The effect of metal (hydr)oxide nano-enabling on intraparticle mass transport of organic contaminants in hybrid granular activated carbon

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Abstract

The overarching goal of this study was to ascertain the changes in intraparticle mass transport rates for organic contaminants resulting from nano-enabled hybridization of commercially available granular activated carbon (GAC). Three different nano-enabled hybrid media were fabricated by in-situ synthesizing titanium dioxide nanoparticles inside the pores of GAC sorbent, characterized, and evaluated for removal of two model organic contaminants under realistic conditions to obtain the intraparticle mass transport (pore and surface diffusion) coefficients. The results validated the two hypotheses that: (H1) the pore diffusion rates of organic contaminants linearly decrease with decrease in cumulative pore volume caused by increase in metal (hydr)oxide nanoparticle content inside the pores of the hybrid GAC sorbent; and (H2) introduction of metal (hydr)oxide nanoparticles initially increases surface diffusivity, but additional loading causes its decrease as the increase in metal (hydr)oxide nanoparticles content continues to reduce the porosity of the GAC sorbent. Nano-enabled hybridization of commercially available GAC with metal (hydr)oxides has the potential to significantly increase the intraparticle mass transport limitations for organic contaminants. Introduction of metal (hydr)oxide nanoparticles inside the pores of a pristine sorbent causes the pore diffusion rates of

organic contaminants to decrease as the cumulative pore volume is reduced. In contrast, the introduction of limited amounts of metal (hydr)oxide nanoparticles appears to facilitate the surface diffusion rates of these contaminants.

Keywords: nanoparticles; pore diffusion; surface diffusion; activated carbon; water; organic contaminant

1. Introduction

Nanotechnology has demonstrated a great potential for resolving major challenges associated with existing small-scale water treatment systems by exploiting the unique size-dependent characteristics of nanomaterials to develop novel high-performance nano-enabled sorbents or catalysts (Qu et al., 2013a). Frequently, nanomaterials are embedded inside commercially available macroporous adsorbents or ion-exchange resin to (1) enable simultaneous removal of multiple contaminants with different chemistries; (2) reduce the size and complexity of the sorbent systems by eliminating the need for multi-modular solutions; and (3) minimize the operations and management (O&M) requirements of a small-scale water treatment system (Savagel and Diallo, 2005; Sylvester et al., 2006; Hristovski et al., 2008a; Lin and SenGupta, 2009; Ali, 2012; Xu et al., 2012; MedPELLI et al., 2015; Dale et al., 2016). Because of these attributes, the nano-enabled hybrid sorbents appear to be particularly advantageous for uses in small, rural, and poor communities of developing countries, which do not have the finances or technological know-how to employ a complex centralized solution for treating water sources contaminated with multiple contaminants (Sarkar et al., 2007; Shannon et al., 2008; Brame et al., 2011).

Driven by the prospects that introduction of nanoparticles in commercially available media could enable simple water treatment without requiring expensive infrastructure changes, significant research has been done to assess the benefits of adding novel nano-enabled properties to traditional adsorbent and ion-exchange media (Qu et al., 2013b; German et al., 2014). For example, granular activated carbon (GAC), which has been proven to be a poor sorbent for treating inorganic contaminants, demonstrated effective removal of arsenic and similar oxyanions after impregnation with metal (hydr)oxide nanoparticles (Zhang et al., 2007; Jang et al., 2008; Hristovski et al., 2009; Cooper et al., 2010; Sandoval et al., 2011). However, much of the published research has focused on enabling commercial sorbents to remove new contaminants beyond their initially designed capabilities, while the adverse impacts of nano-enabled hybridization on the properties of pristine commercial media were frequently overlooked (Rivera-Utrilla et al., 2011). Specifically, only a small number of studies have been conducted to investigate

the losses in organic contaminant or ion-exchange capacities of activated carbon sorbents or ion-exchange resins, respectively (Hristovski et al., 2008a). However, in small packed-bed systems (e.g. point-of-use or point-of-entrance systems), which are typically operated at high hydraulic loading rates and short empty bed contact times (EBCTs), the system's overall performance and design are frequently dominated by the contaminant mass transport mechanisms, and not by the sorption capacity of the media (Fox, 1989; Hand et al., 1989). A negligibly small number of studies have been conducted to assess the overall contaminant mass transport implications of hybridizing traditional sorbents with nanoparticles (Cooper et al., 2010; Sandoval et al., 2011). To illustrate, the effect that metal (hydr)oxide nanoparticles hybridization of GAC has on the organic contaminant mass transport has not been studied, although aspects of the inorganic contaminant mass transport have been explored (Chen et al., 2007; Jang et al., 2008)

Considering that nano-enabled hybridization changes the intraparticle properties of the pristine media (e.g. pore-size distribution and specific surface area), the intraparticle mass transport rates of all contaminants are expected to change. This, in turn, will affect the shape and depth of the mass transfer zone for each contaminant in a packed-bed reactor configuration, and affect the design and operation criteria of the packed-bed reactor to ensure optimum removal of contaminants (Crittenden et al., 2005).

In light of this knowledge gap and its engineering implications, the overarching goal of this study was to ascertain the changes in intraparticle mass transport rates for organic contaminants resulting from nano-enabled hybridization of commercially available granular activated carbon. Under realistic fabrication and operation conditions, it was hypothesized that: (H1) the pore diffusion rates of organic contaminants linearly decrease with decrease in cumulative pore volume caused by increase in metal (hydr)oxide nanoparticle content inside the pores of the hybrid GAC sorbent; and (H2) introduction of metal (hydr)oxide nanoparticles initially increases surface diffusivity, but additional loading causes its decrease as the increase in metal (hydr)oxide nanoparticles content continues to reduce the porosity of the GAC sorbent. The underlying reasoning behind (H1) stems from the fact that introduction of nanoparticles inside media reduces the size of available pores through which the pore controlled intraparticle mass transport (pore diffusion) occurs. Similarly, nano-enabling also changes the surface properties inside the

pores of the media, which consequently affects the nature and intensity of the interactive forces that are engaged in the surface controlled intraparticle mass transport (surface diffusion) of a contaminant. Therefore, to accomplish the overarching goal and address the hypotheses, four task-oriented objectives were achieved: (1) three different nano-enabled hybrid media were fabricated by in-situ synthesizing TiO_2 nanoparticles inside the pores of a commercially available GAC sorbent; (2) the hybrid and pristine GAC sorbents were characterized and compared side-by-side; (3) the adsorption capacities of all sorbents were quantified for two model contaminants under pseudo-equilibrium conditions and continuous-flow conditions using batch and short packed-bed column (SBC) tests, respectively; (4) the intraparticle mass transport (pore and surface diffusion) coefficients were obtained and/or validated by employing existing mathematical and pore-surface diffusion model (PSDM) predictions. Two types of model contaminants (methyl orange and methylene blue) with similar molecular weights and sizes, but different charges in neutral pH ranges (methylene blue is positively charged at $\text{pH} > 4$ and methyl orange is negatively charged at $\text{pH} > 4$) (Mahmoudi et al., 2015) were selected to explore significance of electrostatic interaction in intraparticle mass transport. Titanium dioxide nanoparticles were used to nano-enable the pristine GAC media because of insolubility of this metal oxide in water and its unfavorable affinity to sorb organic contaminants when compared to GAC sorbents. Considering that the nanoparticles were not exposed to light inside the pores of the media, it was assumed that any photocatalytic degradation of the organic contaminants by TiO_2 was negligible compared to adsorption to GAC.

2. Experimental approach

2.1. Fabrication and characterization of hybrid media

A commercially available macroporous lignite-based GAC (Norit HydroDarco 3000 - HD 3000) was impregnated with different TiO_2 nanoparticles amounts by the modified method described by Elton et al. (2013). Hybrid media is termed low dose Ti-GAC (L-Ti-GAC), medium dose Ti-GAC (M-Ti-GAC) and high dose Ti-GAC (H-Ti-GAC).

In brief, 100 mL of wet pristine, as received, GAC was suspended in 100 mL of water solution containing different quantities of titanium(IV) oxysulfate (TiOSO_4). Specifically, TiOSO_4 solution with concentration of 100 g/L, 500 g/L and 1000 g/L was used for synthesis of L-Ti-GAC, M-Ti-GAC and H-Ti-GAC, respectively. The soaked media with the solution were kept in oven at 80 °C for 24 h to hydrolyze TiOSO_4 into TiO_2 . The media was washed with ultrapure water until the rinse water pH > 6, and kept in 10 mM NaHCO_3 buffered solution for further use.

Content of TiO_2 in the nano-enabled hybrid media was determined by gravimetric analysis (Reyes-Gallardo et al., 2013). For this purpose, the media was heated at 700 °C for 1 day to incinerate the organic content. The difference between the ashed solid weight of hybrid and pristine media presented TiO_2 content.

The size and shape of the deposited TiO_2 nanoparticles were analyzed by focus ion beam and scanning electron microscopy (FIB/SEM) (Nova 200 NanoLab UHR FEG-SEM/FIB and FEI XL 30). Spatial distribution of titanium through the hybrid media was observed by energy dispersive X-ray (EDS) elemental mapping. In this study, the finding that Ti was not present in HD-3000 was only confirmed (Hristovski et al., 2009; Jain et al., 2013).

The density, moisture content and porosity of the sorbent media were estimated using pycnometer analysis as described by Sontheimer et al. (1988) and previously applied for hybrid GAC media (Cooper et al., 2010). Specific surface area of the sorbent media was determined using the Brunauer–Emmet–Teller (BET) method, while the pore size distribution was obtained using the Barret-Joyner-Halenda (BJH) method with MicroMeritics Tristar-II 3020 automated gas adsorption analyzer.

Changes in pore width resulting from different amount of TiO_2 nanoparticles inside the hybrid Ti-GAC media were calculated using the BJH data. Cumulative pore volume distribution, measured for pore width in the working range of the instrument from 1.7 to 300 nm, was integrated and separated to domains in accordance to IUPAC classification where micropores have pore width of less than 2 nm, mesopores are from 2 to 50 nm and macropores have pore width of greater than 50 nm (Rouquerol et al., 1994). Weight average values of the pore volumes were calculated for each pore classification range.

Point-of-zero charge (pH_{PZC}) of sorbent media was determined by the pH drift method in 10 mmol KNO_3 background electrolyte solution after 7 days of mildly agitated equilibration (Mustafa et al., 2002). The pH drift method is recommended for porous and large particles that require longer time for equilibration than is allowed by titration or electrophoresis methods (Cristiano et al., 2011).

Determining sorption capacity of all media for the model organic contaminants

To quantify the sorption capacity of the Ti-GAC and pristine GAC media for both model contaminants, batch pseudo-equilibrium sorption tests were conducted. Specifically, a minimum of 11 doses for all GAC media, ranging between 0.01 to 1 g/L of dry media, were exposed to 10 mg/L model contaminants (methyl orange or methylene blue) dissolved in ultrapure water buffered by 10 mM NaHCO_3 and corrected to a $\text{pH}_{\text{FINAL}} = 7.6 \pm 0.2$ with HNO_3 . To prevent any photo-bleaching, amber glass bottles with Teflon lined caps were used as reactor vessels. Samples were continuously agitated for a period of 3 days at $T = 20 \pm 2$ °C, prior to filtering through a GF/F membrane. This contact time was found sufficient for pseudo-equilibration of occur (Hristovski et al., 2008b; MedPELLI et al., 2015). The equilibrium concentrations of the model dyes were determined via UV/VIS spectroscopy (Genesis 20 UV/VIS spectrophotometer) at $\lambda_{\text{METHYL ORANGE}} = 464$ nm and $\lambda_{\text{METHYLENE BLUE}} = 665$ nm. Sorption capacity at pseudo-equilibrium was calculated according to the Eq. (1):

$$q_e = \frac{C_0 - C_e}{D_0} \quad (1)$$

Model contaminant isotherms were developed using the Freundlich isotherm model (Eq. 2) to (1) characterize the pseudo-equilibrium sorption capacity, and (2) develop modeling parameters for continuous-flow packed-bed modeling and enable characterization of the mass transport mechanisms.

$$q_e = KC_e^{1/n} \quad (2)$$

Where q_e is the absorption capacity (mg/g), C_o is the initial concentration of sorbate in solution (mg/L), C_e is the equilibrium concentration of sorbate in solution (mg/L), D_o is the dose of sorbent media (g/L), K is the Freundlich sorption capacity parameter (mg/g)(L/mg)^{1/n}, and $1/n$ corresponds to the unitless Freundlich sorption-intensity parameter.

A regression analysis matrix was generated for experimentally obtained batch sorption data and Freundlich adsorption isotherm model. To validate the significance of the Freundlich model fit, regression analysis was conducted. The validity of the Freundlich model fits was considered statistically significant when the probability factor (p) was lower than 0.05.

Assessing contaminant removal performance under continuous-flow conditions

To assess the removal performance of model organic contaminants under continuous-flow conditions and determine the contaminant mass transport coefficients, a series of SBC tests were conducted for all media with the two model contaminants. In brief, the tested media were tightly and evenly packed with a length of 10 cm in 1.5 cm diameter glass columns and connected to a ceramic piston pump via Teflon tubing to eliminate sorption of the organic contaminants on the test elements. Considering that ratios of column and particle diameters were > 8 ($d_{\text{column}}/d_p > 8.33$), the wall effect on mass transfer was neglected (Knappe et al., 1997; Sandoval et al., 2011). The properties of tested media and operating conditions are summarized in the Supplemental Information - Table S1. An initial dye concentration of 10 mg/L, as a model contaminant, in 10 mM NaHCO₃ buffered ultrapure water with a pH = 7.6 ± 0.3 was used in the tests. The SBC tests were operated at realistic hydraulic loading rates of 1.52 L/s m² (2.22 gal/min ft²) (Westerhoff et al., 2005). Effluent samples were collected in glass vials with Teflon lined septa and analyzed via UV/VIS spectrophotometry at corresponding wavelengths.

The film mass transport and pore-diffusion coefficients for each operating conditions and contaminants were estimated using Gnielinski, Hayduk & Laudie, and Mackie & Meares correlations.

Initial estimates for the external (film) mass transport coefficient (k_f) were calculated using Gnielinski correlation by Eq. 3 - 5 (Sontheimer et al., 1988; Hristovski et al., 2008b; Cooper et al., 2010; Athanasaki et al., 2015):

$$k_f = \frac{[1+1.5(1-\varepsilon)] \times D_l}{d_p} \times (2 + 0.644 \times Re^{1/2} \times Sc^{1/3}) \quad (3)$$

$$Re = \frac{\rho_l \times \phi \times d_p \times v_l}{\varepsilon \times \mu_l} \quad (4)$$

$$Sc = \frac{\mu_l}{\rho_l \times D_l} \quad (5)$$

The liquid diffusivity was determined from a correlation given by Hayduk and Laudie (Eq. 6) (Mertz et al., 1999):

$$D_l = \frac{13.26 \times 10^{-5}}{\mu_l^{1.14} V_b^{0.589}} \quad (6)$$

Constraints: $Re \times Sc > 500$; $0.6 \leq Sc \leq 10^4$; $1 \leq Re \leq 100$; $0.26 \leq \varepsilon \leq 0.935$; where k_f is the external mass transport coefficient (m^2/s); Re is the Reynolds number (unitless); Sc is the Schmidt number (unitless); ε is the bed void fraction (unitless); d_p is the adsorbent particle diameter (m); D_l is the free liquid diffusivity for dyes (m^2/s); μ_l is the dynamic viscosity of water at 20 °C (Ns/m^2); ρ_l is the density of water at 20 °C (kg/m^3); Φ is the particle shape factor (unitless); v_l is the liquid superficial velocity (m/s); Note: in the formula used by Hayduk, V_b is molar volume (cm^3/mol) and μ_l is viscosity of water (centipoise).

The pore diffusion coefficient was calculated using Eq. (7) (Sontheimer et al., 1988; Hristovski et al., 2008b; Cooper et al., 2010; Athanasaki et al., 2015):

$$D_p = \frac{\varepsilon_p \times D_l}{\tau} \quad (7)$$

The tortuosity (τ) was estimated using the correlation for electrolyte solutions based on particle porosity (ε_p) proposed by Mackie and Meares (Eq. 8) (LeVan et al., 1997; Hristovski et al., 2008b; Cooper et al., 2010; Athanasaki et al., 2015):

$$\tau = \frac{(2-\varepsilon_p)^2}{\varepsilon_p} \quad (8)$$

Detailed values of film mass transport and pore-diffusion coefficients and all parameters used for its calculation are summarized in Supplemental Information - Table S1.

Estimating surface diffusion and verifying film and pore diffusion coefficients via Pore Surface Diffusion Modeling

The pore surface diffusion model (PSDM) is a dynamic packed-bed model, which has been successfully used to predict the breakthrough curves and quantify mass transport coefficients of both organic and inorganic contaminants in porous media (Crittenden et al., 1986; Hand et al., 1997; Magnuson and Speth, 2005; Hristovski et al., 2008b; Cooper et al., 2010; Yan et al., 2013; Athanasaki et al., 2015). The PSDM simulations were set up for the experimental conditions identical to those used in SBC tests, with mathematically calculated values of k_f and D_p and fitted values of D_s . The coefficient of determination (R^2), between breakthrough curves obtained experimentally in the SBC tests and predicted by PSDM, allowed verification of calculated values for film and pore diffusion coefficients and selection of the most appropriate values for the surface diffusion coefficient.

3. Results and discussion

3.1. Characterization of the sorbent media

Figure 1 confirms the presence of sphere-like clusters of nanoparticles in all hybrid Ti-GAC media. The backscatter detector used during FIB/SEM analysis differentiated Ti, which is white as a heavier element, from the black background of pristine GAC composed of lighter elements like carbon such as illustrated in Figure S1 of Supplemental Information. Determination of the spatial distribution of Ti via EDS elemental mapping revealed that the TiO_2 was distributed throughout the media in a relatively even pattern for all the synthesized media (Figure S2) although the increase in

nanoparticle precursor concentration during synthesis caused TiO₂ content to increase from 0% in pristine GAC to ~ 8% in L-Ti-GAC, ~ 20% in M-Ti-GAC, and ~ 31% in H-Ti-GAC. This caused the content of nanoparticles inside the pores of GAC to increase, which is particularly emphasized in H-Ti-GAC where the small pores appeared almost completely clogged (see Figure 1d).

<Figure 1>

The observed decrease in particle porosity, caused by the increase in TiO₂ nanoparticle content, was further confirmed by the data describing media's particle porosity. Table 1 summarizes the decrease in particle porosity for the pristine and hybrid media. Addition of ~ 8% of TiO₂ nanoparticles in L-Ti-GAC did not decrease the overall particle porosity of pristine GAC media, which was $\varepsilon_p \sim 0.80$. However, as the TiO₂ content increased to ~ 20%, the particle porosity decreased to $\varepsilon_p \sim 0.78$ in M-Ti-GAC. Similarly, the particle porosity further decreased to $\varepsilon_p \sim 0.75$ in H-Ti-GAC, when the TiO₂ content increased to ~ 31%. Figure 2 shows the same decreasing trend in the differential pore volume with increase in TiO₂ content. Interestingly, however, the differential pore volume appears to be the same for the micropore region of all media (pristine and hybrid GAC). As illustrated in Figure 2, the difference (delta) in differential pore volume starts increasing at $d_{PORE} > 3$ nm suggesting that the pore clogging occurs in the mesopore and lower macropore regions, which are the greatest contributors to tortuosity, pore diffusion limitation, and sorption capacity reduction for large molecules (e.g. methylene blue, NOM, etc.). The estimated average pore width for all ranges further supports this decreasing trend for the mesopores and macropores (Table 1). An interesting deviation from this trend; however, could be observed for the average macropore width of H-Ti-GAC. As summarized in Table 1, the increase in macropore width of H-Ti-GAC is expected because increase in TiO₂ content and clogging of pores slightly greater than 300 nm, will cause creation of new pores with diameters < 300 nm, which would become detectable by instrument.

In contrast, Figure S3 does not suggest a significant change in differential pore surface area among the pristine GAC, L-Ti-GAC, and M-Ti-GAC media although there is

slight decrease in specific surface area with increase in TiO₂ content (Table 1). However, the differential pore surface area significantly decreases in H-Ti-GAC as TiO₂ nanoparticles start to exclude the available surface area from the clogged pores. This trend is expected to seriously affect the surface diffusion mass transport mechanism because of decrease in available surface area on which the contaminants could travel according to the intraparticle mass transport theory (Axe and Trivedi, 2002).

The $pH_{PZC} \sim 6.8$ of the pristine media was similar to values reported in literature (Cheng et al., 2005). With increase of TiO₂ content, pH_{PZC} decreased to ~ 6.4 for L-Ti-GAC, ~ 6.3 for M-Ti-GAC and ~ 5.1 for H-Ti-GAC. Considering that pH_{PZC} of TiO₂ is around 6 (Kosmulski, 2002), pH_{PZC} for H-Ti-GAC is somewhat lower than expected, but not completely surprising considering the TiO₂ nanoparticle formation process generates sulfates, which could not be completely eliminated from the pores of the hybrid media and contribute to a higher number of negative surface charges (Athanasaki et al., 2015). This decrease in media's pH_{PZC} is anticipated to aid surface diffusion of positively charged contaminants because of the electrostatic attraction with the surface of the media. In contrast, it could be anticipated that the increase in electrostatic repulsion between the surface and negatively charged contaminants (e.g. methyl orange) to aid pore diffusion for these types of contaminants.

<Table 1>

<Figure 2>

3.2. Contaminant removal performance of media under pseudo-equilibrium conditions

Figure 3 presents the statistically significant fits of Freundlich adsorption isotherm models ($p < 0.05$) for methyl orange and methylene blue removal by pristine GAC and hybrid Ti-GAC media. The sorption capacity of the hybrid media exhibited a decreasing trend for both contaminants with increase in TiO₂ content. This trend is to be expected because much of the available carbon-based surface area is being replaced or made inaccessible for sorption by the metal oxide nanoparticles, which are not good

sorbents for organic contaminants. Although the increase in TiO_2 content caused a decrease of the media's sorption capacity for both contaminants, the consequent decrease in pH_{PZC} caused decrease in sorption energy of methylene blue as described by the decreasing Freundlich intensity parameter ($1/n$) values. The Freundlich intensity parameter value for the pristine GAC was $1/n \approx 0.14$, and decreased to $1/n \approx 0.11$ for L-Ti-GAC. The $1/n$ value decreased by a factor of two for M-Ti-GAC and H-Ti-GAC, which exhibited values of $1/n \approx 0.07$ and $1/n \approx 0.06$, respectively. In contrast, the Freundlich intensity parameters for sorption of methyl orange by the hybrid media initially remained unchanged, and then increased above the one obtained for the pristine GAC ($1/n \approx 0.14$), suggesting that small amounts of TiO_2 does not have to change energy of sorption environment (L-Ti-GAC $1/n \approx 0.14$), while excess of TiO_2 nanoparticles energetically inhibits the sorption process (M-Ti-GAC $1/n \approx 0.24$ and H-Ti-GAC $1/n \approx 0.31$).

<Figure 3>

3.3. Contaminant removal performance of media under continuous-flow conditions

Figure 4 illustrates the experimentally obtained breakthrough curves from the short packed-bed column tests and the corresponding PSDM predictions for the model contaminants removal by the pristine GAC media and H-Ti-GAC media. To eliminate data overcrowding on the graph, the experimental results and corresponding model predictions for L-Ti-GAC and M-Ti-GAC media are presented in Figure S4 of Supplemental Information. All PSDM simulated breakthrough curves, which were based on the predicted film and pore diffusion coefficients, demonstrated good agreement with the corresponding experimental data ($R^2 > 0.95$) and proved to be suitable for estimation of diffusion coefficients for removal of charged organic compounds by either pristine or hybrid media.

The pristine GAC media breakthrough curves for both model contaminants exhibit similar shapes for intraparticle diffusion controlled mass transport processes, which are characterized by rapid initial and slower later changes in effluent concentrations.

However, the introduction of TiO₂ nanoparticles resulted in a more rapid initial increase and a longer gradual increase in the profiles of the hybrid GAC breakthrough curves. Considering that there is negligible difference in film diffusion coefficient (k_f) caused by the difference in experimental conditions, this trend is expected because the intraparticle mass transport limitations grow with increase in tortuosity and longer intraparticle paths, which were created by the introduction of nanoparticles inside the pores of the GAC (Crittenden et al., 1986; Weber and Smith, 1987; Sontheimer et al., 1988; Badruzzaman et al., 2004; Sperlich et al., 2005; Westerhoff et al., 2005; Hristovski et al., 2008a, 2008b). Pore diffusivity, which is typically the dominant intraparticle mass transport mechanism, is especially affected by this reduction of the cumulative pore volume. As illustrated in Figure 5a, the pore diffusivity coefficient decreases linearly with reduction in the cumulative pore volume ($R^2 \approx 0.92$) for both contaminants. The linear relationships in Figure 5a support the H1 hypothesis “the pore diffusion rates of the organic contaminants linearly decrease with decrease of cumulative pore volume caused by increase in metal (hydr)oxide nanoparticle content inside the pores of the hybrid GAC sorbent”. It has to be noted that the level of this linearity could be affected by other factors. For example, pore properties (pore morphology and size distributions, etc.), material properties (impurities, surface chemistry, charge, etc.), contaminant properties (size, charge, or type of the contaminant), and background water characteristics could affect this trend and its linearity to a greater or lesser extent, which is implied by the difference in fitted slopes for methyl orange and methylene blue (Figure 5a). Specifically, higher D_p values for methyl orange, which stem from the higher free liquid diffusivity when compared to methylene blue ($D_{l-MO} \approx 5.06 \times 10^{-6} \text{ cm}^2/\text{s}$; $D_{l-MB} \approx 4.00 \times 10^{-6} \text{ cm}^2/\text{s}$), describe its much faster diffusion inside the pores of media. However, the greater slope for methyl orange suggests that the introduction of TiO₂ nanoparticles inside the GAC pores may have a stronger impact on the pore diffusion when compared to the impact on diffusion of methylene blue. In contrast, the TiO₂ nano-enabling appeared to initially facilitate methylene blue surface diffusion much stronger than the surface diffusion of methyl orange as illustrated in Figure 5b. This is because increasing the TiO₂ content changed the surface charge to more negative, which consequently affected the nature and intensity of the attractive forces that are engaged in the surface controlled intraparticle

mass transport (surface diffusion) of a methylene blue (positively charged). This initial increase was also evident for methyl orange, but the effect was not as strong as with methylene blue probably because of the negatively charged disposition of methyl orange at $\text{pH} > 4$. Interestingly, however, the TiO_2 increase beyond the content of M-Ti-GAC led to rapid decrease in surface diffusion coefficients for both contaminants, which supports the H2 hypothesis that stated “introduction of metal (hydr)oxide nanoparticles initially increases surface diffusivity, but additional loading causes a decrease as the high metal (hydr)oxide nanoparticle levels continue to decrease the porosity of the GAC sorbent”. This cutoff appears to be somewhere between 20% and 30% TiO_2 in the case of this GAC and model contaminants. This trend could be supported by the interpretation that excessive pore clogging is expected to seriously impact the surface diffusion mass transport mechanism because it causes the available surface area, on which the contaminants could travel, to decrease. In brief, although the surface area is available, it is not accessible by the large contaminant molecules because of the pore size restrictions that are created by excessive introduction of nanoparticles. Consequently, even though dimensions of methyl orange or methylene blue ions are about $\sim 1.4 \times 0.7$ nm (Pelekani and Snoeyink, 2000; Huang et al., 2008), their hydrated radii would hinder their surface diffusions in significantly restricted mesoporous or microporous regions.

<Figure 4>

<Figure 5>

4. Conclusions

When designing nano-enabled media for full-scale packed-bed applications operated under realistic conditions, where the system’s overall performance is frequently dominated by the contaminant mass transport mechanisms, and not by the sorption capacity, it becomes imperative to properly understand how hybridization of commercially available media may affect the intraparticle mass transport rates. Nano-enabled hybridization of commercially available GAC with metal (hydr)oxides has the potential to significantly increase the intraparticle mass transport limitations for organic

contaminants. Introduction of metal (hydr)oxide nanoparticles inside the pores of a
pristine sorbent causes the pore diffusion rates of organic contaminants to decrease as the
cumulative pore volume is reduced. In contrast, the introduction of limited amounts of
metal (hydr)oxide nanoparticles appears to facilitate the surface diffusion rates of these
contaminants. Excessive nano-particle impregnation, however, has the potential to
reverse this beneficial surface mass transport effect. Consequently, proper understanding
of the magnitude of these effects leads towards designing media that enable maximization
of multi-contaminant removal efficiencies, optimization of mass-transfer zones and
packed-bed configurations, and minimization of operational problems.

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599

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Figure Caption

Figure 1. The presence of titanium nanoparticles in a) low dose (L-Ti-GAC), b) medium dose (M-Ti-GAC) and c-d) high dose (H-Ti-GAC) media

Figure 2. Differential pore volume as a function of pore diameter for pristine (GAC) and low dose (L-Ti-GAC), medium dose (M-Ti-GAC) and high dose (H-Ti-GAC) media

Figure 3. Freundlich adsorption isotherms for removal of a) methyl orange (MO) and b) methylene blue (MB) in 10 mM NaHCO₃ buffered ultrapure water after a contact time of 3 days with pristine (GAC), low dose (L-Ti-GAC), medium dose (M-Ti-GAC) and high dose (H-Ti-GAC) media

Figure 4. PSDM prediction and experimental data for removal of a) methyl orange (MO) and b) methylene blue (MB) with pristine (GAC) and high dose (H-Ti-GAC) media

Figure 5. Correlation of a) pore diffusion coefficients and b) surface diffusion coefficients with BJH adsorption cumulative pore properties for removal of methyl orange (MO) and methylene blue (MB) by pristine (GAC), low dose (L-Ti-GAC), medium dose (M-Ti-GAC) and high dose (H-Ti-GAC) media

<Figure 1>

<Figure 2>

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<Figure 5>

Table 1. TiO₂ content, pH_{PZC} and pore properties of pristine GAC and hybrid Ti-GAC media

Media	TiO ₂ content (%)	pH _{PZC}	BET surface area (m ² /g)	Particle porosity (%)	BJH adsorption cumulative volume of pores (cm ³ /g)	Estimated average pore width (nm) ^{a)}		
						Micropores	Mesopores	Macropores ^{b)}
GAC	0.00	6.8	532.19	0.80	0.43	2.00	19.88	114.0
L-Ti-GAC	7.94 ± 1.5	6.4	530.25	0.80	0.39	1.96	18.81	112.1
M-Ti-GAC	20.22 ± 0.2	6.3	495.31	0.78	0.32	1.96	17.49	111.1
H-Ti-GAC	31.46 ± 2.5	5.1	442.15	0.75	0.24	1.95	17.24	115.3

^{a)} Average pore width based on cumulative pore volume expressed for range of micropores (0-2 nm), mesopores (2-50 nm) and macropores (50-270 nm)

^{b)} Expected to increase because of large pores clogging by TiO₂ nanoparticles and creation of new pores with diameter less than 300 nm that are detectable by instrument