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Phytoremediation and Nanoremediation of Heavy Metals from Textile Industry Wastewater Using Coconut Husk Modified Nanoscale Zerovalent Iron and Rapeseed: A Review

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ABSTRACT: The accumulation of metals in different environmental compartments poses a risk to both the environment, human and biota health. The combination of both Phyto and nano remediation techniques have been gaining more attention in this regard. This technique leverage on the unique and specific absorption qualities of plant roots, and employs these inherent processes with the bioaccumulation, translocation, and pollutant degrading capacities of the whole plant as well as cost effectiveness, and potential to treat a broad range of contaminants. This review focuses on phytoremediation and nanoremediaion of metals from wastewater effluents, the use of modified nanomaterials and the advantages and limitations of each strategy.

Keywords: Nanoparticles, NZVI, Remediation, Metals, Adsorbent

Introduction

Environmental pollution has been recognized as one of the significant problems faced globally today. Anthropogenic activities influence biogeochemical cycles via industries and have led to diverse, irreversible changes in our environment (Khairiah *et al.,* 2009). As a result, undesirable effects of poor environmental circumstances on human health are mostly manifested in the environment, predominantly in developing countries where urbanization, industrialization, and rapid population growth occur on an unprecedented scale (Biddut *et al.,* 2015). The crooked disposal of industrial wastes has generated contamination problems since these wastes are disposed of in the environment or are accumulated in water, biota and sediments. Most manufacturing processes are water-based and thereby discharge a high volume of treated or untreated effluents containing heavy metals and organic pollutants into river bodies. Hence, leading to surface and groundwater pollution.

The need for a sustainable and safe water supply is compelling developing countries to develop innovative and economical methods for the purification and treatment of water and wastewater. Many investigations on aquatic organisms have indicated that organic pollutants and heavy metals are ubiquitous with high detection rates and levels (Lee *et al.,* 2012; Desforges *et al.,* 2016). Past studies have reported that exposure to these contaminants might be related to the development of cardiovascular diseases, diabetes, and neurodegenerative diseases (Canterbury *et al.,* 2018) amongst others.

Investigators have been vigorously looking for various removal measures (e.g., advanced oxidation, adsorption, biodegradation, electrochemistry, biodegradation, adsorption, advanced oxidation, reduction, and zero-valent iron (ZVI)) for groundwater and wastewater remediation and treatment, and remediation of radioactive elements and contaminated wastewater (Dias and Petit, 2015; Rivera-Utrilla *et al.,* 2013; Wu *et al.,* 2017). Among the proposed removal methods, nano-phytoremediation is considered promising for its ability to remove heavy metals and organic pollutants, this is because of its affordability and ability to immobilize metals. Nano-phytoremediation is a terminology used for the removal of heavy metals from polluted sites via the simultaneous application of nanomaterials and plants.

"Nanotechnology" is a field of applied science and technology involving the production and study of nanomaterials. Nanomaterials are materials with sizes at the nano-scale (1–100 nm) in at least dimensions and they include nano-objects and nanoparticles (Hristozov *et al.,* 2009; Stone *et al.*, 2010). Nanomaterials are considered excellent remarkable absorbents and catalysts (Gong *et al.,* 2018; Khin *et al.,* 2012) because they have large specific surface areas, more associated sorption sites, lower temperature modification, shorter interparticle diffusion distance, more tunable pore size, and different surface chemistry than other materials (Tang *et al.,* 2014). Nano-remediation involves the use of nanoparticles in the treatment of contaminated water, soil, or air. By adsorbing pollutants, accelerating the reaction, and lowering the hazardous valence to a stable metallic state, this innovative remediation method has shown great efficacy in degrading toxins. Nanoparticle agents used for nano-remediation include carbon-based nanoparticles: Carbon Dots (CDs), Graphene Oxides (GOs), and Carbon Nano Tubes (CNTs) and the non-carbon-based nanoparticles are: nano zerovalent iron (NZVI) and zeolites. Unfortunately, the nanoparticles including the carbon-based nanoparticles used in nano-remediation have been reported to be toxic on human cells especially the lungs and breast. Toxicity is caused by the reactive surface containing the exchangeable ions and penetrating sizes of the nanoparticles. These toxicities are generally ameliorated by amending the reactive surfaces with functional surfactants (Pak *et al.*, 2019). Hence, the nano zerovalent iron (NZVI) have attracted much attention and have been used to remediate environments contaminated by heavy metals due to the rapid growth of nanotechnology but few have been carried out on the use of agricultural and domestic wastes modified with NZVI and the phytoremediation process (Huang *et al.,* 2018; Xue *et al.,* 2018a; Xue *et al.,* 2018b).

Phytoremediation means the use of plant in remediation. This method makes use of the plant roots capacity for uptake and exploits these natural processes in conjunction with the plants' capacity for translocation, bioaccumulation, and pollutant degradation (Negri *et al.,* 1996). Phytoremediation can thus be applied to the environment to reduce high concentrations of several pollutants, such as organic compounds and metals (Ahmadpour *et al.,* 2012; Pilon-Smits and Freeman, 2006). This technology was introduced in the 90's, but already being noted as a green substitute solution to the problem of heavy metal degradation, with great potential, since over 400 plant species have been identified as potential phytoremediators (Lone *et al.,* 2008). Furthermore, according to Ibañez *et al.,* 2015, this process allows the restoration of polluted environments with low costs and low collateral impacts.

In this context, the aim of the present study is to discuss and compare phytoremediation techniques with the use of organic waste modified nanoremediation approach in industrial wastewater while addressing the increasing problem of metallic nanoparticles in aquatic environment.

Phytoremediation of heavy metals in wastewater

Removal of heavy metals along with other contaminants through the application of aquatic plants is the most proficient and cost-effective method of removing heaving metals from wastewater (Guittonny-Philippe *et al.*, 2015, Ali *et al.*, 2013). This approach has garnered overwhelming recognition globally and referred to as a form of '*green technology.*" Selection of aquatic plant species for the accumulation of heavy metal is a very important matter to enhance the phytoremediation process (Galal *et al.*, 2018). According to Mays *et al*. (2001) and Stoltz *et al*. (2002), aquatic plants are the most promising option for the accumulation of pollutants in plant roots and shoots because they always grow a vast root system that benefits them. For hyperaccumulating plants, better transfer of the absorbed metals from industrial wastewater to a plant shoot is important. However, in order to increase the effectiveness of different forms of phytoremediation, it is important to understand the biological processes involved (Pilon-Smits and Freeman, 2006). It is widely accepted that plants, through the release of organic materials, nutrients and oxygen, produce a rich microbial environment that can promote the rapid growth of plants and microbial activity (Masciandaro *et al.*, 2013). In addition, root growth allows the entrance of air and water which possess the ability to alter carbondioxide and oxygen concentrations, reduction, oxidation and osmotic potential, pH and the moisture content of the soil (Lin and Xing, 2008). The interactions between plants and beneficial microorganisms of the rhizosphere can increase plant biomass and tolerance to metals, indicating that microorganisms, such as bacteria, protozoa, fungi and algae, are important components for phytoremediation (Masciandaro *et al.,* 2013). As a result, many bacteria and plants have their own methods for dealing with metals, and depending on the type of contact, the relationship between microbes and plants can either increase or decrease the amount of metal that accumulates in plants (Sharma *et al.,* 2013). For example, mixtures of arbuscular mycorrhizal fungi have been reported to lead to greater absorption and subsequent accumulation of metals in plant tissues (Leung *et al.,* 2013).

Factors that influence phytoremediation in wastewater

The following factors explained below have the potential to affect the uptake of heavy metals (Figure 1)

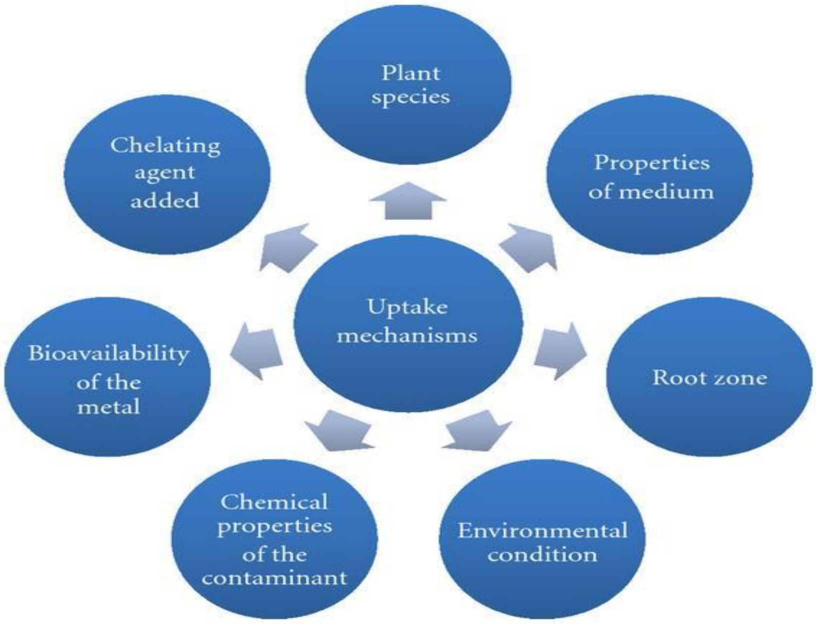

Figure 1: Factor affecting uptake of heavy metals by plants (Source: Bieby *et al.,* 2011)

- *The plant species:* Plant species or cultivars are evaluated for enhanced remediation properties, and those with the best results are chosen. The absorption of a chemical is influenced by the plant species. The phytoextraction technique's success is contingent on the discovery of suitable plant species that hyperaccumulate heavy metals and generate high amounts of biomass when grown and managed according to recognized crop production and management procedures.
- *Properties of medium:* Agronomical methods (pH correction, inclusion of chelators, fertilizers) are being developed to improve remediation. The pH, organic matter, and phosphorus concentration of the soil, for example, influence the quantity of lead absorbed by plants. The pH of the soil is modified to a range of 6.5 to 7.0 to limit lead uptake by plants.
- *The root zone:* In phytoremediation, the Root Zone is of particular relevance. It has the capacity to absorb contaminants and store or metabolize it within plant tissue. Another phytoremediation technique is the degradation of pollutants in the soil by plant enzymes secreted from the roots. Increased root diameter and reduced root extension as a reaction to reduced permeability of the dried soil is a morphological adaptation to drought stress.
- *Vegetative uptake:* Environmental variables have an impact on vegetative uptake. Temperature has an impact on growth ingredients and, as a result, root length. The structure of roots in the field differs from that in the greenhouse. A contaminant-specific hyperaccumulator is required for phytoremediation, specifically phytoextraction. The key to showing the applicability of phytoremediation is to understand mass balance analyses and the metabolic fate of contaminants in plants. Metal uptake by plants is influenced by the metal's bioavailability in the aqueous phase, which is influenced by the metal's retention duration and interactions with other elements found in the water Furthermore, when metals are linked to soil, pH, redox potential, and organic matter content all influence the metal's likelihood to exist in an ionic and plant-available form. Plants have an impact on the soil by lowering the pH and oxygenating the sediment, which influences the

availability of heavy metals. Biodegradable physicochemical variables, such as chelating agents and micronutrients, can increase the bioavailability of heavy metals.

Nanoremediation of heavy metals in wastewater

In Europe and North America, the use of nanoscience and nanotechnology for quality water issues has been in the spotlight of the scientific community. Nanotechnology can help to remove organic and inorganic microscopic pollutants in residual water. The adsorption and the use of membranes with nanomaterials are two techniques employed for removal of heavy metals.

Adsorbents: Adsorption is commonly used for remediation of organic and inorganic pollutants in residual water. Different types of nanomaterials, such as nanosorbents, zeolites and dendrimers, have been used for removal of heavy metals in residual water with exceptional absorption properties (Baruah *et al.,* 2015). For heavy metals removal from aqueous systems, nanosized ferric oxides, magnesium oxides, aluminum oxides, titanium oxides and cerium oxides are commonly used as adsorbents (Hua *et al.,* 2012). These nanomaterials have also been employed to remove heavy metals like arsenic, lead, mercury, copper, cadmium, chromium and Nickel (Qu *et al.,* 2013).

Efficiency of conventional adsorbents is usually limited by the surface area on active sites, the lack of selectivity and the adsorption kinetics (Baruah *et al.,* 2015). The growing development of nanoadsorbents have greatly benefited from their high specific surface area, which is associated with their short intraparticle diffusion distance, tunable pore size, surface chemistry and the characteristics of the sorption site (Qu *et al.,* 2013). CNTs, zeolites and dendrimers are common nanoadsorbents used in residual water to absorb heavy metals. Natural zeolites are aluminosilicates with skeletal structure, containing free spaces filled with large ions and water molecules. These compounds have distinct properties such as the presence of highly efficient adsorbents of various compounds (gaseous mixtures and dissolutions), cation exchangeable property, catalytic property; besides, each type of zeolite adsorbs molecules of a specific size. Recently, different research on nanosorbents have been carried out, including areas like nanobeats, nanocomposites, magnetic nano adsorbents and nanofibrous matrices (Kampalanonwat *et al.,* 2010).

Activated carbon is an adsorbent material prominently used for removal of heavy metals from aqueous solutions. This adsorbent is considered to be inexpensive method. Several researchers have reported the removal of ions of Co(II), Cd(II), Ni(II), Pb(II), Cr(III), Cr(V) and Cu(II) with activated carbon, synthesized from peat, coconut shell, coconut husk and coal (Baruah *et al.,* 2015). Lately, metal-based nanomaterials proved to be better in removing heavy metals than carbon activated; for example, TiO_2, NZVI, nanoparticles and nanosized magnetite for arsenic adsorption (Amin *et al.,* 2014).

Membranes: Membrane filtration is a common process in water treatment. However, the filtration efficiency depends on filtration material being used (Sang *et al.,* 2008) The efficacy of nanofiber membranes in retention of heavy metals, such as Aluminum and Copper (II) in residual water has been highlighted by many other researchers, but their applications are still untapped (Albuquerque *et al.,* 2013). Membranes have high specific surface area and porosity, and form nanofibers mats with complex pore structures. Nano-Ag, TiO_2, zeolites, magnetite and CNTs are some nanomaterials employed for membranes because of their potential properties like affinity to water, low toxicity on humans, high mechanical and chemical stability, high permeability and selectivity and photocatalityc activity (Albuquerque *et al.,* 2013).

Sensors: Nanosensors have been designed for sensing and monitoring tasks of highly toxic heavy metals, like arsenic and mercury. “These nanosensors are characterized by their (i) sensibility for detecting metals at low concentrations, (ii) low cost for monitoring and mapping in indefinite space and time, (iii) portability, that permits in situ measurement, and (iv) autonomy for measuring over an extended period of time. Nanosensors are designed to take advantage of the capacity of modifying physico-chemical behavior in shape, size and composition terms that nanomaterials have (Saez *et al.,* 2004). Some sensors employed for detection, quantification and monitoring tasks of heavy metals at different concentrations are referred to as nanobiosensors. These devices analyze samples called analytes, consisting of a biological receptor for detecting specific substances, a transducer for measuring the reaction of recognition and an amplifier for sending the quantification signal (Saez *et al.,* 2004).

Synthesis of NZVI and phytoremediation strategies

Iron nanoparticles can be synthesized using two methods: top-down and bottom-up. In the former approach large size materials are converted to NZVI with the aid of mechanical and chemical processes such as milling, etching, and/or machining (USEPA, 2010; Crane and Scott, 2012). The latter approach is based on the “growth” of nanostructures atom-by-atom or molecule-by-molecule via chemical synthesis, self-assembling and positional assembling (Li *et al.,* 2006). The top-down approach is what will be used in this study. On the other hand, previous research works have shown that plants can be used for phytoremediation via different physiological processes that allow metal tolerance and absorption capacity (Peuke and Rennenberg, 2005; Pilon-Smits and Freeman, 2006) while categorizing these phytoremediation techniques into: phytofiltration, phytostabilization, phytoextraction, phytovolatilization and phytotransformation (Halder and Ghosh, 2014). However, for the purpose of this review, only the phytoextraction approach will be discussed.

Synthesis of NZVI/BC from eggshells and coconut husks: Eggshells and coconut husks are subjected to the pyrolysis method. This method is the process of converting food and agricultural wastes into biochar, liquid, and gas through thermochemical conversion in the absence of oxygen and under anoxic condition at temperatures from around 200 to 700°C (IBI 2012). Therefore, the nature of each biochar is dependent on the raw material and conditions in which the conversion occurred (Dai *et al.,* 2017). Metals are immobilized mainly via their sorption from the soil onto the biochar, a process favored by high pH, organic matter, functional groups (carboxylic, amine, hydroxyl, carbonyl, alcoholic, and phenolic groups), and large surface area of the latter (Beesley *et al.,* 2010; Beesley and Marmiroli 2011).

Phytoextraction: In this technique, plants store and accumulate metals into their tissues (Nwoko, 2010). This is also referred to as phytoaccumulation, Phyto-absorption or Phyto-sequestration, and is composed of metal uptake from soil or water by plant roots and their translocation to and accumulation in the above ground biomass (Ali *et al.,* 2013; Sekara *et al.,* 2005; Yoon *et al.,* 2006). This is considered as the important phytoremediation technique for removal of heavy metals from polluted soils, sediments or water, although its efficiency is dependent on many factors, such as metal bioavailability, soil properties, metal speciation and plant species and, mainly, on shoot metal concentration and biomass (Ali *et al.,* 2013; Li *et al.,* 2010).

Advantages and limitations of phytoremediation: This is considered to be aesthetically pleasant and (Ali *et al.,* 2013), and generally referred to as a "clean" alternative to chemical plants (Pilon-Smits and Freeman, 2006). This technique is cost-effective in terms of installation and maintenance when compared to other remediation alternatives (Pilon-Smits and Freeman, 2006; Van Aken, 2009). Phytoremediation is also known to be a vital tool in ecological engineering effective for treating large areas (Garbisu and Alkorta, 2003). Additionally, the use of plants in synergistic phytoremediation processes results not only in cleaning the environment, but also in restoring ecosystems (Pilon-Smits and Freeman, 2006). When compared with microbial remediation, it causes fewer disturbances to ecosystems (Doran, 2009).

Also, biomass of plants after phytoremediation and chemical treatment for de-contamination can also be used as an alternative source of energy production (biogas or direct combustion), production of ethanol and bricks, and papermaking (Bell *et al.*, 2014).

However, phytoremediation process takes longer than other forms of clean-up and it is best suited for places where the elements are present within the range of plant roots (Doran, 2009; Pilon-Smits and Freeman, 2006). Furthermore, as stated previously, environmental conditions are contributing factors that determine the efficiency of plant uptake and may not always be adequate for most species. Additionally, soil contamination by different metals requires the use of specific plant species, well-suited or tolerant to the environmental conditions and contamination present. Hence, the application of phytoremediation in these cases require a wide range of research prior to the application of the technology (Danh *et al.,* 2009).

Advantages and limitations of nanoremediation: Nanoremediation based on NZVI has been used to treat chlorinated solvent contamination and trace element contamination, particularly Cr(VI)/ Other contaminants it has the capability to treat are: PAHs, complex chlorinated aromatic compounds (PCBs & pentachlorophenol), and the chlorinated benzenes. This method also offers the potential for rapid and complete treatment without the generation of toxic intermediate degradation of products. NZVI has been reported to be effective across a broad range of soil pHs, temperatures, and nutrient levels (Kharisov *et al.,* 2012). Nanoremediation would also not be subject to conditions that might be inhibitory to biological processes. For example, as yet unpublished laboratory-scale results showed that biomagnetite nanoparticle had a high resistance to inhospitable aquifer conditions (e.g., pH). On the other hand, some drawbacks of this method have been recorded in past studies.

In addition to concerns regarding the reactivity and mobility of NZVI there is little literature regarding the risks that this technology may pose on human and ecological health (Tratnyek and Johnson, 2006). Studies have demonstrated that the toxicity effects of NZVI are limited compared to other nanoparticles (Reijnders, 2006). The ecological impacts of nanoparticles on the environment can be summarized as:

Toxic effect to mammalian nerve cells: Different forms of NZVI (i.e., fresh, aged, and surface modified) are differentially toxic to the rodent nerve cells (Phenrat *et al.,* 2009). Fresh NZVI produced morphological evidence of mitochondrial swelling and cell death. The results revealed that partial or complete oxidation of NZVI reduces its redox activity, agglomeration, sedimentation rate, and toxicity to mammalian cells. Surface modification of NZVI also reduces its toxicity. In the presence of a polymeric coating, toxicity effects are very limited or even absent (Li *et al.*, 2010).

Toxic effect to aquatic life: The effects of NZVI on *Oryzias latipes* and their embryos were investigated, a dose- and time-dependent decrease in superoxide dismutase (SOD) and malondialdehyde (MDA) activities were observed in the embryos. A significant decrease of SOD and glutathione (GSH) activity were also observed in liver and brain samples taken from the adults, but as the exposure time increased, the adults appeared to recover from the exposure by adjusting the levels of antioxidant enzymes (Li *et al.*, 2009).
Toxic effect to microorganisms: NZVI is found to be capable of removing viruses from water by inactivating them and/or irreversibly adsorbing the viruses to the iron (You *et al.*, 2005). A study done by Lee *et al.*, (2008) says that NZVI particles exhibited a bactericidal effect on Escherichia coli that was not observed with other types of iron-based compounds, such as iron oxide nanoparticles, microscale ZVI, and $Fe3^{+}$ ions.

Conclusions

Phytoremediation strategies applied to metal contamination possess a huge potential in removing harmful or excess metals from the environment, since they are considered a "green" approach. However, these techniques are subject to varying factors, such as soil pH, temperature, depth of the contamination and metal species, among others. Hence, it is essential to have a comprehensive understanding of plant physiology, biochemistry and uptake of these contaminants, as well as proper evaluation of possible synergistic effects and specific metal species contamination and further research regarding synthetic approaches to metal phytoremediation, such as the addition of chelators or organic matter to the soil or rhizosphere or the use of transgenic species, which has increased in the last few years. In particular, given that the nanotechnology industry is growing at extremely fast rates, nanoparticle contamination is of increasing concern, and nano particle phytoremediation, or nanoremediation, is being rapidly demonstrated as the possible solution.
This paper also provided an insight into the synthesis of NZVI while establishing its role in the environmental remediation process. With more research work focusing on developing proper techniques to improve the NZVI motility the function of NZVI can be enhanced. Hence, the application of NZVI as a remediation tool appears to be more promising than conventional ZVI (microscale) or other in situ remediation methods. However, continued research effort toward modifying this technology is required to minimize the unexpected adverse environmental impact or potential risks.

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