175 ICAP 7400 Duo) after extraction with *aqua regia* [hydrochloric acid (HCl):nitric acid
176 (HNO₃)1:3]. This Fe concentration is equivalent to 2.80 ± 0.2 mg HA-Goe g⁻¹ sand.

177

178 2.3. Batch adsorption experiments

179 Adsorption isotherms were conducted at different pH (5.5–7.5) to determine the effect of
180 pH on the capacity of HA-Goe colloids to adsorb As(V). The pH values selected for batch
181 adsorption experiments are within the range for groundwater in natural conditions (Ayotte et
182 al., 2011). Batch experiments were carried out at a constant temperature of 20°C and in 50
183 mL polypropylene tubes. Aliquots of the HA-Goe suspension (4 mL, 0.7 g goethite L⁻¹) were
184 placed into a dialysis membrane for phase separation (Spectra/Por 4, 12–14 kDa cutoff) and
185 equilibrated with 20 mL of sodium arsenate (Na₂HAsO₄·7H₂O) solution of increasing As
186 concentrations ranging from 0 to 100 μM. The contact solutions also contained 5 mM CaCl₂
187 as background electrolyte and 5 mM of either 2-(N-morpholino)ethanesulfonic acid (MES
188 buffer, pH 5.5 and 6.5) or 3-(N-morpholino)propanesulfonic acid (MOPS buffer, pH 7.5) to
189 maintain constant pH. Preliminary tests showed that there was no influence of these buffers
190 on the adsorption of As(V) in the experimental conditions used. The HA-Goe suspensions
191 were shaken for 72 h on an end-over-end shaker. Thereafter, a subsample of the contact
192 solution was acidified (2% HNO₃) and the concentration of As in the solutions was
193 determined by ICP-OES (189 nm wavelength). The detection limit (DL) of the ICP-OES for
194 As is 1 μg L⁻¹ and preliminary comparison of the As solutions between inductively coupled
195 plasma mass spectrometry (ICP-MS; DL 0.05 μg L⁻¹) and ICP-OES showed excellent
196 agreement in the 5–50 μg As L⁻¹ range. The concentration of adsorbed As(V) was calculated
197 by subtracting the equilibrium solution concentration from the measured total initial
198 concentrations. All chemicals used in the experiments were of analytical grade and solutions
199 were prepared with Milli-Q water (18.2 MΩ cm⁻¹). The same procedure was adopted for

200 As(V) adsorbed onto HA-Goe-coated sand. For the adsorption experiments, 2 g of HA-Goe-
201 coated sand was placed into a dialysis membrane (12-14 kDa) and equilibrated for 72 h with
202 solutions containing increasing concentrations of As(V) 0-100 μM , 5 mM CaCl_2 and 5 mM
203 MOPS, pH 7.5. The Ha-Goe-coated sand was placed in dialysis membranes to have the same
204 experimental conditions as in the batch experiments with colloidal HA-Goe aggregates.
205 Additionally, a blank sand (Dorsilit 8, quartz sand uncoated) *i.e.* sand without HA-Goe
206 deposited colloids was included, and the As(V) adsorption data were corrected for sorption to
207 this uncoated sand to obtain As(V) adsorbed to the HA-Goe aggregates. All adsorption
208 experiments were conducted in duplicates.

209

210 2.4. Column experiments

211 Column experiments were conducted to evaluate the adsorption of As(V) onto HA-Goe-
212 coated sand at two inlet concentrations and three Darcy velocities 0.12, 0.3 and 1.5 cm h^{-1} .
213 The column experiments (10 columns in total) were run in duplicates for each of three flow
214 rates and two concentrations. Except for the low As(V) concentration where only two flow
215 rates were included (1.5 and 0.3 cm h^{-1}). Glass columns of 2 cm internal diameter and 12 cm
216 length were packed with 51 g of acid washed sand (Dorsilit 8) of which 15 g corresponded to
217 a layer of HA-Goe-coated sand which was located in the middle part of the column. Columns
218 were wet-packed to avoid air entrapment and were fitted with end-caps that contained *o*-rings
219 for sealing and fritted glass filters (P0, pore size 160–250 μm) to facilitate the uniform
220 distribution of the influent solution and prevent any loss of sand during the experiment. The
221 columns were leached bottom-up with a background solution containing 5 mM CaCl_2 and 2
222 mM MOPS pH 7.5 for several pore volumes (PV) to equilibrate the system. Solutions of
223 As(V) (low concentration: $1.01 \pm 0.01 \text{ mg L}^{-1}$ or high concentration: 4.58 ± 0.08 and $4.91 \pm$
224 0.10 mg L^{-1}) were injected for 57–149 PV until the effluent concentration was approximately
225 95% of the inlet concentration, which indicated the HA-Goe-coated sand was nearly saturated
226 with As(V). Thereafter, the columns were flushed with the background solution [without
227 As(V)] until the outflow concentrations were close to baseline. Effluent samples were
228 collected periodically and the concentration of As(V) was determined by ICP-OES after
229 acidification with 2% HNO_3 . Iron was also measured in the effluents and the concentrations
230 were lower than the limit of detection ($0.3 \mu\text{g Fe L}^{-1}$), which indicated no mobilization of
231 goethite during the experiments. During the injection of As(V), the flow was interrupted

232 completely for 24 h to evaluate the effect of extended liquid-solid contact times on the
233 transport of As(V).

234 The transport of bromide (Br⁻), which was added as inert tracer, was also conducted to
235 obtain physical transport parameters and to evaluate if physical non-equilibrium conditions
236 (*i.e.* immobile water region) existed inside the columns. A pulse of 0.6 pore volumes (PV) of
237 1 mM Br⁻ was injected and the effluent samples were analyzed by ion chromatography
238 (Dionex ICS-2000 with AS17-C columns).

239

240 3. Results and Discussion

241 3.1 Arsenate adsorption to humic acid-coated goethite colloids

242 Adsorption isotherms at pH 5.5, 6.5 and 7.5 were conducted to evaluate the effect of pH
243 on the adsorption of As(V) onto HA-Goe colloids. The adsorption data (Figure 2) exhibited
244 the feature of a Langmuir isotherm, formally indicated by:

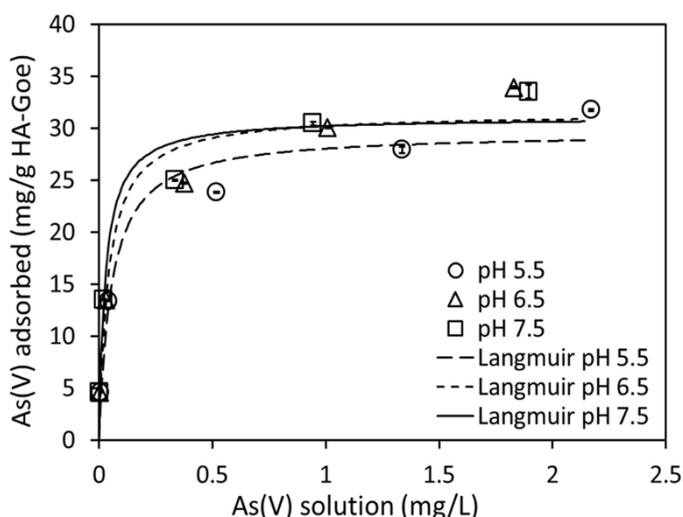
$$245 \quad q = \frac{b \cdot K_L \cdot c_{eq}}{1 + K_L \cdot c_{eq}} \quad \text{Eq. 1}$$

246

247 where, q is the amount of As(V) adsorbed per gram of HA-Goe (mg g⁻¹), c_{eq} denotes the
248 equilibrium concentration of the As(V) in solution (mg L⁻¹), K_L is the Langmuir constant (L
249 mg⁻¹) that relates the affinity of binding sites and b is the adsorption capacity (mg g⁻¹). The
250 adsorption of As(V) was not significantly ($p > 0.05$ level) affected by the pH of the solution
251 (Figure 2). Different from other oxyanions (*e.g.* phosphate), adsorption of As(V) onto
252 goethite has been shown to be less dependent on pH and ionic strength (Antelo et al., 2005).
253 Studies that reported an effect of pH indicated that As(V) adsorption onto goethite generally
254 decreases with increasing pH, particularly at pH above 7 and this effect is more pronounced
255 at high As loading (Dixit and Hering, 2003).

256 In the present study, a relatively high concentration of Ca²⁺ (5 mM) as background
257 electrolyte was used in the adsorption experiments in order to mimic that of contaminated
258 groundwater. The goethite colloids used in this study were coated with humic acids in order
259 to enhance colloidal stability and hence are negatively charged (Zeta potential -37 mV at pH
260 7.3). It is well accepted that functional groups of humic/fulvic substances are prone to form
261 complexes with divalent cations (*e.g.* Ca²⁺) (Weng et al., 2005). Therefore, it is likely that the
262 presence of Ca²⁺ ions may have masked the effect of pH, as Ca²⁺ can enhance the adsorption
263 of As(V) onto iron oxides by increasing the positive charge near the negatively charged
264 surfaces (Antelo et al., 2015).

265



266

267 Figure 2 Adsorption isotherms of As(V) onto humic acid-coated goethite (HA-Goe) colloids
 268 at variable pH. Background electrolyte 5 mM CaCl₂ and 5 mM MES or MOPS. Symbols
 269 represent experimental results and dotted lines the fitted Langmuir model. Standard errors
 270 from duplicate treatments are smaller than the size of the symbols.

271

272 The adsorption capacities calculated from the Langmuir equation were unaffected by the
 273 pH values (t-test, $p > 0.05$ level) and were, on average, 31 mg As g⁻¹ HA-Goe (Table 1).
 274 Values of sorption maxima for goethite reported in literature vary greatly (0.45–61 mg As(V)
 275 g⁻¹ goethite) and direct comparisons are difficult due to the different experimental conditions.
 276 For instance, Wu et al., (2014) measured an adsorption maxima of 61 mg As g⁻¹ at pH 7 for
 277 goethite nanoparticles that have a specific surface area of 293 m² g⁻¹. From the adsorption
 278 isotherm data by Antelo et al., (2005) an adsorption maxima of 11 mg As g⁻¹ was estimated at
 279 pH 7 for goethite material with a surface area of 71 m² g⁻¹. Much lower adsorption capacities
 280 (0.45 mg As g⁻¹ goethite) have been reported in natural iron oxides of lower surface area (2
 281 m² g⁻¹) (Giménez et al., 2007). Over all, the adsorption maxima calculated for HA-Goe used
 282 in this study is high considering that the colloids were stabilized with humic acids which can
 283 decrease As(V) adsorption via electrostatic repulsion or by occupying the reactive surface
 284 sites (Weng et al., 2009). Recently, Otero-Fariña et al., (2017) investigated the adsorption of
 285 As(V) onto bare goethite and goethite coated with humic acids containing different
 286 proportions of carbon (2–8%). They found a decrease in the goethite reactive surface area
 287 from 100 m² g⁻¹ (bare goethite) to about 60 m² g⁻¹ (humic acids coated goethite containing
 288 about 8% C). This decrease in reactive surface area was evidenced also by a 25 to 40%
 289 reduction in the amount of As(V) adsorbed onto goethite containing 4 or 7% C. Similarly,

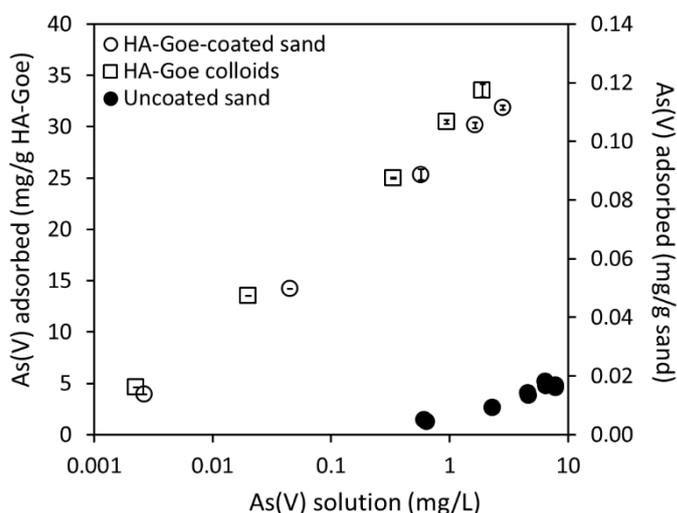
290 humic substances negatively affected the efficiency of granular ferric oxide to remove As(V)
 291 from aqueous solutions as reported by Saldaña-Robles et al., (2017).

292

293 3.2 Arsenate adsorption to humic acid-coated goethite colloids immobilized in quartz 294 sand

295 The adsorption isotherm of the uncoated sand (blank sand) was nonlinear and could be
 296 described by the Langmuir model. The capacity (b) of uncoated sand to remove As(V) from
 297 solution was clearly lower than that of HA-Goe-coated sand ($25 \mu\text{g As g}^{-1}$ uncoated sand vs.
 298 $114 \mu\text{g As g}^{-1}$ coated sand), which corroborated its main function as supportive material for
 299 the HA-Goe aggregates (Figure 3).

300 The comparison of As(V) adsorption onto the surface of HA-Goe-coated sand at pH 7.5
 301 versus that onto the original HA-Goe colloids is shown in Figure 3.



302

303 Figure 3 Semi-log plot of the adsorption isotherm of As(V) onto humic acid-coated goethite
 304 (HA-Goe) colloids in suspension, HA-Goe-coated sand and uncoated sand at pH 7.5.
 305 Background electrolyte 5 mM CaCl_2 and 5 mM MOPS. The standard errors are smaller than
 306 the size of the symbols.

307 The adsorption capacities b for As(V) estimated from fitting the Langmuir model were not
 308 significantly different ($p > 0.05$) between the HA-Goe-coated sand and the colloidal HA-Goe
 309 with b values of 31 and 30 mg As g^{-1} goethite (Table 1). However, the K_L parameter of the
 310 Langmuir equation that reflects the affinity of sorbate to the sorbent was two times larger for
 311 colloidal HA-Goethite compared to that of HA-Goe-coated sand. These results indicate that
 312 there was a more favorable adsorption (*i.e.* stronger adsorption affinity) of As(V) to colloids
 313 in suspension than to those coated on sand particularly, at low As(V) loading. Note that both
 314 adsorption experiments have used an equally high concentration of Ca^{2+} (5 mM) to allow
 315 comparison of As adsorption in equal, and relevant ionic scenarios. At this concentration of

316 Ca^{2+} , aggregation and sedimentation of the HA-Goe colloids was visible during the
 317 experiment. A subsample of the HA-Goe colloidal suspension that was exposed to the contact
 318 solution was taken and the hydrodynamic diameter measured by DLS (>1000 nm) was well
 319 above the size of the original suspension (Figure 1C). Calcium concentrations of 1 mM are
 320 sufficient to cause aggregation of such particles (Bollyn et al., 2016). This means that the
 321 HA-Goe colloidal suspension as used might contain non-colloidal aggregates with lower As
 322 adsorption affinity/capacity than the original suspension which was also low in Ca and
 323 sodium (Na) dominated.

324

325 Table 1 Estimated Langmuir parameters b and K_L and corresponding best fit standard error
 326 for the adsorption of As(V) onto humic acids coated-goethite (HA-Goe) colloids and HA-
 327 Goe-coated sand. The K_L of the original particles at pH 7.5 is significantly (*, $p < 0.05$, t-test)
 328 above that of the coated sand indicating a loss of As affinity of the particles once coated to
 329 sand.

Adsorbant	Langmuir parameters	
	b (mg As(V) g^{-1} HA-goethite)	K_L (L mg^{-1})
HA-Goe colloids		
pH 5.5	29.6 \pm 1.06	18.2 \pm 3.91
pH 6.5	31.5 \pm 1.33	24.2 \pm 6.42
pH 7.5	30.9 \pm 1.23	37.6 \pm 9.69*
HA-Goe-coated sand		
pH 7.5	30.6 \pm 1.03	18.9 \pm 4.10

330

331 3.3 Transport of As(V) in columns containing humic acid-goethite coated sand

332 The Br^- breakthrough curves were fitted to the one-dimensional CDE (one fit per replicate
 333 column) to obtain the parameters pore water velocity (v) and dispersion coefficient (D)
 334 (Šimůnek et al., 1999) that are shown in Table 2. Bromide breakthrough curves were
 335 symmetrical, exhibited no tailing and were well described by the CDE that is based on LEA
 336 ($r^2 = 0.993-0.998$). The optimized dispersion coefficient parameters increased linearly with
 337 increasing pore water velocity but the longitudinal dispersivity (λ) calculated by the ratio
 338 between D and v did not differ greatly. Given that the transport of Br^- was well predicted by
 339 the equilibrium model it was assumed that physical non-equilibrium was negligible in the
 340 columns (Brusseau et al., 1989). The average effective porosity estimated from the Br^- tracer
 341 tests was 0.40 ± 0.01 . The λ values calculated from D and v parameters were subsequently
 342 used to predict As(V) transport based on the CDE model using HYDRUS-1D.

343

344 Table 2 Estimates of the transport parameters dispersion coefficient (D) and pore water
 345 velocity (v) for the convection-dispersion model (CDE) obtained by least-square fit with
 346 STANMOD. Values in parenthesis are corresponding standard deviations of the two column
 347 replicates.

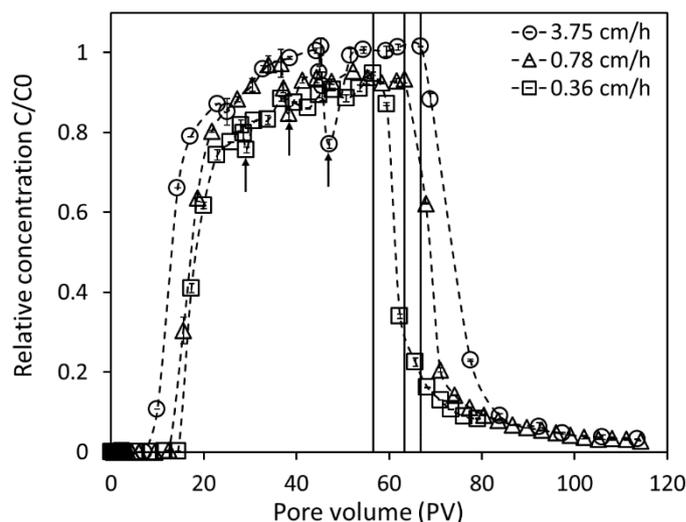
Darcy velocity cm h ⁻¹	D cm ² h ⁻¹	v cm h ⁻¹	λ^{\S} cm	r^2
1.5	0.21 (0.01)	3.75 (0.13)	0.06 ± 0.004	0.998
0.3	0.05 (0.003)	0.78 (0.001)	0.06 ± 0.004	0.995
0.1	0.02 (0.002)	0.36 (0.002)	0.07 ± 0.007	0.993

348 [§]Dispersivity, $\lambda=D/v$

349

350 Column transport experiments were conducted to evaluate the efficiency of HA-Goe in
 351 removing As(V) from contaminated water. Since the results from batch experiments indicated
 352 some adsorption of As(V) onto uncoated sand, additional blank sand columns were included
 353 to understand the transport of As(V) in this system (data not shown). The breakthrough
 354 curves of As(V) in the HA-Goe free (blank) columns were fitted to the nonlinear equilibrium
 355 adsorption model of HYDRUS resulting in b of 2.49 mg As kg⁻¹ sand and K_L of 0.15 L mg⁻¹,
 356 and which corresponded to a retardation coefficient of 1.41.

357 For the column studies, a layer of HA-Goe-coated sand was used to mimic the reactive
 358 barrier after the injection of the HA-Goe colloids in the subsurface. The breakthrough curves
 359 of As(V) at three pore water velocities (3.75, 0.78, 0.36 cm h⁻¹) and initial As(V)
 360 concentration of 4.6–4.9 mg L⁻¹ are shown in Figure 4. All breakthrough curves were
 361 asymmetric with a relatively sharp front after about 14–17 PV and exhibited tailing. The
 362 As(V) breakthrough was considered as complete when the concentration of As in the leachate
 363 was 95% to that of the inlet concentration ($C/C_0 = 0.95$). The adsorption maxima calculated
 364 from the integration of the breakthrough curves was 34.1, 26.4 and 16.2 mg As g⁻¹ HA-Goe,
 365 for columns at 0.36, 0.78 and 3.75 cm h⁻¹ pore water velocities, respectively. This means that
 366 the highest adsorption capacity was observed in the columns with the lowest flow rate, which
 367 can be explained by the longer contact time of As(V) with HA-Goe-coated sand. The
 368 residence times of water in the columns are, depending on flow rates, between 3 and 33 h,
 369 and are relatively short considering that in the batch experiments samples were equilibrated
 370 for 72 h. The total amount of As(V) adsorbed at the lowest velocity (34 mg As g⁻¹ HA-Goe)
 371 is close to the value calculated from the equilibrium batch adsorption experiments (30 mg As
 372 g⁻¹ HA-Goe).



373

374 Figure 4 Breakthrough curves for As(V) at three pore water velocities (0.36, 0.78 and 3.75
 375 cm h⁻¹) and As inlet concentration 4.6–4.9 mg L⁻¹. Arrows denote flow interruption and solid
 376 vertical lines indicate the points when the influent As(V) concentration was reduced to zero.

377

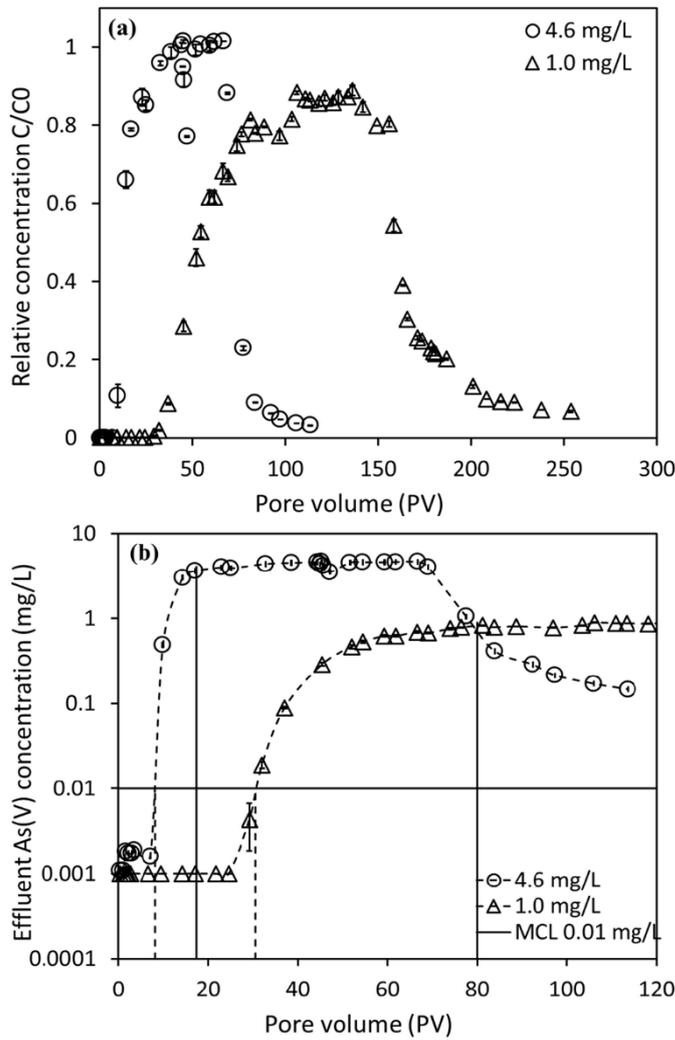
378 The effect of pore water velocity on the transport of As(V) was observed by a leftward
 379 shift of the breakthrough curves (earlier breakthrough) with increasing pore water velocity. In
 380 addition, it was calculated the fraction of previously loaded As(V) that was not recovered in
 381 the leachate in the period after the influent concentration decreased to zero. That non-
 382 recovered fraction was 31.5, 21.5 and 14% for columns at pore water velocities 0.36, 0.78
 383 and 3.75 cm h⁻¹, suggesting that longer residence time allowed stronger As immobilization.
 384 Similar velocity effects on sorption and transport of As(V) have been previously reported in
 385 soils (Darland and Inskip, 1997). These results suggest that sorption-related non-equilibrium
 386 conditions prevailed in the columns. Flow interruptions (24h) were included to further test
 387 non-equilibrium conditions in the columns (Figure 4). The flow interruption is a technique
 388 that has been used to identify non-equilibrium conditions during the transport of solutes in
 389 soils (Brusseau et al., 1989). As shown in Figure 4, a decrease in the concentration of As(V)
 390 was observed in the effluent after resuming the flow, indicating additional sorption and,
 391 hence, non-equilibrium during transport. This decrease was evidently more pronounced in the
 392 columns with the highest pore water velocity (0.78 and 3.75 cm h⁻¹) although a small
 393 decrease was also measured in the columns performed at the lowest pore water velocity (0.36
 394 cm h⁻¹) which suggest that they were likely also under non-equilibrium conditions. On the
 395 basis of flow interruption-mediated effects it is not possible to differentiate between physical
 396 (transport-related) or chemical (sorption-related) non-equilibrium. Because the Br
 397 breakthrough curves were symmetrical and well described by CDE model, physical non-

398 equilibrium was ruled out. Thus changes in the outflow concentrations due to flow
399 interruption are likely indicative of chemical non-equilibrium since there is enough time for
400 As(V) to adsorb onto the adsorbant.

401

402 3.4 Effect of initial concentration on the transport and retention of As(V)

403 The effect of the inlet concentration on the efficiency of HA-Goe-coated sand to remove
404 As(V) was investigated by injecting at the same pore water velocity (3.75 cm h^{-1}) two
405 different concentrations of As(V) (1 and 4.6 mg L^{-1}). These concentrations were selected as
406 they are representative of highly contaminated sites. The injection of a solution of higher
407 concentration translated into a much earlier breakthrough of As(V) (Figure 5). The rapid
408 elution of As(V) can be attributed to saturation of sorption sites. If the WHO limit of $10 \text{ } \mu\text{g L}^{-1}$
409 is considered as the guideline for remediation, about 30 PV (low concentration) and 8 PV
410 (high concentration) of contaminated water were filtered before the concentration in the
411 outflow solution surpassed the standard (Figure 5). This number of PVs (30 and 8) are found
412 between 12 to 14 mg As g^{-1} of goethite in the column for low and high As concentrations, *i.e.*
413 about 40% and 45% of the batch adsorption capacity for the HA-Goe-coated sand.



414

415 Figure 5 Breakthrough curves for As(V) expressed in relative concentrations (a) and effluent
 416 concentration (semi-log plot) (b), at two inlet As(V) concentrations (1 and 4.6 mg L⁻¹)
 417 injected at 3.75 cm h⁻¹ pore water velocity. The solid horizontal line indicates the maximum
 418 concentration limit (MCL) for As in drinking water, the dotted and solid vertical lines is the
 419 number of PVs to reach the MCL and the As sorption maximum of the substrate determined
 420 in batch.

421

422 3.5 Modelling reactive transport of As(V) in columns

423 To further test the LEA and to validate the reactive transport of As(V), the breakthrough
 424 data was modelled with the CDE model in HYDRUS-1D version 4.16. Assuming local
 425 equilibrium-governed adsorption and using the Langmuir parameters (b and K_L) from HA-
 426 Goe-coated sand (Table 1) from the batch experiments, the transport of a sorbing solute *e.g.*
 427 As(V) can be described by:

$$428 \left(1 + \frac{\rho}{\theta} \cdot \left[\frac{b \cdot K_L}{(1 + K_L \cdot c)^2} \right]\right) \cdot \frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2} - v \frac{\delta c}{\delta x} \quad \text{Eq. 2}$$

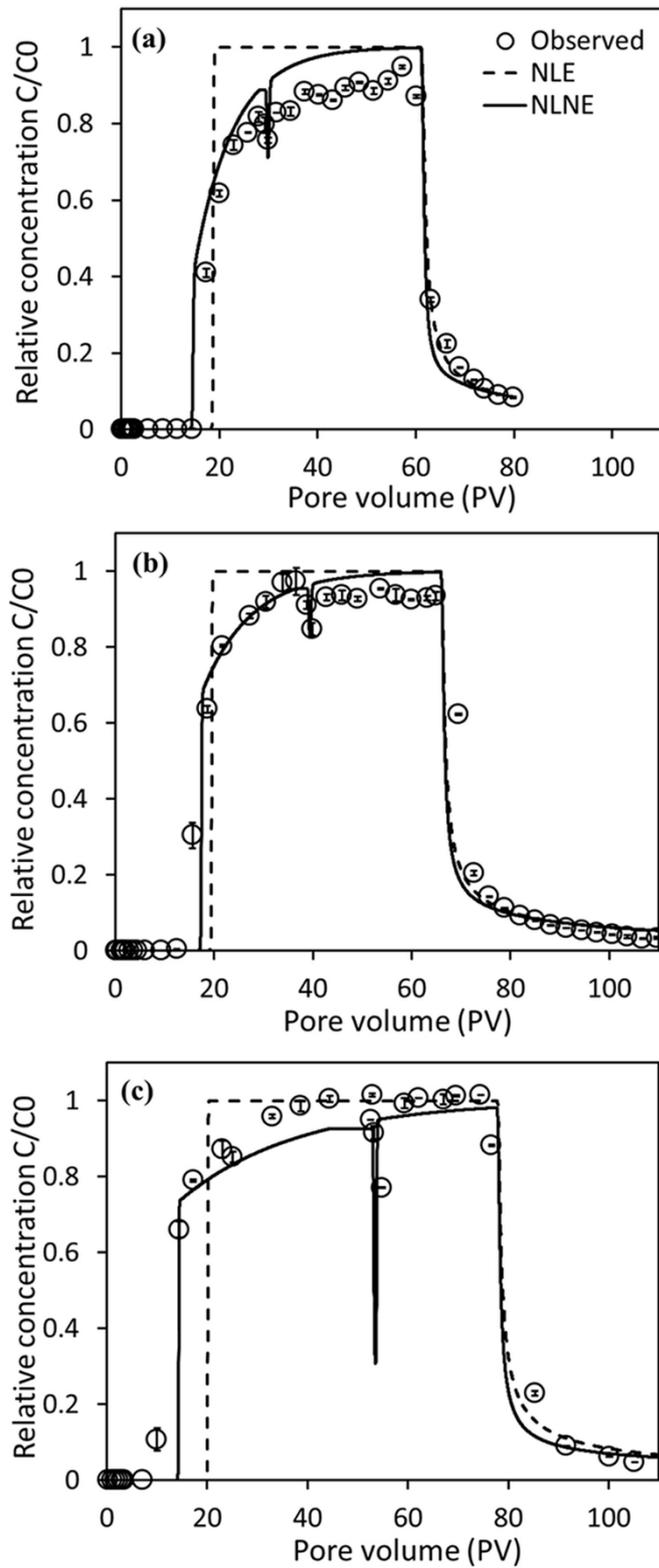
429 where c is the concentration of As(V) adsorbed on equilibrium sites (mg L^{-1}), ρ is the
 430 media bulk density (g cm^{-3}), θ is the porosity of saturated media, D is the hydrodynamic
 431 dispersion coefficient ($\text{cm}^2 \text{h}^{-1}$), v the linear water velocity (cm h^{-1}), t is the time (h), and x the
 432 depth (cm). The linear water velocity (v) is related to the Darcy's flux (q) through the
 433 porosity of the saturated media ($q = v \cdot \theta$). The parameters q , θ , λ , b , K_L are required for
 434 HYDRUS-1D input to model the breakthrough data using the equilibrium nonlinear solute
 435 transport model. The solute transport boundary conditions selected for modelling the
 436 breakthrough data were: flux concentration at the inlet and zero concentration gradient at the
 437 outlet.

438 This nonlinear sorption model with local equilibrium assumption (NLE model)
 439 parameterized with batch sorption parameters (b and K_L) failed to predict As(V) breakthrough
 440 curves from any of the columns with step injections of 4.6–4.9 mg As L^{-1} (Figure 6). The
 441 chemical equilibrium model overestimated the breakthrough time. The reason behind this
 442 deviation has been ascribed either by the overestimation of retardation with the equilibrium
 443 batch adsorption parameters and/or the inability of the solute to reach equilibrium with the
 444 adsorbant during the transport through the sand (Seuntjens et al., 2001). It was observed that
 445 under flow conditions, only about 50% of the HA-Goe sorption sites were occupied and,
 446 hence, the early breakthrough can be due to the by-pass of the As(V)-containing water.
 447 Moreover, the nonlinear equilibrium model was also unable to predict the gradual increase in
 448 the concentration of As(V) in the effluent (*i.e.* sigmoidal shape of breakthrough curve). The
 449 asymmetrical shape of breakthrough curves are better described by non-equilibrium models
 450 (Pang et al., 2002). Considering all indications for non-equilibrium sorption, the two-site non-
 451 equilibrium transport model was explored to model the breakthrough data. The two-site
 452 model considers that the exchange sites are divided into type 1 sites (S_1) that are in
 453 equilibrium with the solution phase and type 2 sites (S_2) on which sorption is considered to be
 454 time-dependent. In case that sorption is described by the Langmuir equation (Eq. 1), the
 455 transport equation for the two-site model is (Šimůnek and van Genuchten, 2008):

$$456 \left(1 + \frac{f \cdot \rho}{\theta} \cdot \left[\frac{b \cdot K_L}{(1 + K_L \cdot c)^2} \right]\right) \cdot \frac{\delta c}{\delta t} = D \frac{\delta^2 c}{\delta x^2} - v \frac{\delta c}{\delta x} - \frac{\alpha \cdot \rho}{\theta} \cdot \left[(1 - f) \cdot \frac{b \cdot K_L \cdot c}{1 + K_L \cdot c} - S_2 \right] \quad \text{Eq. 3}$$

457 where f is the fraction of equilibrium sites (-), α is the first-order kinetic rate coefficient
 458 (h^{-1}), and S_2 the solid phase concentration at site 2 (mg kg^{-1}). The input parameters q , θ , λ , b ,
 459 K_L , f and α are required for HYDRUS-1D to model the data with the nonlinear non-
 460 equilibrium model (NLNE).

461



462

463

464 Figure 6 Observed and modelled breakthrough curves for As(V) in columns containing HA-
 465 Goe-coated sand at three pore water velocities 0.36 cm h^{-1} (a), 0.78 cm h^{-1} (b) and 3.75 cm h^{-1}
 466 (c) and high As(V) inlet concentration. NLE: nonlinear equilibrium model; NLNE: nonlinear

467 non-equilibrium model. The change in concentration at pore volumes 30 (a), 38 (b) and 47 (c)
468 due to 24-h flow interruption.

469 For the equilibrium sites the batch equilibrium adsorption parameters were used, whereas
470 the kinetic parameters (f and α) were obtained with the inverse solution of HYDRUS-1D by
471 fitting the model to the breakthrough data. As shown in Figure 6, the addition of the kinetic
472 parameters allowed for a better match of the predicted breakthrough curves to the observed
473 data, resulting also in RMSE values of C/C_0 that ranged from 0.031–0.038. The values of α
474 increased with increasing pore water velocity (Table 3), which is consistent with previous
475 work (Maraqa, 2001). This kinetic-rate constant describes the sorption/desorption of As(V) in
476 time and is not expected to vary with pore water velocity if the non-equilibrium conditions
477 are mainly due to sorption (chemical non-equilibrium) (Tsang and Lo, 2006). Hence, this
478 finding suggests that physical processes (*i.e.* diffusion) may have also contributed the
479 transport of As(V) in the columns.

480

481 Table 3 Chemical non-equilibrium transport parameters derived from the two-site model with
482 standard error in brackets. Errors are based on fitting duplicate columns individually, *i.e.* $n=2$.

Pore water velocity cm h ⁻¹	α h ⁻¹	f	R ²
0.36	0.004 (0.0001)	0.33 (0.009)	0.988
0.78	0.007 (0.0014)	0.60 (0.028)	0.957
3.75	0.013 (0.0002)	0.53(0.001)	0.967

483

484 The velocities used in this study are comparable to those used in previous reported work
485 where the transport of As was described by non-equilibrium models. The groundwater
486 velocities in the field range widely. Typical groundwater velocities are < 1 m year⁻¹,
487 equivalent to pore water velocities of 2.5 m year⁻¹ or 0.025 cm h⁻¹ in which case equilibrium
488 processes can be considered. The transport of As at groundwater velocities of 0.1–10 cm day⁻¹
489 (pore water velocities 0.02–1 cm h⁻¹) was simulated using the empirical parameters (α and f)
490 obtained from fitting the columns at 0.36 cm h⁻¹. The model predicted that for the highest
491 velocity (10 cm d⁻¹), only 14 mg As g Goe⁻¹ can be adsorbed before exceeding the
492 concentration limit of 10 $\mu\text{g L}^{-1}$ in the effluent water. In contrast, at the lower velocities the
493 equivalent tipping point was close to that determined by batch equilibrium adsorption (about
494 30 mg As g⁻¹ HA-Goe). This indicates that for high flow rates, safety factors should be
495 considered to account for non-equilibrium conditions that can diminish the adsorption
496 efficiency of the adsorbant.

497 This study was limited to investigate the removal of As(V) from spiked water in packed
498 columns. It is speculated that the challenges to adopt the technology in the field are related to
499 non-homogenous deposition of the particles, the effect of competing ions (*e.g.* phosphates)
500 that can interfere in the adsorption reaction and the longevity of the reactive barrier upon
501 conditions that trigger the reductive dissolution of iron oxides. Furthermore, the release of
502 humic acids (used as coating) from the goethite colloids is also a plausible scenario that may
503 affect the efficiency of remediation through mobilization of metal cations (*e.g.* Zn, Cu) that
504 were adsorbed onto the humic acids. All of the above mentioned factors require further study
505 prior the application of this technology in the field.

506

507 **4. Conclusions**

508 The results from batch and column experiments showed that HA-Goe colloids can
509 effectively remove As(V) from contaminated water. This study showed that coagulation and
510 deposition of the HA-Goe within the sand matrix (non-colloidal Goe) only marginally
511 affected the adsorption of As and thus deposited HA-Goe were able to remove similar
512 amounts of As(V) compared to the aggregated HA-Goe colloids alone in suspension. Because
513 of the conditions of pH and ionic strength in contaminated groundwater, it is expected that
514 colloids will aggregate and sediment soon after injection. Therefore, the fact that a very high
515 As(V) adsorption capacity was measured ($30 \text{ mg As g}^{-1} \text{ HA-Goe}$), indicates that this is a
516 promising material for remediation of contaminated sites. The relevance of this finding is that
517 more certainty was gained that aggregation and sedimentation processes may not affect the
518 adsorption properties of colloids in field applications.

519 The experimental breakthrough curves showed that the transport of As(V) exhibited
520 nonlinear and rate-limited reaction. The one dimensional transport model based on LEA
521 failed to correctly describe the breakthrough data and therefore the non-equilibrium model
522 was more appropriate to explain the transport of As(V) in the columns. Because the fitted
523 kinetic rate coefficient was small at the low pore water velocity and large at higher pore water
524 velocities it is likely that the non-equilibrium conditions were related to both diffusion and
525 sorption kinetics. For a successful prediction of As removal in subsurface environments the
526 reactive transport model should include conservative safety factors to account for kinetic-rate
527 expressions and preferential flow paths.

528

529 **Acknowledgments**

530 This work was supported by H2020 EU project “Reground” Grant Agreement N° 641768.
531 www.reground-project.eu/ We thank Dr. Beate Krok (University of Duisburg-Essen,
532 Germany) for providing the stock suspension of goethite colloids.

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Efficient removal of arsenate from oxic contaminated water by colloidal humic acid-coated goethite: batch and column experiments

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Highlights

- Humic acid-coated goethite (HA-Goe) can effectively remediate As(V) polluted water.
- Main advantage of HA-Goe is their high As(V) adsorption capacity (30 mg As g⁻¹).
- HA-Goe colloids retain their sorption capacities after coagulation in sand.
- Non-equilibrium transport model predicts As(V) transport in flow-through conditions.