



Spectroscopic (XAS, FTIR) investigations into arsenic adsorption onto TiO₂/Fe₂O₃ composites: Evaluation of the surface complexes, speciation and precipitation predicted by modelling

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ARTICLE INFO

Keywords:

Arsenic
Composite
Adsorption
EXAFS
FTIR
Surface complexation model

ABSTRACT

Over 50 million people in South Asia are exposed to groundwater contaminated with carcinogenic arsenic(III). Photocatalyst-adsorbent composite materials are popularly developed for removing arsenic in a single-step water treatment. Here, As(III) is oxidised to As(V), which is subsequently removed via adsorption. We previously developed a component additive surface complexation model (CA-SCM) to predict the speciation of arsenic adsorbed onto TiO₂/Fe₂O₃ under different environmental conditions, using surface complexes taken from studies of single-phase minerals. In this work, we critically evaluate this approach, using experimental observations of the surface structures of arsenic adsorbed onto TiO₂/Fe₂O₃. Extended X-ray absorption fine structure spectroscopy (EXAFS) indicates significant As(III) surface precipitation, and the possible formation of tridentate ³C complexes. EXAFS was unable to identify As binding modes for TiO₂ and Fe₂O₃ surface complexes simultaneously, highlighting the challenge of analysing composite surfaces. FTIR and zeta potential analysis indicate that As(III)-Fe₂O₃ surface complexes are protonated at neutral pH, whilst As(III)-TiO₂, As(V)-Fe₂O₃ and As(V)-TiO₂ surface complexes are negatively charged. Our study confirms the speciation predicted by CA-SCM, particularly As(III) surface precipitation, but also introduces the possibility of tridentate As(III) at acidic pH. This study highlights how experiment and modelling can be combined to assess surface complexation on composite surfaces.

1. Introduction

Arsenic is a toxic Group 1 carcinogen (International Agency for Research on Cancer) and long-term exposure to even trace amounts can lead to debilitating and potentially fatal diseases including skin cancer, lung cancer, keratosis, and neurological disorders (Naujokas et al., 2013). 100–200 million people globally are believed to be exposed to arsenic through contaminated groundwater drinking supplies (Raven-scroft et al., 2009; Naujokas et al., 2013). Arsenicosis is particularly prevalent in West Bengal, India, and Bangladesh where previous estimations have suggested that 10 and 50 million people respectively are exposed to water exceeding the World Health Organisation's 10 µg L⁻¹

recommended limit (Chakraborti et al., 2009; Anawar et al., 2011). Unlike many other parts of the world, in the Bengal Basin arsenic is released into anoxic aquifers through the reductive dissolution of iron (hydr)oxides via microbial activity, and arsenic is consequently found as As(III) rather than As(V) (Smedley and Kinniburgh, 2005).

In the +3 oxidation state, arsenite (*i.e.* As(III)) oxyanions are difficult to remove from contaminated water using adsorption or coagulation-flocculation due to their neutral charge (H₃AsO₃ at neutral pH) (Smedley, 2008). In contrast, arsenate (*i.e.* As(V)) oxyanions (HAsO₄²⁻ and H₂AsO₄⁻ at neutral pH) are both (i) more easily removed and (ii) less toxic than H₃AsO₃ (Markley and Herbert, 2009). Consequently, the treatment of As(III)-contaminated water benefits from

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the oxidation of As(III) to As(V) prior to its removal via adsorption. Oxidation of As(III) can be achieved using heterogeneous photocatalysts, such as TiO_2 , and ultraviolet (UV) radiation. However, designing and maintaining treatment plants with multiple treatment steps is challenging, especially in rural areas of low-income countries where there may be a lack of trained and skilled manpower (Kabir and Chowdhury, 2017).

This challenge in engineering photocatalytic oxidation-adsorption water treatments may be overcome by incorporating photocatalytic and adsorption capabilities into a single material (Bullen et al., 2020b; Bissen and Frimmel, 2003). Whilst the benchmark photocatalyst TiO_2 is also an adsorbent that can remove both As(III) and As(V), the application of pure TiO_2 for As(III) remediation via the oxidation-adsorption approach is limited by low arsenic adsorption capacities and weak binding affinities compared to iron oxide adsorbents such as Fe_2O_3 . For example, our previous study found that the adsorption capacities of TiO_2 towards As(III) and As(V) were lower than the adsorption capacities of Fe_2O_3 by 51% and 41% respectively (Bullen et al., 2020a). We also found that for monolayer As(V) adsorption, the Langmuir constant (K_L) was 58% smaller for TiO_2 than for Fe_2O_3 , whilst for multilayer As(III) adsorption, the Freundlich constants (K_F and n) were 59% and 15% smaller for TiO_2 than for Fe_2O_3 . The more weakly bound TiO_2 -adsorbed arsenic is thus more easily displaced than iron oxide-bound arsenic by the competitor ions that are abundant in natural waters, especially phosphate oxyanions (Smedley and Kinniburgh, 2001). Furthermore, we found that the application of pure TiO_2 for the photocatalytic oxidation of As(III) was limited due to photocatalyst deactivation, or photocatalyst fouling, associated with the build-up of As(V) products on the TiO_2 surface that prevent the generation of reactive oxygen species (ROS) intermediates such as the hydroxyl radical (Bullen et al., 2022).

Consequently, of particular interest are composite materials combining the excellent photocatalytic capabilities of TiO_2 with the high As(V) adsorption capacities of iron oxides (Beduk, 2016; Deng et al., 2019; Su et al., 2017; Yu et al., 2013; Zhang and Itoh, 2006). In previous work, we investigated one such composite (meso- $\text{TiO}_2/\text{Fe}_2\text{O}_3$), synthesised by the precipitation of iron oxide onto a mesoporous TiO_2 support. We found that adsorption capacities and adsorption isotherm constants were enhanced after adding Fe_2O_3 to the TiO_2 support (Bullen et al., 2020a), whilst photocatalyst fouling was prevented by the Fe_2O_3 phase adsorbing As(V) more strongly than TiO_2 and also maintaining a local As(III) concentration (Bullen et al., 2022). We developed a kinetic adsorption model to investigate the trade-offs between low material concentrations for effective photocatalysis and high material concentrations for effective adsorption in batch and continuous-flow processes (Bullen et al., 2020b). We subsequently developed a surface complexation model (SCM) to predict changes in the amount of arsenic adsorbed and its speciation as a function of experimental variables such as pH (Bullen et al., 2020a). This SCM was important, in corroboration with transient absorption spectroscopy (TAS) measurements, for explaining differences in the As(III) photocatalytic oxidation kinetics of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ and pure TiO_2 : (i) photocatalytic oxidation kinetics were limited due to parasitic ultraviolet (UV) light absorption by the iron oxide phase; (ii) a heterojunction between TiO_2 and Fe_2O_3 , providing extended charge carrier lifetimes, is not necessarily formed using precipitation synthesis methods; and (iii) photocatalyst fouling occurs more rapidly on the pure TiO_2 photocatalyst than the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite, since the pure TiO_2 surface is more rapidly saturated with adsorbed As(V), which hinders the generation of ROS intermediates from photoexcited holes (Bullen et al., 2022).

However, a knowledge gap remains regarding the structures of arsenic surface complexes on $\text{TiO}_2/\text{Fe}_2\text{O}_3$. This is important for several reasons. Firstly, the strength and stability of surface complexes depends upon their structure (i.e. covalently bonded inner sphere surface complexes are stronger than electrostatic outer sphere complexes, and multi-dentate inner sphere complexes are stronger than mono-dentate

inner sphere complexes). The stability of a surface complex cannot be determined from adsorption capacities or equilibrium constants alone, as the competitive adsorption by phosphate and sulphate that causes the leaching of adsorbed arsenic (Smedley, 2008) will likely displace outer sphere complexes more easily than bidentate inner sphere complexes. The implications are that if the surface complexes are weak, then adsorption media must be used in greater amounts, regenerated more frequently, or a pre-treatment must be used to remove competitor ions (Hou et al., 2020; Peld et al., 2004; Luxton et al., 2008). Secondly, detailed knowledge of the structure of these surface complexes is central to developing surface complexation models (SCM), valuable tools for understanding and predicting the adsorption of arsenic as a function of pH, ionic strength and the presence of competitor ions (Goldberg, 1995; Kanematsu et al., 2013; Bullen, 2021). Accurate SCMs require knowledge of both the binding mode (e.g. mono or bidentate complexation) and the protonation state of the surface complex (to provide the correct pH sensitivity and to model electrostatic interactions).

In previous work (Bullen et al., 2020a), we assumed that the structures of arsenic surface complexes formed on meso- $\text{TiO}_2/\text{Fe}_2\text{O}_3$ were the same as those identified in the literature for single-phase TiO_2 and Fe_2O_3 sorbents (Sverjensky and Fukushima, 2006; Fukushima and Sverjensky, 2007; Kanematsu et al., 2013). The equilibrium constants were optimised to fit experimental pH adsorption edge data. Whilst the adsorption of As(V) onto $\text{TiO}_2/\text{Fe}_2\text{O}_3$ was successfully predicted using the description of arsenic surface complexes on single-phase TiO_2 and Fe_2O_3 , the adsorption of As(III) was not. This required incorporation of a new reaction term that represents the surface precipitation of As(III) (Bullen et al., 2020a) that has been observed experimentally on other iron oxide minerals at pH 7.2–7.4 (Morin et al., 2009).

The aim of the present study was to experimentally evaluate the success of our SCM for predicting the speciation of arsenic adsorbed onto $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites, developing a deeper understanding of the mechanisms by which As(III) and As(V) adsorb and confirming As(III) surface precipitation. We also assess how the synthesis route used to prepare $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites influences adsorption capacity and the structure of the surface complexes formed.

$\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites can be prepared using a wide variety of synthetic routes, yielding a wide range of material structures, such as Fe_2O_3 precipitated onto a mesoporous TiO_2 support (Zhou et al., 2008), nanopowders where TiO_2 is precipitated onto an $\alpha\text{-Fe}_2\text{O}_3$ support (Li et al., 2016), and Fe-doped TiO_2 sol-gel products (Trapalis et al., 2003). Consequently, we investigated the influence of synthesis method on the arsenic adsorption of $\text{TiO}_2/\text{Fe}_2\text{O}_3$, using three previously reported protocols: (1) Fe_2O_3 precipitated onto mesoporous TiO_2 as per our previous study (Bullen et al., 2020a,b, 2022), (2) a faster synthesis route, where Fe_2O_3 is precipitated onto a commercial TiO_2 anatase nanopowder (D'Arcy et al., 2011), and (3) a sol-gel approach, where sources of dissolved Fe and Ti are mixed simultaneously (Trapalis et al., 2003). We used X-ray powder diffraction (XRD) to characterise these three composite adsorbents and we determined their adsorption capacities using batch experiments. We identified the structure of the surface complexes formed between arsenic and $\text{TiO}_2/\text{Fe}_2\text{O}_3$, using a combination of EXAFS, FTIR and zeta potential (ζ) measurements.

2. Materials and methods

Details of the chemical reagents used in this work are provided in Table S1.

2.1. Synthesis of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composites

$\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite materials were synthesised using three different methods. The first two materials were synthesised via the precipitation of iron oxide from ethanolic solution onto a solid TiO_2 support, following previously published procedures (D'Arcy et al., 2011; Zhang and Itoh, 2006). The TiO_2 was either a commercially-sourced anatase

nanopowder (with the final product named *co-precipitate commercial bifunctional*, or *CPCB* hereafter), or a synthesised mesoporous TiO_2 (Liu et al., 2005) (with the final product named *co-precipitate mesoporous bifunctional*, or *CPMB* hereafter). Briefly, 48.48 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 200 mL ethanol to yield a stock solution of 0.6 M iron nitrate. An aliquot of this solution (30 mL) was then added to a beaker containing 1.5 g of either (a) commercial TiO_2 anatase or (b) mesoporous TiO_2 . The beaker was sealed with parafilm and the reaction mixture stirred magnetically for 30 min, before the mixture was left standing on a hot plate (50 °C) overnight to evaporate the solvent. The product was then calcined in a furnace at 300 °C for 10 min, cooled, ground with a mortar and pestle, calcined further at 300 °C for 6 h, and ground to yield a homogeneous powder. In the third method, $\text{TiO}_2/\text{Fe}_2\text{O}_3$ was prepared via a sol-gel synthesis (with the product named *SG* hereafter) (Trapalis et al., 2003). Tetraethyl orthotitanate (TEOT, 5 g) was mixed with a solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ dissolved in ethanol (8.86 g in 12 g). The resulting solution was stirred for 60 min at 50 °C. Concentrated HNO_3 (10 drops) was then added dropwise while stirring to initiate gelation. The mixture was continuously stirred until gelling was completed. The product was calcined at 300 °C for 3.5 h and then crushed to yield a homogeneous powder.

A hematite ($\alpha\text{-Fe}_2\text{O}_3$) reference sample was synthesised. An aliquot of the 0.6 M iron nitrate solution (30 mL) was stirred at 50 °C until all ethanol had evaporated. The product was calcined at 300 °C for 10 min, cooled, ground, calcined further at 300 °C for 6 h, and finally ground to yield a homogeneous powder. An aliquot of the mesoporous TiO_2 precursor used to synthesise CPMB was also kept as a reference sample.

2.2. Materials characterisation

The crystalline phases present in each material were confirmed by X-ray diffraction (XRD), using the Enraf Nonius PDS 120 X-ray diffractometer and a Co tube (40 kV and 30 mA). $\text{TiO}_2/\text{Fe}_2\text{O}_3$ powders were imaged by scanning electron microscopy (SEM), using the LEO 1455 VP SEM, to observe the size distribution and particle morphology.

2.3. Adsorption capacity

$\text{TiO}_2/\text{Fe}_2\text{O}_3$ (1 g L^{-1}) samples were suspended in 0.1 M sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$, 100 mL), buffered to pH 5. Suspensions were spiked with between 20 and 100 mg L^{-1} As(V). Suspensions were shaken for 24 h at room temperature to achieve equilibrium adsorption. An aliquot (10 mL) was extracted by pipette and centrifuged (4000 rpm) for 15 min. An aliquot of the supernatant (5 mL) was then extracted and acidified with 1 M HCl. Experiments with 20 and 100 mg L^{-1} As(V) were performed in duplicate in order to obtain an error estimate for each adsorption isotherm.

The quantity of As(V) adsorbed was determined by subtracting the concentration of aqueous As(V) remaining in the supernatant from the concentration of As(V) originally added. As(V) concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Varian Vista Pro instrument at the Natural History Museum, London. The instrument was calibrated with solutions made from a 1000 mg L^{-1} As standard (Fluka, Sigma Aldrich) diluted with 1 M HCl.

For each adsorption isotherm, errors were calculated using the percentage difference between the duplicate samples at total As(V) concentrations of 20 and 100 mg L^{-1} (Gill, 1997):

$$\% \text{ error} = \left(\frac{\text{difference between repeats}}{\text{mean of repeats}} \cdot 100 \right) \cdot 2 \quad (1)$$

The largest percentage error for each isotherm was chosen to represent the error for that isotherm throughout.

Adsorption isotherms were analysed using the Langmuir adsorption isotherm model:

$$Q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (2)$$

where $Q_{\max}$ is the maximum adsorption capacity (mg As per gram of adsorbent), Q_e is the quantity adsorbed at equilibrium (mg g^{-1}), b is the Langmuir constant (L mg^{-1}) and C_e is the quantity of aqueous As remaining at equilibrium (mg L^{-1}) (D'Arcy et al., 2011). Adsorption isotherm parameters and their uncertainties were determined using non-linear fitting with a Monte-Carlo method and 200 simulations (Hu et al., 2015).

Only As(V) adsorption isotherms were measured, given that the purpose of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite is to catalyse the photooxidation of As(III) and adsorb the As(V) that is subsequently produced. The acetate anion used to buffer the pH in this work may have an influence on measured adsorption capacities through competitive adsorption: (a) one previous study found no significant difference in the number of pore volumes achieved at breakthrough in the column adsorption of As(V) onto iron oxides when 4.2 mM carbonate is added to the influent (0.1 M NaCl and 10 mM piperazine- $\text{N,N}'$ -bis(2-ethanesulfonic acid) (PIPES) buffer) (Schaefer et al., 2020), whilst (b) another study showed a 21% reduction in As(V) adsorption onto iron-oxide coated sand when 23.6 mM carbonate was present (Brechtbühl et al., 2012).

2.4. X-ray absorption spectroscopy (XAS)

Arsenic K-edge XAS spectra were recorded at beamline B18 of Diamond Light Source (Dent et al., 2009). The excitation energy was selected using a Si(111) double crystal monochromator and calibrated by defining the maximum intensity of the fluorescence spectrum of As_2O_3 to be at 11871.7 eV (Smith et al., 2005). High energy harmonics were removed by Cr coated Si mirrors (collimating and focusing). The beam resolution was determined by the Darwin width of the monochromator and the divergence of the collimating mirror (10.0 eV) and is 3.6 eV at the As K-edge. The resulting spectral resolution was 28.6 eV with an energy resolution ($\Delta E/E$) for Si 111 of 1.4×10^{-4} at 2.05–20 keV. The photon flux was 10^{10} – 10^{11} photons s^{-1} . The beam was focused at the sample position using a toroidal mirror to 1×1 mm. Samples were mounted at 45° to both the incident beam and a nine element Fe fluorescence detector (Ortec C-TRAIN) with XSPRESS acquisition electronics that provide accurate deadtime correction. All spectra were recorded in fluorescence mode and the sample-detector distance and incident flux (controlled by a slit) were adjusted to ensure that the total incoming count rate was within the linear range of the detector. Quick EXAFS spectra were recorded from 11600–13200 eV in ~600 s. The spectra were normalised using ATHENA and modelled using ARTEMIS (Ravel and Newville, 2005).

The instrumental conditions were optimised to minimise the oxidation of As(III) induced by the synchrotron X-ray beam. Arsenic trioxide (As_2O_3 , Sigma-Aldrich) and sodium arsenate dibasic heptahydrate ($\text{Na}_2\text{HASO}_4 \cdot 7\text{H}_2\text{O}$, Sigma-Aldrich) were used as reference samples for the As(III) and As(V) K-edge positions, respectively. The As(III) and As(V) components of the XANES spectra were then determined using a linear combination of end-member components using Athena. Photographs of the experimental set-up are presented in the Supporting Information (Figure S2).

2.4.1. Binding modes determined using extended X-ray absorption fine structure (EXAFS)

Suspensions of 20 g L^{-1} $\text{TiO}_2/\text{Fe}_2\text{O}_3$ (100 mL total volume) were prepared in either 50 mM acetate (pH 5) or 50 mM borate (pH 9) buffers and spiked with 100 mg L^{-1} As(III) or As(V). Suspensions were stirred for 24 h to achieve equilibrium adsorption, and the arsenic-adsorbed solid samples were separated from the effluent by gravimetric filtration. The mineral paste was removed and dried for ~1 h under ambient conditions prior to analysis. The solids were stored in sealed opaque tubes (under nitrogen atmosphere) to prevent the oxidation of As(III). Samples, including As_2O_3 and $\text{HNa}_2\text{AsO}_4 \cdot 7\text{H}_2\text{O}$ standards, were ground to a powder and then mixed with cellulose in a ratio of 1:100 by mass. Powders were then pressed into pellets and mounted onto

Table 1

Langmuir adsorption isotherm parameters calculated by non-linear regression. Uncertainties (1σ) in $Q_{\max}$ and b were calculated using a Monte-Carlo method with 200 simulations, as described by Hu et al. (Hu et al., 2015).

Sample	$Q_{\max}$ (mg g ⁻¹)	1σ (68% confidence interval)	b (L mg ⁻¹)	1σ (68% confidence interval)	R^2
CPCB	22.8	21–24.7	0.0376	0.0304–0.0473	0.9943
CPMB	28.5	26.1–31.9	0.1428	0.0869–0.228	0.9785
SG	10.7	7.76–16.1	0.0176	0.0086–0.0407	0.7838

the sample holder with Kapton tape to hold them in position prior to measurements (SI Figure S2).

X-ray absorption near edge spectroscopy (XANES) confirmed that the oxidation state of arsenic was not changed when arsenic stock solutions were mixed with the TiO₂/Fe₂O₃ composites for 24 h at pH 5 and 9, gas purged using nitrogen. The structural parameters (e.g. inter-atomic distances) of arsenic adsorbed onto the TiO₂/Fe₂O₃ composite sorbents were then determined using extended X-ray absorption fine structure (EXAFS) spectroscopy.

The EXAFS, denoted by $\chi(E)$, were extracted from the spectra recorded from the samples and the standard compounds As₂O₃ (arsenolite) and FeAsO₄·2H₂O (scorodite), converted from energy to photoelectron wavenumber (k) and weighted by k^3 . Fourier transforms of the k^3 weighted $\chi(k)$ functions were performed to extract the radial distribution functions $\chi(R)$ using the software ATHENA (Ravel and Newville, 2005).

The EXAFS were fit using ARTEMIS (Ravel and Newville, 2005) and LARCH (Newville, 2013). All fits were performed over a R -range of ~ 1 to ~ 4 Å, except for As(V) and CPMB at pH 5 for which the range was 1–2 Å. A Hanning window was used to define the fit range.

2.5. ATR-FTIR and zeta potential used to identify protonation states

Suspensions of the CPMB TiO₂/Fe₂O₃ composite (1 g L⁻¹, 0.01 M NaCl, pH 7.0 $\pm$ 0.1 fixed with 0.01 and 1 M HCl or NaOH) were spiked with between 0 and 80 mg L⁻¹ As(III) or As(V) and mixed by shaking at room temperature for five days to achieve equilibrium adsorption. Aliquots of each suspension were taken, and the zeta potential was determined using the Malvern Zetasizer Nano. Suspensions were filtered gravimetrically and oven dried at 70 °C to minimise the amount of adsorbed water before ATR-FTIR analysis. ATR-FTIR spectra of the blank and arsenic-sorbed powders were then collected in the range of 400–4000 cm⁻¹, with a 1 cm⁻¹ resolution, using the Perkin Elmer Spectrum Two FT-IR Spectrometer. Spectra were normalised to the intensity of the metal oxide lattice excitation peaks (as these vibrations are expected to be little changed after adsorption and are much more intense than the peaks corresponding to $\nu(\text{As-O})$ stretching vibrations). A blank subtraction was made using FTIR spectra of the samples before arsenic adsorption to provide better resolution of new peaks appearing after arsenic adsorption. Zeta potential measurements and ATR-FTIR spectra were recorded for single-phase meso-TiO₂ and α -Fe₂O₃ reference samples under identical conditions.

3. Results and discussion

3.1. Characterisation of TiO₂/Fe₂O₃ adsorbents

The XRD patterns and assigned peaks are presented in Fig. 1a. Anatase is the major form of crystalline TiO₂ within CPCB (*co-precipitate commercial bifunctional*) and CPMB (*co-precipitate mesoporous bifunctional*), though smaller peaks corresponding to rutile as a minority phase are also identified. Hematite (α -Fe₂O₃) is the only crystalline iron oxide identified in the XRD patterns of CPCB and CPMB. The anatase peaks of CPMB are broader than those of CPCB, suggesting that the synthesised meso-TiO₂ used to prepare CPMB is less crystalline than the commercial TiO₂ nanopowder used to prepare CPCB. The

XRD pattern of the sol-gel synthesised sample, SG, gives small, broad peaks, assigned to anatase and hematite only (with rutile unidentified), showing that SG is poorly crystalline. This is likely due to atomic-scale mixing of Fe and Ti during synthesis and the relatively low calcination temperature (300 °C).

Particle size and morphology were assessed using scanning electron microscopy (SEM, Fig. 1b–d). SEM shows that the CPCB powder has the smallest mean particle size, due to the small dimensions of the anatase TiO₂ nanopowder support, with a maximum particle size of 10 μ m, and most particles < 1 μ m in diameter. The size distribution of CPMB particles is much more disperse, with many 10–30 μ m diameter particles, owing to the less homogeneous meso-TiO₂ powder used as the support. CPMB particles reach a maximum size of 30 μ m. Both CPCB and CPMB have high surface roughness, suggesting large surface areas. The SG sample consists of the largest particles, up to 100 μ m in diameter, with a much smoother surface texture, suggesting a low surface area. SEM images at lower magnification are presented in the Supporting Information (Figure S1).

3.2. Effect of synthesis method on the adsorption capacity

We previously reported the kinetics and equilibrium capacity for the adsorption of As(III) onto a TiO₂/Fe₂O₃ composite prepared via the CPMB synthesis route (Bullen et al., 2020b). Since the TiO₂/Fe₂O₃ composite aims to achieve effective arsenic remediation through coupling photooxidation with adsorption, in the present study we investigated the influence of the synthesis route upon the adsorption capacity of TiO₂/Fe₂O₃ using As(V).

The greatest adsorption capacities at pH 5 are achieved when the iron oxide phase was precipitated onto a solid TiO₂ support, with $Q_{\max}$ values of 22.8 ± 1.8 and 28.5 ± 2.9 mg g⁻¹ for CPCB and CPMB samples respectively, and just 10.7 ± 4.2 mg g⁻¹ for SG, the sol-gel product (Fig. 2). The low adsorption capacity of the sol-gel product is explained by large particle sizes and a smooth surface resulting in a reduced surface area. CPMB has not only the highest As(V) adsorption capacity, but also the greatest Langmuir constant indicating the greatest As(V) binding affinity (0.14 L mg⁻¹ versus 0.038 and 0.018 L mg⁻¹ for CPCB and SG samples respectively, Table 1). Previous work shows that the Fe:Ti surface mass ratio is significantly greater than the Fe:Ti bulk mass ratio when TiO₂/Fe₂O₃ composites are prepared by precipitating iron oxide onto a TiO₂ support (Bullen et al., 2020a). Since the meso-TiO₂ particles used to prepare CPMB are larger than the commercial TiO₂ particles used to prepare CPCB, the Fe:Ti surface enrichment likely increases in the order SG < CPCB < CPMB, further explaining the trend in adsorption capacities. Given the possibility of competitive adsorption from the acetate buffer (Brechtbühl et al., 2012), the absolute adsorption capacities of each material may be higher in an electrolyte-only media such as 0.1 M NaCl.

3.3. Speciation of arsenic adsorbed onto composite TiO₂/Fe₂O₃: structures of surface complexes and surface precipitation

Extended X-ray absorption fine structure (EXAFS) was used to determine interatomic distances and thus identify the major binding modes for arsenic surface complexes formed on single-phase mineral sorbents (Pena et al., 2006; Catalano et al., 2007; Ona-Nguema et al.,

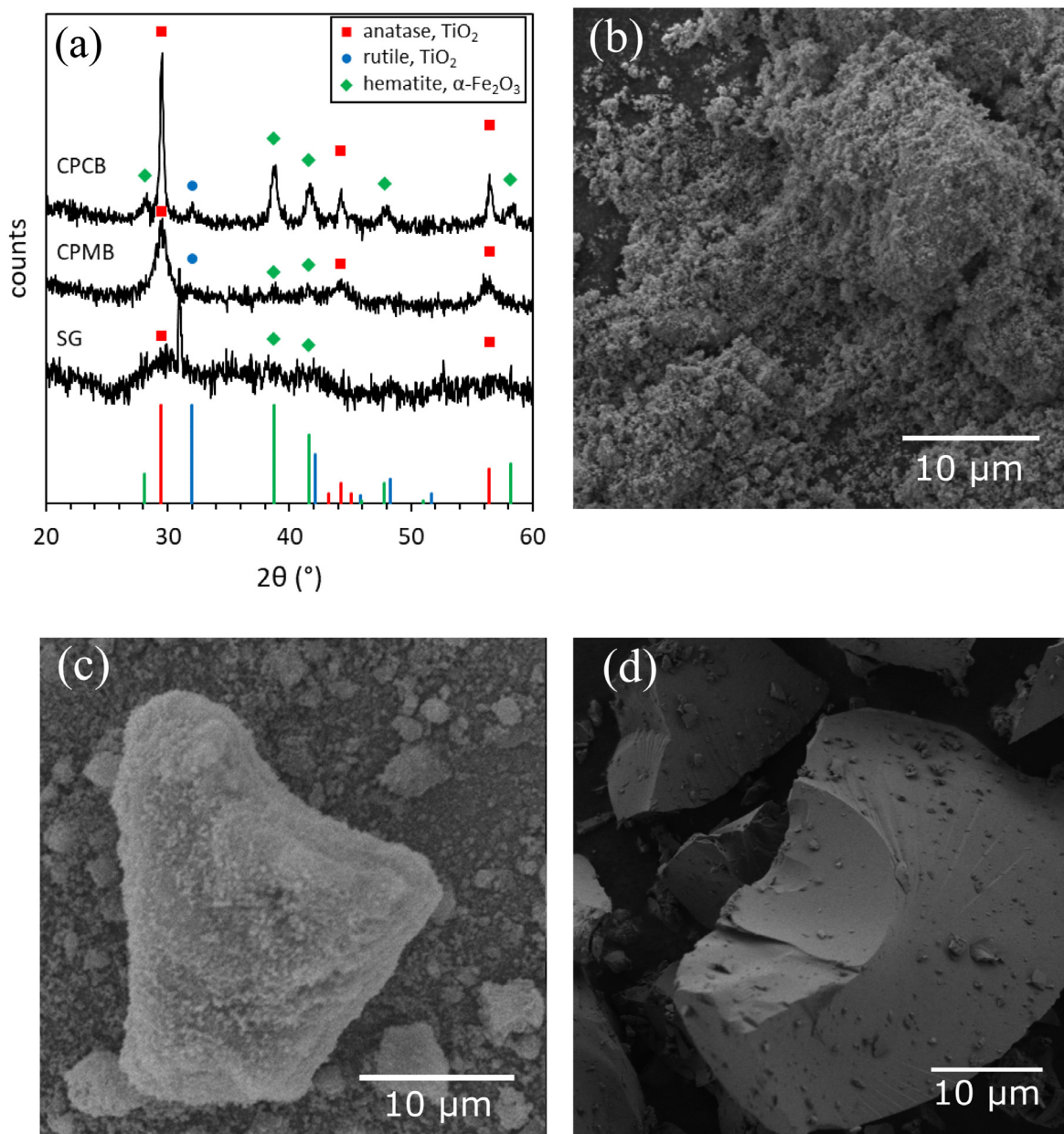


Fig. 1. Characterisation of three TiO₂/Fe₂O₃ composites prepared using different synthesis methods. (a) X-ray diffraction (XRD) patterns confirming the crystal phases within CPCB, CPMB and SG TiO₂/Fe₂O₃ composites. Peaks corresponding to anatase TiO₂ (red squares), rutile TiO₂ (blue circles) and hematite α-Fe₂O₃ (green triangles) phases were identified. XRD patterns have been off-set in the y-axis for clarity. Scanning electron microscopy (SEM) images of TiO₂/Fe₂O₃ composite particles: (b) CPCB, (c) CPMB, and (d) SG. Lower magnification images are presented in the Supporting Information (Figure S1).

2005). EXAFS results were then combined with Fourier transform infrared (FTIR) spectroscopy and zeta potential analysis to determine the protonation states of arsenic surface complexes (Pena et al., 2006). In line with previous studies, we investigated FTIR $\nu(\text{As-O})$ stretching vibrations in the 600–900 cm⁻¹ region (Goldberg and Johnston, 2001; Ela et al., 2013) and FTIR $\nu(\text{AsO-H})$ arsenic hydroxyl stretching vibrations in the 2800–3000 cm⁻¹ region (Myneni et al., 1998).

3.3.1. Insights into the structure of arsenic complexes using EXAFS

The As-Fe and As-Ti interatomic distances determined by EXAFS were used to establish the As(III) and As(V) structures formed on the surface of TiO₂/Fe₂O₃ at pH 5 and 9. The quality of the fitted model against experimental data collected for CPCB, CPMB and SG is presented in Fig. 3. The radial distribution functions (Fig. 3b, Fig. 4b,

S4) all exhibit a peak at ~1.3 Å (not corrected for phase shift). This corresponds to O atoms surrounding the central As for the standards and is also likely to correspond to O for the bicomposite samples. A relatively intense peak at ~3 Å (not corrected for phase shift) is exhibited by As₂O₃ and scorodite, which is due to the presence of As and Fe, respectively, in a second shell. Some samples also exhibit a peak at ~3 Å (not corrected for phase shift) that is more intense for the As(III) samples than for the As(V) samples.

The EXAFS of As₂O₃ and scorodite standards were fit to the crystal structure models of Ballirano and Maras (2002) and Xu et al. (2007), respectively. The degeneracy (N_i) of the scattering paths were taken a priori from the crystal structure. The energy shift (E_0) and passive electron reduction factor (S_0^2) were constrained to be the same for all paths. The fits are shown in Figure S4 and the fit parameters,

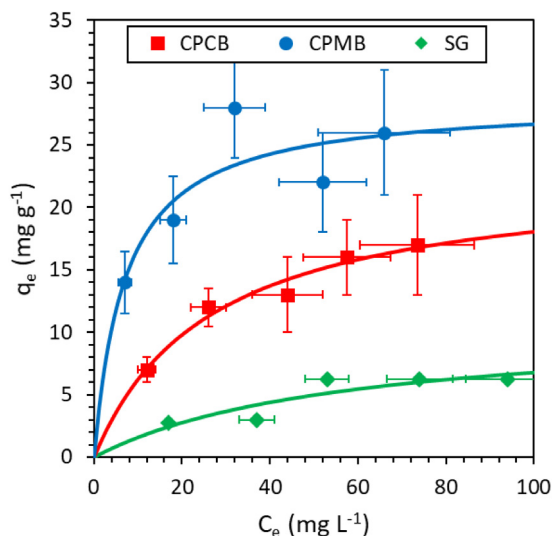


Fig. 2. Adsorption isotherms for As(V) and the three types of $\text{TiO}_2/\text{Fe}_2\text{O}_3$ adsorbent synthesised (CPCB, CPMB, SG). Five data points were collected using each adsorbent. The experimental conditions were 1 g L^{-1} of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite, 20–100 mg L^{-1} total As(V), 0.1 M acetate buffer, adjusted to pH 5 using acetic acid, 24 h shaking time, 100 mL total volume. Error bars are estimated from the difference between duplicates at the lowest and highest concentration respectively, according to Eq. (1). The Langmuir adsorption isotherm model was fit to each data set using non-linear regression, minimising the sum of square residuals (Hu et al., 2015).

where σ^2 and R_i are the mean square displacement and path length respectively, are given in Table S2. Bond lengths of $1.793(8) \text{ \AA}$ for As(III)-O and $3.248(9) \text{ \AA}$ for As(III)-As were determined from the fit to As_2O_3 . The former is within uncertainty of the literature value of $1.786(2) \text{ \AA}$, however, the latter is slightly longer than the literature value of $3.219 \text{ \AA}$. This difference, in addition to the discrepancy of the fit $\sim 3 \text{ \AA}$, could be due to a minor component of claudetite in the otherwise arsenolite form of As_2O_3 . A bond length of $1.69(1) \text{ \AA}$ for As(V)-O, and bond lengths of $3.35(3)$ and $3.38(8) \text{ \AA}$ for As(V)-Fe were determined from the fit to scorodite. These bond lengths are within uncertainty of previously published literature (Table S2) and a model with two Fe shells is in agreement with previous studies (Sherman and Randall, 2003).

The coordination environments of As in the samples were determined from scattering models using paths generated from the structures of As_2O_3 (claudetite and arsenolite), As_2O_5 , hematite and anatase. S_0^2 values of 0.75 for As(III) and 0.85 for As(V), which were determined from the fits to As_2O_3 and scorodite, were fixed for the bicomposites due to the strong correlation between N_i and S_0^2 in the fitting procedure. E_0 was constrained to be the same for all paths and the N_i of paths of similar length were summed. The parameters are given in Table 2 and example fits are shown in Figs. 3 and 4.

The first shell of the As(III) CPCB and CPMB samples prepared at pH 5 was fit to an As-O path. The interatomic distance of $1.79(1) \text{ \AA}$ is within uncertainty of the As-O bond length determined for As_2O_3 ($1.793(8)$; Table S2) and is hence consistent with a trigonal pyramidal arrangement of oxygen around the central As(III) atom (Adra et al., 2015). The coordination numbers determined for the first shell are low ($N=1.8$ and 2.3 respectively, Table 2) and the fits to these bicomposites have a larger E_0 relative to other As(III) compounds (Table 2, Table S2). These values would be consistent with a metallic As^0 component, however, peaks indicative of metal As-As bonds at ~ 2.5 and $4.1 \text{ \AA}$ are not observed in $\chi(R)$ (Schiferl and Barrett, 1969). It is possible that the photocatalyst may have reduced a portion of the As(III) to As(0) under the experimental conditions used to prepare these samples (acidic pH and nitrogen purging). This has been observed previously (Levy et al., 2012). A single scattering path does not fit the second shell well and

results in unreasonable values for the fit parameters, although we found that As-As produced a better fit than As-Fe or As-Ti. Thus, two scattering paths, with an As-As path considered an integral component, were fit to the second shell. Fits with an As-Ti (or As-O) path as the second component resulted in unreasonable values for the fit parameters, whereas an As-Fe path fit the data well (Table 2). The As-As second shell component suggests significant As(III) surface precipitation, which has been observed previously on magnetite (Fe_3O_4) surfaces using high resolution transmission electron microscopy (HR-TEM) (Morin et al., 2009). As(III) is coordinated to ~ 3 Fe at a distance of $3.51 \text{ \AA}$ for the CPCB and CPMB samples at pH 5. This is consistent with the tridentate hexavalent corner-sharing ^3C surface complexes found during adsorption and surface precipitation of As(III) onto magnetite (Fe_3O_4) (Morin et al., 2009). It is not possible to determine whether this tridentate complex is the predominant species formed between As(III) and the Fe_2O_3 surface at pH 5, as bidentate complexes which have shorter As-Fe path lengths (e.g. corner-sharing (^2C) at $3.38 \text{ \AA}$ or mononuclear edge-sharing (^2E) at $2.95 \text{ \AA}$ (Morin et al., 2009)) would be obscured by the significant As-As peak at $3.24 \text{ \AA}$.

The $\chi(R)$ of the As(III) CPCB and CPMB samples prepared at pH 9 have a high amplitude peak at $\sim 1.3 \text{ \AA}$ (compared with the same samples at pH 5, not corrected for phase shift) and As was found to be coordinated to $3(1) \text{ O}$ at a distance of $1.78(1) \text{ \AA}$ (Table 2), as expected for As(III). A second shell is evident in the $\chi(k)$ and $\chi(R)$ of these samples and was fit well by an As-As path (Table 2). The intensity of this shell in the $\chi(R)$ and the degeneracy of this path is lower at pH 9 compared to pH 5 for both CPCB and CPMB, indicating reduced surface precipitation at alkaline pH. No significant As-Fe or As-Ti contributions to the second shell were found, and there is no evidence for tridentate (^3C) As-Fe complexation at either pH 5 or 9.

The $\chi(R)$ of the As(V) samples all exhibit a strong first shell peak, which was fit to an As-O scattering path. The coordination number of ~ 4 and bond length of $\sim 1.69 \text{ \AA}$ determined for all of the samples (Table 2) indicates a tetrahedral arrangement of oxygen about the central As(V) atom (Pena et al., 2006). A weak second shell is exhibited in the $\chi(R)$ of all of samples other than the SG sample prepared for 2 h. Reasonable parameters were only obtained by fitting an As-Ti path (Table 2), with As-As, As-Fe and As-O paths resulting in anomalously high coordination numbers or unreasonable σ^2 values. The As-Ti distances determined for CPCB (pH 5), CPMB (pH 5 and 9) and SG (pH 7) are 3.11 – $3.14 \text{ \AA}$. These are significantly closer to the previously found range of 3.17 – $3.26 \text{ \AA}$ for bidentate binuclear corner-sharing (^2C) complexes on single-phase TiO_2 than the range of 3.59 – $3.61 \text{ \AA}$ for monodentate mononuclear complexes (He et al., 2009). Whilst an As-Fe second shell could not be fit to these samples, As-Fe distances for bidentate binuclear corner-sharing (^2C) complexes are similar ($3.29 \text{ \AA}$ (Arai et al., 2004)), whilst bidentate mononuclear edge-sharing (^2E) distances are only 2.78 – $2.86 \text{ \AA}$ (Arai et al., 2004; Fendorf et al., 1997). An As-O path was additionally fit to the SG sample (Table 2), although, the significance of this path should be treated with caution due to the weak changes in amplitude of $\chi(R)$ and the large uncertainty associated with the degeneracy (Table 2). A second shell could not be fit to the CPMB sample prepared at pH 5.

Despite significant differences in adsorption capacity between the three synthesised composites (Fig. 2), EXAFS does not indicate any effect of the synthesis method on the structure of adsorbed arsenic (Table 2).

3.3.2. Insights into protonation state using zeta potential and FTIR

Zeta potential and FTIR analysis were used to determine the protonation states of arsenic surface complexes. We focused on the CPMB material given that (a) it has the greatest adsorption capacity of the three composites studied herein (Fig. 2), and (b) we developed surface complexation model (SCM) for this material in a previous work (Bullen et al., 2020a), allowing us to compare the experimentally identified complexes with those predicted by modelling. We also previously investigated the adsorption kinetics of this material, and investigated

Table 2

Parameters determined by fitting EXAFS spectra of bicomposite materials, where N is the degeneracy of the path, E_0 the energy shift, σ^2 the mean square displacement, and R_i the bond length in Å. S_0^2 (passive electron reduction factor) values of 0.75 were used for As(III) and 0.85 for As(V). The experimental conditions were 20 g L⁻¹ TiO₂/Fe₂O₃, 100 mg L⁻¹ As(III) or As(V), 50 mM acetate (pH 5) or borate (pH 9) buffer, and 24 h mixing to achieve equilibrium adsorption.

Sorbate	Sorbent	pH	Scattering path	N	E_0	σ^2	R_i
As(III)	CPCB	5	As–O	1.8(4)	13(3) ^a	0.001(1)	1.79(1)
			As–As	3(1) ^a	13(3) ^a	0.003(3)	3.24(2)
			As–Fe	3(1) ^a	13(3) ^a	0.008(3)	3.51(3)
As(III)	CPMB	5	As–O	2.3(6)	13(4) ^a	0.002(1)	1.79(1)
			As–As	3(2) ^a	13(4) ^a	0.003(3)	3.24(1)
			As–Fe	3(2) ^a	13(4) ^a	0.010(4)	3.51(3)
As(III)	CPCB	9	As–O	3(1)	10(1) ^a	0.003(2)	1.78(1)
			As–As	2(1)	10(1) ^a	0.004(6)	3.23(2)
As(III)	CPMB	9	As–O	3.2(2)	10(1) ^a	0.002(1)	1.78(1)
			As–As	1(1)	10(1) ^a	0.003(4)	3.22(1)
As(V)	CPCB	5	As–O	4(1)	5(4) ^a	0.002(1)	1.68(1)
			As–Ti	3(7)	5(4) ^a	0.01(2)	3.11(2)
As(V)	CPMB	5	As–O	4(2)	8(5)	0.001(3)	1.69(3)
As(V)	CPCB	9	As–O	4(1)	7(4) ^a	0.003(1)	1.69(1)
			As–Ti	2(4)	7(4) ^a	0.01(2)	3.12(9)
As(V)	CPMB	9	As–O	4.2(7)	8(2) ^a	0.001(1)	1.69(5)
			As–Ti	2(2)	8(2) ^a	0.009(1)	3.12(1)
As(V)	SG	7	As–O	4(1)	9(3)	0.002(1)	1.69(1)
			As–O	4(9)	9(3) ^a	0.014(3)	2.70(9)
			As–Ti	1(1)	9(3) ^a	0.002(7)	3.14(4)

^aConstrained to be the same for indicated paths.

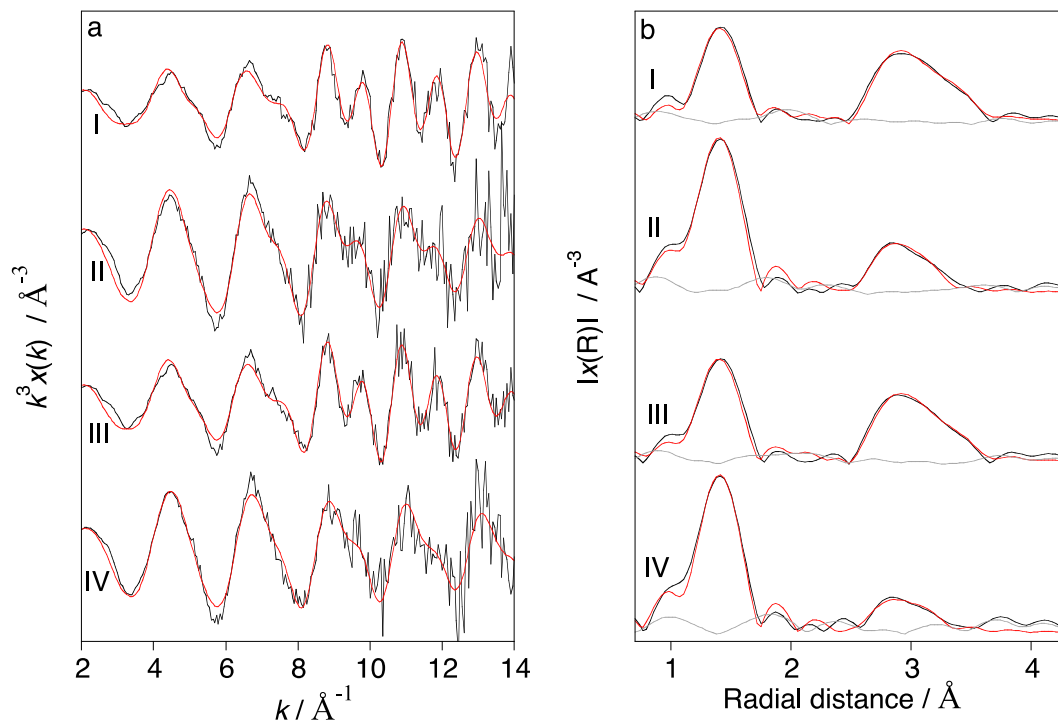


Fig. 3. The As(III) (a) $k^3\chi(k)$ (black) and (b) $\chi(R)$ (black) for (I) CPCB pH 5, (II) CPCB pH 9, (III) CPMB pH 5 and (IV) CPMB pH 9. The fit (red) and residual in $\chi(R)$ (grey) are shown. The experimental conditions were 20 g L⁻¹ TiO₂/Fe₂O₃, 100 mg L⁻¹ initial As(III), and 50 mM acetate buffer (pH 5) or 50 mM borate buffer (pH 9), with 24 h shaking to achieve equilibrium adsorption. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

how the choice of batch versus continuous-flow treatment and operating conditions would influence the lifetime of a filter using CPMB media (Bullen et al., 2020b). α -Fe₂O₃ and the mesoporous TiO₂ support were used as reference samples, to better understand results collected for the composite material, given the challenges in deconvoluting the EXAFS signal between Fe₂O₃ and TiO₂ contributions.

The zeta potential of α -Fe₂O₃ and CPMB decreases with increasing adsorption of both As(V) and As(III) (Fig. 5a,b). However, the rate of change in zeta potential with increasing surface coverage is approximately 4–5 times greater for As(V) than As(III). EXAFS analysis identified bidentate As(V)-TiO₂ surface complexes, and As(V)-iron oxide surface complexes are generally considered to be bidentate (Adra et al.,

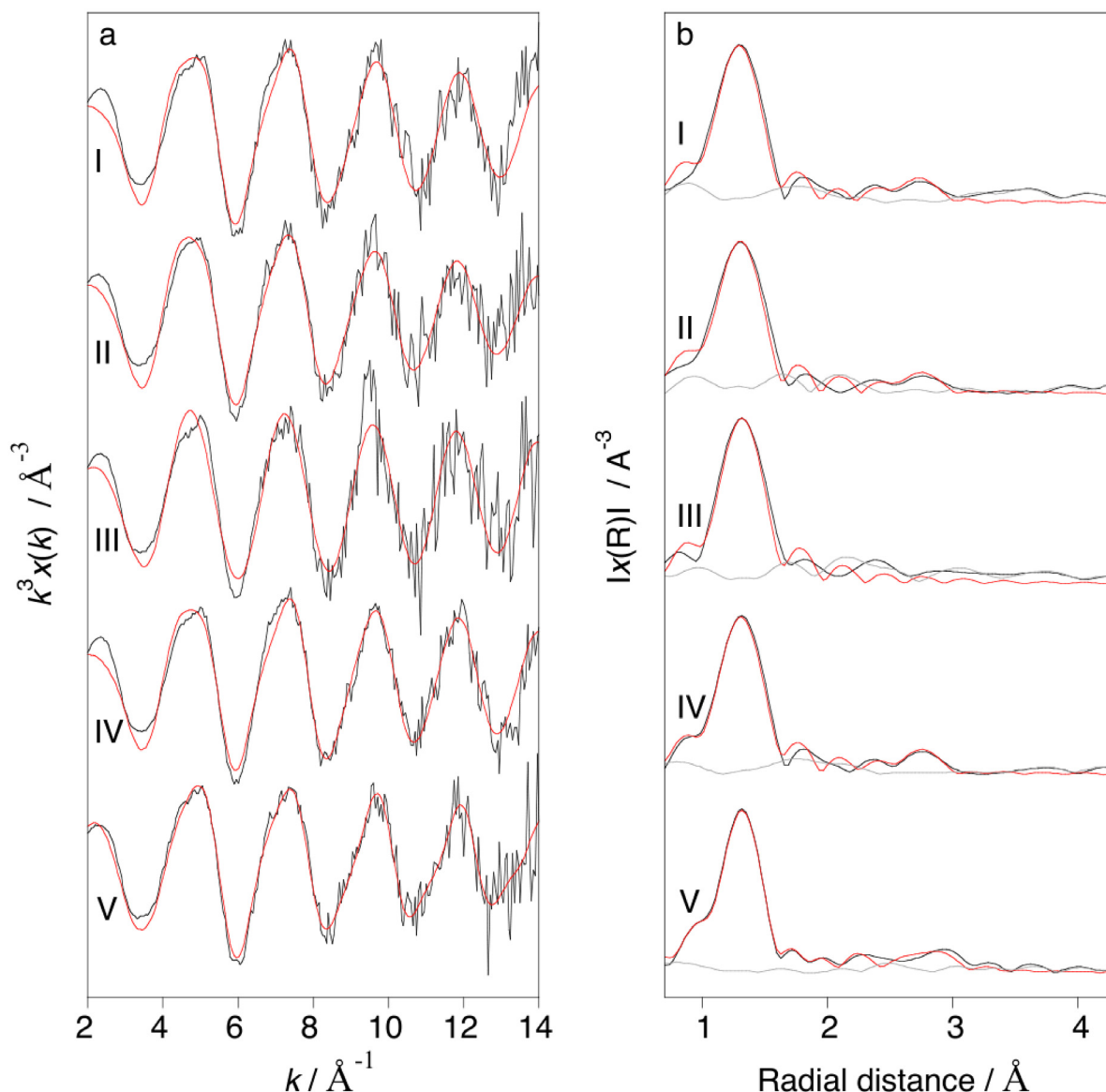


Fig. 4. The As(V) (a) $k^3\chi(k)$ (black) and (b) $\chi(R)$ (black) for (I) CPCB pH 5, (II) CPCB pH 9, (III) CPMB pH 5, (IV) CPMB pH 9 and (V) SG pH 7. The fit (red) and residual in $\chi(R)$ (grey) are shown. The experimental conditions were 20 g L⁻¹ TiO₂/Fe₂O₃, 100 mg L⁻¹ initial As(V), and 50 mM acetate buffer (pH 5) or 50 mM borate buffer (pH 9), with 24 h shaking to achieve equilibrium adsorption (except for (V) SG pH 7, which was only shaken for 2 h only). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2015; Ona-Nguema et al., 2005) for which the maximum charge is -1 . Consequently, zeta potential analysis suggests that adsorbed As(III) must be present as a combination of -1 (deprotonated) and electrostatically neutral (protonated) species. The latter species could be found both through the tridentate 3C complexes that are potentially formed on the hematite surface, i.e. $(>FeO)_3As$ (Section 3.3.1), or through bidentate $(>FeO)_2AsOH$ and monodentate $>FeAs(OH)_2$ complexes. The zeta potential of meso-TiO₂ suspensions is already significantly negative prior to the adsorption of arsenic (-25 mV) and is consequently slow to decrease with arsenic adsorption.

A detailed assignment of IR peaks referenced against literature spectra is given in the Supporting Information (Tables S3 and S4). The FTIR spectra of CPMB and Fe₂O₃ and TiO₂ reference samples before the adsorption of arsenic are presented in Fig. 6. All metal oxide samples show a broad peak between 2500 and 3600 cm⁻¹ due to $\nu(O-H)$ stretching vibrations, most intense at 3355 cm⁻¹ for α -Fe₂O₃ and 3234 cm⁻¹ for meso-TiO₂, and with at an intermediate value of

3333 cm⁻¹ for CPMB (Fig. 6b). No narrow peaks within this region are observed before the adsorption of arsenic.

After adsorption of As(III), the iron oxide containing samples (α -Fe₂O₃ and CPMB) both show new peaks between 2850 and 2990 cm⁻¹ with a weak but significant intensity of $\sim 1\%$ absorption (Fig. 7a). As(III)-sorbed TiO₂ does not show new peaks in this region, and neither do any of the As(V)-containing samples. The $\nu(O-H)$ stretching vibrations of hydroxyls within aqueous inorganic arsenic species appear at lower frequencies than the $\nu(O-H)$ stretch of H₂O (e.g. 3011 cm⁻¹ for HAsO₄²⁻ versus 3615 and 3450 cm⁻¹ for H₂O) (Myneni et al., 1998), i.e. in the same region as the new vibrations identified in Fig. 7a. As(III) reaches greater protonation states at less acidic pH values than As(V), both in the aqueous and surface-adsorbed phases (Dixit and Hering, 2003; Kanematsu et al., 2013) and stretching $\nu(O-H)$ vibrations at ~ 2930 and 2860 cm⁻¹ are only observed for As(V) adsorbed onto α -Fe₂O₃ under acidic conditions (Wang et al. Fig. 3c) (Wang et al., 2015). The pattern of new $\nu(O-H)$ peaks in samples containing Fe₂O₃ and As(III) at pH 7, Fe₂O₃-As(V) samples at acidic pH, but not in

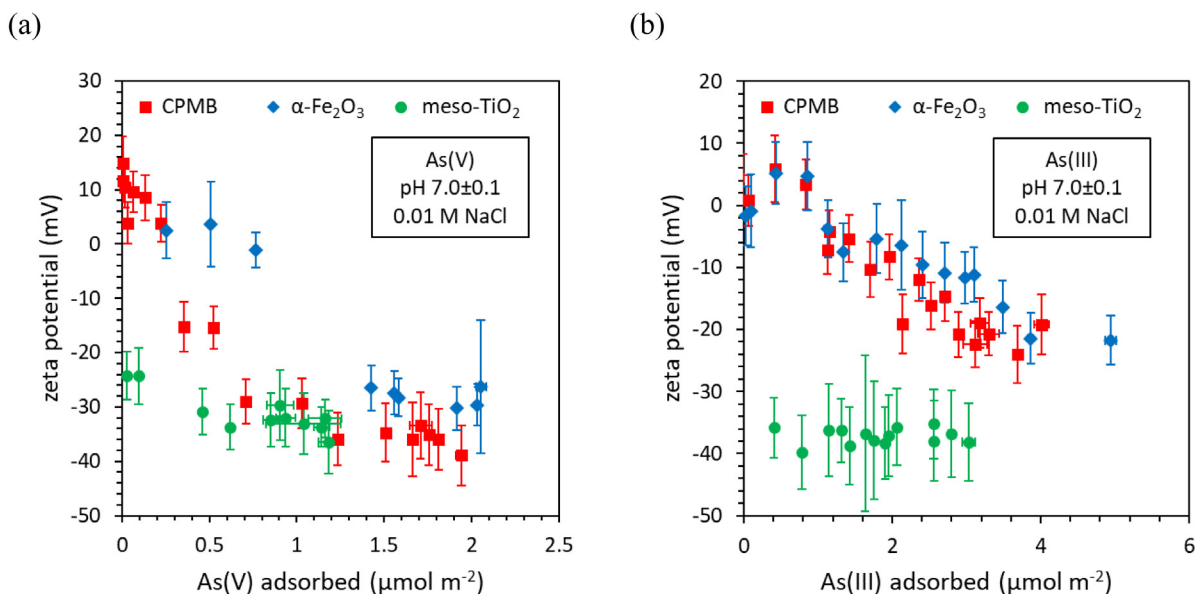


Fig. 5. The influence of arsenic adsorption on the zeta potential of mineral suspensions. The changes in zeta potential with increasing adsorption of (a) As(V) and (b) As(III) for suspensions of CPMB (red squares), α -Fe₂O₃ (blue diamonds) and meso-TiO₂ (green circles). The experimental conditions were 1 g L⁻¹ solid concentration, 0 to 74 mg L⁻¹ total As, 0.01 M NaCl, pH 7.0 $\pm$ 0.1.

pure TiO₂ samples or samples containing As(V) at pH 7, suggests that these new peaks correspond to ν (AsO–H) stretching vibrations. Elsewhere, ν (AsO–H) stretching vibrations have been identified between 2900, 2955 and 3076 cm⁻¹ for As-containing minerals such as adamite (Sumin de Portilla, 1976), vladimirite, and picroparmacolite (Makreski et al., 2017), and ν (AsO–H) stretching vibrations at 2855 and 3052 cm⁻¹ have been predicted using density-functional theory (DFT) for As(III) adsorbed onto ferrihydrite (Dzade and De Leeuw, 2018).

The presence of new ν (O–H) peaks after the adsorption of As(III) onto iron oxide-containing samples α -Fe₂O₃ and CPMB is accompanied by new δ (O–H) peaks at 1380–1470, 1100–1255 and 1030–1070 cm⁻¹ (Fig. 7b), close to the δ (AsO–H) vibration of aqueous H₃AsO₃ at 1250 cm⁻¹ (Bahfenne and Frost, 2010). In meso-TiO₂, the 1000–1600 cm⁻¹ region is dominated by decreased IR absorption due to the loss of adsorbed carbonate. The absence of new ν (O–H) peaks after the adsorption of arsenic observed in the As(III)-TiO₂ sample and the As(V)-containing samples is accompanied by an absence of new δ (O–H) peaks (though As(V) adsorbed onto α -Fe₂O₃ under acidic conditions shows both ν (O–H) peaks at $\sim$ 2930 and $\sim$ 2860 cm⁻¹ and δ (O–H) peaks at 1350 and 1100 cm⁻¹ (Wang et al., 2015, Fig. 3c)). This pattern of presence-versus-absence suggests that these peaks are not due to metal oxide surface hydroxyls, but instead due to the hydroxyl group on protonated Fe₂O₃-As(III) surface complexes. Consequently, the absence of ν (AsO–H) and δ (AsO–H) in As(V)-containing samples indicates that As(V) complexes on CPMB, meso-TiO₂ and α -Fe₂O₃ are deprotonated at pH 7 (in agreement with the trend of decreasing zeta potential as As(V) is adsorbed onto CPMB). EXAFS identified bidentate As(V)-TiO₂ surface complexes, indicating that As(V) is present on the TiO₂ surface of these composites as ($>$ -TiO₂)₂AsO₄⁻, and most likely on the Fe₂O₃ surface as ($>$ -FeO)₂AsO₄⁻ (Adra et al., 2015; Ona-Nguema et al., 2005).

The value of the ν (As–O) stretching frequency depends on the As–O bond order, and is therefore used to identify dominant arsenic surface complexes by comparing the position of ν (As–O) absorption bands against IR spectra for aqueous arsenic species at different pH values, for which the protonation states are well known (Myneni et al., 1998; Goldberg and Johnston, 2001; Pena et al., 2006). For all As(V) samples, absorption at 933 cm⁻¹ was weak (Fig. 7e), suggesting an absence of As(V) surface complexes with the double bond localised

on a single As=O group (i.e. no ($>$ SO)₂HAsO₂ complexes). Increased absorbance at $\sim$ 808 cm⁻¹ is likely due to ν (As–OM), where oxygen is complexed to a metal, i.e. Fe or Ti at the mineral surface (Pena et al., 2006; Ela et al., 2013). Absorbance between 808 and 933 cm⁻¹ suggests deprotonation (delocalisation of the As=O double bond charge across two or three As–O groups results in absorbance at 850 cm⁻¹ and 855 cm⁻¹ respectively Myneni et al., 1998). This agrees with analysis of the zeta potential and the ν (O–H) region.

For As(III), all three samples show increased absorption at 790 cm⁻¹, corresponding to uncomplexed oxygen (Fig. 7d) (Ela et al., 2013). This agrees with zeta potential analysis, confirming that adsorbed As(III) is partially present as negative surface complexes as well as neutral complexes. The strong absorption of As(III)-sorbed Fe₂O₃ at 680 cm⁻¹ corresponds to ν (As–OH), either indicating a significant presence of protonated surface complexes, or a significant amount of arsenic hydroxide surface precipitates (Bullen et al., 2020a; Ona-Nguema et al., 2005). Absorbance at 680 cm⁻¹ is less significant for meso-TiO₂ than Fe₂O₃, suggesting that As(III) surface complexes are protonated to a greater extent on the Fe₂O₃ surface than the TiO₂ surface at pH 7, in agreement with analysis of the ν (O–H) region. Meso-TiO₂ shows a small peak at 920 cm⁻¹ corresponding to uncomplexed ν (As–O) for As(V), suggesting that some As(III) had been oxidised between sample preparation and analysis, which is not surprising given the photocatalytic nature of TiO₂.

3.3.3. Comparison of arsenic speciation predicted by surface complexation modelling (SCM) with EXAFS, zeta potential and FTIR observations

We recently developed a component additive surface complexation model (CA-SCM) for the CPMB TiO₂/Fe₂O₃ composite (Bullen et al., 2020a), which predicts the adsorption of arsenic using a combination of non-interacting TiO₂ and Fe₂O₃ surface components (Davis et al., 1998). This model was developed using the extended triple layer model (ETLM) and the surface complexes selected by Sverjensky and Fukushima for single-phase goethite (FeOOH) and for single-phase TiO₂ surfaces as a starting point (Sverjensky and Fukushima, 2006). Equilibrium constants for the formation of each surface species were optimised to improve the quality of fit between the model and experimental pH adsorption edge data. Having identified some of the characteristics of arsenic adsorbed onto the TiO₂/Fe₂O₃ composite surface, we now use experimental

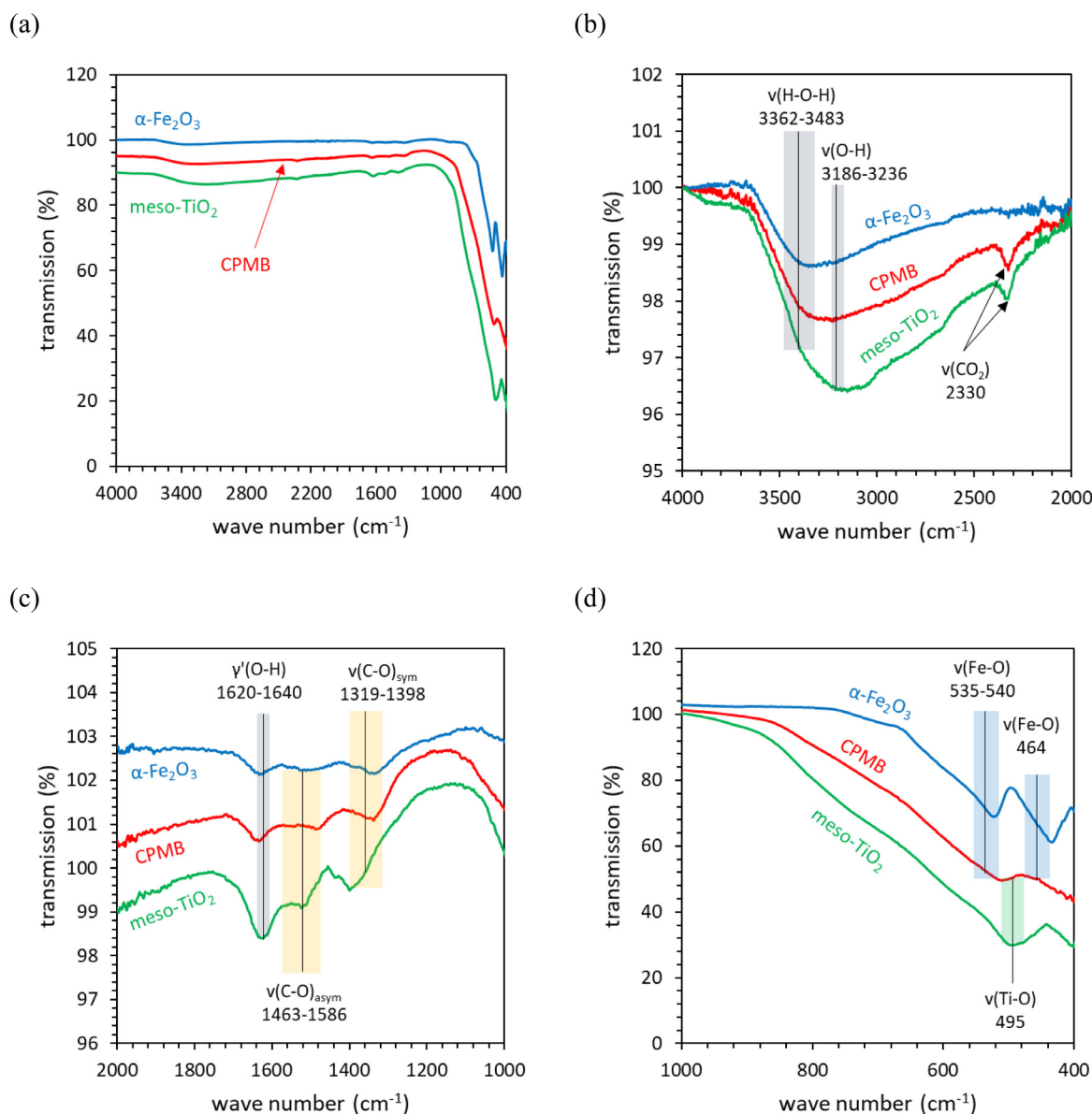


Fig. 6. ATR-FTIR spectra of the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite CPMB and the two reference samples ($\alpha\text{-Fe}_2\text{O}_3$ and meso-TiO_2) before adsorption of arsenic. Spectra in panels (a) and (b) have been shifted in the y-axis for clarity. References for the peak assignment are presented in Table S3.

analysis to evaluate the surface structures predicted by the CA-SCM. The results are summarised in Fig. 8.

Firstly, the surface complexation model (SCM) required a multilayer adsorption reaction (*i.e.* surface precipitation) to fully capture the extent of adsorption when describing As(III) adsorption isotherms at pH 7 (Bullen et al., 2020a). This is supported by EXAFS analysis, where the As–As second shell path suggests significant surface precipitation of As(III) on the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ surface at both pH 5 and 9. The greater magnitude of the second-shell signal and higher coordination number when the pH drops from 9 to 5 indicates increasing surface precipitation. This agrees with aqueous geochemical calculations using the software PHREEQC, which predict that precipitation is more favourable below pH 9 (Bullen et al., 2020a). Neither the SCM nor EXAFS provided any evidence for As(V) surface precipitation between pH 5 and 9, though As(V) surface precipitation under acidic conditions can be observed elsewhere (Jia et al., 2006).

Secondly, the SCM predicts the protonated bidentate As(III)- Fe_2O_3 surface complex, $(>\text{FeO})_2\text{AsOH}$, as the dominant species at pH 5 and

9 (Bullen et al., 2020a). In the SCM, deprotonated $(>\text{FeO})_2\text{AsO}^-$ is a minority component, increasing with pH. Whilst FTIR spectra showed evidence of significant As(III) protonation, zeta potential measurements suggest a partial negative charge of adsorbed arsenic at pH 7, in agreement with the SCM. EXAFS however, suggested the presence of tridentate (^3C) As(III)- Fe_2O_3 complexes at pH 5 which are neither protonated nor negatively charged, and are not featured in the SCM speciation. EXAFS did not identify bidentate As(III)- Fe_2O_3 complexes, perhaps due to overlap of this peak with the As–As path. EXAFS and zeta potential measurements reveal little information about the nature of As(III)- TiO_2 surface complexes, however FTIR supports the presence of deprotonated As(III) surface complexes at pH 7. This corresponds with the SCM predictions of deprotonated As(III)- TiO_2 species: $(>\text{TiO})_2\text{AsO}^-$ at pH 5, gradually switching to outer sphere/hydrogen-bonded $>\text{TiOH}_2^+ - \text{AsO}(\text{OH})_2^-$ beyond pH 7 (Bullen et al., 2020a).

Thirdly, the SCM predicts that the bidentate species $(>\text{FeO})_2\text{AsO}_2^-$ and $(>\text{TiO})_2\text{AsO}_2^-$ are the dominant forms of adsorbed As(V) at pH 5 (Bullen et al., 2020a). At pH 9, the SCM predicts that As(V) adsorbed

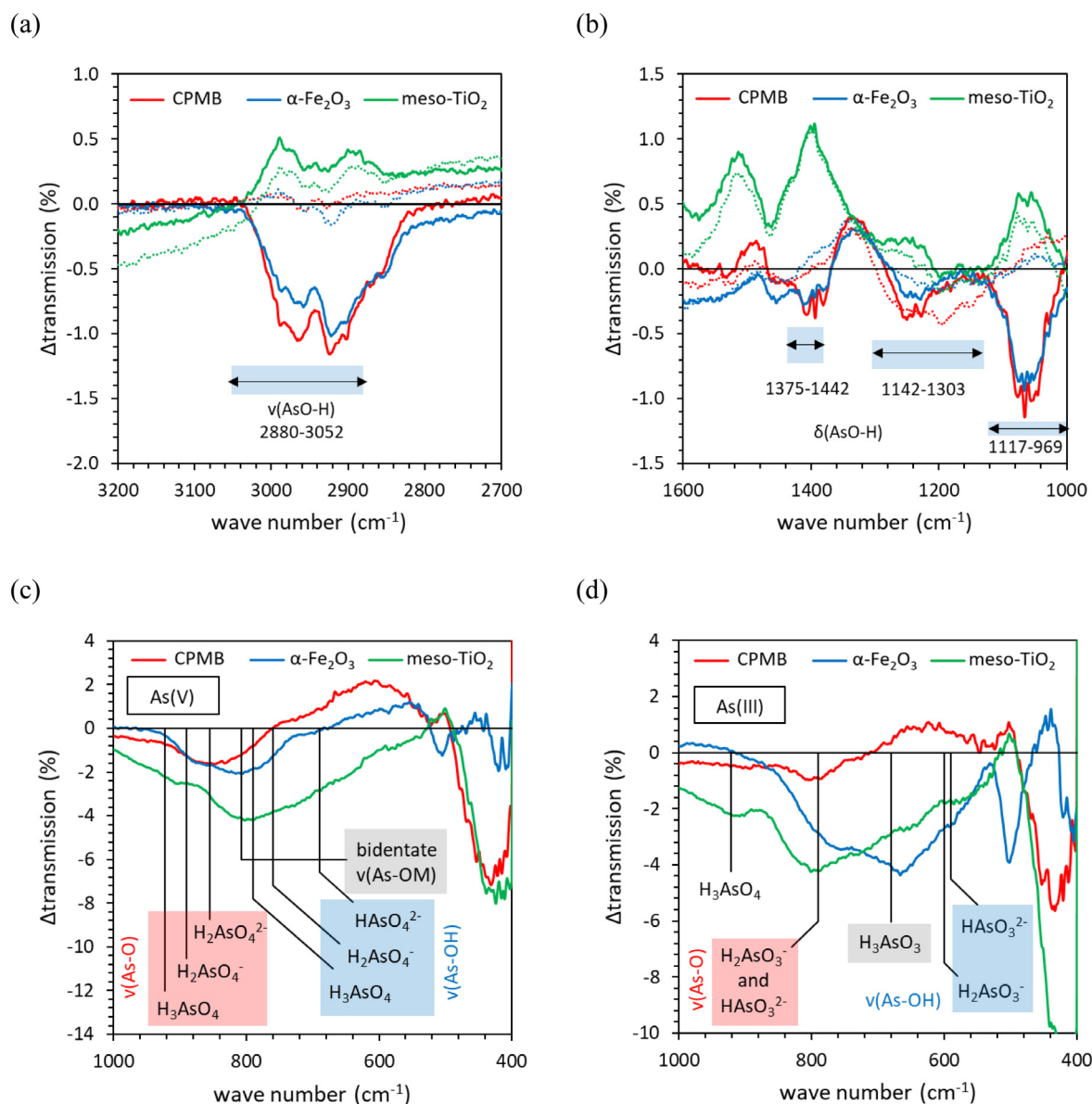


Fig. 7. Changes in infrared absorption (ATR-FTIR spectroscopy) after adsorption of As(V) and As(III). Spectra are presented for CPMB (red) alongside $\alpha\text{-Fe}_2\text{O}_3$ (blue) and meso- TiO_2 (green) reference samples. (a) The $\nu(\text{AsO-H})$ stretching region and (b) the $\delta(\text{AsO-H})$ deformation region of samples after As(III) adsorption (solid lines) and As(V) adsorption (dotted lines). (c) and (d) present the $\nu(\text{As-O})$ stretching region for samples after adsorption of As(V) and As(III) respectively. The experimental conditions were 1 g L^{-1} adsorbent concentration, 0 to 74 mg L^{-1} total As, 0.01 M NaCl, pH 7.0 ± 0.1 . Samples were filtered gravimetrically and dried in the oven prior to ATR-FTIR analysis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

onto the Fe_2O_3 surface is a 50:50 mix of bidentate ($>\text{FeO})_2\text{AsO}_3^-$ and monodentate $>\text{FeOAsO}_2^{2-}$ whilst As(V) adsorbed onto the TiO_2 surface is present as monodentate $>\text{TiOAsO}_3^{2-}$ only. EXAFS does not reveal information about the nature of the surface complexes formed between As(V) and the Fe_2O_3 surface, however, zeta potential and FTIR data indicate that these surface complexes are deprotonated and negatively charged, therefore supporting the SCM. EXAFS identified bidentate binuclear corner-sharing (^2C) As(V)- TiO_2 surface complexes at both pH 5 and 9, whilst FTIR spectra indicated that these complexes are deprotonated at pH 7. This agrees with the $(>\text{TiO})_2\text{AsO}_2^-$ complex predicted by the SCM at pH 5, however the prediction of monodentate $>\text{TiOAsO}_3^{2-}$ disagrees with the EXAFS observation of bidentate $(>\text{TiO})_2\text{AsO}_2^-$ at pH 9.

EXAFS provides a better fit for As(V) using the As(V)-Ti second shell, rather than As(V)-Fe and this is contrary to expectations, given that the Fe_2O_3 surface has a greater affinity for As(V) adsorption than

TiO_2 (Bullen et al., 2020a) and that we previously identified an iron oxide surface enrichment on the $\text{TiO}_2/\text{Fe}_2\text{O}_3$ composite prepared via this procedure (Bullen et al., 2020a). This may be due to uncertainties created by the overlap between As-Ti and As-Fe signals, e.g. bidentate binuclear corner-sharing (^2C) distances are 3.17–3.26 Å for As(V)-Ti (He et al., 2009) and ≈ 3.29 Å for As(V)-Fe (Arai et al., 2004). This highlights potential challenges when using EXAFS to determine binding modes on composite adsorbent samples.

In summary, experimental analysis generally supports the speciation of adsorbed arsenic predicted by our previous surface complexation model (Fig. 8). The first difference is that EXAFS analysis introduces the possibility of tridentate (^3C) $(>\text{FeO})_3\text{As}$ surface complexes at pH 5. These complexes were not necessary to achieve a good fit between the SCM and experimental pH adsorption edges. A second difference is found in the SCM predicting monodentate $>\text{TiOAsO}_3^{2-}$ at pH 9, whilst EXAFS only identified bidentate As(V)- TiO_2 complexes. The overall

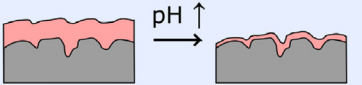
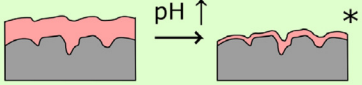
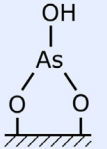
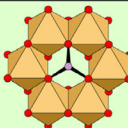
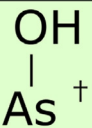
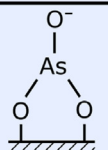
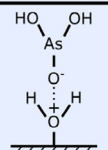
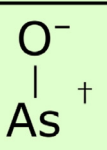
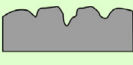
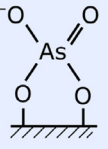
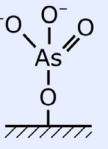
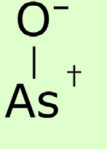
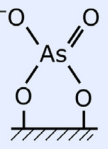
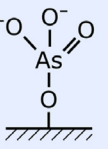
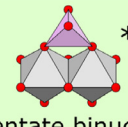
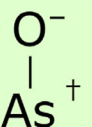
	Adsorption mechanism	Surface Complexation Model	Experiment (EXAFS*, ζ^+ , FTIR $^+$)
As(III)	precipitation		
	Fe ₂ O ₃		 * tridentate (^3C , pH 5)  (pH 7)
	TiO ₂	 $\xrightarrow{\text{pH } \uparrow}$ 	 (pH 7)
As(V)	precipitation	no precipitation 	no precipitation* 
	Fe ₂ O ₃	 $\xrightarrow{\text{pH } \uparrow}$ 	 (pH 7)
	TiO ₂	 $\xrightarrow{\text{pH } \uparrow}$ 	 * bidentate binuclear (^2C , pH 5 and 9)  (pH 7)

Fig. 8. A comparison of information gained regarding the likely properties of arsenic adsorbed onto TiO₂/Fe₂O₃ composites using (left) the speciation predicted by surface complexation modelling and (right) characteristics suggested by experimental analysis (EXAFS, zeta potential and FTIR). Arrows indicate where the pH is increased from 5 to 9.

agreement between the SCM and experimental observations, however, indicates that the ETLM developed by Sverjensky and Fukushima for single-phase minerals (Sverjensky and Fukushima, 2006) can be used to predict the speciation of arsenic adsorbed onto composite minerals using the component additive approach (Davis et al., 1998). A summary of the key speciation of arsenic adsorbed onto TiO₂/Fe₂O₃ composites between pH 5 and 9 proposed by combining the SCM with the experimental observations is given in Fig. 9.

4. Conclusion

This study aimed to use spectroscopic techniques to experimentally evaluate the speciation of adsorbed arsenic as predicted by surface complexation modelling (SCM) (Bullen et al., 2020a).

EXAFS identified significant As(III) surface precipitates, whilst no As(V) precipitation was identified. EXAFS also provided evidence for tridentate (^3C) As(III)-Fe₂O₃ surface complexes and bidentate binuclear corner-sharing (^2C) As(V)-TiO₂ surface complexes. A combination of

FTIR and zeta potential data indicated protonated As(III)-Fe₂O₃ complexes, deprotonated As(III)-TiO₂ complexes, and deprotonated As(V)-TiO₂ and As(V)-Fe₂O₃ complexes. With the exception of the ^3C complex, these results support the surface complexes used in our previous modelling study, highlighting that the best-fit surface complexes provided by the extended triple layer model (ETLM) for single-phase surfaces are likely appropriate for modelling adsorption with a range of similar composite mineral systems.

This study found that identifying the binding modes of arsenic adsorbed onto each of the TiO₂ and Fe₂O₃ phases of the TiO₂/Fe₂O₃ composite simultaneously was not possible due to the significant peak overlap. This highlights the challenges in characterising composite adsorbent materials and indicates that experimental observation and modelling are complementary when understanding the surface complexes formed on composite adsorbents. The final speciation provided by the combined assessment of model and experiment should be considered when investigating titania-iron oxide composites for arsenic remediation in future studies.

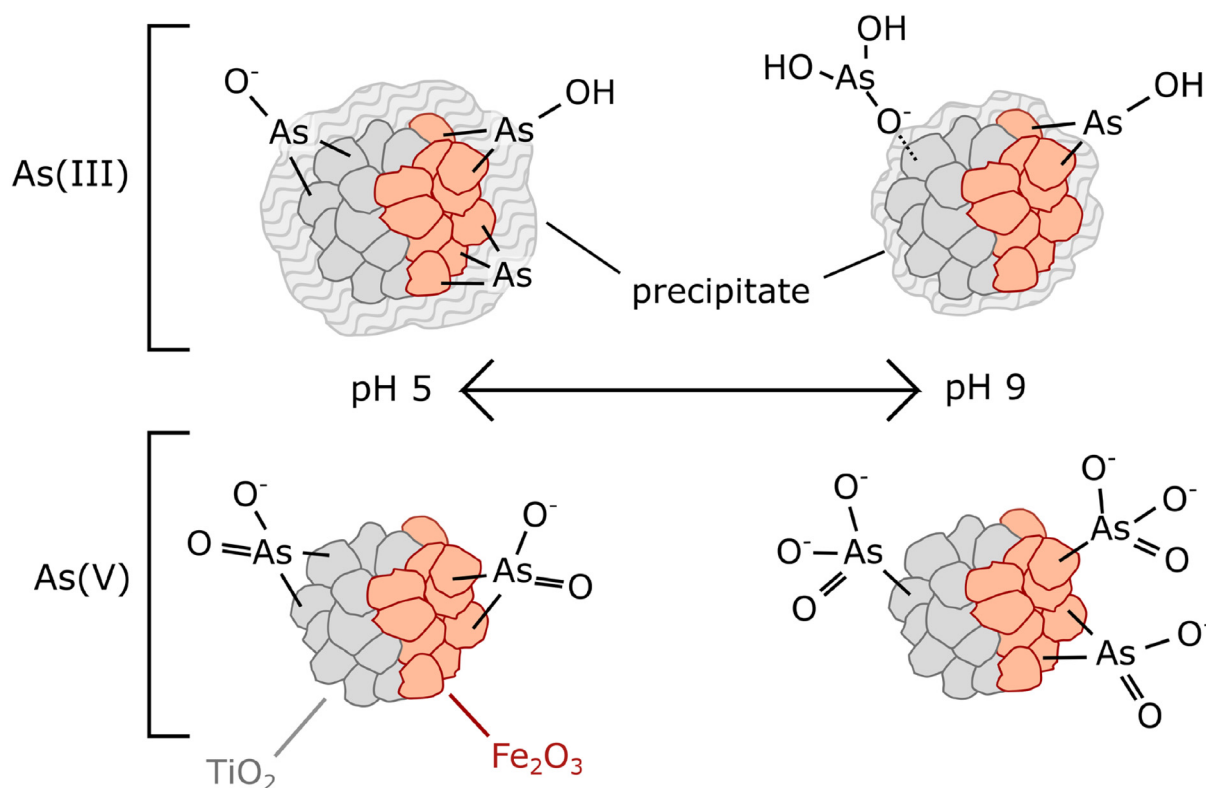


Fig. 9. Summary of likely arsenic surface complexes (and precipitation effects) between pH 5 and 9, determined through a combination of surface complexation modelling (SCM) and experimental evidence. The TiO₂ and Fe₂O₃ nano-crystallite phases contributing to each TiO₂/Fe₂O₃ particle are presented in grey (left-hand half) and red (right-hand half) respectively. The As(III) surface precipitate is indicated by the wave-patterned background.

CRedit authorship contribution statement

Jay C. Bullen: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Chaiapat Lapinee:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Laura A. Miller:** Software, Validation, Formal analysis, Writing – review & editing, Visualization. **Florence Bullough:** Formal analysis, Investigation, Resources, Writing – original draft. **Andrew J. Berry:** Conceptualization, Methodology, Investigation, Software, Validation, Writing – review & editing, Supervision. **Jens Najorka:** Formal analysis, Investigation, Resources. **Giannantonio Cibin:** Conceptualization, Methodology, Investigation, Resources. **Ramon Vilar:** Conceptualization, Supervision, Project administration, Writing – review & editing, Funding acquisition. **Dominik J. Weiss:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge the Royal Thai Government, the University of Phayao, the Engineering and Physical Sciences Research Council (EPSRC), United Kingdom [grant number EP/N509486/1], and the EPSRC Centre for Doctoral Training in the Advanced Characterisation of Materials (CDT ACM), United Kingdom [grant number EP/L015277/1] for funding. The authors also thank the Natural History Museum, UK for XRD analysis, and Diamond Light Source Ltd, Oxford, UK for XAS analysis [grant number B18SP11226].

Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.rsufri.2022.100084>.

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