

Development of Nanomaterial Adsorbent Media and Packed Bed Column for the Arsenic Removal from Water: A Review

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ABSTRACT

Metal oxides nanomaterials can be synthesized using multiple synthesis techniques and the resulting media (titanate nanofibers, nanostructured spheres, and nanoparticle impregnated surfaces) can be assessed for their potential to remove an important environmental pollutant in water (arsenate). The hypothesis is that nanotechnology offers the ability to control, characterize, and tailor the fabrication of materials for specific applications. Arsenic is selected as a representative environmental pollutant because of recent regulatory changes to a lower maximum contaminant level and its ability to form strong inner-sphere complexes with metal (hydr)oxides. A comparison of different types of metal (hydr)oxide nanomaterials indicate that titanium, zirconium, and iron (hydr)oxides are the most suitable materials because of their ability to remove arsenic and low toxicity of the base metal, which potentially be released into drinking water. Several metal (hydr)oxide nanomaterial media based upon titanium, zirconium and iron can be synthesized to create hybrid ion exchange media, modified granular activated carbon media, metal (hydr)oxide nanofibers and extremely porous nanostructured spheres. Each synthesis platform produces nanomaterial media capable of being used in a pack-bed continuous flow configuration, including titanate nanofibers because they are fused together by precipitation and drying into strong media. The field of nanotechnology is rapidly evolving, and this work demonstrates how a small mass quantity of nanomaterials can be synthesized and characterized to provide data to scale-up in order to facilitate comparisons against existing technologies. The protocol includes the use of batch arsenic adsorption experiments, short bed adsorber column tests, and calculate pore surface diffusion models.

Keywords: Nanomaterial, packed bed continuous flow configuration, arsenate, HIX media, percolate, pore surface diffusion model.

I INTRODUCTION

There are 20 countries where groundwater arsenic contamination episodes in the world are known. However, the world's 4 biggest cases of groundwater contamination and the worst sufferings of the people have been in Asia. **Warangal is one of the major towns in Andhra Pradesh with a population of more than 10 lakhs and several toxic pollutants are released by various ways of human activities.** Arsenic can exist in air, water, soil, or food, and all of these present potential pathways for human exposure. Very low concentrations of arsenic are common in soil; however, in areas within the vicinity of arsenic-rich deposits, the natural concentration of arsenic in soil can increase over a thousand fold. In these areas, it is common to find ground water that is also contaminated with high concentrations of arsenic. For this reason, concentrations of arsenic in ground water are often much higher than those in surface water. This is a particular problem in India, where naturally occurring arsenic contaminates wells used by millions of people. Since the discovery of the buckyballs by Curl, Kroto, and Smalley in 1985, the new field of nanotechnology has rapidly emerged in the past 20 years (Curl *et al.* 2001). Nanotechnology, which is defined as "understanding and control of matter at dimensions of roughly 1 to 100 nanometers, where unique phenomena enable novel applications," is making significant impact on our everyday lives (Martin and Mitchell, 1998; Narr *et al.*, 2007). The unique phenomena that enable novel applications of the nanomaterials are

direct consequence of the dimensions of the nanomaterials. The new promises that nanotechnology offers have spurred the industry to focus their research and investments on developing new applications for the nanomaterials. Although used in many fields such as medicine, biotechnology and electronics, the beneficial applications of nanotechnology in drinking water treatment are only recently initiated (Roco, 2005; Yonzon *et al.*, 2005; Simon, 2005; Stylios *et al.*, 2005; Glenn, 2006). According to Narr *et al.* (2007), current research attempts in water and wastewater nanotechnology are aimed at using photocatalytic properties of TiO₂ to remove nitrates or non-biodegradable organics, and using zero valent iron to remove halogenated hydrocarbons. Although research in the area of heavy metal removal by nanomaterials is also underway, very little attention has been dedicated to this important issue (Narr *et al.*, 2007). As a result of their size, nanomaterials can exhibit an array of unique novel properties which can be utilized in development of new heavy metal treatment technologies and improvement of existing ones. Some of their properties, such as high surface area, self assembly, high specificity, and other properties make them an excellent candidate for removal of heavy metals from water by adsorption. Metal hydroxide nanomaterials could allow for better heavy metal removal properties of an adsorbent compared to conventional porous metal hydroxide adsorbents. Two common approaches for using nanomaterial adsorbents in full-scale application are either suspended adsorbent or packed bed reactors. Unfortunately, it may be extremely difficult to remove essentially 100% of the nanomaterials in suspended

adsorbent reactors, even if the nanomaterials have unique properties (e.g. magnetic) (Colvin, 2006). It is far more likely that packed bed reactors with some form of aggregated nanomaterial adsorbent media may be utilized to prevent release of nanomaterials into finished water. One potential platform to use nanomaterials in packed bed reactors is to aggregate the nanomaterials using binding agents. These new materials may become intra-particle diffusion limited, would limit the overall removal performance of the treatment media in a packed bed system. As such, addressing the issue of contaminant mass transport is critical in assessing the viability of nanomaterial adsorbents in full-scale systems. It may be possible to minimize mass transport resistance by synthesizing nanostructured adsorbents (eg. nanofibers, nanostructured spheres etc.) or nanomaterial deposited surfaces. Nanomaterial packed bed adsorbing media could be engineered to maximize mass transfer kinetics by allowing rapid access of the contaminants to high surface area and by controlling the type of internal mass transport. Pore diffusion, for example, could be facilitated by engineering an adsorbent with high porosity. The external mass transport could be controlled by engineering the adsorbent particle size during the fabrication process considering that external mass transport is in large dependent on the adsorbent particle size. Nanomaterials deposited on specific surfaces could yield hybrid materials exhibiting other properties in addition to the initial properties of nanomaterials. In brief, by utilizing nanomaterials as adsorbent media, more efficient packed bed absorbers could be engineered allowing for less expensive and smaller treatment systems capable of economically removing contaminants from drinking water at a municipal treatment scale or in a single dwelling point of use applications. Arsenic is a Class A human carcinogen classified by the International Agency for Research on Cancer (IARC), and has been one of the major concerns associated with water in many regions of the world as an emerging contaminant (Dutta *et al.*, 2004; Nikolaidis *et al.*, 2004; Xu *et al.*, 2002). Arsenic is naturally found in the soil and the water, but it is also accruing as a result of anthropogenic sources (Matschullat, 2000; Smedley and Kinniburgh, 2002).

Consequences of Excess Arsenic in drinking water:

- (a) Arsenic poisoning can produce effects on skin and nerves
- (b) The skin may become dry and hard, peripheral nerves can start getting affected and muscle weakness can result. It can also lead to cancer.
- (c) If a continuous dose of arsenic is taken though drinking water, it leads to death primarily due to kidney failure.



Fig 1 Effects of arsenic exposure

II TECHNOLOGIES & LIMITATIONS

Arsenic removal technologies all suffer from one or more drawbacks, limitations and scope of application. Adsorption is evolving as a front line of defense. Selective adsorption utilizing biological materials, mineral oxides, activated carbons, or polymer resins, has generated increasing excitement (Benjamin *et al.*, 1996). The use of carbon extends far back into history. Its origin is impossible to document. Charcoal was used for drinking water filtration by ancient Hindus in India, and carbonized wood was a medical adsorbent and purifying agent in Egypt by 1500 b.c. (Cheremisnoff *et al.*, 1980). Modern activated carbon industrial production was established in 1900–1901 to replace bone-char in sugar refining (Bansal *et al.*, 2005). Powdered activated carbon was first produced commercially from wood in Europe in the early 19th century and was widely used in the sugar industry. Activated carbon was first reported for water treatment in the United States in 1930 (Mantell, 1968). Activated carbon is a crude form of graphite with a random or amorphous highly porous structure with a broad range of pore sizes, from visible cracks and crevices, to crevices of molecular dimensions (Hamerlinck *et al.*, 1994). Carbon surface chemistry has been reviewed (Bansal *et al.*, 2005). Brunori *et al.*, (2005) also utilized red mud for treating contaminated waters and soils with particular attention to the Italian regulatory system. The sorption of arsenic (III) by acid treated spent bleaching earth, an industrial waste produced during the bleaching of crude palm oil was studied to examine the possibility of utilizing this material in

water treatment systems (Mahramanlioglu et al., 2004). Maximum adsorption occurred at pH 9.0. The adsorption capacity was 0.46 mmol/g. The column studies were also carried out to simulate water treatment processes. The capacity values obtained in column studies were found to be greater than the capacity values obtained in batch studies.

Manganese oxides minerals have important environmental chemistry uses. They readily oxidize and adsorb many reduced species such as As (III) (Manning et al., 2002). Synthetic birnessite has been extensively investigated because it is representative of many naturally occurring manganese oxides. Na⁺ and K⁺ substituted birnessites are phyllosulfates, possessing layered sheet structures with edge-sharing Mn octahedral (Drits et al., 1997). Arsenic removal from drinking water by monocomponent fixed-bed adsorption of phosphate and arsenate using two natural manganese oxides was investigated by Ouvrard et al. (2002). This surface chemistry depends upon the activation conditions and temperatures employed. Activation refines the pore structure. Mesopores and micropores are formed yielding surface areas up to 2000 m²/g (Mohan, et al., 2005). Acidic and basic activation carbon exists according to the Steenberg's classification (Mattsom., 1971). The acidic groups on activated carbons adsorb metal ions (Corapcioglu., 1987). Surface area may not be a primary factor for adsorption on activated carbon. High surface area does not necessarily mean high adsorption capacity (Perrich., 1981). Nanocrystalline titanium dioxide's (TiO₂) ability to remove arsenate and arsenite and to photocatalytically oxidize As(III) was evaluated (Pena et al., 2005). The nanocrystalline TiO₂ was prepared by hydrolysis of a titanium sulfate solution (Meng et al., 2003). The adsorption mechanism for As(III) and As(V) on nanocrystalline titanium dioxide was also established using electrophoretic mobility (EM) measurements, Fourier transform infrared (FTIR) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, and surface complexation modeling (Pena et al., 2006). Jing et al. (2005) investigated the adsorption mechanisms of monomethylarsonic acid [CH₃AsO(OH)₂] (MMA) and dimethylarsinic acid [(CH₃)₂AsO(OH)] (DMA) on nanocrystalline titanium oxide (TiO₂) using X-ray absorption spectroscopy (XAS), surface charge and zeta potential measurements, adsorption edge, and surface complexation modeling. The experimental data was explained by the charge distribution multi-site complexation model (Machesky et al., 2001) with the triple plane option under the constraint of the XAS evidence. The monolayer adsorption capacity was not calculated. Bang et al. (2005) studied a novel granular titanium dioxide (TiO₂) for groundwater arsenic removal. More arsenate was adsorbed than arsenite on TiO₂ at pH 7.0. The adsorption capacities for As(V) and As(III) were 41.4 and 32.4 mg/g TiO₂, respectively. This TiO₂ had similar adsorption capacities for As(V) and As(III) (approximately 40 mg/g) using simulated Bangladesh groundwater. Nakajima et al. (2005) also investigated the combined use of TiO₂-photocatalyst and an adsorbent with high

adsorption ability for As(V), under photo-irradiation. Swedlund and Webster (1999) synthesized ferrihydrite and studied its use to remove As(III) and As(V) from water. Synthesis was performed by rapidly raising the pH from 2.0 to 8.0 for different concentrations of Fe(NO₃)₃·9H₂O and 0.1M NaNO₃ by the addition of NaOH (0.1–5.0 M). The oxide formed as a red/brown, loose gelatinous precipitate, aged for 18–24 h prior to adsorption experiments. X-ray diffraction of the freeze-dried product showed two broad characteristic ferrihydrite peaks. Application of Fe(II) instead of Fe(III) was advantageous, because the dissolved oxygen used for oxidation of Fe(II) causes partial oxidation of As(III). Furthermore iron(III) (hydr)oxides formed in this way have higher sorption capacities. Multiple additions of Fe(II) followed by aeration further increase As(III) removal. A competitive coprecipitation model with As(III) oxidation was established. Roberts et al. (2004) studied the arsenic removal by oxidizing naturally present Fe(II) to iron(III) (hydr)oxides by aeration. These iron(III) species precipitated with adsorbed arsenic. Jezeque and Chu (2006) investigated titanium dioxide for pentavalent arsenate removal from water. Adsorption isotherms measured at pH 3 and 7 generally followed the Langmuir model. The maximum uptake capacity ranged from 8 mg/g at pH 3 to 2.7 mg/g at pH 7. Addition of phosphate resulted in a significant reduction in arsenate adsorption.

Most remediation methods discussed more effectively remove arsenic from water containing high initial arsenic concentrations (usually >100 mg/L) but residual arsenic concentrations exceed the 0.05 mg/L water quality standard used in most countries. Conventional and non-conventional treatment technologies for aqueous arsenic remediation were compared (Vigneswaran et al., 2002). In villages in India, a highly successful technology may not succeed in rural areas unless it fits into the rural circumstances and is well accepted by the masses. Technology development is only possible when a partnership exists involving proper village level participation.

Experiments studied the metal trapping ability of treated red mud and the subsequent release of these trapped metals at low pH conditions. The treated red mud exhibited a high metal trapping capacity and metal release at low pH was generally low. The removal capability of treated red mud was increased using more mud in contact with the solution. After 48 h, only 35% of As (corresponding to an absolute value of 230 g/L) was removed with 2 g/L, but the percentage significantly increased up to 70% (corresponding to an absolute value of 400 g/L) with 10 g/L.

Modified calcined bauxite was also used for As(III) and As(V) remediation from ground water (Ayoob et al., 2007) in batch and column modes. The optimum pH was 7.0 for both As(III) and As(V). Adsorption was unaffected by temperature variations (Bhakat et al., 2006).

The concentration variations at the column outlet were deduced simply by conductivity and pH measurements. These macroscopic-scale data enabled phenomenological information to be obtained on the surface reactions involved. Two behaviors were found. When surface complexation alone occurred, adsorption isotherms could be rapidly and accurately measured by a series of column experiments. However, when surface complexation was coupled with anion exchange, the system was far more complex. Direct detection of arsenate breakthrough from the conductivity and pH signals was no longer possible. Column experiments were conducted using different particle sizes and flow rates. Transport was influenced by non-linear adsorption and intraparticle diffusion. Total adsorption capacity varied with the flow rate and particle size. Results were interpreted using the effective diffusivity of arsenate in the grain as a single adjustable parameter by a transport model including the Langmuir adsorption and mass transfer. Diffusivities between 0.6 and $7.0 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ were calculated which included intraparticle diffusion. Batch adsorption and oxidation experiments were conducted with TiO_2 suspensions in 0.04M aqueous NaCl. The challenge water contained phosphate, silicate, and carbonate competing anions. The adsorption followed pseudo-second-order kinetics. The TiO_2 was effective for As (V) removal at $\text{pH} < 8$. Maximum As (III) removal occurred at $\text{pH} 7.5$. The adsorption capacity of nanocrystalline TiO_2 of As(V) and As(III) was much higher than that for fumed TiO_2 (Degussa P25) and granular ferric oxide. More than 0.5 mmol/g of As (V) and As(III) was absorbed by the TiO_2 at an equilibrium arsenic concentration of 0.6Mm. Competing anions had a moderate effect on the adsorption capacities of the TiO_2 for As(III) and As(V) at a neutral pH. In the presence of sunlight and dissolved oxygen, As(III) (26.7Mm or 2 mg/L) completely photocatalytically oxidized within 25 min to As(V) in a 0.2 g/L TiO_2 suspension. The adsorption of As(V) and As(III) decreased the point of zero charge of TiO_2 from 5.8 to 5.2, suggesting the formation of negatively charged inner-sphere surface complexes for both arsenic species. The EXAFS study indicated that As(V) and As(III) formed bidentate binuclear surface complexes as evidenced by an average Ti-As(V) bond distance of 3.30 Å and Ti-As(III) bond distance of 3.35 Å. The FTIR bands caused by vibrations of the adsorbed arsenic species remained at the same energy levels at different pH values. Consequently, the surface complexes on TiO_2 maintained the same non-protonated speciation at pH values from 5 to 10, and the dominant surface species were $(\text{TiO})_2\text{AsO}_2^-$ and $(\text{TiO})_2\text{AsO}^-$ for As(V) and As(III), respectively. Adsorption of As(V) and As(III) on commercially available titanium dioxide (TiO_2) suspensions (Hombikat UV100 and Degussa P25) was investigated versus pH and initial adsorbate concentration (Dutta et al., 2004). More As(V) and As(III) adsorb onto Hombikat UV100 particles than onto Degussa P25 particles. Adsorption of As(V) was $>$ As(III) onto TiO_2 suspensions at pH 4 while the capacity of As(III) was greater at pH 9. The Langmuir and Freundlich isotherm

equations interpreted the adsorption of arsenic onto TiO_2 suspensions. XAS data demonstrated that MMA and DMA formed bidentate and monodentate inner-sphere complexes with the TiO_2 surface, respectively. The charge and zeta potential behaviors of TiO_2 as a function of ionic strength suggested that the point of zero charge (PZC) and the isoelectric point of TiO_2 were identical at pH 5.8. Adsorption of MMA and DMA on TiO_2 shifted the isoelectric point to pH 4.1 and 4.8, respectively. This indicated the formation of negatively charged surface complexes occurred. An effective oxidation of As(III) into As (V) was obtained when As (III) solution was stirred and irradiated by sunlight or xenon lamp in the presence of TiO_2 suspension resulting 89% As (V) removal after 24 h. Lanthanum hydroxide (LH), lanthanum carbonate (LC), and basic lanthanum carbonate (BLC) remove As (V) from aqueous solutions. These lanthanum compounds were effective at a concentration of $<0.001 \text{ Mm}$. Dissolution was appreciable at initial pH values <4.3 , <4.3 , and <4.0 for LH, LC and BLC, respectively. Arsenic removal followed first-order kinetics in the neutral pH range, and the order of the rate constants was $\text{LH} > \text{LC} > \text{BLC}$. The optimum pH range was 3–8 for LH, 4–7 for LC, and 2–4 for BLC. Two arsenic uptake mechanisms were proposed: (i) adsorption by the exchange of CO_3^{2-} and (or) OH groups with arsenic ions in neutral to alkaline pH where La does not dissolve and (ii) precipitation of insoluble lanthanum arsenate, LaAsO_4 , in acidic pHs. Iron oxides, oxyhydroxides and hydroxides, including amorphous hydrous ferric oxide (FeO-OH), goethite (-FeO-OH) and hematite ($\text{-Fe}_2\text{O}_3$), are promising adsorbents for removing both As(III) and As(V) from water (Saha et al., 2005). Amorphous Fe(O)OH has the highest adsorption capability since it has the highest surface area. Surface area is not the only criterion for high removal capacities of metal ions and other mechanisms (ion exchange, precipitation) play an important role. Most iron oxides are fine powders that are difficult to separate from solution after. Therefore, the EPA has proposed iron oxide-coated sand filtration as an emerging technology for arsenic removal at small water facilities (Thirunavukkarasu et al., 2003). Another shortcoming of amorphous FeOOH is its tendency to form low surface area crystalline iron oxides during preparation, greatly reducing its As removal capacity. Different types of ferrihydrites, iron hydroxide and iron oxides were prepared and tested. Some recent studies are now discussed. Ranjan et al.(2003) synthesized hydrous ferric oxide, for arsenic sorption. As(V) sorption strongly depended on the system's concentration and pH, while As(III) sorption was pH insensitive.

Till now no work was found on use of nanotechnology in water treatment in a continuous flow packed bed column and earlier research was not concentrated on modeling of packed bed configuration for arsenic removal. Arsenic is a poisonous element and is a cumulative poison. So far **very limited technologies are available** to reduce the Arsenic content to acceptable levels of 0.02 ppm or lower.

III OBJECTIVES & METHODOLOGY

(a) OBJECTIVES:

- (i) Evaluate the feasibility of using titanate based nanofiber matrices as media in a packed bed column.
- (ii) Develop porous nanostructured ZrO_2 spheres suitable for arsenate treatment in a packed bed column setup.
- (iii) Develop the iron (hydr)oxide nanomaterials with different structures to obtain hybrid ion-exchange (HIX) media.
- (iv) Evaluate the impact of synthesis conditions on the arsenic removal.
- (v) Evaluate the impact of synthesis conditions on the distribution of iron (hydr)oxide nanomaterials derived from Fe(II) inside GAC media oxidized with $KMnO_4$, and the consequent impact on arsenic removal.
- (vi) Develop a model to predict the arsenic breakthrough curve of an adsorber packed with adsorbents fabricated using the two platforms: (1) nanostructured adsorbents and (2) nanomaterial deposited surfaces.

(b) METHODOLOGY:

- (i) Commercially available metal oxide nanopowders can be obtained and Stock suspensions with concentrations of 1 g/L can be prepared by suspending the nanopowders in nano-pure water with conductivity $< 1.1 \mu S/cm$ and sonicating for 15 minutes in an ultrasonic bath at 90 W/L to allow disaggregation of the particles and homogenization of the suspension. Nanopowder removal can be evaluated by separating the nanopowder from the suspension via centrifugation and filtration with $0.2 \mu m$ and $2.5 \mu m$ pore size filters. The concentrations of the nanopowder supernatant and the filtrate can be evaluated. To select one nanopowder media, the adsorption capacities of the commercial nanopowders exhibiting the highest arsenate removal in the screening experiments can further be studied through isotherm experiments.

- (ii) Based on the findings from the nanoparticle characterization experiments, the nanoparticle aggregates can be separated from the suspension by filtration. A proprietary synthetic method, developed by SolmeteX, using a solution of $FeCl_3$ in alcohol can be used to synthesize HIX by precipitation of Fe(III) as iron (hydr)oxide under alkaline conditions. Short bed adsorber (SBA) tests can be conducted on the HIX and virgin IX media with the highest adsorption capacities.
- (iii) Arsenate can be analyzed using a graphite furnace atomic absorption spectrophotometer (GF-AAS). The development and design of hybrid ion exchange media containing nanoparticles should consider the impact of the nanoparticle impregnation process onto the ion exchange performance of the media. Fabrication methods that can allow more even distribution of the nanoparticles throughout the media pores could contribute to a higher adsorption capacity and separation factor of the HIX media. Nanostructured zirconium oxide spheres can be fabricated by modifying a synthesis method developed for the preparation of a porous resin loaded with crystalline hydrous ZrO_2 .
- (iv) Modeling is useful tools to mathematically describe and predict adsorption of a contaminant in equilibrium and continuous
- (v) flow setting. Although many different models can be used to describe the equilibrium adsorption, Freundlich adsorption isotherm model can be selected for the purposes of the work because the parameters describing the adsorption can be used in pore surface diffusion model. The pore surface diffusion model can be used to validate and predict the contaminant breakthrough of continuous flow column adsorbents.

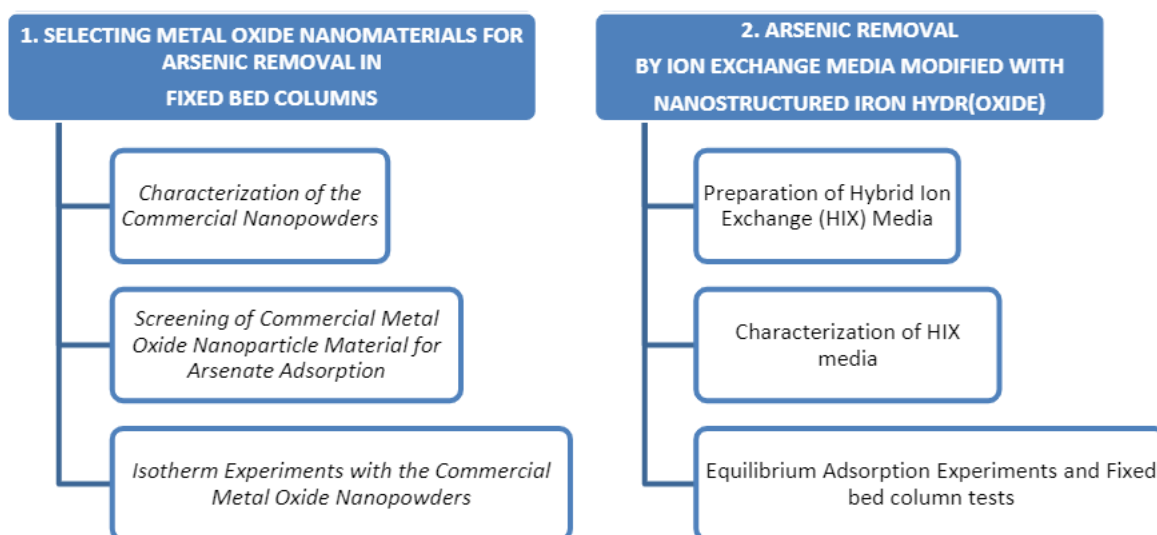


Fig 2

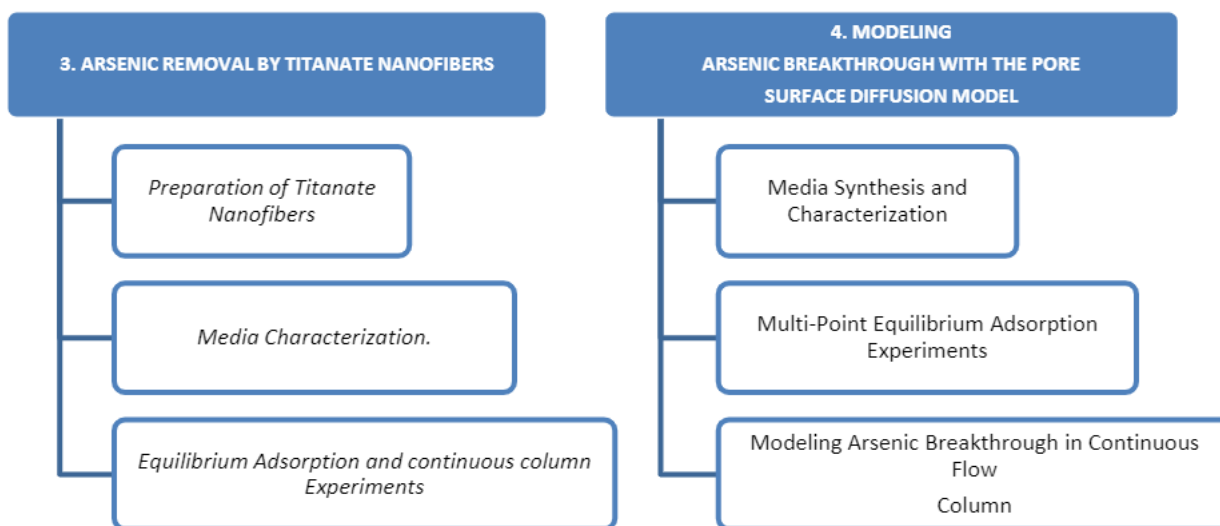


Fig 3

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