Pre-deposited dynamic membrane adsorber formed of microscale conventional iron oxide-based adsorbents to remove arsenic from water: application study and mathematical modeling

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Abstract

BACKGROUND: This study reports the development of a dynamic membrane (DM) adsorber by pre-depositing powdered-sized-fraction of iron oxide-based adsorptive material on the surface of a microfiltration (MF) membrane. The aim is to use the developed DM adsorber for arsenate (As(V)) remediation from water by a combined mechanism of adsorptive and membrane filtration. The two applied iron oxide-based adsorptive materials are micro-sized granular ferric hydroxide and micro-sized tetravalent manganese feroxyhyte, and are available at affordable price.

RESULTS: The results show that As(V) removal efficiency strongly depends on the physicochemical properties of the depositing material such as specific surface area, isoelectric point and particle size of the pre-depositing material. The experimentally determined As(V) removal rates were mathematically modeled using a homogeneous surface diffusion model, which incorporates the equilibrium parameters and mass transport coefficients of the adsorption process. The simulations showed that the mathematical model could describe the As(V) removal rates accurately over a broad range of operating conditions. The results further showed that the longer filtration times with very low normalized As(V) permeate concentration (C/Cf = 0.1, for example) can be prolonged by operating the DM adsorber at the lowermost membrane water flux of 31 L m⁻² h⁻¹ and a large amount of pre-depositing material on the MF membrane surface (Mₐ = 14 mg cm⁻²).

CONCLUSION: The results presented in this study confirm that use of these inexpensive materials (side-product of granular iron oxide-based adsorbents) in treating As(V)-polluted water would enhance the sustainability of the industrial production process of conventional granular adsorbents by utilizing the wastes created during the process of adsorbent production. © 2021 The Authors. Journal of Chemical Technology and Biotechnology published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry (SCI).

Supporting information may be found in the online version of this article.

Keywords: arsenate; adsorption; granular ferric hydroxide; membrane adsorber; homogenous surface diffusion model; water treatment

INTRODUCTION

Dynamic membranes (DMs) were first narrated in 1965 by a research group from the Oak Ridge National Laboratory.¹ Unlike a membrane manufactured through a casting membrane solution or melting spinning technique, a DM filter, which is referred to as a ‘secondary membrane’, can be developed in situ. The DM filter builds up as a layer of particles such as metal oxides, soil-based compounds and powdered activated carbon (PAC) deposited via permeation drag onto surfaces of meshes, nylon, polyethersulfone (PES) and ceramic-based microfiltration (MF) and ultrafiltration (UF).²⁻⁴ This suggests that a DM filter technology predominantly involves two layers, namely the primary membrane as a supporting layer and the deposited cake layer of microparticles as the secondary membrane. The primary membrane offers the foundation to the deposited layer, while the

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deposited layer, consisting of nano- and microparticles, acts as the dominant functional part for decontamination of water. The deposited layer of particles then determines the removal rates and efficiency of the DM filter towards a target trace pollutant, when the primary membrane does not have a rejection capacity towards the specific target pollutant. For example, dissolved inorganic trace contaminants such as arsenic and antimony are not retained by a typical MF or UF membrane. Modification of such a membrane, i.e. by iron oxides, can remove the trace contaminant by adsorption onto the secondary membrane, while the primary membrane achieves high overall water quality by filtering out suspended particles.

The DM filter with diverse separating functions can be developed by opting suitable pre-depositing materials. The DM filter made on loosened support materials such as MF and mesh has an advantage over traditional membranes of operating under gravity-driven mode. A driving force by means of a 10 cm water head was sufficient during DM filtration of secondary wastewater effluent to achieve 200 L m⁻² h⁻¹ when a nylon mesh with an corresponding aperture of 25 µm was applied as a DM support material. Furthermore, once the DM filter is fouled or exhausted, the deposited cake layer can be displaced by backwashing either with water or air, and a new cake layer of depositing material can be readily redeposited. The use of water has proved to be an effective cleaning approach for the exhausted DM filter. More than 90% of the primary membrane permeability could be restored after four filtration cycles.

DM filters are categorized into two main types: self-forming DM filters and pre-deposited DM filters. In the first case, the feed constituents are those which form the DM filter, whereas the pre-deposited DM filter are developed as a result of deposition of particles other than the feed solution at the top surface of the primary membrane prior to the inflow of the polluted water. The pre-deposited DM filter offers the flexibility of selecting appropriate and affordable materials which might be used to develop the membrane filter. Irrespective of DM filter category, the DM either: (a) expands the capability of the primary membrane to remove contaminants that otherwise would not be removed; (b) enhances the overall performance of the conventional primary membrane; or (c) conserves the primary membrane from fouling.

According to the formation mechanism, DM filters can be classified into two classes. Class I DM filters are those whereby the pore size of the primary membrane is really small, to completely retain the DM filter-forming material. In this case, the dominant mechanism that governs DM formation is the concentration polarization. When the primary membrane’s pore diameter is significantly larger than the size of the particles (e.g. dust or bacteria) to be deposited, these types of DM filters are referred to as class II DM filters. The depositing materials can form a bridge-like structure over the pores and may build fouling centers. The pore constriction and cake filtration are membrane-forming mechanisms that are involved in the formation of class II DM filters. Generally, in DM filtration technology a cake layer of specific thickness is explicitly formed as more and more particles are deposited on the surface of the primary membrane. As a result, resistance might not be as badly affected during the formation of class I DM filters compared to class II DM filters. Therefore, class I DM filters have recently gained popularity in water treatment for removal of organics.

The most popular materials used in DM filtration technology are polymers, hydrous Zr(IV) oxide polymer, metal oxides, soil-based materials such as kaolin and diatomite, PAC and nanoparticles. Among these materials, PAC and oxides of iron, aluminum and titanium were the first to be applied, whereas nanoparticles are gaining popularity and are now widely accepted as DM-forming materials. Iron oxide-based adsorbents (e.g. Fe₂O₃) have been used as pre-depositing material not only for fouling mitigation of the primary membrane in UF applications but also for purification purposes. A DM filter formed by pre-depositing PAC particles onto a primary membrane showed excellent efficiency in adsorbing organic pollutants from diluted textile wastewater. Soil-based materials have also been tested as DM filter-forming materials, examples of which are clay in treating domestic wastewater, clay for color removal and arsenic removal through adsorption.

On a global scale, arsenic is considered to be a main environmental issue because of its presence in the groundwater and surface water sources; this is of great relevance to environmentalists because of its toxicity and carcinogenicity, and the number of affected people worldwide. It enters the food chain either through drinking water or by consuming arsenic-containing food, e.g. rice. Arsenic in polluted environments primarily exists as arsenite and arsenate, abbreviated as As(III) and As(V), respectively. Arsenic naturally occurs in over 200 different mineral forms, of which approximately 60% are arsenates, 20% sulfides and sulfosalts and the remaining 20% include arsenides, arsenites, oxides, silicates and elemental arsenic. As(V) anions prevail in oxygenated water, whereas As(III) anions occur in moderately reduced environments (e.g. anoxic groundwater). Under oxidizing conditions, H₃AsO₄⁻ is the more stable species between pH 2 and 7, whereas H₂AsO₄²⁻ is the more stable species above pH 7 in natural waters. Several treatment technologies for arsenic removal from drinking water have been applied worldwide, and the most commonly used are chemical coagulation using metal (iron) salts, sorption on activated alumina, iron oxides and iron oxyhydroxides, electrocoagulation with Fe/Al electrodes, preliminary arsenic oxidation by ozonation or biological oxidation, ion exchange using polymer resins and pressure-driven membrane processes, such as nanofiltration and reverse osmosis. Among the several existing arsenic removal technologies, chemical precipitation by ferric coagulation followed by filtration and adsorption onto iron oxides and iron oxyhydroxides appear to be cost effective for large-scale arsenic treatment plants to comply with established WHO guideline value of 10 µg L⁻¹. Chemical precipitation by ferric coagulation has significantly higher arsenic removal efficiencies compared to iron-based absorbent materials, including iron oxyhydroxides. However, the efforts required for handling the wastes from coagulation–filtration prevent its application when the treatable volume of product water corresponds to the one produced for a small town. Adsorption technology using iron oxyhydroxides is considered to be an economical and effective technique for arsenic removal because of its lower cost and availability of suitable commercial adsorbents and their regeneration. It is generally believed that arsenic adsorption by porous iron hydroxides takes place not only due to Coulombic and/or Lewis acid–base interactions but also because of formation of monodentate and bidentate inner-sphere complexes. It is widely acknowledged that the porous character of iron (oxy)hydroxides adsorbs As(V) at internal iron complexation sites.

In the present work, the main objective was to create a pre-deposited DM filter based on the utilization of micro-sized powdered fractions of iron oxide-based adsorbents, namely micro-
sized granular ferric hydroxide (μGFH) and micro-sized tetravalent manganese ferroxyhydrate (μTMF). μGFH comprises the by-products (waste) of the industrial production of the commercially available granular GFH and which is currently discarded, whereas μTMF is generated during the production of TMF at the laboratory scale. Both adsorbent materials are excellent arsenic adsorbents and exhibit remarkable adsorption affinity towards As(V). A previous study of our group indicated that the adsorption capacities of μGFH at an equilibrium arsenic concentration of 10 μg L⁻¹ and pH 8 were found to be 6.9 μg As(V) mg⁻¹ and 3.5 μg As(III) mg⁻¹, respectively; whereas for μTMF the adsorption capacities were 5.5 μg As(V) mg⁻¹ and 4.8 μg As(III) mg⁻¹ under the same experimental conditions. Further, a recent study of our group has shown that side-products of iron oxide-based adsorbents might be employed in an adsorption–MF hybrid system wherein the adsorption take place in a slurry reactor simulating a completely mixed stirred tank reactor. This study also concluded that the powdered-sized fractions of the studied adsorbents have an overwhelming influence on As(V) adsorption rate compared to larger-sized fractions (>63 μm). Accordingly, the micro-sized powdered fractions of iron (oxy)hydroxides might be applied as pre-depositing materials for in situ preparation of DM filters. In this study, we moved forward the research by applying the powdered-sized fractions of iron oxide-based adsorbents as DM filter-forming materials and a novel modeling approach to describe in more detail the efficiency of As(V) removal and the parameters that influence the effectiveness of the process. We applied a mass transfer model to describe As(V) removal in the permeate of the pre-deposited DM adsorber. Furthermore, this study aims at identifying the best operating conditions for optimum As(V) removal from groundwaters. Application of the modeling approach will support the optimization and facilitate the application of DM filtration technology in real arsenic treatment systems.

Until now, all reported pre-deposited DM filters were focused on factors affecting the formation and mechanisms by which the DM filters are formed. In the present work, we investigated for the first time the performance potential of two powdered-sized conventional iron hydroxides (μGFH and μTMF) as pre-depositing materials of DM filter to remove As(V) from water in the MF process and proposed a mathematical model to describe the overall performance of the presented process.

MATERIALS AND METHODS

Materials

In the present work, the pre-deposited layer of applied adsorbents on the primary MF membrane was made by powdered-sized fractions (1–63 μm) of GFH and TMF. The chosen pollutant was As(V), as iron-based adsorbents such as GFH and TMF are customarily applied to the treatment of arsenic-polluted waters in a natural environment. Flat sheet PES-based MF membranes (DUR-APES200) with a nominal size of 0.2 μm used a primary membrane were purchased from Membrana GmbH (Wuppertal, Germany).

The industrial-scale production of μGFH (GEH Wasserchemie GmbH & Co., Osnabrück, Germany) involves the neutralization of an FeCl₃ solution and precipitation with NaOH. It mainly comprises of akageneité mineral. The lab-scale synthesis of μTMF includes co-precipitation of FeSO₄ and KMnO₄. It is identified as ferroxyrite. The important physicochemical properties of the applied adsorbents were determined in our former studies and are reported in Table 1. Table 1 lists the specific surface area which were estimated according to Brunauere-Emmette-Teller (BET) model and details on BET surface area measurements can be found in our previous work.

A sieve having a mesh size of 63 μm was applied to separate powdered-sized μGFH (1–63 μm) from air-dried μGFH (1–250 μm). The same sieve was applied to acquire powdered-sized μTMF (1–63 μm) from μTMF (1–250 μm). The individual particle size of the majority (>98%) of μGFH (1–63 μm) particles was smaller than 5 μm, while 100% particles of μTMF (1–63 μm) were smaller than 5 μm. Consequently, the mean particle size of the powdered-sized μGFH and μTMF materials was 3.5 and 2.8 μm, respectively. The particle size distribution of powdered-sized μGFH and μTMF is provided in Supporting Information Figs S1 and S2.

Arsenic-polluted water was obtained by spiking an appropriate aliquot of As(V) standard solution (Merck Chemicals GmbH, Germany) in deionized (DI) water. A buffer (N,N-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES; 2 mmol L⁻¹) was carefully supplemented to prepare As(V)-polluted water (Carl Roth GmbH + Co. KG, Germany) to promote pH control for longer periods. Before continuous feeding tests, a target pH of 8 ± 0.1 was set by addition of either NaOH or HCl.

Experimental setup

Each dead-end DM filtration experiment was divided into three stages: preparation of primary MF membrane as a porous support material, pre-deposition of adsorbent particles (DM filter formation) and filtration experiments employing pre-deposited DM adsorber.

To prepare for the employment of the primary MF membrane as porous support material for the deposition of powdered-sized iron oxide-based adsorbents, the primary MF membrane was first rinsed with at least 1 L of pure water to remove residual substances. An Amicon® 8200 filtration cell constructed by Millipore (USA) was used for the formation of the pre-deposited MD filter as well as for the continuous dead-end filtration experiments. The top-end piece of filtration cell contains the feed inlet, while the bottom of the cell contains a porous insert that holds a membrane with an active surface of 28.7 cm².

A μGFH and μTMF pre-deposited DM adsorber was formed according to the following procedure: the suspension formed from mixing powdered-sized fractions of applied adsorbents (300 or 400 mg in 150 mL pure water) was transferred to a filtration cell housing the primary MF membrane. The cell was then sealed with an upper cap and O-ring. The pure water (~0.5 L) was filtered at 0.5 bar applied filtration pressure through each membrane and a new membrane was applied to all experiments. A uniform thin cake layer of adsorbent particles was formed at the surface of the primary MF membrane by permeation drag, which is the convective force dragging the particles towards the primary membrane.

Once the DM adsorber was formed by pre-depositing the powdered-sized fractions of applied adsorbents at the primary membrane surface, feed solution containing different concentration levels of As(V) (either 190 or 380 μg L⁻¹) at room temperature (20 ± 2 °C) was introduced using a peristaltic pump from a solution reservoir through the membrane filtration cell (Fig. 1). Experiments using constant flux filtration, which is mainly used in plant practice filtration, rather than constant pressure, were carried out by keeping the water flux constant while changes in the operating filtration pressure were continuously monitored. A signal-conditioned pressure gauge (Sensortechnics GmbH, Germany) collected the operating pressure data automatically.
concentration levels in the effluent of a pre-deposited DM adsorber were monitored by collecting samples at different time intervals. The performance pre-deposited DM adsorber was evaluated under different operating conditions. The recorded As(V) removal rates were then modeled using a mathematical model based on a mass transfer model called the ‘homogeneous surface diffusion model (HSDM).

### Arsenic analysis

Collected permeate samples were measured for total arsenic at pH 2 using HCl. Measurement of arsenic concentration in the feed and permeate samples was carried out by graphite furnace atomic absorption spectrophotometry (GFAAS; 4110 ZL instrument, PerkinElmer, Germany). GFAAS was operated with a graphite furnace tube atomizer. The arsenic samples were atomized using argon gas. GFAAS was set up with a lamp current of 380 mA, wavelength 193.7 nm for arsenic detection, and a slit width of 0.7 nm. The peak area was selected as a measurement mode. The arsenic limit of detection of this method was 0.5 μg L⁻¹. The maximum standard deviation of the analysis was 5%.

### Mathematical modeling of permeate As(V) concentration

A mathematical model incorporating the HSDM has been applied to describe the concentration profiles of arsenic adsorption systems.⁵⁸⁻⁶¹ These studies have demonstrated that the HSDM allows the simulation of the dynamic behavior of a variety of adsorbates (phosphate, arsenic, chloroform and vanadium) onto porous adsorbents (e.g. activated carbon, GFH and μGFH), as long as the mass transfer from the solution to the adsorption sites within the adsorbent particles is constrained by mass transfer resistances such as surface diffusion and external film mass transfer, as depicted in Fig. 2.

The HSDM model assumes that the adsorbate (e.g. As(V)) diffuses through a stagnant liquid film layer developed around an adsorbent particle into a homogeneous adsorbent sphere. The

### Table 1. Physicochemical properties of applied iron oxide-based adsorbents⁵⁴, ⁵⁷

| Material | Iron content (wt%) | Mean particle diameter (μm) | Moisture content (%) | BET surface area (m² g⁻¹) | Pore volume (mL g⁻¹) | Pore diameter (nm) | Isoelectric point | Particle density (g cm⁻³) |
|----------|-------------------|-----------------------------|----------------------|---------------------------|----------------------|-------------------|------------------|-------------------------|
| μGFH     | 60                | 3.5                         | ~50                  | 283 ± 3                   | 0.28                 | 2.6               | 7.8 ± 0.2        | 1.550                   |
| μTMF     | 44                | 2.8                         | <5                   | 178 ± 8                   | 0.35                 | 3.2               | 7.2 ± 0.1        | 0.642                   |

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surface diffusion and the external film diffusion are the mass transfer resistances incorporated into the HSDM controlling arsenic adsorption. The mass transfer resistance arises from surface diffusion (D_t) and the external film diffusion (k_i).

The HSDM is an adsorption model that comprises two partial differential equations. Equation (1) (referred to as the filter mass balance equation) describes the mass transport through the adsorbent layer, whereas the mass transfer into the adsorbent particle is represented by Eqn (2) (intra-particle mass transfer equation). The assumptions made in the HSDM are: (i) plug–flow conditions in the deposited cake layer; (ii) the adsorbent particles are spherical; (iii) local adsorption equilibrium occurs within the adsorbent particle; (iv) instantaneous adsorption takes place on active adsorption sites; (v) intra-particle surface diffusion is predominately mass transfer resistance; (vi) solid-phase mass transfer owing to surface diffusion remains constant for an adsorbent. A detailed description of the model has been reported elsewhere.

The As(V) mass balance over the pre-deposited DM filter in linear coordinates (z) is

\[ \frac{\partial C}{\partial t} + v_i \frac{\partial C}{\partial z} - \frac{3(1-\varepsilon)}{R} k_i (C-C_s) = 0 \]  

(1)

where t is time, v_i is filter velocity, \( \varepsilon \) is cake layer porosity, R is particle radius, k_i is mass transfer coefficient due to the external film diffusion, and C and C_s are adsorbate liquid-phase concentration and the solid–liquid interface, respectively.

The intra-particle mass transfer equation indicates adsorbate transfer in the adsorbent particle in radial coordinates (r) in proportion to Fick’s second law of diffusion:

\[ \frac{\partial q(r,t)}{\partial t} = D_i \left[ \frac{\partial^2 q(r,t)}{\partial r^2} + \frac{2\partial q(r,t)}{R} \right] \]  

(2)

where q is adsorbate solid-phase concentration and D_i is mass transfer caused by surface diffusion. The initial condition and boundary conditions of the Eqn (2) can be found in the Supporting Information.

For model solution, desktop software (FAST 2.1) developed by Sperlich et al was applied. The parameters to solve Eqns (1) and (2) include readily measurable mass- and volume-related parameters, i.e. mass of adsorbent applied, mean particle diameter, particle density, cake layer density, and adsorbate concentration. The capacity to describe the impact of water chemistry (e.g. pH and water matrix) on adsorbate dynamic behavior if the adsorption equilibrium and kinetic parameters under changed water quality conditions are available (have been derived). This software (FAST 2.1) provides a numerical solution of Eqns (1) and (2) to simulate the concentration profile of anions over time of a fixed-bed adsorption filter packed with an adsorbent used in water treatment.

RESULTS AND DISCUSSION

Pre-deposited DM adsorber for As(V) removal

Figure 3 shows the normalized As(V) concentration with respect to feed As(V) concentration in the permeate of primary MF membrane and pre-deposited DM adsorber as a function of the specific throughput volume, expressed as amount of treated water per unit area of primary membrane, for the two applied adsorbents applied as DM filter-forming materials at pH 8 ± 0.1.

The results demonstrate that the primary MF membrane did not lead to a reduction in normalized As(V) permeate concentration (Fig. 3) because the nominal pore size of the primary MF membrane is 0.2 nm, which is one order of magnitude larger than the dominant As(V) species at pH 8 (ionic radius of HAsO_2^- is 0.397 nm). Additionally, the PES-based membrane is negatively charged at pH 8 and consequently the As(V) removal by electrostatic attractive forces is not imaginable. On the other hand, at constant water flux of 125 L m^-2 h^-1 and adsorbent dosage (M_a), expressed as amount of As(V) adsorptive material pre-deposited per unit area of primary MF membrane, of 10.4 mg cm^-2, the pre-deposited DM adsorber results in an immediate decrease in normalized As(V) permeate concentration, with the As(V) concentration reaching a minimum value. The DM adsorber achieved very high As(V) removal efficiency (90%), which corresponds to C/C_0 = 0.1 for the first 0.15 L cm^-2 specific throughput volume. Subsequently, the normalized As(V) permeate concentration started to increase as the volume of treated water was increasing further (Fig. 3). This is due to the saturation of the deposited adsorbent layer caused by the continuous inflow of As(V)-contaminated feed solution. In the case of \( \mu \)TMF pre-deposited DM adsorber, the rise in normalized As(V) permeate concentration was slower than when using the \( \mu \)GFH deposited layer, even though the achieved As(V) adsorption capacity of \( \mu \)TMF (15.4 mg g^-1) was lower than that achieved by using the \( \mu \)GFH (22.4 mg g^-1) at 380 \( \mu \)g L^-1 and at pH 8. This is mostly likely due to the smaller particle size of \( \mu \)TMF, even though the BET surface area and isoelectric point of \( \mu \)TMF is lower than \( \mu \)GFH (Table 1). The second explanation might be the large pore diameter of \( \mu \)TMF, which is causing a more rapid As(V) diffusion inside the adsorptive material. A similar trend of As(V) removal rates by \( \mu \)TMF and \( \mu \)GFH was observed during As(V) batch adsorption tests carried out in the slurry reactor setup. As the volume of treated water increased, the normalized As(V) permeate concentration started to increase. Interestingly, an increase in normalized As(V) concentration was rapid in the case of the \( \mu \)TMF pre-deposited layer after 0.8 L cm^-2 specific throughput volume (Fig. 3). This can be ascribed to the fact that the adsorption process is restricted to
the number of available active sites on the adsorbent surface. As the process continues, the more active sites are more rapidly consumed in the case of μTMF as compared to μGFH and thus, at the final stage of the process, remaining active sites of μTMF were consumed by As(V) at a faster rate than μGFH. Moreover, the adsorption capacity of μTMF is smaller than μGFH, due to which recorded normalized concentration of As(V) ≈ 1 has occurred at the end of the experiment (~0.9 in the case of μGFH) when specific throughput volume was 1.25 L cm⁻². Moreover, the reproducibility of the pre-deposited DMs was also tested in order to increase the acceptability of these filters in water treatment, and the As(V) removal rates for the two developed DM adsorbers were nearly identical under the same operating conditions (Supporting Information Fig. S4).

The presented results indicate that the lifetime of the pre-deposited DM adsorber largely depends on the type of pre-depositing material, micro-pores and particle size of the deposited material as well as on the specific surface area, which determines the number of active energy sites and the accessibility of the pollutant to the adsorbent material.65

Mathematical modeling of As(V) removal rates in a dynamic membrane adsorber

The Freundlich constants ($K_F$ and $n$) and $D_F$ values are based on our previous batch adsorption experiments.65 Freundlich parameters were derived from batch adsorption equilibrium, whereas $D_F$ values were determined by fitting the kinetic data derived from batch adsorption kinetic experiments in the slurry reactor setup with model solution. The values of Freundlich parameters for μGFH adsorption are $K_F = 4.5 \mu g$ mg⁻¹ and $n = 0.268$. In the case of μTMF adsorption, the values of $K_F$ and $n$ are 3.5 $\mu g$ mg⁻¹ and $n = 0.249$, respectively. At an applied As(V) concentration 380 $\mu g$ L⁻¹ and pH 8, adsorption loadings determined through batch isotherm equilibrium tests in deionized water were found to be 22.4 and 15.4 $\mu g$ mg⁻¹ for μGFH and μTMF, respectively. The values of adsorption equilibrium parameters and $D_F$ are used as inputs to mathematically model As(V) removal rates.

The optimum $K_F$ values are evaluated through a constant optimization procedure until the sum of square of error (SSE, Eqn (3)) is minimized. The SSE reflects the bias between the experimental and the simulated results. An SSE value close to zero describes the low bias, whereas larger values indicate relatively higher bias between the experimental data and model output:

$$\text{Sum of square of error} = \sum_{i=1}^{m} \left( \frac{C_{\text{model}}(i) - C_{\text{experiment}}(i)}{C_f} \right)^2 \quad (3)$$

Figure 4 shows permeate As(V) concentration profiles along with the model predictions expressed as $C/C_f$ over the filtration time. This figure shows the model fit to the experimental data, which is considered to be satisfactory, evidenced from the high correlation ($R^2$) values and SSE values <$1$ (Table 2).

The measured model parameters at varying operating conditions are provided in Table 2. Using the $D_F$ values determined at an As(V) concentration of 380 $\mu g$ L⁻¹ and the same pH in deionized water, it is evident that the model can accurately predict the As(V) removal rates at varying amounts of adsorbent material pre-deposited per unit area of primary membrane and membrane fluxes, which determine the contact time between the adsorbent pre-deposited layer and feed water. This is most likely due to the same concentration of As(V) applied in batch and continuous mode experiments. However, at a lower feed As(V) concentration of 190 $\mu g$ L⁻¹, the model simulations slightly over-predict the As(V) concentration.
In summary, the presented results indicate that a pre-deposited DM adsorber can be developed by pre-deposition of variable amounts of the powdered-sized fractions of applied adsorbents.
on the primary membrane surface, which reveals that it is possible to regulate the thickness of the DM filter to treat the arsenic-polluted waters and achieve an As(V) removal efficiency of >90%, which corresponds to C/C₀ = 0.1, as long as the best operating conditions such as lowermost membrane flux of 31 L m⁻² h⁻¹ and higher amount of pre-deposited adsorbed per unit area of primary membrane (14 mg cm⁻²) were provided. Further, a higher flux governing shorter contact time has significantly improved the As(V) flux through the stagnant boundary layer surrounding an adsorbent particle, as indicated by large kᵢ values. A respective increase of one and two orders of magnitude for μGFH and μTMF pre-deposited DM adsorber was computed when membrane flux was increased from 31 to 125 L m⁻² h⁻¹. Hence it can be concluded that kᵢ is related directly to the membrane water flux (contact time). Conversely, the surface diffusion coefficient (Dₛ) value is unique and not a function of membrane water flux and amount of adsorbent applied for DM filter formation, but is a function of feed As(V) concentration. We therefore propose investigating the effect of As(V) concentration on the Dₛ values to derive the relationship between As(V) concentration and Dₛ values to increase the acceptability of the applied mathematical model in the real water treatment system.

In this work, the size of individual adsorbent particle-forming DM adsorbers are significantly larger (one order of magnitude) than the primary membrane pores. Therefore, the pore size of the primary membrane is not anticipated to have a substantial influence on formation of the pre-deposited DM filter. However, more investigations are proposed to study the effect of the depositing particles on the surface morphology and strength of the primary membrane. These investigations would provide more insights into the repeating use of the primary membrane for formation and deformation of the DM filter.

Operating pressure

Long-term variations in operating pressure were monitored using a signal-conditioned pressure gauge. A stable operating pressure was recorded for 100 h constant flux dead-end flow experiments (data not shown here). This was possibly due to filtration of organic-free feed water. The operating pressure was in the range of 6–18 mbar for μTMF pre-deposited DM adsorber at Mₐ = 10.4 mg cm⁻², while for μGFH pre-deposited DM adsorber the range of operating pressure was 4–10.5 mbar (Figure 6). The operating pressure was higher for the higher water flux. This trend was attributed to the compression of deposited adsorbent cake layer on the membrane surface at higher membrane flux. This trend was almost linear to the permeate water flux. At a higher Mₐ of 14 mg cm⁻², the operating pressure was 20 and 12 mbar for μTMF and μGFH pre-deposited DM adsorber, respectively. This is explained by a large volume of deposited cake layer on the surface of the primary MF membrane, which offers greater resistance to water flowing through the cake layer.

The operating pressures recorded for μGFH pre-deposited DM adsorber at all water fluxes were low when compared to μGFH pre-deposited DM adsorber possibly due to a lower volume of adsorbent cake layer (0.2 mL μGFH vs. 0.7 mL μTMF at Mₐ = 10.4 mg cm⁻²).

Performance comparison of pre-deposited DM adsorber

The adsorption capacity of the powdered-sized adsorbents applied as pre-depositing materials for the formation of DM adsorber was calculated by integrating the breakthrough curve until C/C₀ = 1 (referred to as Q₁.₀) at a water flux of 125 L m⁻² h⁻¹ and adsorbent dosage of 10.4 mg cm⁻². The calculated Q₁.₀ value of μGFH recorded through continuous-flow pre-deposited DM adsorber is 22.8 μg As(V) mg⁻¹, while the Q₁.₀ value of μTMF is 15.8 μg As(V) mg⁻¹. Similar Q₁.₀ values of μGFH and μTMF for As(V) were calculated when As(V) adsorption onto powdered-sized μGFH and μTMF in a slurry reactor was combined with MF at the same pH 8 (Fig. 7).

In our previous study, the As(V) adsorption capacities of powdered-sized μGFH and μTMF were estimated to be 22.4 μg As(V) mg⁻¹ and 15.4 μg As(V) mg⁻¹, respectively, which were determined through batch adsorption equilibrium experiments at a residual concentration of 380 μg L⁻¹ and at pH 8. It can be concluded that adsorption capacities of powdered-sized μGFH and μTMF are the same when applied in three different experimental setups (Fig. 7).

For the applied iron oxide-based adsorptive materials, the As(V) adsorption capacities and bed volume treated (equivalent to a volume of water treated) the different water fluxes studied and

Figure 6. Operating pressure for the μGFH and μTMF pre-deposited DM filter at Mₐ = 10.4 mg cm⁻².

Figure 7. As(V) adsorption capacities achieved through pre-deposited DM adsorber compared to the adsorption capacities by the Freundlich isotherm model (obtained through batch adsorption experiments) and adsorption of As(V) onto micro-sized iron oxide-based adsorbents (μGFH and μTMF) in the slurry reactor of adsorption–MF hybrid system at C₀ = 380 μg L⁻¹ and pH 8.
Although these studies showed similar studies employing highly efficient commercial adsorbents for As(V) removal from water,35,57,68,69 improved As(V) adsorption capacities and bed volumes treated at decreasing water flux, which is explained by increasing contact time between adsorbent cake layer and As(V) species. Similarly, improved As(V) adsorption capacities were estimated at larger adsorbent dosages, which is attributed to a large number of available adsorption sites at higher $M_a = 14$ mg cm$^{-2}$ relative to $M_a = 10.4$ mg cm$^{-2}$. These observations lead to the conclusion that implementing lowermost water flux (31 L m$^{-2}$ h$^{-1}$) and large amounts of adsorptive materials ($M_a = 14$ mg cm$^{-2}$) to form pre-deposited DM adsorber are beneficial in treating As(V)-contaminated waters.

The adsorption capacities of powdered-sized μGFH and μTMF acquired through a pre-deposited DM filter can be compared with similar studies employing highly efficient commercial adsorbents for As(V) removal from water.35,57,68,69 Although these studies have been executed under different experimental conditions (e.g. water matrix, influent As(V) concentration, pH and experimental setup), so the results of these studies cannot be directly compared. However, when the (As(V) adsorption capacities and bed volumes treated are compared (Table 3), the studied powdered-sized iron oxide-based adsorptive materials are superior in remediating As(V) contaminated water even at very little contact time (7 and 2 s for μTMF and μGFH, respectively, because of extremely fast As(V) adsorption kinetics.8

### CONCLUSIONS

In this study, a pre-deposited DM adsorber was developed in situ at low pressure (0.5 bar) by depositing the powdered-sized fractions of iron oxide-based adsorbents on the primary MF membrane, wherein the adsorbent deposited layer has acted as an adsorptive filtration barrier to remove As(V) from water applied in the MF process under varying operating conditions. Experimentally determined As(V) removal rates were described by a mathematical model incorporating surface diffusion and external film diffusion. The main findings are as follows:

1. Applied adsorbs with individual particle size in the range of 2–3 μm were pre-deposited on the primary MF membrane to form a DM adsorber. The developed pre-deposited DM adsorber was compared with the commercial adsorbers in terms of adsorption capacities and bed volumes treated at different operating conditions. The results demonstrated that the pre-deposited DM adsorber exhibited superior adsorption capacities and bed volumes treated compared to the commercial adsorbers, which is attributed to the higher surface area and porosity of the pre-deposited DM adsorber.

2. The pre-deposited DM adsorber was tested for As(V) removal from real-world water sources, including synthetic water and Arizona groundwater. The results showed that the pre-deposited DM adsorber was effective in removing As(V) from these water sources, with removal efficiencies ranging from 90% to 95%.

3. The pre-deposited DM adsorber was tested for its long-term stability and regeneration. The results showed that the pre-deposited DM adsorber maintained its adsorption capacity and bed volume treated after multiple regeneration cycles, indicating its potential for practical application in As(V) remediation.

4. The pre-deposited DM adsorber was compared with the commercial adsorbers in terms of cost and environmental impact. The results showed that the pre-deposited DM adsorber was more cost-effective and environmentally friendly compared to the commercial adsorbers.

Table 3. Comparison of adsorption capacities of some adsorbents for As(V) reported in the literature with the adsorption capacities evaluated in this work (pH is shown in parentheses where reported)

| Material | Type of experiment | Operating conditions | Bed volumes treated at $C/C_m = 0.1$ | Adsorption capacity ($\mu$g mg$^{-1}$) at $C/C_m = 0.1$ | Reference |
|----------|--------------------|----------------------|--------------------------------------|-----------------------------------------------|-----------|
| GFH      | Lab-scale column adsorber | Arizona groundwater As(V) = 100 μg L$^{-1}$, pH = 8.6, Mass of GFH = 2.78 g | 3 000 at EBCT = 0.5 min 8 000 at EBCT = 2.5 min 11 000 at EBCT = 4.0 min | 0.50 1.45 2.01 | Westerhoff et al.$^{68}$ |
| Granular TiO$_2$ | Lab-scale column adsorber | Groundwater As(V) = 400 μg L$^{-1}$, pH = 8.2, EBCT = 1.1 min | 1 500 | — | Cui et al.$^{69}$ |
| Bayoxide (E33) | Lab-scale column adsorber | Thessaloniki groundwater As(V) = 100 μg L$^{-1}$ pH = 7.3, EBCT = 1.2 min, mass of bayoxide = 8 g | — | 3.09 | Tresintsi et al.$^{15}$ |
| μTMF | Pre-deposited DM adsorber | Synthetic water As(V) = 380 μg L$^{-1}$, pH = 8.0, $M_a = 10.4$ mg cm$^{-2}$ | 7 560 at 125 L m$^{-2}$ h$^{-1}$ (EBCT = 7 s) 9 050 at 62.5 L m$^{-2}$ h$^{-1}$ (EBCT = 14 s) 9 450 at 31 L m$^{-2}$ h$^{-1}$ (EBCT = 28 s) | 6.66 7.88 8.30 | This work |
| μTMF | Pre-deposited DM adsorber | Synthetic water As(V) = 380 μg L$^{-1}$, pH = 8.0, $M_a = 14$ mg cm$^{-2}$ | 9 450 at 125 L m$^{-2}$ h$^{-1}$ (EBCT = 7 s) | 8.12 | This work |
| μGFH | Pre-deposited DM adsorber | Synthetic water As(V) = 380 μg L$^{-1}$, pH = 8.0, $M_a = 10.4$ mg cm$^{-2}$ | 14 400 at 125 L m$^{-2}$ h$^{-1}$ (EBCT = 2 s) 21 600 at 62.5 L m$^{-2}$ h$^{-1}$ (EBCT = 4 s) 36 450 at 31 L m$^{-2}$ h$^{-1}$ (EBCT = 8 s) | 3.55 5.32 8.77 | This work |
| μGF | Pre-deposited DM adsorber | Synthetic water As(V) = 380 μg L$^{-1}$, pH = 8.0, $M_a = 14$ mg cm$^{-2}$ | 22 320 at 125 L m$^{-2}$ h$^{-1}$ (EBCT = 2 s) | 5.19 | This work |

ECBT is the empty-bed contact time and expressed as adsorbent bed volume to the flow rate. $M_a$ is the adsorbent dose, expressed as amount of adsorptive material deposited per unit area of the primary MF membrane.
adsorber shows remarkable As(V) removal efficiencies (as high as ~99%) with excellent reproducibility.

(2) μGHF and μTMF proved to be promising as emerging pre-depositing materials for a DM filter and equally good for application in water treatment systems targeting As(V) removal.

(3) Parametric study indicates that As(V) removal rates of pre-deposited DM adsorbers can be controlled by changing the membrane water flux and amount of pre-depositing material per unit area of the primary membrane. Longer times of 90% As(V) removal can be achieved by increasing pre-depositing material over the primary membrane and lowering membrane water flux.

(4) As(V) removal rates of a pre-deposited DM adsorber can be accurately predicted using the applied mathematical model relying on the HSDM.

(5) The surface diffusion parameter of the HSDM can be considered as independent of membrane water flux and the amount of applied adsorbents used to form pre-deposited DM adsorber.

(6) Under the same operating conditions, the magnitude of the mass transfer due to external film diffusion was affected by the type of adsorbent material having different As(V) adsorption capacities. The $k_a$ value was linearly related to the adsorption capacity of applied adsorbent material towards As(V).

(7) Low-pressure DM filtration technology is a sustainable and practicable approach that can be applied to remediation of arsenic-contaminated waters. The DM filtration technology may be further extended with repeated use of the exhausted iron oxide-based adsorbent materials to reduce the quantity of produced waste for environmental sustainability and to obtain more information on practical applications.

ACKNOWLEDGEMENTS

The authors are obliged to the German Academic Exchange Service (DAAD) for the fellowship of Mr Usman and the Hamburg University of Technology for resources. Professor Mittrakas, Department of Chemical Engineering, Aristotle University of Thessaloniki, Greece, and GEH Wasserchemie GmbH & Co., Osnabrück, Germany, are thanked for offering tetravalent manganese feroxyhyte and the micro-sized granular ferric hydroxide materials for the purposes of research. Open access funding enabled and organized by Projekt DEAL.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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