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Chapter 13

Titanium Dioxide-Based Hybrid Ion-Exchange Media for Simultaneous Removal of Arsenic and Nitrate

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The goal of this study was to develop an inexpensive and easy to fabricate titanium dioxide-based hybrid ion-exchange media (Ti-HIX) and assess its potential to remove arsenic and nitrate from water. Different Ti-HIX media were fabricated via in-situ formation of TiO_2 nanoparticles within the pores of three different commercially IX resins; the Ti-HIX media were characterized; and the arsenic and nitrate removal potential of the most economically feasible Ti-HIX media was assessed in model water under batch pseudo-equilibrium conditions. The Ti-HIX media were characterized with content ranging between 11% and 21% TiO_2 per media dry mass. The TiO_2 exhibited form of anatase nanoparticles. The Freundlich adsorption intensity parameters (1/n) for all the Ti-HIX media were < 1 implying favorable adsorption for arsenic. The estimated maximum adsorption capacity for arsenic expressed per mass of titanium ranged between 16.6 mgAs g^{-1} Ti, 24.9 mgAs g^{-1}Ti, and 27.3 for different types of tested Ti-HIX media, and was several fold higher than similar reported values in the literature.

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Nitrate removal performance of the base ion-exchange resins used in synthesis of the Ti-HIX media was not adversely impacted by the synthesis process.

Introduction

Many small and rural communities around the world lack the financial and technical capabilities to construct, maintain and operate complex and expensive treatment systems capable of simultaneously removing multiple contaminants from their groundwater sources. However, with the ever-increasing need for potable water and increasing regulations impacting small systems, a possibility exists to employ small and simple point-of-entry or point-of-use treatment systems in small communities. These systems could offer an inexpensive and simple alternative which is capable of simultaneously removing a wide range of inorganic contaminants with different chemistries such as arsenic and nitrate.

Arsenic is widely naturally occurring element within the earth's crust, with an average abundance of approximately 2 ppm (*1*, *2*). Besides the natural geological sources, like the dissolution of arsenic-bearing rocks, soil erosion and weathering; various anthropogenic activities such as mining and smelting of metal ores, combustion of fossil fuels and use of arsenical pesticides are also contributing to groundwater contamination with arsenic (*2*, *3*). Because of its chronic and acute toxicities and carcinogenic properties, the International Agency for Research on Cancer, the US National research Council, and the US Environmental Protection Agency (US EPA) consider arsenic as toxin and human carcinogen prone to cause cancer in the bladder, lungs, skin, liver and prostate (*4–6*). To limit the exposure to arsenic, US EPA decreased its maximum contaminant level (MCL) in drinking water from 50 μg/L to 10 μg/L in 2002 and mandated all public water systems to comply with this 10 μg/L standard by 2006 (*7*).

Nitrate is one of the most widespread pollutants of groundwater in many developed and developing countries (*8*). In addition to occurring naturally, the main sources of nitrate contamination in groundwater include intensive use of chemical fertilizers and manure in crop production, and poor wastewater treatment and collection (*9*, *10*). Although traditionally nitrate itself has been considered relatively non-toxic to humans, new studies suggest that various types of cancer and disruption of the endocrine system have also been attributed to nitrate in drinking water in addition to the problems associated with methemoglobinemia (*11*, *12*). Currently, the Maximum Contaminant Level (MCL) set by the USEPA for nitrate in drinking water is 10 mg/L NO_3-N; however, it would not be surprising if the US EPA decreases the MCL value for nitrate in the near future.

Driven by the newest toxicological findings, the increase in regulatory pressure has spurred the need to develop new and inexpensive or improve existing technologies capable of better removing arsenic and nitrate, two anions with distinctly unique chemistries. Nitrate is a stable, highly soluble ion that does is difficult to remove by traditional coagulation or adsorption processes because of its unique non-coordinating ligand chemistry. With exception to biological treatment, which does not work for small drinking water systems, the only

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cost-efficient way for nitrate treatment is via strong base ion-exchange process. In contrast, arsenic has a unique chemistry which allows it to exist as an oxo-anion in natural waters regardless of whether it exists in arsenite (+3) or arsenate (+5) form (*13–15*). Both these species of arsenic can adsorb onto metal (hydr)oxide surfaces by forming stable inner-sphere bidentate ligands (*16*). This property of arsenic has made metal (hydr)oxides good candidates for use as absorbents for arsenic treatment (*17*). Because of their low cost, iron (hydr)oxides have been the primary candidates for development of hybrid media that could simultaneously remove arsenic and other contaminants from water (*17*, *18*). However, their dissolution at low pH and affinity for silica at high pH may limit their use and regeneration potential (*19*). Titanium dioxide has offered a promise as an alternative metal (hydr)oxide media that could replace iron (hydr)oxides, but the unique chemistry and high cost of titanium based precursors needed to inexpensively synthesize titanium dioxide have created a barrier for developing inexpensive and easy to fabricate titanium dioxide-based hybrid media capable of simultaneous removal of multiple contaminants (*20*).

The goal of this study was to develop an inexpensive and easy to fabricate titanium dioxide-based hybrid ion-exchange media (Ti-HIX) and assess its potential to remove arsenic and nitrate from water. To achieve this goal, three task-oriented objectives were addressed: (1) different hybrid ion-exchange (HIX) media were fabricated via in-situ formation of TiO_2 nanoparticles within the pores of three different commercially ion-exchange (IX) resins; (2) the Ti-HIX media were characterized; and (3) the arsenic and nitrate removal potential of the Ti-HIX media was assessed in model water under batch pseudo-equilibrium conditions.

Experimental Approach

Fabrication of the Titanium Dioxide-Based Hybrid Ion-Exchange Media

The hybrid media were fabricated by in-situ synthesis of TiO_2 nanoparticles within the pores of commercially available nitrate selective IX resins (Table 1). Briefly, 50 mL of strong base IX resin were soaked in 100 mL of ultrapure water (< 1 μS cm^{-1}) for a period of 24 hours to achieve proper hydration of the resin. An aliquot of 100 mL of saturated TiO^{2+} precursor solution was prepared by slowly dissolving 124 g of $TiOSO_4$ salt (ACS grade, Sigma-Aldrich) in ultrapure water at an elevated temperature of 80°C. After decanting the excess water, the hydrated IX resin was mixed with 100 mL of the TiO^{2+} precursor solution. Two mixing times, 5 minutes and 6 hours, were used in mixing the precursor solution with the IX resin to assess the impact of mixing time on TiO_2 content of the Ti-HIX media. For large scale manufacturing, shorter mixing times are preferred because they allow process streamlining and cost reduction. Upon mixing, the TiO^{2+} precursor was converted to TiO_2 via a 24 hour hydrolysis at 80 °C. The hydrolysis process is illustrated with Equation 1:

$$TiO^{2+} + 2H_2O \rightarrow TiO(OH)_2 + 2H^+ \rightarrow TiO_2 + H_2O \qquad (1)$$

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Two hydrolysis conditions were used to understand the effect that excess precursor solution might have on the TiO_2 content of the Ti-HIX media. The first condition entailed decanting of the excess TiO^{2+} precursor solution after the mixing, while the second condition involved hydrolysis without any removal of the excess TiO^{2+} precursor solution. The first condition is more economically sound from a cost reduction perspective than the second one because the decanted precursor solution could be reused for fabrication of other media.

Table 1. Strong Base Ion-Exchange Resins Used in Fabrication of the Titanium Dioxide-Based Hybrid Ion-Exchange Media

Media Name	*Manufacturer*	*Functional groups*	*Exchange capacity (meq/mL)*	*Dp (mm)*
Dowex NSR-1	Dow Chemical Co.	Quaternary amine	1.4	0.3-1.2
A-520E	Purolite	Quaternary ammonium	0.9	0.3-1.2
SIR-100-HP	Resintech	$R\text{-}N\text{-}R3^{+}Cl^{-}$	0.85	0.3-1.2

Using these synthesis variations, twelve different Ti-HIX media were fabricated from three commercially available IX resin. Upon fabrication, all Ti-HIX media were rinsed in ultrapure water to remove the excess sulfuric acid generated during the synthesis process and soaked in 5% NaCl overnight to convert the resin back in the chloride form. The Ti-HIX media was then repeatedly rinsed with ultra pure water to remove excess NaCl and stored wet.

Characterization of the Titanium Dioxide-Based Hybrid Ion-Exchange Media

The TiO_2 content of the media was quantitatively determined by a gravimetric analysis which involved drying of approximately 6g Ti-HIX media at 104 ± 1 °C to remove any moisture and consequent ashing at 550 °C until constant mass was achieved to remove any carbon content or impurities. This process produced pure TiO_2, which was confirmed by X-ray diffraction (XRD). High resolution XRD (Pananalytical X'Pert Pro) was used to determine the crystalline structure of the TiO_2, and focus ion beam and scanning electron microscope with energy dispersion X-ray microanalysis (FIB/SEM-EDX) techniques were employed to determine the size and the shape of the TiO_2 nanoparticles within the pores of the media (Nova 200 NanoLab UHR FEG-SEM/FIB).

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Removal of Arsenic and Nitrate by the Titanium Dioxide-Based Hybrid Ion-Exchange Media

Batch equilibrium tests were conducted with the most economically feasible hybrid ion-exchange media at a final pH of 7.7 ± 0.2 in 5 mM $NaHCO_3$ buffered ultrapure water (<1 μS cm^{-1}). A realistic initial arsenate concentration of $C_0 \approx$ 120 μgAs L^{-1} was used to assess the arsenic removal capacities of the media and compare them to their untreated counterparts. To determine the best Ti-HIX media, two criteria, production cost and TiO_2 content, were considered. Additional batch equilibrium tests with the lowest performing hybrid ion-exchange media were conducted at four additional pH values, 6.3 ± 0.2, 7.7 ± 0.2, 8.3 ± 0.2, and 8.9 ± 0.2 to assess the impact of naturally occurring pH environments on arsenic adsorption capacity of the media. Nitrate removal potential of the media was assessed by conducting batch equilibrium tests in same water matrix (5 mM $NaHCO_3$ buffered ultrapure water) characterized with a final pH of 7.6 ± 0.3 and a low initial nitrate concentration of 5 mg L^{-1} (1.3 NO_3-N), to minimize the effects that high nitrate concentrations might have on the nitrate/chloride selectivity.

Isotherms were developed for arsenic and nitrate adsorption and analyzed using Freundlich adsorption model (Equation 2):

$$q = KC_E^{\frac{1}{n}} \tag{2}$$

where q is the adsorption capacity ([M] adsorbate $[M]^{-1}$ adsorbent; K is the Freundlich adsorption capacity parameter ([M] adsorbate $[M]^{-1}$ adsorbent)$([L]^3$ $[M]^{-1}$ adsorbate$)^{1/n}$, C_E is the equilibrium concentration of adsorbate in solution ([M] adsorbate $[L]^{-3}$), and $1/n$ is the Freundlich adsorption intensity parameter (unitless).

Arsenic was analyzed using inductively couple plasma mass spectrometry (ICP-MS) (ThermoScientific X-Series) according to US EPA method 200.8; while nitrate was analyzed using ion chromatography (IC) (Dionex IS-2000) according to method US EPA method 300.0 (*21*).

Results and Discussion

Media Characterization

Figure 1 illustrates the titanium dioxide content of the fabricated Ti-HIX media which ranged between 11% (6.7% as Ti) and 21% (12.9% as Ti) by dry resin mass. This broad range was caused to great extent by the high variability in the TiO_2 content of the Resintech media and suggests that this media might be the most susceptible to changes in fabrication conditions. In general, however, most of the Ti-HIX media were characterized with TiO_2 contents which were close to the average value of 16.4% (9.8% as Ti content).

The TiO_2 content data suggests that short mixing periods result in media with higher TiO_2 content. A mixing time of 6 hours without decanting the excess precursor solution resulted in similar TiO_2 contents as the 5 minute mixing times with or without decanting. However, when the excess precursor was decanted, the

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prolonged mixing of the media resulted in lower TiO_2 content probably because of attrition of the IX resin and/or reequilibration of the TiO^{2+} between the bulk solution and the pores of the IX resin. Higher metal (hydr)oxide content typically relates to higher adsorption capacity of the metal (hydr)oxide impregnated media. When the metal (hydr)oxide contents of the media are similar or higher, shorter mixing times are preferred if the fabrication process is to be scaled up because of lower fabrication costs. Additionally, reusing the excess precursor solution for fabrication of other Ti-HIX media further reduces the cost of production, which makes the Ti-HIX media fabricated by mixing the IX resin for 5 minutes and decanting the excess precursor solution most economically sound.

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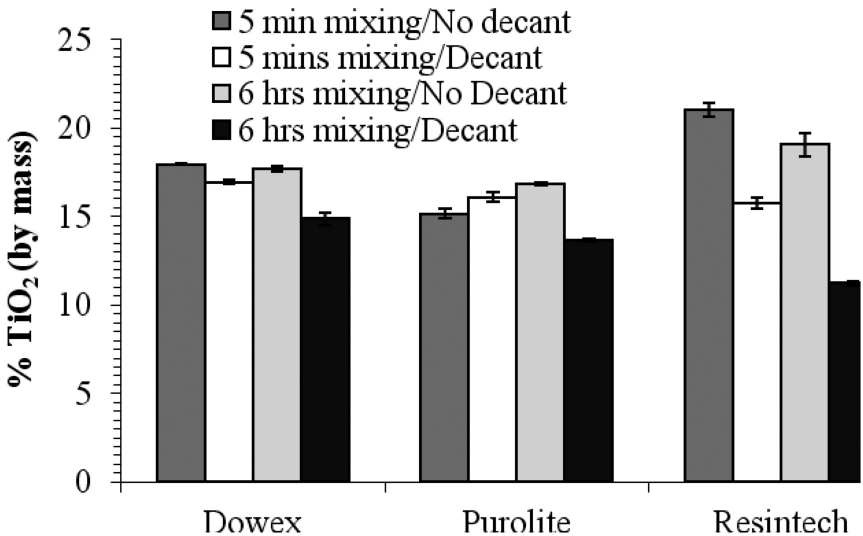

Figure 1. Titanium dioxide content of fabricated titanium dioxide-based hybrid ion-exchange media under different synthesis conditions and with three different ion-exchange resins. Error bars represent standard deviations.

FIB/SEM analysis revealed that titanium dioxide is evenly distributed through the Ti-HIX media (Figure 2a). The backscatter detector used during the FIB/SEM analysis differentiated between heavier elements such as titanium (white areas in Figures 2a and 2b) and lighter elements such as carbon, nitrogen, oxygen and hydrogen (darker areas in Figures 2a and 2b). As seen in Figure 2b, the in-situ hydrolysis resulted in formation of clusters of spherical nanoparticles within the pores of the IX resin. The nanoparticles ranged between 50 nm and 90 nm in size and had similar morphology as commercially available TiO_2 nanopowders (*20*). Although the FIB/SEM images suggested an amorphous TiO_2 structure, X-ray diffraction analysis revealed that the nanoparticles have the crystalline structure of anatase (Figure 3). Furthermore, the XRD data implied that the IX resin had no impact on the crystalline structure of the TiO_2 nanoparticles.

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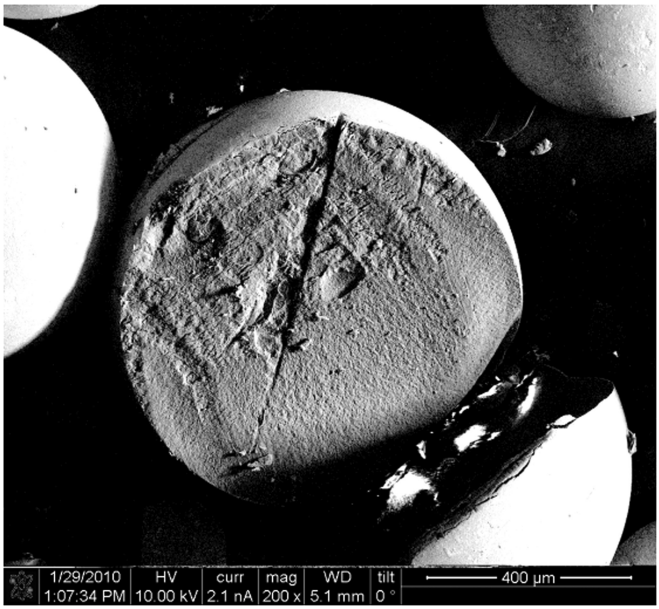

Figure 2a. Focus Ion Beam/Scanning Electron microscope image of a crossection of titanium dioxide-based hybrid ion-exchange media. Even distribution of white areas thoughout the media implies even distribution of heavier elements such as titanium.

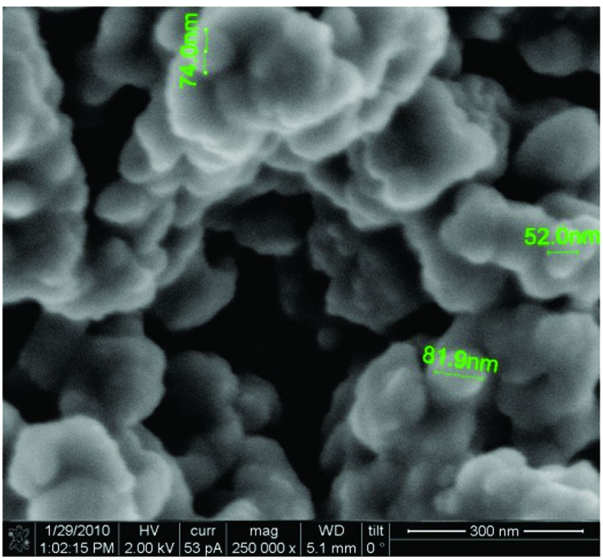

Figure 2b. Focus Ion Beam/Scanning Electron microscope image of a pore inside the titanium dioxide-based hybrid ion-exchange media showing white clusters of titanium dioxide nanoparticles coating the pores of the ion-exchange resin.

Arsenic Removal by the Titanium Dioxide-Based Hybrid Ion-Exchange Media

Figure 4 compares the arsenic adsorption isotherms for the untreated IX resin and the Ti-HIX media fabricated via the most economically sound synthesis conditions (mixing time of 5 minutes followed by decanting of the excess precursor solution and 24 hr hydrolysis). By the isotherms grouping, it is obvious that the Ti-HIX exhibit similar arsenic adsorption capacities, with Purolite Ti-HIX exhibiting negligibly higher adsorption capacity, and Resintech Ti-HIX exhibiting negligible lower adsorption capacity under these conditions. The arsenic removal performance of the untreated IX resin was one to three orders of magnitude lower than the hybrid media demonstrating the fact that high arsenic adsorption capacity is a direct result of the TiO_2 nanoparticle modification of the media.

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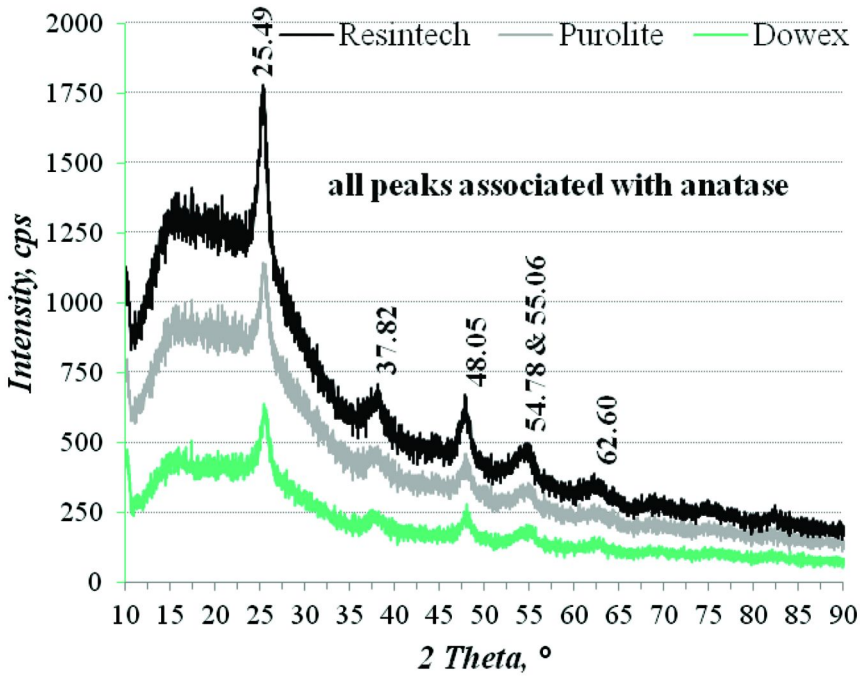

Figure 3. X-Ray diffraction peaks indicate existence of anatase crystalline structure of the synthesized titanium dioxide nanoparticles within the hybrid ion-exchange media.

Freundlich adsorption capacity parameters expressed per gram of dry mass of media are also presented in Figure 4; while normalized Freundlich capacity parameters expressed per gram of metal (titanium) are summarized in Table 2 together with the Ti contents of the tested media. For better comparison with other metal (hydr)oxide media used in arsenic adsorption, Table 2 also summarizes the maximum adsorption capacities expressed per gram of metal (titanium) and estimated for C_0 = 100 μgAs L^{-1}. The estimated maximum adsorption capacities (q_0) for the Ti-HIX media were 16.6 mgAs g^{-1} Ti, 24.9 mgAs g^{-1}Ti, and 27.3 mgAs g^{-1}Ti for the Resintech Ti-HIX, Dowex Ti-HIX and Purolite Ti-HIX, respectively. These values are several fold higher than the values published for other metal (hydr)oxide materials when normalized to gram of metal. The lowest performing Resintech Ti-HIX exhibited almost three times greater adsorption capacity per g of titanium than the commercially available TiO_2 nanopowder (*22*); while this factor was even greater for the ferric (hydr)oxide based media (Table 2).

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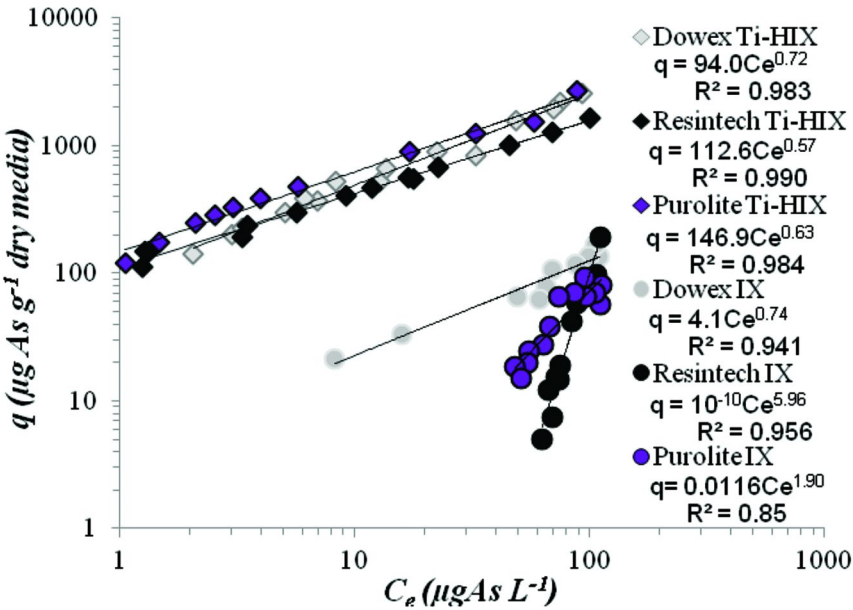

Figure 4. Arsenic adsorption isotherms for the untreated IX resin and the titanium dioxide-based hybrid ion-exchange media fabricated via the most economically sound synthesis conditions. Final pH = 7.7 ± 0.2; 5 mM $NaHCO_3$ buffered ultrapure water; $C_0 \approx 120$ μgAs L^{-1}.

The Freundlich adsorption intensity parameters (1/n) for all the Ti-HIX media were < 1 and were similar to the values reported for other metal (hydr)oxides (*19*, *22*, *23*). A value of 1/n < 1 implies a low energy of adsorption and good performance in waters with low arsenic concentrations (*24*).

Table 2. Comparison of Metal Contents and Estimated Maximum Arsenic Adsorption Capacity Values (q_0 for C_0 = 100 µgAs L^{-1}) for the Titanium Dioxide-Based Hybrid Ion-Exchange Media and Published Values for Other Metal (Hydr)oxide Based Media Evaluated under Comparable Conditions

Media Type	*Freundlich Capacity Parameter K**	*Metal Content (Fe, Zr, Ti)*	*Est. Max. Adsorption Capacity q_0 (mgAs g^{-1})*
Dowex Ti-HIX	924.5	~10.2%	24.9
Purolite Ti-HIX	1520.2	~9.7%	27.3
Resintech Ti-HIX	1191.7	~9.4%	16.3
TiO_2 nanopowder [pH ~ 6.7] (*22*)	NA	~60%	7.0
TiO_2 nanopowder [pH ~ 8.4] (*22*)	**NA**	**~60%**	**2.8**
Zr-GAC (lignite) (*23*)	**NA**	**~12%**	**8.6**
Zr-GAC (bituminous) (*23*)	**NA**	**~9.5%**	**12.2**
ZrO_2 nanopowder (*22*)	**NA**	**~74%**	**3.5**
ZrO_2 nanostructured spheres (*25*)	**NA**	**~74%**	**2.4**
Fe-GAC [pH ~ 6.4] (*26*)	**NA**	**~60%**	**6.4**
Fe-GAC [pH ~ 8.3] (*26*)	**NA**	**~60%**	**1.6**

* (µg As g^{-1} metal)(L μg^{-1} As)$^{1/n}$.

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Figure 5 illustrates the effect of pH on arsenic adsorption for Resintech Ti-HIX, which exhibited negligibly lower adsorption capacity when compared to the other two HIX media. It is expected that arsenate adsorption would be the highest at pH ≈ 6.3 and lowest at pH ≈ 8.3 because anatase surface is more negatively charged at higher pH. Additionally, at pH ≈ 8.3, the $HAsO_4^{2-}/H_2AsO_4$ ratio is about 46 compared to 0.65 at pH ≈ 6.3, implying that almost all of the arsenate would be present in the more negative form, resulting in greater repulsion forces than at pH ≈ 6.3, and consequently causing greater energy required for the adsorption to occur. This increase in required energy for adsorption to occur would be manifested through reduced adsorption capacity and increase in the value of the Freundlich adsorption intensity parameter (1/n) at same sorben dosages and initial arsenic

concentrations. Interestingly, however, the isotherm data suggests that that the adsorption capacity did not changed between pH ≈ 6.3 and 8.3 much, suggesting that electrostatic repulsion was abated probably as a result of the Donnan effect created by the positively charged quaternary amine ion-exchange groups (*27*). The expected trends associated with increase in pH were observed at pH ≈ 8.9, which is much higher than typically encountered for many metal (hydr)oxides (*23*), making the media suitable for arsenic treatment of waters with much higher pH.

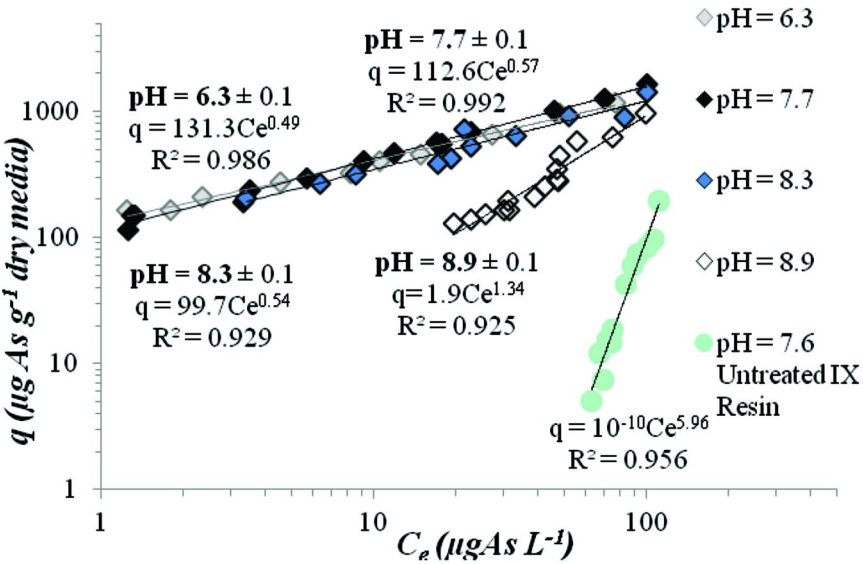

Figure 5. The effect of pH on arsenic adsorption for Resintech titanium dioxide-based hybrid ion-exchange media (5 mM $NaHCO_3$ buffered ultrapure water; $C_0 \approx 120$ µgAs L^{-1}).

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Nitrate Removal by the Titanium Dioxide-Based Hybrid Ion-Exchange Media

Figure 6 illustrates the nitrate removal performance of both hybrid ion-exchange media and the ion-exchange resins. The data fitted with the Freundlich isotherm model implies that there is negligible reduction in the nitrate removal performance after the media was impregnated with the TiO_2 nanoparticles. This suggests that the introduction of TiO_2 nanoparticles within the pores of the IX resin did not block the strong base ion-exchange sites responsible for removing the nitrate ions.

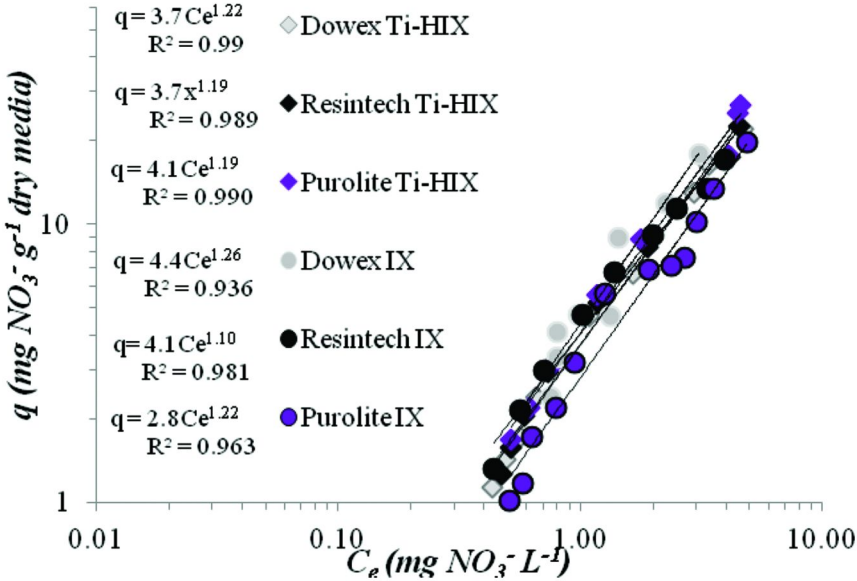

Figure 6. Nitrate removal performance of both titanium dioxide-based hybrid ion-exchange media and the ion-exchange resins.

Conclusions

This concept study demonstrated that a simple and inexpensive fabrication process can be developed to fabricate titanium dioxide-based hybrid ion-exchange media which exhibit high adsorption capacities for arsenic. The base ion-exchange resin could have a minor impact on titanium content of the final product and consequent arsenic removal performance, but an optimization study that engages in selection of the most suitable media could provide for even better performing hybrid media. It is imperative, however, that the media's performance is further examined under realistic conditions involving continuous flow test with naturally occurring water matrices to better understand and optimize the media.

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