RSC Advances

Inorganic Nano-Adsorbents for the Removal of Heavy Metals and Arsenic: A Review

Journal:	*RSC Advances*
Manuscript ID:	RA-REV-02-2015-002714.R1
Article Type:	Review Article
Date Submitted by the Author:	12-Mar-2015
Complete List of Authors:	Ray, Phoebe; University of New Orleans, Shipley, Heather; University of Texas at San Antonio, Civil and Environmental Engineering

Inorganic Nano-Adsorbents for the Removal of Heavy Metals and Arsenic: A Review

Phoebe Zito Ray and Heather J. Shipley,*[1†]

*University of New Orleans, Dept. of Chemistry, 2000 Lakeshore Dr., New Orleans, LA 70148

[†]University of Texas-San Antonio, Dept. of Civil and Environmental Engineering, One UTSA Circle, San Antonio, TX 78249

Abstract

Adsorption is widely popular for removal of heavy metals due to its low cost, efficiency, and simplicity. The focus of this review will be the use of inorganic adsorbents engineered at the nanoscale. The applicability of iron oxide (hematite, magnetite and maghemite), carbon nanotubes (CNT), and metal oxide based (Ti, Zn) and polymeric nanoadsorbents are examined. The advantages and limitations of the type of nanoadsorbent and its functionality are evaluated. Current developments and next generation adsorbents are also reviewed. Finally, scopes and limitations of these adsorbents will be addressed while investigating the types of metal ions that are harmful.

1 Introduction

The anthropogenic release of heavy metals into the environment is becoming a global epidemic.[1, 2] These species can enter natural waters through release of wastewater, industrial activity[3] and domestic effluents.[4, 5] In 1988, Nriagu and Pacyna published a quantitative assessment of

[1] To whom correspondence may be addressed Heather J. Shipley One UTSA Circle San Antonio, TX 78249, fax 210-458-6475, heather.shipley@utsa.edu

emission studies in Western Europe, the United States and the Soviet Union.[6] They concluded that "mankind" was the biggest contributor in the deployment of trace metals into the environment.[6] Almost 30 years later, the release of heavy metals into the environment continues to be a worldwide issue. Although anthropogenic sources cause much of the environmental pollution, heavy metals can also be introduced into the environment through natural sources. Natural sources of heavy metals can include weathering, erosion from rock and soil, rainwater.[7] Natural sources of heavy metal release into the environment are dominated by interfaces between solids, liquids and gases.[8] These interfacial interactions, especially between natural solids (rock) and aqueous solutions (water), can contribute to the release or accumulation of heavy metals into the environment.[8] These processes occur through mineral dissolution, precipitation, and sorption/desorption of chemical species, which can evolve to become pollutants in soils and groundwater.[8] This combination of natural and anthropogenic sources can cause heavy metals to accumulate and as a result, have toxic effects to humans and other living organisms.[9-11] According to the United States Environmental Protection Agency (EPA), the most toxic heavy metals include arsenic, copper, mercury, nickel, cadmium, lead and chromium.[12] The ingestion of these metals can cause a number of health issues, such as severe developmental and neurological disorders over relatively short time periods or even death.[12]

Currently, the most common methods to remove heavy metals from water and wastewater are ion exchange,[13-15] reverse osmosis,[16, 17] chemical precipitation,[18] electrochemical treatment[19-21], membrane filtration[22], floatation[23], and adsorption.[1] The most recognized method for heavy metal treatment is adsorption.

The many advantages of adsorption are that it is versatile, it does not require high amounts of energy, large amounts of water or additional chemicals. [24, 25] In developing countries

where access to large amounts of power and financial resources can be an issue, this simple and cheap process would be a viable option. The mechanistic process of adsorption allows versatility in the design and use of the adsorbent. The two most common methods used for adsorption are the batch method and column or flow method. The batch method is where the adsorbate is added to the sorbent in an aqueous suspension under continuous mixing or agitation.[26] A column or flow method uses a continuous flow of liquid through a fixed bed of the adsorbent. The flow of the liquid through the fixed bed it set a fixed rate. The flow method is typically applied in industrial settings.

In order to measure and classify adsorption systems, isotherms are generated. Isotherms are curves that are based on computational expressions that follow the Gibbs adsorption isotherm, which predicts the thermodynamic conditions for interfacial systems.[27] The nature of the curve and the initial slope can be observed and used to give the relationship between solute adsorption mechanisms at the surface of the solid, the pressure, and the type of adsorption isotherm to classify the system.[28] An isotherm can be used to describe and identify the mechanism of adsorption between the solute and the substrate surface as well as the adsorption capacity of adsorbent.[28] There are many adsorption isotherms (Adamson and Gast 1997), the two most commonly observed types of isotherms are Langmuir and Freundlich. Generally, the curve generated from the Langmuir isotherm shows an initial slope dependent on the rate of change of available sites on the particle with increasing solute adsorbing to the sites.[28] As more solute is adsorbed, there is a decreased chance that additional species can find an adsorption site, and the curve will form a plateau.[28]

The Freundlich equation is similar to the Langmuir equation in that it produces a graphical representation of the amount of solute adsorbed on the surface of the substrate

(adsorbent), at which this sorption occurs. The difference, however, is that the Langmuir adsorption isotherm gives the amount of solute adsorbing on the external surface of the adsorbent in the form of a monolayer.[29] Therefore, in theory, it represents the equilibrium distribution of ions between the solid and liquid phase.[29] The Freundlich adsorption isotherm empirically describes the adsorption characteristics for the liquid-solid interface.[29]

Other key parameters addressed were those that control adsorption of a solute onto an adsorbent are pH, temperature, concentration of the solute and adsorbent, and the surface area available on the surface of the adsorbent. The articles that are discussed in this review provide a comprehensive analysis giving details of each of the aforementioned parameters. One should also mention that the articles presented in this review provided extensive characterization of their nanomaterials using transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) theory, and other techniques. Though these techniques are important and were accounted for, they will not be mentioned in this review. The main focus will be on the performance of the inorganic nanoadsorbents when they are in contact with heavy metal ions.

Adsorption is widely popular for removal of heavy metals due to its low cost, efficiency, and simplicity.[30] According to a review article published by Bailey *et al*, to consider an adsorbent to be “low cost” it has to be abundant in nature, originated from waste or by-products, or is minimally processed.[31] Adsorbents can be purchased commercially, engineered at the nanoscale, or prepared from agricultural waste as raw materials. There have been many published methods in the last decade that focus on using materials such as agricultural raw materials[32-39], biomaterials, polymers, metal oxides, and others to remove heavy metals from

water.[40, 41, 42] The focus of this review will be the use of inorganic adsorbents engineered at the nanoscale. Nanomaterials are generally defined as having at least one dimension in the range of 1-100 nm.[42] A nanomaterial possesses certain properties and morphologies that make it a great candidate as an adsorbent for removing heavy metals from contaminated waters, including enhanced surface area in comparison to bulk particles. The larger surface area per mass allows more sites for surface chemistry. They also have the ability to be tuned with different chemical species to increase their functionality toward specific targets.[43] In the case for heavy metal removal, particles can be surface functionalized to increase the affinity for a specific ion. The research reported in this review covers pertinent literature from 2004-2014 focusing on the removal of heavy metal ions in synthetic solutions, natural waters and wastewater.

This article will provide a thorough review covering the types of inorganic nanoadsorbents and the type of metal ions being removed. The applicability of iron oxide (hematite, magnetite and maghemite), carbon nanotubes (CNT), and metal oxide based (Ti, Mn, Zn) and polymeric nanoadsorbents are examined. The advantages and limitations of the type of nanoadsorbent and its functionality are evaluated. Current developments and next generation adsorbents are also reviewed. Finally, scopes and limitations of these adsorbents will be addressed while investigating the types of metal ions that are harmful.

2 Inorganic Nano-Adsorbents

2.1 Heavy Metals being removed

A number of simple or complex metal ions and species pose serious health threats to humans and other animals and must be removed from the environment, including arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and Zinc (Zn). These metals, often in the form of complex ions, are present due to the erosion of natural

materials and anthropogenic sources (industrial wastewater).[12] In the last ten years, many research groups have investigated the use of nanoparticles for heavy metal removal due to their high surface area and ability for their surfaces to be functionalized in order to increase efficiency or adsorption capability.[44] Inorganic nanoadsorbents that will be covered in this review include magnetic nanoparticles, carbon nanotubes (CNT), metal-oxide based nanoparticles, and polymeric nanoadsorbents.

2.2 Iron Oxide Nanomaterials

The growing interest in the use of iron oxide nanoparticles for heavy metal clean-up is due to their simplicity and resourcefulness. The three phases of iron oxide discussed in this article, are the magnetic phase-magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_4) and non-magnetic, hematite (α-Fe_2O_3). These phases can be synthesized using a wide range of techniques from sol-gel, thermal decomposition, hydrothermal, solvothermal, and chemical vapor deposition. They can also be synthesized into different structural morphologies like nanochains,[45] flowers,[46] cauliflower-like structures,[47] nanotubes,[48] nanorods[30] and nanoparticles.[33] This article will review nanoparticles made of these three phases of iron oxide, with varying sizes and experimental parameters that were used during the adsorption process.

2.2.1 Magnetite (Fe_3O_4) and Maghemite (γ-Fe_2O_4)

It is a challenge to separate and recover sorbent materials from water that has become contaminated. Magnetic versions of iron oxide sorbent nanomaterials offer a viable solution to collect and remove toxic species. This advantage is because they can be easily removed from the system by simply applying an external magnetic field. There have been many reports on the use of MNPs for cleanup of heavy metals including arsenic,[49] chromium,[49-51] cobalt,[52] copper, lead,[51] and nickel[52] from aqueous synthetic solutions and natural water systems. The experimental

conditions for the adsorption of these ions onto the MNPs vary. However, the highlights covered are the morphology of the nanoadsorbent, how it was synthesized, the adsorption efficiency, what type of heavy metal ions were being removed and the type of sample matrix, i.e. "natural water samples" or lab prepared.

2.2.1.1 Nanoparticles, Nanotubes, rods and other morphologies

Magnetite nanoparticles are ideal adsorbents for arsenic species due to their affinity for arsenate and arsenite and simple removal from solution using low magnetic fields.[53] Shipley *et al*. conducted arsenic adsorption studies along with examining the effect of common aquatic contaminants (sulfate, silica, calcium, bicarbonate, dissolved organic matter, phosphate, magnesium and iron). Adsorption experiments took place in a sealed vessel containing 100 µg/L As (V) with 0.5 g/L magnetite nanoparticles in Houston tap water and 39 µg/L total arsenic contaminated groundwater from Brownsville, TX with 0.5 g/L magnetite nanoparticles. About 83 µg/L of arsenate was adsorbed within one hour from the spiked Houston tap water. For the arsenic contaminated groundwater, the amount of arsenic in solution was reduced to 10 µg/L in less than 10 mins and 5 µg/L within one hour. The results correlated well with the Langmuir isotherm model and demonstrated that magnetite nanoparticles have the ability to remove arsenic species from water in the presence of other species such as phosphates and carbonates. The use of a representative wastewater and drinking water samples exemplifies the application for household use; however, the authors note that more research is needed to apply toward industrial applications.[53]

In 2013, Roy *et al* removed Cu (II), Zn (II) and Pb (II) from water using maghemite nanotubes (MHNT).[48] They synthesized the maghemite nanotubes using a template free microwave irradiation and determined adsorption kinetics.[54] In order to evaluate the adsorption

capacity of the metal ion to the MHNTs, Langmuir and Freundlich isotherm models were applied.[54] The Langmuir isotherm showed better correlation to the observed behavior for the adsorption of the metals onto the MHNTs than the Freundlich model.[48] At an initial concentration of 100 mg/L, favorable adsorption was observed for all metal ions tested in this study (Table 1). In 2013, Karami reported the use of magnetite nanorods for heavy metal ion removal from lab prepared aqueous solutions containing Fe^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Cu^{2+} ions.[30] They previously presented a method for preparation of uniform magnetite nanorods via pulsed electosynthesis method.[55] Adsorption/desorption studies were carried out and fit to isotherms in order to determine the capacity of the magnetite nanorods. Both Langmuir and Freundlich isotherm models were applied, and the Langmuir isotherm demonstrated a better fit to the data.[30] The nanorods, due to their high surface area, showed increased metal ion adsorption at pH 5.5, representative of natural groundwater.[30] A comparison between the magnetite nanorods with the maghemite nanotubes synthesized by Roy *et al was* conducted.[30, 54] Furthermore, the adsorption capacities of the nanorods versus the nanotubes using solutions containing Cu^{2+}, Zn^{2+}, and Pb^{2+} were compared.[30] The nanorods showed higher adsorption capacity for Zn^{2+} and Pb^{2+} but lower adsorption capacity for Cu^{2+} when compared to the nanotubes.[30] Karami attributed the lower Cu^{2+} adsorption due to the morphology of the nanorods.[30] They attributed the adsorption mechanism for the nanorods to electrostatic forces between the negatively charged adsorbent and positive metal ions.[30] After adsorption experiments, the nanorods were removed via low magnetic field.[30] Although both groups created a representative sample solution in the lab, they did not test their nanoadsorbents using natural water samples. In a natural water sample, there are many other types of ions present that can compete for adsorption onto the particle surface. In addition, natural organic matter (NOM) can

coordinate metals and change their adsorption behavior. To really determine if the nanoadsorbent will be applicable outside the laboratory and in practical applications, it must be tested accordingly.

2.2.1.2 Functionalized MNPs

The next few paragraphs will discuss attempts to increase the performance of MNPs by functionalization of the particle surface with various chemical species in order to hone in on specific affinities of the heavy metal ions and remove them from water. While such approaches can improve performance, they also add cost and complexity to adsorbent preparation.

In order to increase efficiency and to avoid interference from other metals ions, MNPs have been functionalized in order to tune their adsorption ability, creating a more effective process.[44, 56] Warner *et al* engineered superparamagnetic MNPs from iron oxide via high temperature deposition according to a previously published method[57] and functionalized (tuned) their surface to match the affinity of specific classes of heavy metal contaminants.[56] The ligands attached to the magnetite through ligand exchange reaction of lauric acid were as follows to yield functionalized magnetic nanoparticle sorbents: ethylenediamine tetraacetic acid (EDTA); l-glutathione (GSH); mercaptobutyric acid (MBA); a-thio-w-(propionic acid) hepta(ethylene glycol) (PEG-SH); and meso-2,3-dimercaptosuccinic acid (DMSA). The functionalized magnetic nanoparticles EDTA, GSH, MBA, PEG-SH, and DMSA had varying affinities for each metal (refer to table 1). [56] The addition of a flexible ligand shell allowed for the incorporation of a wide range of functional groups into the shell while leaving the Fe_3O_4 nanoparticle properties intact.[56] The Warner group spiked Colombia River water with seven metals (Table 1), and compared the results to commercial adsorbents as well as un-functionalized MNPs to measure the efficiency of the modified particles.[56] The use of river water spiked with heavy metals allows

for a system representative of natural waters. The natural organic matter present in the river water causes some interference due to adsorption to the MNPs, thus blocking the active surface sites. The fact that the Warner group was able to get high binding affinity for these metals in spiked river water suggests these particles may be practical for environmental applications. Discussion regarding recyclability was not mentioned in this paper; however, it is conceivable that the used iron oxide particles could be regenerated by removal of the adsorbed metals and then reused for additional adsorption. Without such regeneration, the cost and amount of nanomaterials increase. Regeneration itself may pose practical and cost barriers, especially since iron oxide materials are soluble in the acidic media that would likely be used to remove the adsorbed metals.

Ge *et al* reported novel Fe_3O_4 MNPs modified with 3-aminopropyltriethoxysilane (APS) and copolymers of acrylic acid (AA) and crotonic acid (CA) as polymer shells (Fe_3O_4@APS@AA-co-CA MNPs).[44] The use of a polymer shell prevented inter-particle aggregation and improved dispersion stability of the nanostructures.[44]

Ge *et al* concluded that the polymer modified MNPs successfully removed metal ions (Table 1) and from lab prepared aqueous solutions and that these particles were reusable.[44] They performed recyclability studies using 0.1 M H^+ and found the metal ion adsorption capacity remained constant after 4 cycles.[44] The polymer coating assisted in preventing dissolution of the metal oxide core under these acidic conditions. In 2005, Hu *et al* published a paper using maghemite nanoparticles synthesized via a sol gel method[58] to remove Cr (VI) from wastewater generated from a metal-processing plant.[59] According to the EPA, the acceptable level of chromium in drinking water is no more than 0.1 mg/L.[12] The most common methods of removing hexavalent chromium from wastewater effluent are chemical precipitation, reverse

osmosis, and electrochemical methods.[59] However, there are many disadvantages with these approaches, with high cost being at the top of the list.[59] Hu *et al* utilized adsorption technologies in an effort to efficiently remove Cr (VI) at low cost.[59] They used maghemite nanoparticles as solid adsorbents to remove Cr (VI) ions, and then were able to regenerate the adsorbent.[59] The regenerative studies were performed by controlling the pH.[59] After a suitable eluent was used for desorption, 0.01 M sodium hydroxide was found to be the most effective at returning the particles to their active form.[59] After six cycles, the Cr capacity of maghemite remained unchanged.[59] In the case of maghemite nanoparticles, almost all of the adsorption active sites are all located on the exterior of the nanoparticle's surface. Compared to a porous adsorbent, this means that the adsorption of the Cr (VI) ions onto the maghemite particle site is faster due to the accessibility of the external active sites.[59] Once all the active sites are occupied, equilibrium is reached.[59] Hu *et al* found pH 2.5 to be the optimum conditions for Cr (VI) removal.[59] Hu *et al* was able to demonstrate that the maghemite nanoparticles were successful at adsorbing Cr(VI) ions however, representative wastewater samples typically have a pH 6-9.[60]

The EPA lists mercury as a contaminant in drinking water with maximum contaminant level of 2 μg L^{-1}. Long term exposures can cause kidney damage.[12] In 2014, Qi *et al* published a water-soluble magnetite superparamagnetic nanoparticles (MSPNPs) in attempt to provide a fast, selective adsorbent to remove mercury (Hg^{2+}) from water.[61] In water, the polymeric molecules act as a binder for any metal ions present; therefore, becoming a "carrier" of metal ions from treated water.[62] They synthesized these particles using an efficient polymer combined with the MSPNPs to functionalize the magnetic nanoparticle as previously published.[63, 64]

The effect of polymer modification on the surface of (M-MSPNPs) was tested on the removal of Hg^{2+} from water. This was done using the batch method and a shaking speed of 350

rpm.[61] Adsorption studies compared MSPNPs and M-MSPNPs at pH 7 (refer to table 1 for details). Isotherm calculations were used to describe the behavior of the adsorption of Hg^{2+} to the M-MSPNPs. The data fit to both Langmuir and Freundlich models although the Langmuir was moderately better. The adsorption behavior described by the Langmuir model indicates the formation of a monolayer complex between the coated polymer and Hg^{2+}.[61] Therefore, the authors infer that no more complex molecules can form on the first layer.[61] The effect of pH and salinity were studied in order to obtain data representative to real water samples. Both did not have a significant effect on the adsorption of Hg^{2+} to the M-MSPNPS. A sample collected from Jinji Lake located in China, was spiked with Hg^{2+} and adsorption experiments were performed. The model water sample gave insight as to the influence of coexisting ions and the potential effect they had on the adsorption of Hg^{2+} to the M-MSPNPs. The adsorption interaction was due to complex formation between the polymer ligand on the M-MSNPS and Hg^{2+}.[61] Regenerative studies were performed using 2-mercaptoethanol (a strong complexing agent) to effectively remove the bound Hg^{2+} from the M-MSPNPs after treatment.[61] After 3 cycles the percent removal was higher than 98 %.[61]

The authors compared the removal efficiency of the M-MSPNPs to other reported studies using different adsorbents to remove Hg^{2+} from water.[61] M-MSPNPs were one of the most efficient and quickest at removing Hg^{2+}.[61] This article was rich in data to show that these M-MSPNPs would be applicable to solve real world heavy metal contamination.

In addition to the studies highlighted in this article, there have been several other articles on functionalizing the surface of magnetic particles.[65-71]

2.3 Hematite (α-Fe_2O_3)

The use of a non-magnetic phase of iron oxide, hematite (α-Fe_2O_3), has been considered as a stable, low cost material for use in sensors, catalysis and environmental applications.[72] The synthesis of iron oxide into hierarchical nanostructures with distinct shapes is of interest due to their novel properties compared to bulk materials.

The role of nanohematite as an adsorbent for the removal of heavy metal ions from spiked tap water was examined by Shipley *et al*.[73] This study provided a comprehensive elucidation into the adsorption properties of nanohematite (α-Fe_2O_3) to certain heavy metal ions in solution. Commercially bought nanohematite particles were used (refer to table one for details). The parameters that were investigated included loading and exhaustion studies, the effect of pH and temperature, as well as the its performance in the presence of multiple metals in solution.[73] A representative groundwater sample was prepared by spiking treated tap water with the heavy metals of interest. Batch adsorption studies were performed and the spent nanohematitie particles were removed from solution via filtration. The effect of temperature on the adsorption of metals to the nanohematite was carried out at pH 6 and illustrated that metal adsorption increased with increasing temperature.[73] The effect of pH was studied to observe surface charge effects on adsorption. An increase in pH correlated with an increase in metal adsorption to the nanohematite. The surface chemistry was attributed to the presence of hydroxyl groups located on the exterior of the nanohematite particles which allowed for specific binding to the heavy metal ions.[73] Freundlich isotherm model was applied to describe the behavior of the experimental data at all three temperatures (refer to table 1 for details). The model proved that adsorption of Pb (II), Cd (II) and Cu (II) were endothermic processes and Zn(II) to be exothermic.[73] Exhaustion studies showed that the nanohematite could be recycled up to four cycles before adsorption ability was compromised. This paper provided great detail

into the use of nanohematite as an adsorbent for metal removal. The use of spiked tap water proved that this adsorbent could be used in treatment. A similar paper was published by Grover *et al* investigating the adsorption and desorption behavior of bivalent metals to hematite nanoparticles.[74]

In order to increase the surface area and efficiency of hematite, studies have been published on hierarchical structures used as adsorbents to remove heavy metals from aqueous solutions. Liang *et al* synthesized self-assembled 3D flower-like α-Fe_2O_3 structures for water treatment use.[72]

Figure 1 illustrates the α-Fe_2O_3 microflowers that were synthesized via hydrothermal treatment.[72] The size of the microflower was between 5-7 microns, however the size of each "petal" was on the nanoscale, thus allowing for the enhanced surface area and properties found with typical nanomaterials.[72] These were advantageous for water treatment due to their unique structural characteristics, which enables separation and regeneration.[72]

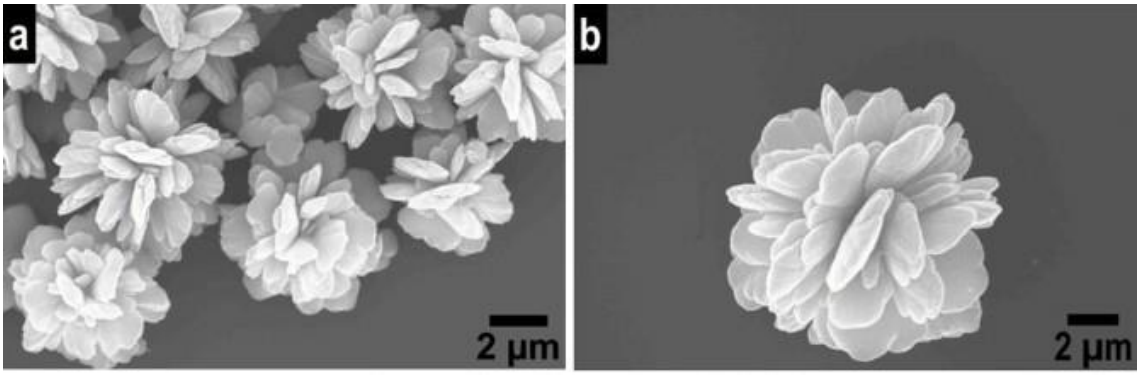

Figure 1. SEM images of α-Fe_2O_3 microflowers after hydrothermal treatment at 150 °C for 12 h.[72] Reprinted from Ref. 72, Copyright 2015, with permission from Elsevier.

The flower-like structure prevents flocculation, and the enhanced surface area with multiple spaces and pores provide many active sites for interaction with pollutants.[72] The novelty of these microstructures compared to other 3D flower oxides is in the simplicity of the synthesis route. In

order to investigate the potential application of the α-Fe_2O_3 microflowers for water treatment, adsorption isotherms were observed. Both Langmuir and Freundlich adsorption models were considered (equations 1 and 2 respectively). The Langmuir model showed the best fit with correlation coefficients above 0.999 when compared to the Freundlich model.[72] Therefore it can be inferred that the adsorption behavior of the heavy metal ions (Table 1) onto the α-Fe_2O_3 microflowers is a monolayer adsorption process.[72] There is no mention of regenerative studies, how the spent particles were removed from solution, or surface area measurements. The solutions containing heavy metals were prepared in the lab and no mention of environmental applicability was made. There have been other α-Fe_2O_3 microstructures synthesized for wastewater treatment. Some worth mentioning were in the shape of cauliflower[47], nanosheets,[75] 3D self-assembled iron hydroxide nanostructures[76] and nano-flowers.[77, 78] The two former studies reported the removal of dyes from wastewater and not metal ions. The latter studies with the iron oxide nanoflowers reported heavy metal removal applications.

Other reports for the use of bulk hematite as adsorbents for heavy metal removal have been published.[79-81] However, since the focus of this article is on inorganic nanoadsorbents for heavy metal removal, these will not be discussed in great detail.

2.3.1.1 Iron Oxide Scopes and Limitations

Iron oxide limitations include poor recovery (hematite) and the size of the particle can be a factor on its overall performance.[37] In the case of MNPs, if they are too small (< 12 nm) magnetic separations would require large external magnetic fields to overcome opposing forces, which can lead to costly gradient separators.[82, 83] The research discussed above did not mention the possibilities of scaling up the syntheses for the iron oxide nanomaterials in order to

demonstrate their real world application to remove heavy metals from wastewater effluent. However, iron oxide is abundant, relatively non-toxic and cheap.

2.4 Carbon Nanotubes with other metals/supports

Carbon nanotubes are often combined with other metals or types of support in effort to enhance their overall adsorption, mechanical optical, and electrical properties.

A study published by Di *et al*, reported the use of carbon nanotubes as a support for the rare earth element cerium (Ce) in the form of cerium oxide (CeO_2).[84] The researchers reported rare earth elements in the hydrous oxide form demonstrated high-adsorption capacity for anions therefore by supporting ceria nanoparticles onto CNTs (CeO_2/ACNTs), they would create a novel adsorbent for wastewater treatment.[84] Hydrous oxides of rare earth elements have previously been found to have a high affinity for anions such as fluoride, arsenate and phosphate.[85, 86] Synthesis of the aligned carbon nanotubes (ACNTs) was achieved via previously published method[87] by catalytic decomposition of hydrocarbon.[84] The ceria nanoparticles were 6 nm in diameter. A solution containing $CeCl_3$ was added in small volumes to the CNTs to make a CeO_2/ACNTs support.[84] It is well known that the addition of nitric and sulfuric will add –OH and –COOH functional groups to CNTs. The CeO_2/ACNTs were functionalized with the aforementioned acids and the effect of pH, adsorption capacities, isotherm results and comparison to other adsorbents were reported. Di *et al* found that the pH was the most important parameter when considering the binding of the metal ion to the CeO_2/ACNTs.[84] They evaluated adsorption pH effects from pH 3.0-7.4, pH 7 being the optimal value.[84] Adsorption studies were performed at 25°C and the CeO_2/ACNTs demonstrated high Cr (VI) adsorption efficiency from water with variable pH rages (3.0-7.4).[84] Langmuir and Freundlich isotherm algorithms were applied and the results showed an adsorption capacity two times higher when compared to other

adsorbents (refer to table 2).[84] There was no mention of recyclability or use of actual wastewater samples. Also, the use of rare earth elements for environmental remediation can be costly. Other reports have been published on the use of cerium oxide nanoparticles to remove heavy metal ions from pure water but without the CNT support.[88, 89,90]

Gupta *et al* published a study using CNTs as a support for magnetic iron oxide.[91] They combined the adsorption properties of CNTs with the magnetic properties of iron oxide into a "composite" adsorbent to remove chromium from water.[91] They studied the adsorption of chromium due to its heavy use in tanneries, glass and mining industries.[91] Chromium is a known contaminant and health hazard. The MWCNTs were purchased commercially and purified and functionalized using nitric acid. Ferric chloride hexahydrate and ferrous chloride tetrahydrates were added to a suspension of MWCNTs and after 2 h, ammonium hydroxide was added to precipitate the iron oxides.[91] The MWCNTs/nano-iron oxide composite was then filtered and dried.[91] Batch experiments were performed to study the adsorption capacity of activated carbon, MWCNTs and a MWCNTs/nano-iron oxide composite.[91] The results from the adsorption studies were compared, and the MWCNTs/nano-iron oxide composite was better at adsorbing chromium when compared to the MWCNTs and the activated carbon (refer to table 2).[91] The iron oxide nanoparticles have surface oxygen atoms, which can provide additional adsorbing sites for the chromium.[91] The presence of these oxygen atoms also increases the surface charge, which can contribute to electrostatic interaction with the chromium.[91] Effect of pH on the adsorption of chromium and the MWCNTs/nano-iron oxide composite was evaluated. At a pH range of 5-6, maximum adsorption capacity was observed. Other parameters were investigated (contact time, agitation time, and loading studies)[91] but no isotherm models were applied and regenerative studies were not mentioned. The MWCNTs/nano-iron oxide composites were not

tested using real world samples, however, wastewater is typically between pH 6-9[60] which suggest these composites may be environmentally applicable.

2.4.1.1 CNTs Scopes and Limitations

Toxicity of CNTs has been a growing concern since their discovery in the early 90s.[92] Many reports have surfaced regarding health concerns[93, 94] Alternative methods such as using CNT sheets[95] have been implemented in an effort to remove heavy metals from water without the serious health[96, 97] and environmental risks.[98] The other drawbacks with using CNTs are their low removal efficiency and limited selectivity.[99] Also, the sorption capacities for metal ions are very low because the walls of carbon nanotubes are not reactive.[62] However, the CNTs can be easily modified by chemical treatment[100, 101] to correct these issues. Future directions for the CNTs discussed in the previous sections would be to test their performance using real world samples and help with environmental remediation and cleanup. In order to do this, the synthesis of these carbon nanomaterials would need to be scaled up which could become costly in some cases.

2.5 Metal oxide nanoadsorbents

The use of metal oxides for treatment provides a low cost adsorption technology. Metal oxides can include ferric oxides (refer to iron oxide section for in-depth discussion), titanium (Ti),[102, 103] cerium (Ce),[88, 89] and Zinc (Zn). When produced at the nanoscale, metal oxides can have increased surface area and possess favorable sorption to heavy metals.

2.5.1 Titanium

The ninth most abundant element in the Earth's crust is titanium.[104] It is cheap and its oxide is chemically inert. Titanium dioxide (TiO_2) has many applications. It has been used over a wide

range of applications from photovoltaics, photocatalysis, H_2 sensing, lithium batteries and as an adsorbent for the removal of contaminants in polluted waters.[104] It's also used extensively as a pigment in paints, food, pharmaceuticals and cosmetics. In addition to titanium dioxide, titanates have also been used as adsorbents. Layered titanates can be formed into sheets,[105] fibers,[106] hierarchical shapes such as flowers,[107, 108] and composites.[109, 110] These shapes contribute to increased surface area and higher ion exchange capabilities.[107] The difference between the two is that titanate works through an ion exchange process.

2.5.1.1 TiO_2 and Titanate

Arsenic removal and recovery is a huge concern and challenge. Arsenic is introduced into the environment via wastewater effluent from industries and in many parts of the world in groundwater which poses a threat to people who drink unpurified well water. Luo *et al* performed extensive work on the removal and recovery of arsenic using TiO_2.[111] They acquired wastewater from a copper smelting company that contained an average concentration of 3310 mg/L As (III), 24 mg/L Cu, 5 mg/L Pb, and 369 mg/L Cd.[111] The pH of the solution was 1.4 but was adjusted to 7 for the adsorption batch experiments. Titanium dioxide was synthesized by hydrolysis of titanylsulfate at 4°C.[111] The authors made no mention of the size of the TiO_2 and did not provide images. Surface area was measured and is reported in table 3. Regenerative studies were investigated. The spent TiO_2 was collected through membrane filtration, and then the "filter cake" was mixed with a basic solution. The solid was collected and reused in the batch adsorption method. Luo *et al* reported 21 successive treatment cycles using the regenerated TiO_2. Arsenic was recovered by pre-concentrating the extracted solutions (TiO_2 included), and further precipitated as a result of cooling.[111] Adsorption kinetic experiments were performed using batch method. Results were fit with a pseudo second-order kinetic model with

an R value greater than 0.999 and a rate constant of 0.84 g/mg-h. A majority of the arsenite was adsorbed in less than one hour reach about 100 mg/g which was steady state and remained there for 25 hours, the initial concentration was 3310 mg/L.[111] Since As (III) forms "inner-sphere bidentate binuclear complexes",[112] it will bind to the OH surface sites on the TiO_2.[111] This result was confirmed using Extended X-ray Absorption Fine Structure spectroscopy (EXAFS), XPS and surface complexation modeling. Attempts to implement this technique to full scale were limited. The authors state that the TiO_2 used in this study was expensive in comparison to the process that was currently in place to remove arsenic at the copper smelting plant (metal hydroxide process).[111] Nonetheless, this paper provided extensive work on the removal and recovery of arsenic from real world samples. Furthermore, TiO_2 exhibited great regenerative studies which may reduce the overall cost in the future for the copper smelting plant.[111]

Engates and Shipley studied the adsorption of metal ions (refer to table 3) to commercial TiO_2 nanoparticles and TiO_2 anatase bulk particles.[113] San Antonio tap water was spiked with heavy metals in effort to have a model polluted water sample.[113] Adsorption studies were carried out for single and multi-metal adsorption. Exhaustion experiments were also performed. The authors reported large adsorption capacities for the TiO_2 nanoparticles compared to bulk particles.[113] The data correlated to Langmuir isotherm model indicating a monolayer adsorption on the surface of the TiO_2 nanoparticles. The TiO_2 nanoparticles also exhibited strong adsorption rates when compared to the bulk particles. Exhaustion results showed that at pH 6, TiO_2 nanoparticles exhausted after 3 cycles and at pH 8 after 8 cycles.[113] These results support the possibility of TiO_2 nanoparticles to be a potential remediation for heavy metal removal from contaminated waters. Other reports by this group studied regeneration of TiO_2 nanoparticles for heavy metal removal.[114]

Layered protonated titanates have become the latest sensation in solar cells, lithium ion batteries, and as adsorbents.[104, 105] According to Lin *et al*, "unfolded" titanate nanosheets have a high theoretical cation exchange capacity due to the presence of exchangeable cations intercalated in the interlayers.[104, 105] This ability makes them good adsorbents through ion exchange. Layered protonated titanate nanosheets (LPTN) were produced using a one-pot synthesis of titanium n-butoxide with urea at low temperatures. The urea was added to govern the production of NH_4^+ ions into the TiO_6 layers.[105] Extensive characterization of different crystal phases and structures were investigated. Sample number "400-7" was found to be the best model adsorbent for this study. Adsorption studies using Pb^{2+} as the model pollutant and an organic dye, methylene blue with the LPTN were conducted. Results are reported in table 3. Isotherm models were applied, Langmuir describing the best fit for the data. Favorable adsorption was observed for Pb^{2+} with the LPTN. The authors state the mechanism of adsorption for the Pb^{2+} onto the LPTN was due to the negative zeta potential of the LPTNs in water.[105] This negative potential created an electrostatic bond between the cationic Pb^{2+} and the surface of the negative LPTN.[105, 115] Furthermore, the Pb^{2+} ions were intercalated into the interlayers of the LPTNs, thus making it a successful adsorbent for Pb^{2+} removal from water.[105] No natural water samples were used for this study so it is unclear whether other metals or ions could interfere with the intercalation of Pb^{2+}ions in the LPTN interlayers. However, the LPTN shows promise for industrial applicability for its ability to remove inorganic and organic contaminants (methylene blue) from water.

Additional structures of layered titanates have been used as adsorbents to remove heavy metals from solution. Titanate nanofibers were synthesized by Yang *et al* to remove radioactive contaminants and metals from contaminated water. The fibers were synthesized under

hydrothermal conditions and consisted of two TiO_6 octahedra connected to form layers (figure 2 below).[106, 116, 117]

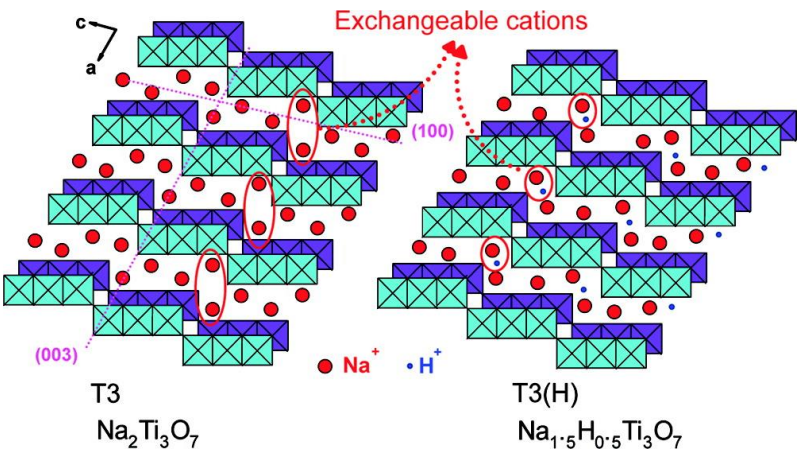

Figure 2. Schematic of the nanofiber structures.[106] Reprinted with permission from Yang *et al*. Copyright 2015 American Chemical Society.

The layers have the ability to carry negative electrical charges and contain exchangeable sodium cations.[106] The titanate nanofibers were synthesized via hydrothermal treatment and then subsequently dried into a white powder. The white powder product was collected and labeled "T3". Excess "T3" was then dried a second time at 483 K to obtain "T3(H)".[106] The T3 phase was $Na_2Ti_6O_{13}$ and the T3(H) phase was $Na_{1.5}H_{0.5}Ti_3O_7$.[106] The authors hypothesized that the mechanism of sorption of the pollutant cations onto the fibers was due to the induction of structural changes that permanently trap them inside the layers of the adsorbent.[106] To test the adsorption performance of the T3 and T3(H) titanante nanofibers, isotherm and sorption studies were investigated (refer to table 3).[106] In brief, Yang *et al* found that the T3(H) fibers were better at selectively binding to the Pb^{2+} and radioactive ions than the T3 fibers.[106] In order to be an effective adsorbent for radioactive elements, the titanante nanofibers had to permanently trap the radioactive cations and Pb^{2+} for safe disposal.[106] The release of these cations was investigated via centrifugation and basic treatment. No release of the Pb^{2+} ions was observed. The authors concluded that the fibers were trapping the ions and could be stored without causing secondary

contamination.[106] Large-scale synthesis and industrial use of the titanate nanofibers was discussed but not applied.

The last two sections discussed the use of sheets and fibers as inorganic nanoadsorbents for heavy metal removal. Other groups have taken these titanate structures a step further and have prepared hierarchical titanate structures, titanate nanoflowers (TNF), in an effort to improve the overall surface area.[107]

Huang *et al* reported a study using TNF to remove heavy metal ions from wastewater (refer to table 3 for details). The idea behind using the TNF vs. TNT or TNW is the titanate flowers have ultra-thin nanosheets which can prevent aggregation, and provide strong mechanical properties when applied in water flow systems.[107] The TNF, TNT and TNW were all synthesized using an alkaline hydrothermal method and further acidified to convert them into a protonated form.[107] To get each form, the synthesis time for TNF was 45 minutes, TNT was 2 h and TNW was 6 h.[107] The authors believed that the TNF was an intermediate product of the TNT since it is a flowerlike aggregate of many sheets.[107] Competitive adsorption studies using TNF, TNT, and TNW were performed using a ternary system containing Zn (II) Ni (II) and Cd (II). TNF adsorbed to all three of the cations better than TNT and TNW.[107] Adsorption isotherms were studied and compared among the titanate nanostructures. The TNF showed the largest adsorption capacity when compared to the TNT and TNW which was about 1.5×10^{-3} mol/g Pb(II) compared to 6×10^{-4} mol/g Pb(II) for TNW and 4×10^{-4} mol/g Pb(II) for TNT. Adsorption kinetics for the titanate nanostructures was considered in effort to design a treatment plan for practical environmental application. The TNF exhibited the fastest adsorption for Pb (II) compared to TNT and TNW (refer to table 3 for actual values).[107] The authors argue that the ultra-thin nanosheets are able to transport heavy metal ions through the space in-between the nanosheets

making a “tunnel”.[107] The tunnels increase the diffusion rate of the Pb (II) ions and the thin width of the nanosheet allows for quick access from the surface active sites to the interlayer of the titanate.[107, 118] The use of titanate nanoflowers as adsorbents for heavy metals in a model pollutant system showed great promise. It would be interesting to see how the TNF would perform in a real wastewater sample. There was no mention of the effect of pH in this study; however, the authors did mention that the synthesis is simple and feasible for scale up considerations.[107]

2.5.1.2 TiO_2 supports/composites

In order to create a synergistic effect, TiO_2 and titanate can be combined with other materials as a support or composite to enhance their properties. Cadmium is a toxic heavy metal that can cause harmful health issues (hypertension, cancer, bone sores). It is introduced into the environment through mining, smelting, and alloy manufacturing.[110] Sharma *et al* developed a titanium nanocomposite (TiO_2-AM) by in situ doping acrylamide (AM) into titanium during a sol-gel reaction[119] in order to develop a low cost adsorbent for cadmium removal.[110] The addition of the acrylamide to the TiO_2 forms a composite with free amide groups, which can increase the binding capacity of titanium to other metals.[110] Figure 3 illustrates the proposed mechanism of adsorption. The TiO_2-AM performance as an adsorbent for Cd (II) was demonstrated through sorption kinetics. Initially, the removal of Cd (II) was fast and more than 50 % was adsorbed in 30 minutes then reached equilibrium at 1.5 h.[110] The authors report that the initial fast rate of Cd (II) removal was due to the many unoccupied sites in the TiO_2-AM composite and the adsorption was due to a “chemisorption phenomenon".[110]

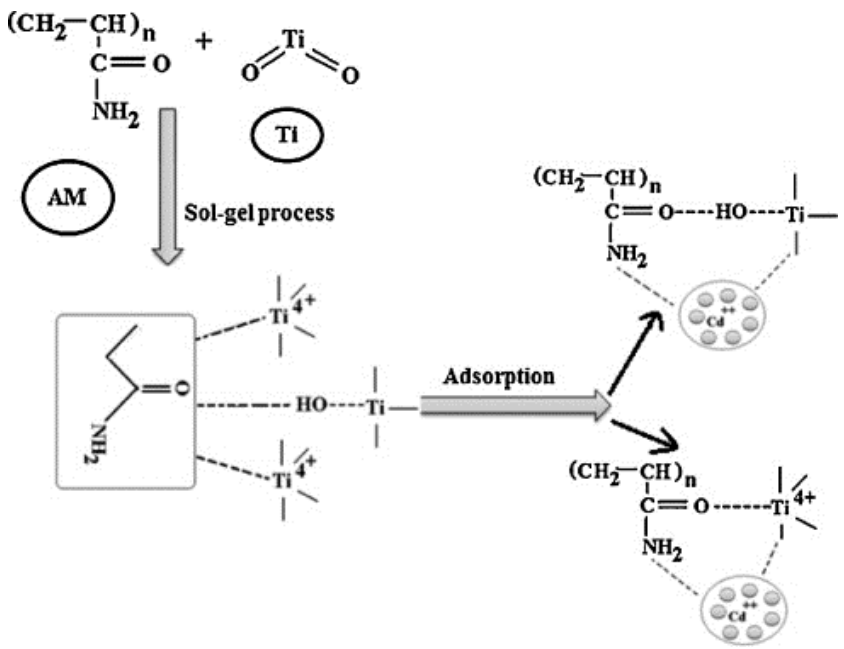

Figure 3. Proposed structure of the nanocomposite synthesis and reaction pathways for the adsorption of Cd(II) by the nanocomposite.[110] Reprinted from Ref. 110, Copyright 2015, with permission from Elsevier.

The effect of pH was considered at a range from 2.0-10 with pH 8 being the optimum value for Cd (II) adsorption.[110] Sharma *et al* mentioned that Cd is very sensitive to changes in the pH due to the polar interaction of the charged Cd^{2+} species and the oxygen on the TiO_2.[110] Since wastewater is composed of many different types of cations and anions, the TiO_2-AM nanocomposite was placed in separate solutions containing anions (Cl^-, $(SO_4)^{2-}$ and $(CO_3)^2$) and cations (Pb^{2+}, Cu^{2+}, Co^{2+}, Zn^{2+}) with cadmium.[110] These ions interfere with the binding to the TiO_2-AM nanocomposite and have a negative impact on adsorption as wells as forming complexes with the cadmium making it challenging to remove from the wastewater.[110] The increasing concentration of the anions decreased the adsorption capacity for the cadmium.[110] The cations showed an interference of less than 10 % which is not significant for Cd (II) removal.[110] Adsorption isotherms were studied and the Cd (II) data best fit to the Langmuir model.[110] This is indicative of monolayer adsorption capacity. In order to test the regenerative

ability of the TiO_2-AM nanocomposite, desorption studies were performed. After the fifth cycle, the authors observed a decrease in the adsorption efficiency and desorption efficiency. The synthesis of TiO_2-AM nanocomposite did require a lot of time and the temperature for adsorption was a little higher than room temperature. However, the fact that it can be regenerated through five cycles does show promise as a scale up adsorbent for industrial applications. The TiO_2-AM nanocomposite was not used in natural water systems; however, the extensive research investigating its performance in the presence of interference ions gave promising results. Other studies were reported for titania composites. Byrne *et al* published a paper on mercury removal by adsorption and photocatalysis using silica-titania composites (STCs).[109] Without illumination (adsorption only), the STCs removed 90 % of mercury when compared to unmodified TiO_2 (Degussa P25). The combination of photocatalysis and adsorption to simultaneously remove organic pollutants from aqueous solution is an innovative technology that has potential for environmental applications. The pH value of these systems was lower than actual reports of pH values for wastewater (pH 6-9).[60] No natural water samples were used in this study.

2.5.1.3 TiO_2 coatings

Generally, coating the surface of TiO_2 nanoparticles is a method used to increase adsorption and improve technology for removal of heavy metals in aqueous solution. As discussed previously, humic acid (HA) is a form of natural organic matter (NOM) found in the aquatic environment. It is known that NOM plays an important role in the sorption of heavy metals and other toxic pollutants.[120] Coating with HA applies a polyanionic coating onto metal oxides, which can change the surface chemistry properties.[121] Chen *et al* coated humic acid onto TiO_2 through mechanical agitation from a previously published method.[120, 121] Figure 4 shows the effect of HA interactions on HA-TiO_2 when the solution conditions were changed. However,

the main purpose for the inclusion of figure 4 was to show the proposed structure and coating of the HA on to nano-TiO_2.[121]

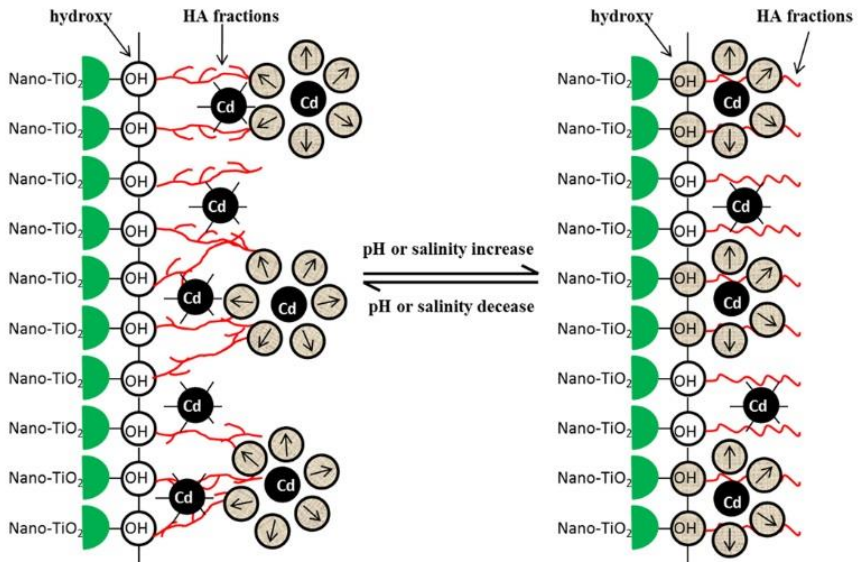

Figure 4. Effect of HA fractions on HA-TiO_2 during different solution conditions.[121] Reprinted from Ref. 121, Copyright 2015, with permission from Elsevier.

Coating nano-TiO_2 with HA added phenolic groups to the surface and interacted with terminal OH groups on the surface of the nano-TiO_2.[121] The authors chose Cd (II) as a model pollutant and studied the effect of pH, role of salinity and performed adsorption experiments. Overall, the results showed that HA-TiO_2 increased adsorption to Cd (II) compared to nano-TiO_2. It was suggested that this was due to the fact that the presence of HA modifies the bioavailability of heavy metals in aquatic systems.[121] Both salinity and pH changed adsorption interactions of Cd (II) to the nanoparticles. High pH and salinity contributed to electrostatic attraction between the charges on the particle. Low salinity facilitated covalent bond interactions.[121] The HA-TiO_2 showed a moderate increase in adsorption when compared to the nano-TiO_2 (refer to table 3). Adsorption isotherms were calculated and the Freundlich model showed the best fit.[121] Overall, this study provided insight as to how HA and nano-TiO_2 interacted with heavy metals in a representative environmental sample. It would be interesting to observe the interactions of HA-

TiO_2 with binary and ternary solutions containing other heavy metals. Regenerative studies were not performed.

2.5.1.4 Titanium Scopes and Limitations

Limitations of TiO_2 for applications in water treatment is mainly due to its small particle size which can lead to expensive filtering treatment.[122] However, much progress has been made to address this issue using innovative nanocomposites containing TiO_2 or titanate with polymers, metals and humic acid[121] as previously discussed. The hydrothermal methods for TiO_2 nanomaterials seem to be the most economical when it comes to scaling up the reactions for water treatment. Another concern is the emerging studies reporting on the toxicity of TiO_2 based nanomaterials.[123-125]

2.5.2 ZnO nanoparticles

There is limited literature on the use of zinc oxide as an adsorbent to remove heavy metals in solution. Typically, its used to treat H_2S contamination.[126] Nonetheless, it is widely popular for use in other technologies such as gas sensing, photocatalysis and solar cells.[127] It is considered nontoxic to the environment. The many surface hydroxyl groups make it a promising candidate for heavy metal adsorption in aquatic systems.

ZnO nanoparticles were used as an adsorbent to remove Zn(II), Cd (II) and Hg (II) ions from aqueous solutions in a study reported by Sheela *et al*.[128] The ZnO nanoparticles were synthesized using the precipitate method then dried and calcined at 400°C.[128] The batch method was employed to measure the adsorption of the heavy metal ions onto ZnO nanoparticles. The metal ions adsorbed onto the ZnO at different concentrations, however, Hg (II) had the highest maximum adsorption (refer to table 3 for details). The authors state that this was because Hg (II) has the smallest hydrated ionic radii (compared to Zn and Cd), which allowed it to move faster in

solution and reach the adsorption sites on the ZnO particle.[128] Also, Hg has a higher electronegativity value when compared to the other cations. The effect of pH and temperature on adsorption was studied with the maximum value at 5.5 and 30ºC respectively.[128] Isotherm models were applied and the adsorption data fit well to both Langmuir and Freundlich. The mechanism for sorption between the cations and ZnO nanoparticles could be due to both ion exchange and adsorption processes.[128] The authors infer that if ion exchange process is occurring then the ions must be moving either through the channels within the crystal lattice or the pores of ZnO mass.[128] Previous studies have reported on metal ions replacing cations with surface hydroxyl groups.[129] The experimental data collected from the pH studies supported this finding. Further work was done looking at adsorption kinetics, contact time and thermodynamics. Natural water samples were not used in this study and no regenerative experiments were considered. Published work by Salehi *et al* engineered Chitosan-zinc oxide nanoparticles for dye removal with potential to remove other pollutants.[130]

In order to improve the adsorption efficiency of ZnO, Wang *et al* fabricated hollow ZnO hollow microspheres using a previously published hydrothermal method.[131],[127] They compared the adsorption performances of commercial ZnO nanopowder, ZnO nanoplates[132] and activated carbon with the ZnO hollow spheres (table 3). Adsorption studies were carried out using the batch method. In every case, the ZnO hollow microspheres had the highest adsorption performance. Furthermore, no saturation was observed with Cu (II) concentrations higher than 2000 mg/L. This high adsorption value was close to the ZnO nanoplates (surface area 147 m^2/g)[132] however, the ZnO hollow microspheres have much less specific surface area 46 m^2/g.[127] Previous literature along with XPS and DRIFT measurements, confirm that hydroxyl groups on the surface of the ZnO hollow microspheres are interacting with the cation species forming Cu-

O, Pb-O or Cd-O by Lewis interactions.[133] Langmuir and Freundlich Isotherm models were applied to study the behavior of each adsorbent. The commercial ZnO fit to Langmuir isotherm model suggesting monolayer adsorption. The ZnO hollow microspheres fit to both Langmuir and Freundlich models, indicating monolayer adsorption and multilayer adsorption. The authors explain that the structure of the ZnO hollow microspheres plays an important role in the adsorption behavior.[127] The ZnO nanosheets are cross-linked in the porous hollow spheres creating non-polar and polar surfaces. Depending on the electronegativity of the metal, either the Langmuir or Freundlich behaviors will predominate. For example, metals with low electronegativity will fit well with Langmuir-type adsorption behaviors. There was no report of the regenerative ability for the ZnO hollow microspheres. Also, they would be unstable in strong acid or alkali solutions.[127] The environmental applicability of the ZnO hollow microspheres is unknown due to the lack of research using natural water samples.

2.5.3 ZnO nanoplates and nanosheets

Wang *et al* synthesized micro/nanostructured porous ZnO nanoplates for use as an adsorbent for heavy metal removal.[132] They were synthesized via solvothermal methods using ethylene glycol to control the morphology and subsequent annealing. The ZnO nanoplates are porous with two terminal non-polar planes.[132] The authors realized the ethylene glycol (EG) played a roles in the morphology of the ZnO nanoproducts.[132] The more EG they added, the more changes in morphology was observed.[132] The nanosheets evolved into plates, particles and finally microspheres. Adsorption studies were performed with Cu (II) ions as the model pollutant. ZnO nanoplates were compared to commercial ZnO nanopowder (table 3). A noteworthy mention is that the adsorption behaviors for each ZnO nanomaterial were different. The ZnO nanoplate was best described using the Freundlich model which indicates that the adsorption occurs on a

heterogeneous surface.[132] Whereas the ZnO nanopowder was best fit to the Langmuir model, suggesting monolayer adsorption onto a uniform surface.[132] The mechanism for adsorption of Cu(II) ions onto the ZnO nanoplates was due to their structure and many pores.[132] In theory, the pore walls should contain many polar sites within the plates. Once the plates are subjected to air and water, hydroxyl radical groups should form on the sites. These results were confirmed by FTIR. In reference to the Cu (II) interaction with the ZnO nanoplates, the Cu (II) can react with the hydroxyl groups through Lewis interactions.[132] The authors also state that the adsorbed hydrated Cu (II) ions can form Cu-OH through hydrolysis and further form Cu-O-Cu on the walls of the pores.[132] This confirms the behavior of Freundlich because multilayer adsorption is occurring. This phenomenon is shown in an illustration provided by the author (Figure 5 below).[132]

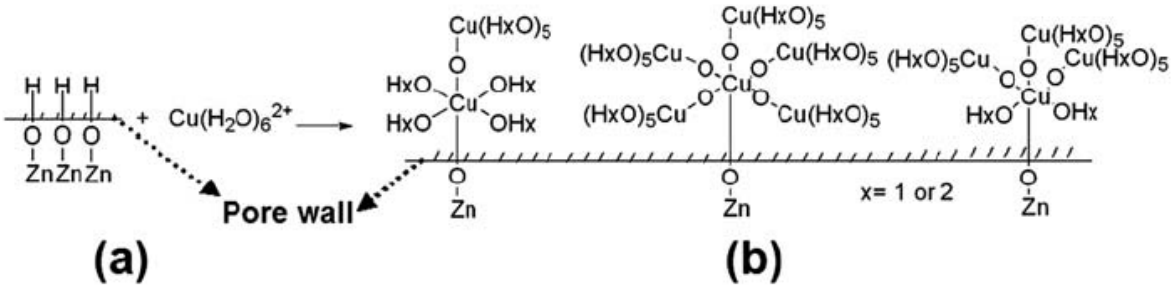

Figure 5. An adsorptive illustration of Cu(II) ions on the polar sites of pore walls within the porous ZnO nanoplates.[132] Reproduced from Ref. 132 with permission from The Royal Society of Chemistry.

Chromate anions and methyl orange were selected to investigate the possibility of anionic interference.[132] No adsorption of these anions was observed for the ZnO nanoplates. The authors comment that further work is needed to study regenerative life. No studies were conducted to study the performance of the ZnO nanoplates in wastewater.

An article published by Ma *et al* used ZnO nanosheets for Pb^{2+} removal. ZnO nanosheets were synthesized using a hydrothermal method with zinc nitrate and thiourea in water.[134] Their objective was to use the ZnO nanosheets as an adsorbent while simultaneously doping them with Pb^{2+} and use the properties of the Pb^{2+} to then create a secondary nanoadsorbent, in this case ZnO/PbS heterostructured nanocomposite.[134] The ZnO/PbS nanocomposite would then have wide range of functionalities including photocatalysis.[134]

Adsorption studies were implemented using the batch method. After adsorption, the ZnO nanosheets with the adsorbed Pb^{2+} were treated hydrothermally as previously mentioned. The mechanism of adsorption for the Pb^{2+} onto the ZnO nanosheets was due to the hydroxyl groups on their surface.[134] The metal ions in solution reacted with the hydroxyl groups, which was demonstrated by the high removal capacity. Once the Pb^{2+} adsorbed to the surface of the ZnO nanosheets, the products formed were PbO_2 or PbS.[134] Both of which have good photoelectric abilities. The effect of pH was not considered during the adsorption studies. However, the objective of this study was focused on creating a functional ZnO/PbS nanocomposite.[134] Future studies should consider heavy metal removal from actual water and wastewater samples using these nanocomposites. Other studies have reported the use of ZnO nanosheets for cadmium removal.[135]

2.5.4 ZnO Scopes and Limitations

There is limited literature on the use of ZnO as an adsorbent to remove pollutants from aqueous solutions. Other studies have used ZnO to load onto supports in effort to create a hybrid adsorbent. Kikuchi *et al* published an extensive analysis on the effect of ZnO loading onto activated carbon.[136] There have been reports of coating the surface of ZnO with humic acid to remove phenanthrene but no mention of its applicability for heavy metal removal was made.[120]

Other studies have reported on the use of semiconductor nanocrystals, notably, ZnS. Amiri *et al* published work on the development of CdS/ZnS core-shell nanoparticles for heavy metal removal from aqueous solutions.[137, 138] Zan *et al* used ZnS nanocrystals for Hg(II) removal. These studies will not be mentioned further because the focus of this discussion is dedicated to the use of ZnO nanomaterials.

2.5.5 Metal Oxides Scopes and Limitations

There are a few limitations to using nanosized metal oxides as adsorbents. Reducing metal oxides to nanoscale sizes can increase surface area, but this increase can also cause instability.[139] As a result of being unstable, they become more prone to agglomeration due to the presence of van Der Waals forces and other interactions.[140] Once these interactions occur, they lose high capacity, selectivity and develop poor mechanical strength. To circumvent these limitations, metal oxides are typically incorporated into supports or other bulk adsorbents.[139]

2.6 Polymeric Nanoparticles

Polymeric nanoparticles were developed in the 1960s for use in gel permeation chromatography.[141] These adsorbents are typically made up of polystyrene or polyacrylic ester matrix. They are currently used in the removal of organic pollutants from natural and wastewaters. They possess physical properties including large surface area, perfect mechanical rigidity, tunable surface chemistry and pore size distribution and are reasonably regenerative.[140] These novel properties allow polymeric nanoparticles to be applied for use in drug delivery,[142] optics,[143] and water treatment.[62] They can also be incorporated with other particles making them extremely versatile. This section will be devoted to the practical application of polymeric nanoparticles for the removal of heavy metals ions for water treatment.

The use of polymer-based inorganic hybrid adsorbents was an alternative to try and overcome the limitations of the use of metal hydroxides as adsorbents namely, issues with mass transport and pressure drops using flow systems.[140] The solution was to impregnate or coat the particles with polymers (refer to functionalized MNPs section 2.2.1.2) or fabricate a hybrid adsorbent in a polymer matrix.[140] Kumar *et al* developed a bi-metal doped micro and nano multi-functional polymeric adsorbent to remove fluoride and arsenic (V) from wastewater.[25] They synthesized polymeric beads through suspension polymerization and incorporated Al and Fe salts during the polymerization step.[25] Briefly, the prepared polymeric beads were then carbonized and activated in a tube furnace. Four different adsorbents were synthesized using different metal loadings and were labeled as APH-04 (4g Fe salts), APH-22 (2g Al and Fe salts), APH-40 (4 g Al salts) and PH22BM-A (APH-22 beads that were crushed by ball milling to 200 nm).[25] Adsorption experiments were performed using batch method with solution of arsenic and fluoride (refer to table 4 for details). The Fe-doped micro sized beads had a larger As capacity than the Al-doped beads and the Al-doped beads had a larger fluoride capacity than the Fe-doped beads.[25] Overall, the PH22BM-A nanoparticles showed the highest adsorption capacity for the As and fluoride.

The authors' state that the large surface area combined with the large number of active sites available was the reason for its superior adsorption performance.[25] The surface interactions and proposed mechanism of the metal doped polymeric beads after As and fluoride adsorption is described in figure 6. Langmuir and Freundlich isotherm models were studied to describe the adsorption behavior of the adsorbents. The Freundlich isotherm correlated with the data better than the Langmuir model suggesting multilayer adsorption with heterogeneous surface energies.[25]

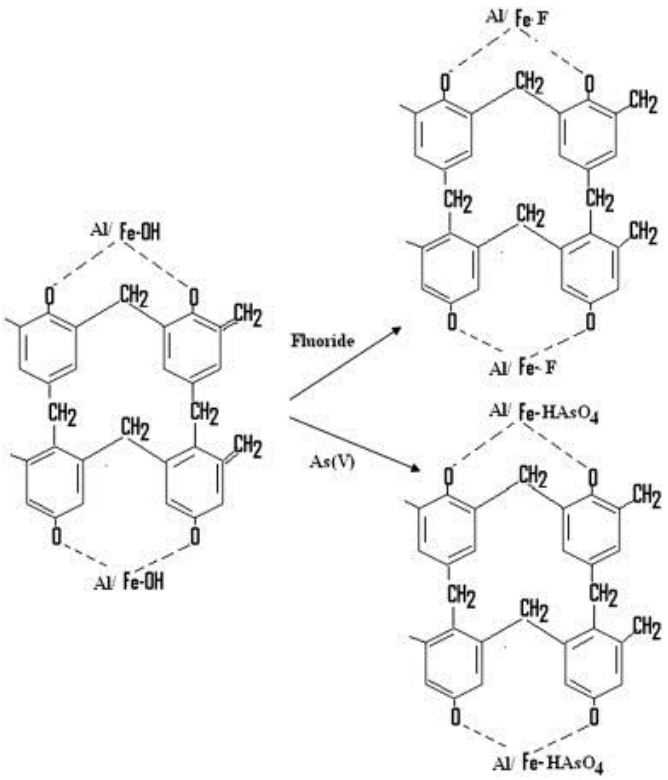

Figure 6. The postulated molecular structure of phenolic polymeric beads after the adsorption of fluoride and As(V) ions.[25] Reprinted from Ref. 25, Copyright 2015, with permission from Elsevier.

The effect of pH was studied and the maximum variation of pH observed with PH22-BM-A was around 0.7 therefore a suitable pH range was between 6.0-7.5.[25] No real world samples were used in this study. The authors mentioned a limitation of using PH22-BM-A in a flow method for wastewater treatment would require a binder phase to prevent entrainment of the nanoparticles.[25] Regenerative studies were being considered in future research.

2.6.1.1 Polymeric Scopes and Limitations

The last section covered the use of polymeric adsorbents and how they have been used as adsorbents for heavy metal removal in water. The drawbacks of this adsorbent include synthesis challenges and the difficulty of implementing into environmental application. Pan *et al* stated that even though polymeric adsorbents have excellent properties, for example structure, pore

sizes and tunable functional groups, the molecular design still has some flaws.[140] The ability to make it highly selective for a given pollutant is a challenge and recovery can be costly if a low purity polymer is used.[140] It is also noted that the adsorption capacities of polymeric adsorbents are low and regeneration is required in order to reuse them resulting in high occupational costs.[140]

3 Next Generation

3.1 Organic-Inorganic hybrids

The last three sections discussed the design and use of inorganic nanoadsorbents for heavy metal removal in water in extensive detail. Qi *et al* states that the next generation adsorbents for heavy metal removal are organic-inorganic hybrids due to their "unique quality of combining the functionality of organic compounds with the stability of inorganic compounds".[144] According to Wang *et al*, inorganic frameworks have various geometries, flexible coordination behaviors and assorted connectivity's which inhibit the presence of large structural pores and channels.[145 146, 147] On the other hand, metal organic frameworks possess rich structural chemistry and integrity as well as potential applications in catalysis, ion-exchange, and gas storage.[145-147]

A report on the fabrication of a new organic-inorganic hybrid zinc phosphate with 28 ring channels was published for the use of heavy metal removal from water. The use of organic amine ligands enables a route for the synthesis of large channels into an inorganic framework. The synthesis of these organic-inorganic hybrids (NCU-1) took about 2 days using hydro(solvo)thermal reactions.[145] Figure 7 shows a proposed illustration of the NCU-1 structure. For applicability for heavy metal removal, NCU-1 was added to aqueous solutions containing Co, Hg, and Cd (refer to table 5 for more details).

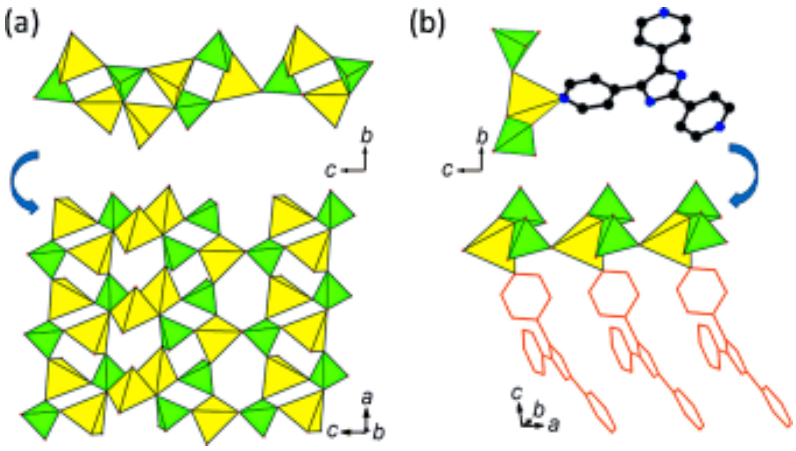

Figure 7. Two types of chains in NCU-1: a) the inorganic $_{\infty}[Zn_4(HPO_4)_2(PO_4)]^+$ chain with three-, four-, and six-membered rings; b) the organic–inorganic hybrid $_{\infty}[Zn(H_2L)(HPO_4)(PO_4)]^-$ chain. Blue and black circles represent N and C atoms, respectively. The H atoms are omitted for clarity.[145] Reprinted from Ref. 145, Copyright 2015, with permission from John Wiley and Sons.

The adsorbent was removed from the water via centrifugation. The NCU-1 was capable of removing metal ions from solutions however, the percentages were quite low (table 5).[145] The authors contribute the non-coordinating N atoms of the 2,4,5-tri(4-pyridyl)-imidazole in the wall of NCU-1 for the interaction with incoming metal ions.[145] The NCU-1 organic-inorganic hybrid showed promise for environmental applicability but more research is needed to assess its potential.

In order for organic-inorganic hybrids to be used in large-scale water remediation plants, Arkas *et al* states the technique has to be low cost, marginally non-toxic in reference to the types of chemical used, and have low energy requirements.[148] In effort to meet these requirements, they created an organic-inorganic hybrid through biomimetic silification process in water.[148] The mechanism for sorption kinetics was determined using the batch method. The authors state that the sorption mechanism is directed by electrostatic attractions between the negatively charged silica and positively charged metal ions.[148] Furthermore, the ionic radius of the cation is correlated to the sorption rate of the metal on the silica.[148] With that being said, the larger the ionic radius, the less likely it will remain solvated to compete with the silanols.[149] Zeta potential

measurements were performed as a function of pH and the PEI-silica nanospheres had an isoelectric point around 8 due to the presence of a protonated amino group of the polymer.[148] Sorption isotherms were calculated to study the behavior of adsorption. The PEI-silica nanoparticles were compared to the polymer-free silica nanoparticles. Langmuir-type adsorption occurred for all metal ions (table 5) and the PEI-silica nanoparticles performed better than the polymer-free silica nanoparticles. In addition to heavy metals, the authors tested the PEI-silica nanoparticles for the sorption of polycyclic aromatic hydrocarbon (PAHs). The nanomaterials demonstrated success for sorption of heavy metals and PAHs through electrostatic interactions and the formation of a charge transfer complex between the PAH and tertiary amino groups.[149] More tests are needed to implement these in wastewater treatment. No regenerative studies were mentioned.

Chitosan-based porous organic-inorganic hybrid membranes supported on nylon film were prepared as a proposed metal adsorbent.[144] The inorganic support was glycidoxypropyltrimethoxysilane (GPTMS) and chitosan was used as the organic component.[144] This paper was focused on the synthesis and characterization of these organic-inorganic hybrids. Figure 8 shows a cross section of the membranes.[144] No adsorption studies or kinetics were measured in this study. A few noteworthy mentions regarding the potential application for these membrane structures as adsorbents would be the use of chitosan as the organic component of these hybrid structures. Chitosan is an aminopolysaccharide, (cationic polymer) produced from N-deacetylation of chitin.[150] It has high content of amino groups ($-NH_2$) and hydroxyl groups ($-OH$) which make it a good binder toward heavy metals.[150] The use of a membrane increases the compatibility between the organic and inorganic polymers making the hybrid structure stable.[144]

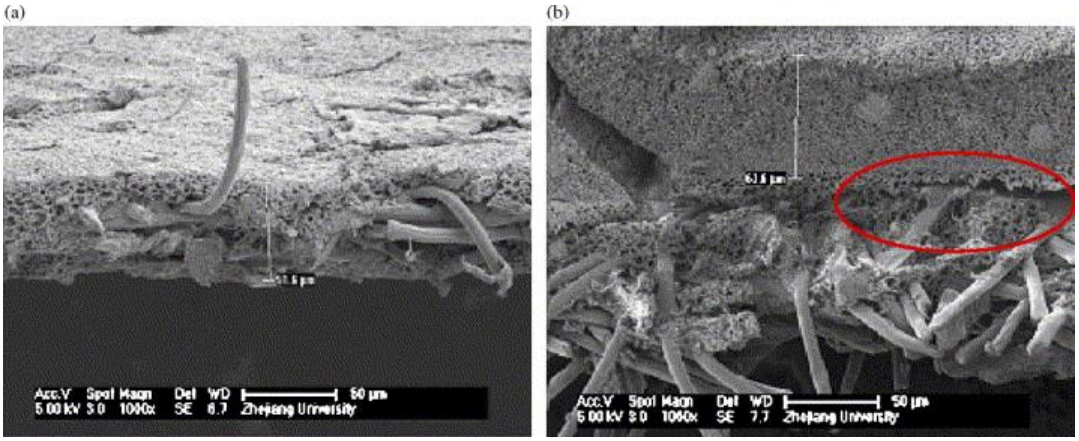

Figure 8. SEM of cross-section of nylon membrane (a) and hybrid membrane imprinted with 15% PEG 20 000 (b). Scale bar for (a) 51.6 μm; (b) 61.6 μm (magnification: 1000).[144] Reprinted from Ref. 144, Copyright 2015, with permission from Elsevier.

The stable organic-inorganic support and use of chitosan would make this a very good potential adsorbent for heavy metal removal. Since this review is focused on inorganic nanoadsorbents removing heavy metal ions from water, no further discussion will take place.

The use of precious metals such as Pd (II) has increased in many fields and its applications include jewelry, electronics, medical devices etc. Human health risks have emerged due to the ability of Pd (II) to react with proteins, DNA, thiol-containing aminos, and cause cellular damage. Therefore, the release and accumulation of Pd (II) into the environment is a growing concern. Awual *et al* presented a study where they demonstrated Pd (II) detection and removal using a functionalized ligand immobilized nano-conjugate adsorbent based on organic-inorganic combination.[151]

The DHDM ligand was then immobilized in mesoporous silica under vacuum creating the functionalzed ligand immobilized nano-conjugate adsorbent (NCA).[151] Sorption experiments for NCA were performed via single batch and multi-component methods. The effect of pH was studied and the temperature was constant (refer to table 5 for details). A filtration system was used to remove the sorbent from solution after each time interval. Kinetics were measured and

evaluated at different Pd (II) ion concentrations. NCA was reused in multiple cycles in order to test the recyclability and its long-term use. The maximum adsorption for Pd (II) was at pH 1.5 which is considerably lower than industrial wastewater (6-9).[60] The authors noticed the formation of hydroxyl and hydroxyl-chloride species when the pH was adjusted to 5.[151] In order to understand the behavior of adsorption processes occurring with NCA and Pd(II), isotherms were employed. The NCA adsorption data fit well to the Langmuir isotherm which implies that the interaction between the PD(II) ions and NCA is classified as monolayer coverage.[151] The presence of other ions in relation to Pd(II) adsorption onto NCA was investigated. The studies included mixing Cu^{2+}, Zn^{2+}, Ag^{+}, Al^{3+},Cd^{2+}, Co^{2+}, Fe^{3+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Ca^{2+}, Ru^{3+} and Pt^{2+} with Pd(II) ions. It can be said with confidence that the Pd(II) adsorption on to the surface of NCA was not affected by the presence of these ions.[151] A solution of thiourea and HCl was used to aid the process and after 10 cycles the sorption efficiency was marginally lower.[151] This study presented an organic-inorganic adsorbent, NCA, for Pd (II) detection and recovery.[151] The novelty of this adsorbent is that it can simultaneously detect and removed Pd (II) from water. Regenerative and interference ion studies suggest that it could be suitable for acidic environmental applications. However the versatility of this adsorbent for other metals is hindered by the maximum adsorption pH value of 1.5, which is considerably lower than typical wastewater conditions.

These next generation nanoadsorbents have increased innovation for environmental remediation of heavy metals in solution. The creative design and versatility of these adsorbents allow for simultaneous detection and removal for heavy metals as previously discussed. According to Sanchez *et al*, the integration of organic and inorganic nanomaterials produces a high level of elementary functions in a small volume. [152] The general physical properties of these

hybrids are thermal stability, superior mechanical properties, permeability, electronic properties and can be found in an excellent article published by Sanchez *et al*.[152]

4 Conclusions and Prospects

Over the last decade, considerable research on the use of inorganic nanoadsorbents for adsorption of heavy metals has shown great progress. The use of adsorbents addresses the need for viable, simple solutions for heavy metal removal worldwide.

The survey of 155 articles (2004-2014) provides evidence that work is being done to remove heavy metals from wastewater using inorganic nanoadsorbents. It is clear that metal oxides and CNTs are the most widely studied and utilized materials as nanoadsorbents for heavy metal removal in aqueous solutions. Most notably, ZnO hollow nanospheres[127] and ZnO nanoplates[132] showed complete removal of Cu (II) in aqueous solutions. Hierarchical structures such as flower-like shapes of Fe_2O_3,[46, 72, 78] titanium.[107] were engineered to enhance the properties of metal oxides for heavy metal removal. Each of these unique hierarchical type structures demonstrated enhanced adsorption capabilities when compared to non-modified nanoparticles.

The increased popularity of the use of polymeric nanoadsorbents to remove heavy metals from solution has also shown great promise for practical industrial applications. Kumar *et al* demonstrated the capabilities of synthesized Al- and Fe-doped polymeric nanocomposite, PH_22_BM_A, through the dramatic and efficient loadings of fluoride (100 mg/g) and arsenic (V) 40 mg/g.[25] The polymeric nanoadsorbent was synthesized in effort to prepare a multi-functional adsorbent for water treatment.[25]

One of the most important parameters of an adsorbent is the ability for regeneration and reuse. This is especially important from an economic perspective when converting to large scale industrial settings. Overall, the Fe_xO_x nanomaterials showed the greatest ability for regeneration.

Most notably, Hu *et al* was able to regenerate spent magnetite nanoparticles up to 6 cycles to remove Cr (VI) from wastewater effluent.[153] The CNTs showed great potential as adsorbents for a wide range of heavy metals including radioactive elements.[154] However, there was very limited research on CNT regeneration or exhaustion. Titanium dioxide showed the most promise for regeneration, particularly the work performed by Hu *et al*, where no exhaustion of the TiO_2 was observed after numerous cycles in multiple metal solutions.[114] Luo *et al* regenerated spent TiO_2 for 21 cycles for As (III) removal from industrial wastewater.[111] Like the CNTs, more research is needed to improve the recyclability of ZnO, and polymeric nanoparticles. For future work with these materials, it is important that regeneration studies be conducted so that the ability of these materials to be reused is understood.

Despite their wide use, nanoparticles can inadvertently cause secondary pollution due to their small size and "hard to separate" suspensions in aqueous solutions.[127] This inability to separate can influence the mobility and bioavailability of heavy metals in the environment. This can cause an increase in the toxicity of the nanomaterials and cause side effects. The next generation adsorbents, organic-inorganic hybrids, are a viable solution to the limitations of the use of nanoparticles. The organic-inorganic hybrid combines the properties of organic functional groups and utilizes the stable inorganic supports to create a novel hybrid capable of removing heavy metal ions from water. Section 3.1 provided the most recent advances of heavy metal removal utilizing the novel properties of these structures.

Despite their limitations, inorganic nanoadsorbents have proven their applicability to remove heavy metals from aqueous and real world samples. Alternative techniques to adsorption include membrane filtration, chemical precipitation, electrochemical methods and ion exchange but their use can become costly and cause other forms of secondary pollution. By addressing the

limitations of recyclability and separation, the use of nanoadsorbents for heavy metal removal is a practical, simple, process. Furthermore the flexibility in design as shown through the many examples of flowers, tubes, spheres and nanocomposites as well as the ability to functionalize the surface of the nanoadsorbents, gives great promise for use as a global water treatment technology.

5 References

1. Fu, F.; Wang, Q., Removal of heavy metal ions from wastewaters: a review. *J. Environ. Manage.* **2011,** *92*, (3), 407-418.
2. Naser, H. A., Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: A review. *Mar Pollut Bull* **2013,** *72*, 6-13.
3. Mendoza, O. T.; Hernández, M. A. A.; Abundis, J. G.; Mundo, N. F., Geochemistry of leachates from the El Fraile sulfide tailings piles in Taxco, Guerrero, southern Mexico. *Environmental Geochemistry and Health* **2006,** *28*, 243-255.
4. Fu, F.; Wang, Q., Removal of heavy metal ions from wastewaters: A review. *Journal of Environmental Management* **2011,** *92*, (3), 407-418.
5. Naser, H. A., Assessment and management of heavy metal pollution in the marine environment of the Arabian Gulf: A review. *Mar Pollut Bull* **2013**, 6-13.
6. Nriagu, J. O.; Pacyna, J. M., Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* **1988,** *333*, (12), 134-139.
7. Wang, S.; Mulligan, C. N., Effect of natural organic matter on arsenic release from soils and sediments into groundwater. *Environmental Geochemistry and Health* **2006,** *28*, 197-214.
8. Jr., G. E. B.; Foster, A. L.; Ostergren, J. D., Mineral surfaces and bioavailability of heavy metals: A molecular-scale perspective. *Proc. Natl. Acad. Sci. U. S. A.* **1999,** *96*, 3388-3395.
9. Lim, S.-R.; Schoenung, J. M., Human health and ecological toxicity potentials due to heavy metal content in waste electronic devices with flat panel displays. *Journal of Hazardous Materials* **2010,** *177*, (1–3), 251-259.
10. Karlsson, K.; Viklander, M.; Scholes, L.; Revitt, M., Heavy metal concentrations and toxicity in water and sediment from stormwater ponds and sedimentation tanks. *Journal of Hazardous Materials* **2010,** *178*, (1–3), 612-618.
11. Madoni, P.; Romeo, M. G., Acute toxicity of heavy metals towards freshwater ciliated protists. *Environmental pollution* **2006,** *141*, (1), 1-7.
12. Agency, U. S. E. P. Water: Drinking Water Contaminants. http://water.epa.gov/drink/contaminants/index.cfm#Inorganic (01/07/2015),
13. Akieh, M. N.; Lahtinen, M.; Vaeisaenen, A.; Sillanpaeae, M., Preparation and characterization of sodium iron titanate ion exchanger and its application in heavy metal removal from waste waters. *J. Hazard. Mater.* **2008,** *152*, (2), 640-647.
14. Ismail, A. A.; Mohamed, R. M.; Ibrahim, I. A.; Kini, G.; Koopman, B., Synthesis, optimization and characterization of zeolite A and its ion-exchange properties. *Colloids Surf., A* **2010,** *366*, (1-3), 80-87.
15. Qiu, W.; Zheng, Y., Removal of lead, copper, nickel, cobalt, and zinc from water by a cancrinite-type zeolite synthesized from fly ash. *Chem. Eng. J. (Amsterdam, Neth.)* **2009,** *145*, (3), 483-488.
16. Dialynas, E.; Diamadopoulos, E., Integration of a membrane bioreactor coupled with reverse osmosis for advanced treatment of municipal wastewater. *Desalination* **2009,** *238*, (1–3), 302-311.
17. Mohsen-Nia, M.; Montazeri, P.; Modarress, H., Removal of Cu2+ and Ni2+ from wastewater with a chelating agent and reverse osmosis processes. *Desalination* **2007,** *217*, (1–3), 276-281.

18. Meunier, N.; Drogui, P.; Montané, C.; Hausler, R.; Mercier, G.; Blais, J.-F., Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate. *Journal of Hazardous Materials* **2006,** *137*, (1), 581-590.
19. Hunsom, M.; Pruksathorn, K.; Damronglerd, S.; Vergnes, H.; Duverneuil, P., Electrochemical treatment of heavy metals (Cu2+, Cr6+, Ni2+) from industrial effluent and modeling of copper reduction. *Water research* **2005,** *39*, (4), 610-616.
20. Deng, Y.; Englehardt, J. D., Electrochemical oxidation for landfill leachate treatment. *Waste Management* **2007,** *27*, (3), 380-388.
21. Rana, P.; Mohan, N.; Rajagopal, C., Electrochemical removal of chromium from wastewater by using carbon aerogel electrodes. *Water research* **2004,** *38*, (12), 2811-2820.
22. Qdais, H. A.; Moussa, H., Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination* **2004,** *164*, (2), 105-110.
23. Yuan, X. Z.; Meng, Y. T.; Zeng, G. M.; Fang, Y. Y.; Shi, J. G., Evaluation of tea-derived biosurfactant on removing heavy metal ions from dilute wastewater by ion flotation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2008,** *317*, (1–3), 256-261.
24. Jang, M.; Chen, W.; Cannon, F. S., Preloading Hydrous Ferric Oxide into Granular Activated Carbon for Arsenic Removal. *Environmental science & technology* **2008,** *42*, (9), 3369-3374.
25. Kumar, V.; Talreja, N.; Deva, D.; Sankararamakrishnan, N.; Sharma, A.; Verma, N., Development of bi-metal doped micro- and nano multi-functional polymeric adsorbents for the removal of fluoride and arsenic(V) from wastewater. *Desalination* **2011,** *282*, 27-38.
26. Buergisser, C. S.; Cernik, M.; Borkovec, M.; Sticher, H., Determination of nonlinear adsorption isotherms from column experiments: an alternative to batch studies. *Environmental science & technology* **1993,** *27*, (5), 943-948.
27. Levan, M. D.; Vermeulen, T., Binary Langmuir and Freundlich Isotherms for Ideal Adsorbed Solutions. *J Phys Chem* **1981,** *85*, 3247-3250.
28. Giles, C. H.; MacEwan, T. H.; Nakhwa, S. N.; Smith, D., Studies in Adsorption. Part XI.* A System of Classi$cation of Solution Adsorption Isotherms, and its Use in Diagnosis of Adsorption Mechanisms and in Measurement of Specific Surface Areas of Solids. *J. Chem. Soc.* **1960**, (0), 3973-3993.
29. Dada, A. O.; Olalekan, A. P.; Olatunya, A. M.; Dada, O., Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rice Husk. *IOSR Journal of Applied Chemistry* **2012,** *3*, (1), 38-45.
30. Karami, H., Heavy metal removal from water by magnetite nanorods. *Chem. Eng. J. (Amsterdam, Neth.)* **2013,** *219*, 209-216.
31. Bailey, S. E.; Olin, T. J.; Bricka, R. M.; Adrian, D. D., A Review of Potentially Low-Cost Sorbents for Heavy Metals. *Water research* **1999,** *33*, (11), 2469-2479.
32. Arshadi, M.; Soleymanzadeh, M.; Salvacion, J. W. L.; SalimiVahid, F., Nanoscale Zero-Valent Iron (NZVI) supported on sineguelas waste for Pb(II) removal from aqueous solution: Kinetics, thermodynamic and mechanism. *J. Colloid Interface Sci.* **2014,** *426*, 241-251.
33. Cheng, Z.; Gao, Z.; Ma, W.; Sun, Q.; Wang, B.; Wang, X., Preparation of magnetic Fe3O4 particles modified sawdust as the adsorbent to remove strontium ions. *Chem. Eng. J. (Amsterdam, Neth.)* **2012,** *209*, 451-457.
34. Gupta, V. K.; Ali, I., Removal of lead and chromium from wastewater using bagasse fly ash-a sugar industry waste. *J. Colloid Interface Sci.* **2004,** *271*, (2), 321-328.

35. Hamadi, N. K.; Chen, X. D.; Farid, M. M.; Lu, M. G. Q., Adsorption kinetics for the removal of chromium(VI) from aqueous solution by adsorbents derived from used tires and sawdust. *Chem. Eng. J. (Amsterdam, Neth.)* **2001,** *84*, (2), 95-105.
36. Kumar, R.; Bishnoi, N. R.; Garima; Bishnoi, K., Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass. *Chem. Eng. J. (Amsterdam, Neth.)* **2008,** *135*, (3), 202-208.
37. Phuengprasop, T.; Sittiwong, J.; Unob, F., Removal of heavy metal ions by iron oxide coated sewage sludge. *J. Hazard. Mater.* **2011,** *186*, (1), 502-507.
38. Rao, M. M.; Reddy, D. H. K. K.; Venkateswarlu, P.; Seshaiah, K., Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste. *J Environ Manage* **2009,** *90*, (1), 634-43.
39. Srivastava, V. C.; Mall, I. D.; Mishra, I. M., Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA). *Chem. Eng. J. (Amsterdam, Neth.)* **2007,** *132*, (1-3), 267-278.
40. Garg, U. K.; Kaur, M. P.; Garg, V. K.; Sud, D., Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. *J. Hazard. Mater.* **2007,** *140*, (1-2), 60-68.
41. Mohan, D.; Singh, K. P.; Singh, V. K., Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth. *Ind. Eng. Chem. Res.* **2005,** *44*, (4), 1027-1042.
42. Kurniawan, T. A.; Sillanpää, M. E. T.; Sillanpää, M., Nanoadsorbents for Remediation of Aquatic Environment: Local and Practical Solutions for Global Water Pollution Problems. *Crit. Rev. Environ. Sci. Technol.* **2012,** *42*, 1233-1295.
43. Savage, N.; Diallo, M., Nanomaterials and Water Purification: Opportunities and Challenges. *Journal of Nanoparticle Research* **2005,** *7*, (4-5), 331-342.
44. Ge, F.; Li, M.-M.; Ye, H.; Zhao, B.-X., Effective removal of heavy metal ions Cd2+, Zn2+, Pb2+, Cu2+ from aqueous solution by polymer-modified magnetic nanoparticles. *J. Hazard. Mater.* **2012,** *211-212*, 366-372.
45. Wang, H.; Chen, Q.-W.; Chen, J.; Yu, B.-X.; Hu, X.-Y., Carboxyl and negative charge-functionalized superparamagnetic nanochains with amorphous carbon shell and magnetic core: synthesis and their application in removal of heavy metal ions. *Nanoscale* **2011,** *3*, (11), 4600-3.
46. Cao, C.-Y.; Qu, J.; Yan, W.-S.; Zhu, J.-F.; Wu, Z.-Y.; Song, W.-G., Low-Cost Synthesis of Flowerlike α-Fe2O3 Nanostructures for Heavy Metal Ion Removal: Adsorption Property and Mechanism. *Langmuir* **2012,** *28*, (9), 4573-4579.
47. Cheng, X.-L.; Jiang, J.-S.; Jin, C.-Y.; Lin, C.-C.; Zeng, Y.; Zhang, Q.-H., Cauliflower-like a-Fe2O3 microstructures: Toluene–water interfaceassisted synthesis, characterization, and applications in wastewater treatment and visible-light photocatalysis. *Chem Eng J* **2014,** *236*, 139-148.
48. Roy, A.; Bhattacharya, J., Removal of Cu(II), Zn(II) and Pb(II) from water using microwave-assisted synthesized maghemite nanotubes. *Chemical Engineering Journal* **2012,** *211-212*, 493-500.
49. Badruddoza, A. Z. M.; Bin Zakir Shawon, Z.; Rahman, M. T.; Hao, K. W.; Hidajat, K.; Uddin, M. S., Ionically modified magnetic nanomaterials for arsenic and chromium removal from water. *Chem. Eng. J. (Amsterdam, Neth.)* **2013,** *225*, 607-615.
50. Lei, Y.; Chen, F.; Luo, Y.; Zhang, L., Three-dimensional magnetic graphene oxide foam/Fe3O4 nanocomposite as an efficient absorbent for Cr(VI) removal. *J. Mater. Sci.* **2014,** *49*, (12), 4236-4245.

51. Tan, L.; Xu, J.; Xue, X.; Lou, Z.; Zhu, J.; Baig, S. A.; Xu, X., Multifunctional nanocomposite Fe3O4@SiO2-mPD/SP for selective removal of Pb(II) and Cr(VI) from aqueous solutions. *RSC Adv.* **2014,** *4*, (86), 45920-45929.
52. Ngomsik, A.-F.; Bee, A.; Talbot, D.; Cote, G., Magnetic solid-liquid extraction of Eu(III), La(III), Ni(II) and Co(II) with maghemite nanoparticles. *Sep. Purif. Technol.* **2012,** *86*, 1-8.
53. Shipley, H.; Yean, S.; Kan, A.; Tomson, M., A sorption kinetics model for arsenic adsorption to magnetite nanoparticles. *Environ Sci Pollut Res* **2010,** *17*, (5), 1053-1062.
54. Roy, A.; Bhattacharya, J., A binary and ternary adsorption study of wastewater Cd(II), Ni(II) and Co(II) by γ-Fe2O3 nanotubes. *Sep. Purif. Technol.* **2013,** *115*, 172-179.
55. Karami, H.; Chidar, E., Pulsed-electrochemical synthesis and characterizations of magnetite nanorods. *Int. J. Electrochem. Sci.* **2012,** *7*, 2077-2090.
56. Warner, C. L.; Addleman, R. S.; Cinson, A. D.; Droubay, T. C.; Engelhard, M. H.; Nash, M. A.; Yantasee, W.; Warner, M. G., High-Performance, Superparamagnetic, Nanoparticle-Based Heavy Metal Sorbents for Removal of Contaminants from Natural Waters. *ChemSusChem* **2010,** *3*, (6), 749-757.
57. Sun, S.; Zeng, H.; Robinson, D. B.; Raoux, S.; Rice, P. M.; Wang, S. X.; Li, G., Monodisperse MFe_2O_4 (M = Fe, Co, Mn) Nanoparticles. *JACS* **2003,** *126*, 273-279.
58. Kang, Y. S.; Rishud, S.; Rabolt, J. F.; Stroeve, P., Synthesis and characterization of nanoparticle-size Fe3O4 and g-Fe2O3 particles. *Chem Mater* **1996,** *8*, 2209–2211.
59. Hu, J.; Chen, G.; Lo, I. M. C., Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles. *Water Res.* **2005,** *39*, (18), 4528-4536.
60. Acheampong, M. A.; Meulepasa, R. J. W.; Lens, P. N. L., Removal of heavymetals and cyanide from gold mine wastewater. *J Chem Technol Biotechnol* **2009,** *85*, 590-613.
61. Qi, X.; Li, N.; Xu, Q.; Chen, D.; Li, H.; Lu, J., Water-soluble Fe_3O_4 superparamagnetic nanocomposites for the removal of low concentration mercury(II) ions from water. *RSC Adv.* **2014,** *4*, (88), 47643-47648.
62. Khaydarov, R. A.; Khaydarov, R. R.; Gapurova, O., Water purification from metal ions using carbon nanoparticle-conjugated polymer nanocomposites. *Water Res.* **2010,** *44*, (6), 1927-1933.
63. Park, J.; An, K.; Hwang, Y.; Park, J.-G.; Noh, H.-J.; Kim, J.-Y.; Park, J.-H.; Hwang, N.-M.; Hyeon, T., Ultra-large-scale syntheses of monodisperse nanocrystals. *Nature Materials* **2004,** *3*, 891-895.
64. Jiang, J.; Gu, H.; Shao, H.; Devlin, E.; Papaefthymiou, G. C.; Ying, J. Y., Bifunctional Fe3O4–Ag Heterodimer Nanoparticles for Two-Photon Fluorescence Imaging and Magnetic Manipulation. *Advanced Materials* **2008,** *20*, (23), 4403-4407.
65. Feitoza, N. C.; Goncalves, T. D.; Mesquita, J. J.; Menegucci, J. S.; Santos, M.-K. M. S.; Chaker, J. A.; Cunha, R. B.; Medeiros, A. M. M.; Rubim, J. C.; Sousa, M. H., Fabrication of glycine-functionalized maghemite nanoparticles for magnetic removal of copper from wastewater. *J. Hazard. Mater.* **2014,** *264*, 153-160.
66. Hanif, S.; Shahzad, A., Removal of chromium(VI) and dye Alizarin Red S (ARS) using polymer-coated iron oxide (Fe3O4) magnetic nanoparticles by co-precipitation method. *J. Nanopart. Res.* **2014,** *16*, (6), 1-15.
67. He, F.; Wang, W.; Moon, J.-W.; Howe, J.; Pierce, E. M.; Liang, L., Rapid removal of Hg(II) from aqueous solutions using thiol-functionalized Zn-doped biomagnetite particles. *ACS Appl. Mater. Interfaces* **2012,** *4*, (8), 4373-4379.

68. Yong-Mei, H.; Man, C.; Zhong-Bo, H., Effective removal of Cu (II) ions from aqueous solution by amino-functionalized magnetic nanoparticles. *J Hazard Mater* **2010,** *184*, 392-399.
69. Liu, J.-f.; Zhao, Z.-s.; Jiang, G.-b., Coating Fe3O4 Magnetic Nanoparticles with Humic Acid for High Efficient Removal of Heavy Metals in Water. *Environ. Sci. Technol.* **2008,** *42*, (18), 6949-6954.
70. Yantasee, W.; Warner, C. L.; Sangvanich, T.; Addleman, R. S.; Carter, T. G.; Wiacek, R. J.; Fryxell, G. E.; Timchalk, C.; Warner, M. G., Removal of Heavy Metals from Aqueous Systems with Thiol Functionalized Superparamagnetic Nanoparticles. *Environ. Sci. Technol.* **2007,** *41*, (14), 5114-5119.
71. Song, J.; Kong, H.; Jang, J., Adsorption of heavy metal ions from aqueous solution by polyrhodanine-encapsulated magnetic nanoparticles. *Journal of colloid and interface science* **2011,** *359*, (2), 505-11.
72. Liang, H.; Xu, B.; Wang, Z., Self-assembled 3D flower-like α-Fe2O3 microstructures and their superior capability for heavy metal ion removal. *Mater. Chem. Phys.* **2013,** *141*, (2-3), 727-734.
73. Shipley, H.; Engates, K.; Grover, V., Removal of Pb(II), Cd(II), Cu(II), and Zn(II) by hematite nanoparticles: effect of sorbent concentration, pH, temperature, and exhaustion. *Environ Sci Pollut Res* **2013,** *20*, (3), 1727-1736.
74. Grover, V. A.; Hu, J.; Engates, K. E.; Shipley, H. J., Adsorption and desorption of bivalent metals to hematite nanoparticles. *Environmental Toxicology and Chemistry* **2012,** *31*, (1), 86-92.
75. Koo, H. Y.; Lee, H.-J.; Go, H.-A.; Lee, Y. B.; Bae, T. S.; Kim, J. K.; Choi, W. S., Graphene-Based Multifunctional Iron Oxide Nanosheets with Tunable Properties. *Chem. - Eur. J.* **2011,** *17*, (4), 1214-1219, S1214/1-S1214/10.
76. Fei, J.; Cui, Y.; Zhao, J.; Gao, L.; Yang, Y.; Li, J., Large-scale preparation of 3D self-assembled iron hydroxide and oxide hierarchical nanostructures and their applications for water treatment. *Journal of Materials Chemistry* **2011,** *21*, (32), 11742-11746.
77. Zhong, L.-S.; Hu, J.-S.; Cao, A.-M.; Liu, Q.; Song, W.-G.; Wan, L.-J., 3D Flowerlike Ceria Micro/Nanocomposite Structure and Its Application for Water Treatment and CO Removal. *Chem. Mater.* **2007,** *19*, (7), 1648-1655.
78. Zhong, L.-S.; Hu, J.-S.; Liang, H.-P.; Cao, A.-M.; Song, W.-G.; Wan, L.-J., Self-Assembled 3D Flowerlike Iron Oxide Nanostructures and Their Application in Water Treatment. *Advanced Materials 18*, 2426-2431.
79. Giménez, J.; Martínez, M.; de Pablo, J.; Rovira, M.; Duro, L., Arsenic sorption onto natural hematite, magnetite, and goethite. *Journal of Hazardous Materials* **2007,** *141*, (3), 575-580.
80. Jeon, B.-H.; Dempsey, B. A.; Burgos, W. D.; Royer, R. A.; Roden, E. E., Modeling the sorption kinetics of divalent metal ions to hematite. *Water research* **2004,** *38*, (10), 2499-2504.
81. Mamindy-Pajany, Y.; Hurel, C.; Marmier, N.; Roméo, M., Arsenic (V) adsorption from aqueous solution onto goethite, hematite, magnetite and zero-valent iron: Effects of pH, concentration and reversibility. *Desalination* **2011,** *281*, (0), 93-99.
82. Cotten, G. B.; Eldredge, H. B., Nanolevel Magnetic Separation Model Considering Flow Limitations. *Separation Science and Technology* **2002,** *37*, (16), 3755-3779.
83. Parham, H.; Rahbar, N., Solid phase extraction–spectrophotometric determination of fluoride in water samples using magnetic iron oxide nanoparticles. *Talanta* **2009,** *80*, (2), 664-669.

84. Di, Z.-C.; Ding, J.; Peng, X.-J.; Li, Y.-H.; Luan, Z.-K.; Liang, J., Chromium adsorption by aligned carbon nanotubes supported ceria nanoparticles. *Chemosphere* **2006,** *62*, 861-865.
85. Zhang, Y.; Yang, M.; Huang, X., Arsenic(V) removal with a Ce(IV)-doped iron oxide adsorbent. *Chemosphere* **2003,** *51*, (9), 945-952.
86. Tokunaga, S.; Hardon, M. J.; Wasay, S. A., Removal of fluoride ions from aqueous solution by multivalent metal compounds. *Int. J. Environ. Studies* **1995,** *48*, (1), 17-28.
87. Cao, A.; Zhu, H.; Zhang, X.; Li, X.; Ruan, D.; Xu, C.; Wei, B.; Liang, J., Hydrogen storage of dense-aligned carbon nanotubes. *Chem. Phys. Lett.* **2001,** *342*, 510-514.
88. Recillas, S.; Colon, J.; Casals, E.; Gonzalez, E.; Puntes, V.; Sanchez, A.; Font, X., Chromium VI adsorption on cerium oxide nanoparticles and morphology changes during the process. *J. Hazard. Mater.* **2010,** *184*, (1-3), 425-431.
89. Sun, W.; Li, Q.; Gao, S.; Shang, J. K., Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles: Part B. Integration with silica monoliths and dynamic treatment. *Chemical Engineering Journal* **2012,** *185–186*, (0), 136-143.
90. Cao, C.-Y.; Cui, Z.-M.; Chen, C.-Q.; Song, W.-G.; Cai, W., Ceria Hollow Nanospheres Produced by a Template-Free Microwave-Assisted Hydrothermal Method for Heavy Metal Ion Removal and Catalysis. *J. Phys. Chem. C* **2010,** *114*, (21), 9865-9870.
91. Gupta, V. K.; Agarwal, S.; Saleh, T. A., Chromium removal by combining the magnetic properties of iron oxide with adsorption properties of carbon nanotubes. *Water research* **2011,** *45*, 2207-2212.
92. Iijima, S., Helical Microtubules of Graphitic Carbon. *Letters to Nature* **1991,** *354*, 56-58.
93. Bottini, M.; Bruckner, S.; Nika, K.; Bottini, N.; Bellucci, S.; Magrini, A.; Bergamaschi, A.; Mustelin, T., Multi-walled carbon nanotubes induce T lymphocyte apoptosis. *Toxicology Letters* **2006,** *160*, (2), 121-126.
94. Muller, J.; Huaux, F.; Lison, D., Respiratory toxicity of carbon nanotubes: How worried should we be? *Carbon* **2006,** *44*, (6), 1048-1056.
95. Tofighy, M. A.; Mohammadi, T., Adsorption of divalent heavy metal ions from water using carbon nanotube sheets. *J. Hazard. Mater.* **2011,** *185*, (1), 140-147.
96. Poland, C. A.; Duffin, R.; Kinloch, I.; Maynard, A.; Wallace, W. A. H.; Seaton, A.; Stone, V.; Brown, S.; MacNee, W.; Donaldson, K., Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nat Nano* **2008,** *3*, (7), 423-428.
97. Smith, C. J.; Shaw, B. J.; Handy, R. D., Toxicity of single walled carbon nanotubes to rainbow trout, (Oncorhynchus mykiss): Respiratory toxicity, organ pathologies, and other physiological effects. *Aquatic Toxicology* **2007,** *82*, (2), 94-109.
98. Rao, G. P.; Lu, C.; Su, F., Sorption of divalent metal ions from aqueous solution by carbon nanotubes: A review. *Sep. Purif. Technol.* **2007,** *58*, 224-231.
99. Moghaddam, H. K.; Pakizeh, M., Experimental study on mercury ions removal from aqueous solution by MnO2/CNTs nanocomposite adsorbent. *J. Ind. Eng. Chem. (Amsterdam, Neth.)* **2014**, Ahead of Print.
100. Gupta, V. K.; Agarwal, S.; Saleh, T. A., Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *J Hazard Mater* **2011,** *185*, 17-23.
101. Chen, C. L.; Wang, X. K.; Nagatsu, M., Europium adsorption on multiwall carbon nanotube/iron oxide magnetic composite in the presence of polyacrylic acid. *Environmental science & technology* **2011,** *185*, 17-23.

102. Debnath, S.; Ghosh, U. C., Equilibrium modeling of single and binary adsorption of Cd(II) and Cu(II) onto agglomerated nano structured titanium(IV) oxide. *Desalination* **2011,** *273*, (2-3), 330-342.
103. Guan, X.; Du, J.; Meng, X.; Sun, Y.; Sun, B.; Hu, Q., Application of titanium dioxide in arsenic removal from water: A review. *J. Hazard. Mater.* **2012,** *215-216*, 1-16.
104. Bavykin, D. V.; Friedrich, J. M.; Walsh, F. C., Protonated Titanates and TiO2 Nanostructured Materials: Synthesis, Properties, and Applications. *Advanced Materials* **2006,** *18*, (21), 2807-2824.
105. Lin, C.-H.; Wong, D. S.-H.; Lu, S.-Y., Layered Protonated Titanate Nanosheets Synthesized with a Simple One-Step, Low-Temperature, Urea-Modulated Method as an Effective Pollutant Adsorbent. *ACS Appl. Mater. Interfaces* **2014,** *6*, (19), 16669-16678.
106. Yang, D.; Zheng, Z.; Liu, H.; Zhu, H.; Ke, X.; Xu, Y.; Wu, D.; Sun, Y., Layered Titanate Nanofibers as Efficient Adsorbents for Removal of Toxic Radioactive and Heavy Metal Ions from Water. *J. Phys. Chem. C* **2008,** *112*, (42), 16275-16280.
107. Huang, J.; Cao, Y.; Liu, Z.; Deng, Z.; Tang, F.; Wang, W., Efficient removal of heavy metal ions from water system by titanate nanoflowers. *Chem. Eng. J. (Amsterdam, Neth.)* **2012,** *180*, 75-80.
108. Lee, Y.-C.; Yang, J.-W., Self-assembled flower-like TiO2 on exfoliated graphite oxide for heavy metal removal. *J. Ind. Eng. Chem. (Amsterdam, Neth.)* **2012,** *18*, (3), 1178-1185.
109. Byrne, H. E.; Mazyck, D. W., Removal of trace level aqueous mercury by adsorption and photocatalysis on silica-titania composites. *J. Hazard. Mater.* **2009,** *170*, (2-3), 915-919.
110. Sharma, A.; Lee, B.-K., Cd(II) removal and recovery enhancement by using acrylamide–titanium nanocomposite as an adsorbent. *Appl Sur Sci* **2014,** *313*, 624-632.
111. Luo, T.; Cui, J.; Hu, S.; Huang, Y.; Jing, C., Arsenic Removal and Recovery from Copper Smelting Wastewater Using TiO2. *Environmental science & technology* **2010,** *44*, (23), 9094-9098.
112. Pena, M.; Meng, X.; Korfiatis, G. P.; Jing, C., Adsorption Mechanism of Arsenic on Nanocrystalline Titanium Dioxide. *Environmental science & technology* **2006,** *40*, (4), 1257-1262.
113. Engates, K. E.; Shipley, H. J., Adsorption of Pb, Cd, Cu, Zn, and Ni to titanium dioxide nanoparticles: effect of particle size, solid concentration, and exhaustion. *Environ. Sci. Pollut. Res.* **2011,** *18*, (3), 386-395.
114. Hu, J.; Shipley, H., Regeneration of spent TiO2 nanoparticles for Pb (II), Cu (II), and Zn (II) removal. *Environ Sci Pollut Res* **2013,** *20*, (8), 5125-5137.
115. Rafatullah, M.; Sulaiman, O.; Hashim, R.; Ahmad, A., Adsorption of copper (II), chromium (III), nickel (II) and lead (II) ions from aqueous solutions by meranti sawdust. *Journal of Hazardous Materials* **2009,** *170*, (2–3), 969-977.
116. Yang, D. J.; Zheng, Z. F.; Zhu, H. Y.; Liu, H. W.; Gao, X. P., Titanate Nanofibers as Intelligent Absorbents for the Removal of Radioactive Ions from Water. *Advanced Materials* **2008,** *20*, (14), 2777-2781.
117. Bancroft, G. M.; Metson, J. B.; Kanetkar, S. M.; Brown, J. D., Surface studies on a leached sphene glass. *Nature* **1982,** *299*, 708-710.
118. Tang, Y.; Gong, D.; Lai, Y.; Shen, Y.; Zhang, Y.; Huang, Y.; Tao, J.; Lin, C.; Dong, Z.; Chen, Z., Hierarchical layered titanate microspherulite: formation by electrochemical spark discharge spallation and application in aqueous pollutant treatment. *Journal of Materials Chemistry* **2010,** *20*, (45), 10169-10178.

119. Sharma, A. K.; Lee, B.-K., Lead sorption onto acrylamide modified titanium nanocomposite from aqueous media. *Journal of Environmental Management* **2013,** *128*, (0), 787-797.
120. Yang, K.; Xing, B., Sorption of Phenanthrene by Humic Acid-Coated Nanosized TiO2 and ZnO. *Environmental science & technology* **2009,** *43*, (6), 1845-1851.
121. Chen, Q.; Yin, D.; Zhu, S.; Hu, X., Adsorption of cadmium(II) on humic acid coated titanium dioxide. *Journal of colloid and interface science* **2012,** *367*, 241-248.
122. Aguado, J.; van Grieken, R.; López-Muñoz, M.-J.; Marugán, J., A comprehensive study of the synthesis, characterization and activity of TiO2 and mixed TiO2/SiO2 photocatalysts. *Applied Catalysis A: General* **2006,** *312*, (0), 202-212.
123. Magrez, A.; Horváth, L.; Smajda, R.; Salicio, V.; Pasquier, N.; Forró, L.; Schwaller, B., Cellular Toxicity of TiO2-Based Nanofilaments. *ACS Nano* **2009,** *3*, (8), 2274-2280.
124. Gerloff, K.; Fenoglio, I.; Carella, E.; Kolling, J.; Albrecht, C.; Boots, A. W.; Förster, I.; Schins, R. P. F., Distinctive Toxicity of TiO2 Rutile/Anatase Mixed Phase Nanoparticles on Caco-2 Cells. *Chemical Research in Toxicology* **2012,** *25*, (3), 646-655.
125. Zhu, X.; Zhou, J.; Cai, Z., TiO2 Nanoparticles in the Marine Environment: Impact on the Toxicity of Tributyltin to Abalone (Haliotis diversicolor supertexta) Embryos. *Environmental science & technology* **2011,** *45*, (8), 3753-3758.
126. Flytzani-Stephanopoulos, M.; Sakbodin, M.; Wang, Z., Regenerative Adsorption and Removal of H2S from Hot Fuel Gas Streams by Rare Earth Oxides. *Science* **2006,** *312*, (5779), 1508-1510.
127. Wang, X.; Cai, W.; Liu, S.; Wang, G.; Wu, Z.; Zhao, H., ZnO hollow microspheres with exposed porous nanosheets surface: Structurally enhanced adsorption towards heavy metal ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2013,** *422*, (0), 199-205.
128. Sheela, T.; Nayaka, Y. A.; Viswanatha, R.; Basavanna, S.; Venkatesha, T. G., Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles. *Powder Technology* **2012,** *217*, (0), 163-170.
129. Erdem, E.; Karapinar, N.; Donat, R., The removal of heavy metal cations by natural zeolites. *Journal of colloid and interface science* **2004,** *280*, (2), 309-314.
130. Salehi, R.; Arami, M.; Mahmoodi, N. M.; Bahrami, H.; Khorramfar, S., Novel biocompatible composite (Chitosan-zinc oxide nanoparticle): Preparation, characterization and dye adsorption properties. *Colloids Surf., B* **2010,** *80*, (1), 86-93.
131. Jing, Z.; Zhan, J., Fabrication and Gas-Sensing Properties of Porous ZnO Nanoplates. *Advanced Materials* **2008,** *20*, (23), 4547-4551.
132. Wang, X.; Cai, W.; Lin, Y.; Wang, G.; Liang, C., Mass production of micro/nanostructured porous ZnO plates and their strong structurally enhanced and selective adsorption performance for environmental remediation. *J. Mater. Chem.* **2010,** *20*, (39), 8582-8590.
133. Ballerini, G.; Ogle, K.; Barthés-Labrousse, M. G., The acid–base properties of the surface of native zinc oxide layers: An XPS study of adsorption of 1,2-diaminoethane. *Applied Surface Science* **2007,** *253*, (16), 6860-6867.
134. Ma, X.; Wang, Y.; Gao, M.; Xu, H.; Li, G., A novel strategy to prepare ZnO/PbS heterostructured functional nanocomposite utilizing the surface adsorption property of ZnO nanosheets. *Catal. Today* **2010,** *158*, (3-4), 459-463.

135. Khan, S. B.; Rahman, M. M.; Marwani, H. M.; Asiri, A. M.; Alamry, K. A., An assessment of zinc oxide nanosheets as a selective adsorbent for cadmium. *Nanoscale Research Letters* **2013,** *8*, (1), 377-377.
136. Kikuchi, Y.; Qian, Q.; Machida, M.; Tatsumoto, H., Effect of ZnO loading to activated carbon on Pb(II) adsorption from aqueous solution. *Carbon* **2005,** *44*, (2), 195-202.
137. Amiri, O.; Emadi, H.; Hosseinpour-Mashkani, S. S. M.; Sabet, M.; Rad, M. M., Simple and surfactant free synthesis and characterization of CdS/ZnS core-shell nanoparticles and their application in the removal of heavy metals from aqueous solution. *RSC Adv.* **2014,** *4*, (21), 10990-10996.
138. Amiri, O.; Hosseinpour-Mashkani, S. M.; Mohammadi Rad, M.; Abdvali, F., Sonochemical synthesis and characterization of CdS/ZnS core-shell nanoparticles and application in removal of heavy metals from aqueous solution. *Superlattices Microstruct.* **2014,** *66*, 67-75.
139. Hua, M.; Zhang, S.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q., Heavy metal removal from water/wastewater by nanosized metal oxides:A review. *J Hazard Mater* **2012,** *211-212*, 317-331.
140. Pan, B.; Pan, B.; Zhang, W.; Lv, L.; Zhang, Q.; Zheng, S., Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chemical Engineering Journal* **2009,** *151*, (1–3), 19-29.
141. Kunin, R., The use of macroreticular polymeric adsorbents for the treatment of waste effluents. *Pure Appl Chem* **1976,** *46*, 205-211.
142. Vauthier, C.; Bouchemal, K., Methods for the Preparation and Manufacture of Polymeric Nanoparticles. *Pharm Res* **2009,** *26*, (5), 1025-1058.
143. von Werne, T.; Patten, T. E., Preparation of Structurally Well-Defined Polymer−Nanoparticle Hybrids with Controlled/Living Radical Polymerizations. *Journal of the American Chemical Society* **1999,** *121*, (32), 7409-7410.
144. Xi, F.; Wu, J.; Lin, X., Novel nylon-supported organic-inorganic hybrid membrane with hierarchical pores as a potential immobilized metal affinity adsorbent. *J. Chromatogr. A* **2006,** *1125*, (1), 38-51.
145. Wang, C.-M.; Lee, L.-W.; Chang, T.-Y.; Chen, Y.-C.; Lin, H.-M.; Lu, K.-L.; Lii, K.-H., Organic-Inorganic Hybrid Zinc Phosphate with 28-Ring Channels. *Chem. - Eur. J.* **2015,** *21*, (5), 1878-1881.
146. Moore, P. B.; Shen, J., An X-ray structural study of cacoxenite, a mineral phosphate. *Nature* **1983,** *306*, 356-357.
147. Davis, M. E.; Saldarriaga, C.; Montes, C.; Garces, J.; Crowdert, C., A molecular sieve with eighteen-membered rings. *Nature* **1988,** *331*, 698-699.
148. Arkas, M.; Tsiourvas, D., Organic/inorganic hybrid nanospheres based on hyperbranched poly(ethylene imine) encapsulated into silica for the sorption of toxic metal ions and polycyclic aromatic hydrocarbons from water. *J. Hazard. Mater.* **2009,** *170*, (1), 35-42.
149. Silva, L. C. C. d.; Santos, L. B. O. d.; Abate, G.; Cosentino, I. C.; Fantini, M. C. A.; Masini, J. C.; Matos, J. R., Adsorption of Pb2+, Cu2+ and Cd2+ in FDU-1 silica and FDU-1 silica modified with humic acid. *Microporous and Mesoporous Materials* **2008,** *110*, 250-259.
150. Lazaridis, N. K.; Kyzas, G. Z.; Vassiliou, A. A.; Bikiaris, D. N., Chitosan Derivatives as Biosorbents for Basic Dyes. *Langmuir* **2007,** *23*, 7634-7643.
151. Awual, M. R.; Hasan, M. M.; Znad, H., Organic-inorganic based nano-conjugate adsorbent for selective palladium(II) detection, separation and recovery. *Chem. Eng. J. (Amsterdam, Neth.)* **2015,** *259*, 611-619.

152. Sanchez, C.; Julian, B.; Belleville, P.; Popall, M., Applications of hybrid organic-inorganic nanocomposites. *Journal of Materials Chemistry* **2005,** *15*, (35-36), 3559-3592.
153. Hu, H.; Wang, Z.; Pan, L., Synthesis of monodisperse Fe3O4@silica core-shell microspheres and their application for removal of heavy metal ions from water. *J. Alloys Compd.* **2009,** *492*, (1-2), 656-661.
154. Shao, D.; Hu, J.; Wang, X., Plasma induced grafting multiwalled carbon nanotube with chitosan and its application for removal of UO2+2, Cu2+, and Pb2+ from aqueous solutions. *Plasma Processes Polym.* **2010,** *7*, (12), 977-985.

Tables

Table 1 FexOx Nanoadsorbents used for Heavy metal removal

	Shape and size (nm)	Surface Area (m^2/g)	Optimal pH	Magnetic Saturation (emu/g)	Targeted Heavy metals	Isotherm model or sorption capacity	Performance	Regenerative/Number of cycles	Sample Matrix	Ref
Iron Oxide-Magnetite (Fe_3O_4) and Maghemite (γ-Fe_2O_4)										
Fe_3O_4 nanoparticle	spheres; 19.3	60	8	–	As (V)	Langmuir q_m (mg/g)	1.19	–	groundwater and spiked tap water	53
					As (III)		1.13			
γ-Fe_2O_3	spheres; 10	178	2.5	3.3	Cr (VI)	Freundlich q_e (mg/g)	19.2	yes/6	effluent from metal processing plant	59
Fe_3O_4 nanorods	rods; 55-65, length 900-1000		5.5	89	Fe(II)	Langmuir (mg/g)	127.01	yes/5	metal ions from aqueous solution	30
					Pb(II)		112.86			
					Zn(II)		107.27			
					Ni(II)		95.42			
					Cd(II)		88.39			
					Cu(II)		79.1			
Fe_3O_4-MSPNPs	spheres; 13	–	7	N/A	Hg (II)	Langmuir (mg/g)	36.495	yes/3	metal ions from aqueous solution and spiked Jinji Lake water	61
Fe_3O_4-MBA	spheres; 7.9 ± 1.2	108	7.8	59.8	Co,Cu,Ag,Cd, Hg,Pb,Tl	Sorbent efficiency (10^5 L/S)	Pb>Cu>Ag>Co, Cd>Hg>Tl	–	Spiked Colombia River water	56
Fe_3O_4-GSH	spheres; 7.7 ± 1.3	111.6		47.4			Pb>Hg>Cu>Ag>Cd>Co>Tl			
Fe_3O_4-PEG-SH	spheres; 8.2 ± 1.4	86.33		62.5			Pb>Cu>Hg>Ag>Cd>Co>Tl			
Fe_3O_4-DMSA	spheres; 7.2 ± 2	114		53.8			Hg>Pb>Ag>Cu>Tl>Cd>Co			
Fe_3O_4-EDTA	spheres; 8.2 ± 1.3	106.8		66			Hg, Pb, Ag>Cu, Co, Tl>Cd			

Fe_3O_4@APS@AA-co-CA	spheres; 15-20	–	5.5	52	Cd(II)	Langmuir (mg/g)	29.6	yes/4	metal ions from aqueous solution	44
					Zn(II)		43.4			
					Pb(II)		166.1			
					Cu(II)		126.9			
γ-Fe_2O_3 nanotubes	tubes; 10–15, length 150-250	321.638	6	68.7	Cu(II)	Langmuir (mg/g)	111.11	–	metal ions from aqueous solution	48
					Zn(II)		84.95			
					Pb(II)		71.42			
Iron oxide-hematite (α-Fe_2O_3)										
3D flower-like α-Fe2O3	flower-like; 5000-7000	–	12.7	N/A	As (V)	Langmuir (mg/g)	41.46	–	metal ions from aqueous solution	72
					Cr (VI)		33.82			
hematite nanoparticles	spheres; 37.0	31.7	6 and 8.0	N/A	Pb (II)	Freundlich q_e (mg/g)	3.11	yes/4	metal ions from aqueous solution, spiked San Antonio tap water	73
					Cd (II)		0.51			
					Cu(II)		0.051			
					Zn (II)		0.31			
Cauliflower-like α-Fe_2O_3	cauliflower-like; 340-500	31.57	3	N/A	Cr (VI)	Langmuir q_m (mg/g)	17.27	–	metal ions from aqueous solution	47
					Pb (II)		32.54			

Table 2 CNT Nanoadsorbents used for Heavy metal removal

Type of Nanoadsorbent	Shape and size	Length (μm)	Surface Area (m^2/g)	Optimal pH	Targeted Heavy metals	Isotherm Model (best fit)	performance	Regenerative?	Sample Matrix	Ref
CeO_2/ACNT	tubes; 20-80 nm; ceria 20 nm	200		7	Cr (VI)	Langmuir q_m (mg/g)	31.55	–	metal ions from aqueous solution	84
MWCNT/nano-iron oxide	tubes; o.d. 30-50 nm; iron oxide 18 nm	10 to 20	92	7	Cr (III)	-	90 % adsorption after 60 min contact time	–	metal ions from aqueous solution	91

Table 3 Metal Oxide Nanoadsorbents used for Heavy metal removal

Type of Nanoadsorbent	Shape and size	Surface area (m^2/g)	Optimal pH	Targeted Heavy metals	Isotherm Model or sorption capacity	Performance	Regenerative?/# of cycles	Sample Matrix	Ref
TiO_2/Titania									
TiO_2	-	196	6 to 7	As(III)	-	Decrease from 3310mg/L to 27 µg/L	yes/21 cycles	Wastewater from copper smelting plant	111
TiO_2 nanoparticles	spheres; 8.3 nm	185	8	Pb (II)	Langmuir q_m (mg/g)	83.04	yes/no exhaustion observed	Aqueous lab solutions/spiked tap water	113
				Cd (II)		15.19			
				Ni (II)		6.75			
Layered protonated titanate nanosheets (LPTNs) (400-7)	nanosheets; thickness 2-15 nm; interlayer distance 0.78 nm	379	5	Pb (II)	Langmuir q_m (mg/g)	366 mg/g	-	Aqueous lab solutions	105
$Na_2Ti_3O_7$-T3	nano fibers	-	Between 6 and 7	Ba (II)	Sorption saturate capacity (mg/g)	160.64	-	Aqueous lab solutions	106
				Sr (II)		55.20			
				Pb(II)		279.45			
$Na_{1.5}H_{0.5}Ti_3O_7$-T3(H)	nano fibers	-	Between 6 and 7	Ba (II)		130.44		Aqueous lab solutions	
				Sr (II)		49.94			
				Pb(II)		244.26			
Titanate Nanoflowers (TNF)	flowers; 600-1100 nm	290	-	Pb(II)	Langmuir q_m (mg/g)	304.3	-	Aqueous lab solutions	107
				Cd (II), Ni (II),Zn (II)		168.6, 88.05, 98.1			
Titanate Nanotubes (TNT)	tubes; Length 200 nm, outer dia. 7-10 nm	230		Pb(II)		147.4			
				Cd (II), Ni (II),Zn (II)		76.76, 40.09, 44.67			
Titanate Nanowires (TNW)	wires; Length 10 µm, dia. 40-240 nm	30		Pb(II)		106.19			
				Cd (II), Ni (II),Zn (II)		47.55, 24.83, 27.66			
TiO_2-AM	spheres;100µm	-	8	Cd (II)	Langmuir q_m (mg/g)	323	yes/5 cycles	Aqueous lab solutions	119

silica-titania composites (STC-0.25-12)	spheres; 45-90 µm	796	4	Hg	-	90 % Hg removal after 60 minutes	-	Aqueous lab solutions	109
ZnO									
ZnO nanoparticles	spheres; 26 nm	-	5.5	Zn (II)	Langmuir q_m (mg/g)	357	-	Aqueous lab solutions	129
				Cd (II)		387			
				Hg (II)		714			
ZnO hollow microspheres	spheres; 5-20 µm Interior nanoplate pores; 10-15 nm	46	6	Pb (II)	Freundlich q_e (mg/g)	> 160	-	Aqueous lab solutions	128
			Between 4 and 6	Cu (II)	Freundlich q_e (mg/g)	> 1400			
			6	Cd (II)	Langmuir q_m (mg/g)	28.1			
ZnO Nanoplates	plates; 10-15 nm thick; pore dia. 5-20 nm	147	Between 4 and 6	Cu (II)	Freundlich q_e (mg/g)	1600	-	Aqueous lab solutions	133
ZnO Nanosheets	squares; sides 1 µm; nanoscale thickness	-	-	Pb (II)	Removal Capacity η (mg/g)	6.7	-	Aqueous lab solutions	135
ZnO Nanosheets	Sheets; thickness 10 nm	-	5	Cd (II)	Langmuir q_m (mg/g)	99.6	-	Aqueous lab solutions	136

Table 4 Polymeric Nanoadsorbents used for Heavy metal removal

Nanoadsorbent	Shape and Size	Surface Area (m^2/g)	Optimal pH	Targeted Heavy metals	Isotherm Model	Performance	Regenerative?	Sample Matrix	Ref
Activated polymeric bead with 4g Fe salt (APH_04)	spheres; 0.8 mm	378	6-7.5	As (V)	Freundlich q_e (mg/g)	1.37	-	Aqueous lab solutions	25
				Flouride		0.19			
Activated polymeric bead with 2g each Fe and Al salt (APH_22)	spheres; 0.8 mm	292		As (V)		0.57			
				Flouride		1.77			
Activated polymeric bead with 4g Al salt (APH_40)	spheres; 0.8 mm	340		As (V)		0.86			
				Flouride		1.28			
Activated polymeric bead with 2g each Fe and Al salt-crushed (PH22BM_A)	spheres; 100 nm	764		As (V)		3.47			
				Flouride		3.03			

Table 5 Organic-Inorganic Nanoadsorbents used for Heavy metal removal

Nanoadsorbent	Shape and size	Surface area (m^2/g)	Optimal pH	Targeted Heavy metals	Isotherm Model	Max Adsorption/ capacity (mg/g)	Performance	Regenerative?/ Number of cycles	Sample Matrix	Ref
Organic–Inorganic Hybrid Zinc Phosphate with 28-Ring Channels	Refer to figure 39	-	-	Co	-	1.32	22.42 % removed after 1 h	-	aqueous lab solutions	146
				Cd		7.12	63.38 % removed after 1 h			
				Hg		16.08	80.17 % removed after 1 h			
Nano-conjugate Adsorbent (NCA)	200 µm	412	1.5	Pd (II)	Langmuir q_m	213.67	Equilibrium for Pd(II) adsorption in 30 min	yes; 10	aqueous lab solutions	152
Hybrid PEI-Silica	non-porous spheres; 305 ± 76 nm	20.6	6.2	Pb(II)	Langmuir q_m	632.91	100 % sorption after 2 days	-	aqueous lab solutions	149
				Cd(II)		595.24				
				Hg (II)		389.11				