



Nanomaterial for inorganic pollutant remediation

Muhammad Noor Hazwan Jusoh^{1,*}, Chi Nam Yap¹, Tony Hadibarata¹, Hisyam Jusoh², Mohamed Zuhaili Mohamed Najib³

¹Department of Civil Construction Engineering, Faculty of Engineering Science, Curtin University, CDT 250, Miri, 98009, Sarawak, Malaysia

²Geo TriTech, No. 17, Persiaran Perdana 15A, Pinji Perdana, 31500, Lahat, Perak, Malaysia

³School of Civil Engineering, Faculty of Civil Engineering, Universiti Teknologi Malaysia, Malaysia

Abstract

Heavy metal (loids) in wastewater persists as a contagious and non-biodegradable environmental pollutant. With the ever rising of nanotechnologies in various field, there is a mass flux of heavy metal (loid)s being transmitted in many water sediments includes wastewater and rivers in which difficult to eliminate through conventional treatment processes. The introduction and development of nanomaterials have been increasingly utilized. Their high absorption capacity and unique properties in eliminating heavy metal pollutants and other nano pollutants have been extensively used in the remediation of inorganic pollutants. This review study illustrates the different types of nanomaterials that are utilized in various treatment process such as nano zero-valent iron (nZVI), carbon nanotubes and titanium dioxide nanoparticles (TiO₂NPs). The mechanism of each nanomaterial and also its advantages and disadvantages are being portrayed. The identified factors affecting their efficiency in eliminating heavy metal and other inorganic pollutants are briefly described.

Keywords :

Heavy metals; Inorganic pollutants; Nanomaterials; Polymer; Water treatment

1 Introduction

Pollution is defined as the introduction of contaminants into the natural environment that causes adverse changes. Nowadays with the advancement of industrial technology, the productions of most industries have produced large amounts of inorganic pollutants in their processes. The discharge of wastewater from industries and commercial activities are the main source of toxic inorganic substances causing a detrimental effect on human health and the surrounding ecosystem. This has been criticized as a serious threat to the issue of environmental pollution concerning industrialization in developing countries. In fact, inorganic pollutants could continuously accumulate, posing high toxicity and penetrability upon living organisms causing damage to human being and other species in the long-term (Zhang and Li, 2017). Nanomaterials typically any material that can be synthesized with particle size < 100 nm (Zhang et al., 2016). At this dimension size and nanoscale, nanomaterials have greater reactivity and absorption capability as compared to their bulk-size materials. It consists of unique morphological and physiochemical properties that could stabilize or absorb heavy metal ions effectively which reduce their movement and bioavailability.

Inorganic nanomaterials consist of several entities including transition metal, metal oxides, sulfides nanomaterials, carbon-based nanomaterials such as graphene, silica-based nanomaterials and other nanocomposites (Lu et al., 2017) (Karthick Kannan et al., 2019). Each nanomaterial has different physical and chemical properties and therefore, required different processes. Nanomaterials are widely used in removing heavy metal ions (Nizamuddin et al., 2018), dyes (Nizamuddin et al., 2018), arsenic ions (Lal et al., 2020) and other inorganic pollutants. However, there are some limitations in its application considering high cost, poor recyclability and environmental concern.

2 Types of nanomaterials

Nanomaterials have been numerously applied and synthesis to eliminate inorganic pollutants concurrent with both treatment processes and industrial systems. The following sections will be described the nanomaterial in terms of characteristic, mechanism, advantages and disadvantages. The summarizes of several nanomaterials for the remediation of water pollution are illustrated in Table 1. While in Table 2 listed the advantages and disadvantages of polymers in nanocomposite membranes.

2.1 Nano zero-valent iron (nZVI)

Nano zero-valent iron (nZVI) has been used widely in various environmental remediation to eliminate the contaminations in groundwater and wastewater by inorganic and organic pollutants (Calderon and Fullana, 2015). The nZVI nanomaterials are conceived as a core-shell structure whereas metallic iron is at the core

* Corresponding Author.

Email Address : mn.hazwan@curtin.edu.my

<https://doi.org/10.33086/etm.v1i1.2037>

Received from 30 March 2021;

Received in revised from 30 April 2021;

Accepted 30 April 2021;

Available online 30 April 2021;

and the shell is comprised of a layer of iron oxide (Zhu et al., 2019). The core is functioning as a positive donor with reducing factors while the shell is operated as an electron receiver causes for absorption and surface complexation reaction to occur (Calderon and Fullana, 2015).

The excel of nZVI in eliminating pollutants is attributed to the nano dimension size (Pang et al., 2018). The large specific surface area of nZVI provides a high chance of pollutants attaches to the surface binding site leading to a fast reaction rate. Also, iron oxide shell prompted the absorption rate of pollutants which has proved the nanomaterials efficiency (Sheng et al., 2016). Sheng et al. (2016) stated in their study that the development of nZVI is considered as low-cost production and forming unarmful by-product which promoted environmentally friendly absorbents. However, nZVI is tended to aggregate due to its high reactivity and nano dimension size that resulted in instability and poor mobility of the material (Cumbal et al., 2003). Thus, supporting agents and stabilizer are required to overcome the consequences of aggregate. In certain cases, the supporting agent like organic polymer and inorganic shells also have failed in the reaction process causing to accumulate of nanoparticles. The reaction of precursor materials with reducing agents (sodium borohydride and hydrazine hydrate) for the formation of nanomaterials could produce toxic substances that would harm human health and the environment.

2.2 Carbon nanotube

Activated carbon was known as an effective absorbent in eliminating inorganic pollutants but limited for the pollutants that existed in the nanoscale. Therefore, carbon nanotubes are introduced exists in single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) (Ihsanullah et al., 2016). The structure of SWCNTs is made up of graphene sheet rolled up to form hollow tubes with walls one atom thick whereas MWCNTs comprises of multiple concentric cylinders that are one atom thick sheets of carbon which combine to form an interlayer and diameter of approximately 1.4 nm (Dai, 2002). Carbon nanotube utilized an adsorption mechanism to remove heavy metal (loid)s in sediment. The absorption of heavy metal pollutants through carbon nanotube are exceptionally complex which include precipitation, physical adsorption, electrostatic attraction, and chemical interaction between the heavy metal(loid) ions and the surface functional groups of CNTs (Li et al., 2003). The SWCNTs and MWCNTs showed a high absorption rate due to large specific area, nano size, graphene materials and hollow structures. Furthermore, both can be enhanced through functionalization with O, N, P containing group on the surface of the carbon nanotubes to have better dispensability and specific surface area (Adeleye and Keller, 2014). Nonetheless, the disadvantages of using MWCNTs is that the particles are easily aggregate and are extremely hydrophobic because of great van der Waals interaction forces within the particles. Hence, rendering the absorption capacity and effectiveness (Sundararajan and K Ghosh, 2011). For SWCNTs, the particles have high persistence and could accumulate in the food chain thereby pose risks to human health and the environment as the particles can hinder the absorption of phosphorus on aquatic sediments (Patra et al., 2017)(Sierra and Morante-Zarcelero, 2018).

2.3 Nano-hydroxyapatite particles (nHAp)

Nano-hydroxyapatite particles (nHAp) is another nanomaterial that extensively utilized in soil remediation and disinfecting wastewater especially on absorbing heavy metal loid such as copper (II), lead(II), and cadmium(II) (Silva et al., 2017). The nHAp mainly utilize on the exchange of fractions but varies depending on the opposing pollutants or reactants, for instance, the mechanism for stabilizing lead (Pb) involve dissolution and precipitation while the absorption of cadmium (Cd) uses surface complexation

and intraparticle diffusion (He et al., 2013). Mobasherpour et al. (2011) also found the same observation that nHAp utilizes ion exchange and surface complexation in eliminating nickel (Ni) in sediments. Due to its unique crystal structure and chemical composition, nHAp consist of a large specific area which proved to have a high absorption rate and capacity for heavy metal. Other advantages of nHAp including having low water solubility and high solidity under reducing and oxidizing conditions, having good cyto-compatibility (Yang et al., 2016). The nHAp is also flexible as having a high capability of functionalization with different molecules. In term of environmental aspect, nHAp are recyclable, biocompatibility and non-toxicity.

2.4 Titanium Dioxide Nanoparticles (TiO₂NPs)

Titanium dioxide nanoparticles (TiO₂NPs) can be found widely in commercial products such as toothpaste, cosmetic, pigments as well as in water and air treatment segments including photocatalysis process in air and water purification (Chen et al., 2012). TiO₂NPs possess unique photocatalytic properties which include acid and alkaline resistance, photochemical corrosion and non-toxicity traits (Zhu et al., 2019). The reaction of TiO₂NPs with the light produced free radicals with high catalyst activity which in turn generate strong photooxidation and reduction capability. Thereby, catalyze the photodecomposition of various organic substances and some inorganic substances. Besides, the TiO₂NPs have displayed the capability to stabilize the mobility, aggregation and detoxify the toxicity of co-existing pollutants (Fan et al., 2017). The strong electrostatic attraction, large specific area and nano size of the material have led the materials to act as excellent inorganic pollutant absorbance (Cai et al., 2019). In ions exchange, the TiO₂NPs presence in the sediment had hindered the movement of the released heavy metal (loid) ions from seeping into the water phase (Zhang et al., 2007). Thus, avoid creating secondary pollution. The alteration of metal (loid) ions geochemical speciation using TiO₂NPs, a part of heavy metal ions occurring in the level of exchangeable (EXC), carbonate (CAR) and iron-manganese (IMO) exchange functional group for sediment ageing. However, TiO₂NPs poses threats toward the aquatic ecosystem as the particles inhibit the growth of aquatic cell on various algae species, lipid peroxidation and photosynthesis inhibit in algae (Chen et al., 2012). It is due to the cyto-ultrastructure disorder and rapid accumulation at the algae cell surface (Chen et al., 2012).

2.5 Graphene Nanomaterial (GNMs)

Graphene or graphene oxide is a single layer of graphite at a nanoscale. The material is made up of sp² allotropic carbon atoms arranged in a two-dimensional hexagonal honeycomb lattice structure (Awad et al., 2020). The graphene nanomaterials (GNMs) absorbs inorganic pollutants and heavy metal (loids) through the porous structure (Farré et al., 2009). Graphene consists of high surface area, enhanced active site, large delocalized -electron systems and decent chemical stability (Gopalakrishnan et al., 2015). It also shows decent electrical and thermal conductivity and high strength (Awad et al., 2020). As such, graphene has been synthesized in many ways and methods due to its flexibility. Graphene is commonly synthesis through mechanical peeling, chemical oxidation-reduction and carbon nanotube conversion (Farré et al., 2009). Among all, graphene oxide (GO) and reduced graphene oxide (RGO) are often produced due to their superior absorption features despite its disadvantage (Ali et al., 2019). The GO is synthesis through the chemical oxidation of graphene while RGO is produced through the reduction of GO. However, GNMs also possess several weaknesses (Chatterjee et al., 2014). Despite its physiochemical properties, graphene could form irreversible collections of graphite through the stacking of - electrons and van der Waals interactions (Awad et al., 2020). The accumulation char-

acteristic can deter the mobility of the particles, minimize specific surface area thereby decreasing the GNMs effectiveness (Ali et al., 2019). Also, GNMs have a possibility to contaminate aquatic ecosystem due to rapid diffusion of surface activity in the water environment that caused water eutrophication (Ali et al., 2019).

2.6 Stabilized Nano-chlorapatite (nCLAP)

Apatite materials are one of the ideal phosphate-based materials used for removing heavy metal in wastewater due to their extraordinary chemical structure. Among all, chlorapatite (CLAP) is one of the ideal materials as it is highly stable for immobilization of heavy metal (loids) under oxidising and reduction conditions. Besides, the absorption rate of heavy metal is high and non-toxicity produced which are the dominant characteristics of CLAP (Liu and Zhao, 2007). Liu and Zhao (2007) also claimed that the CLAP could detoxify and stabilize the unstable function sites of heavy metal into stable fractions through precipitation, ion exchange and absorption processes. Nonetheless, CLAP also has difficulty in terms of the small specific area and low solubility that caused rapid reactivity at polluted sediment (Cai et al., 2019). Therefore, stabilized nano-chlorapatite (nCLAP) is developed and introduced to provide better efficiency, deliverability and well-dispersed absorbance in comparison to CLAP (Cai et al., 2019). Wan et al. (2018) indicated that Rha-stabilized nCLAP substantially efficiency in the stabilization of lead(II) and cadmium(II)

in contaminated deposits, accelerate the transformation from mobile fraction to immobilize fraction through precipitation or adsorption processes. However, the disadvantage of nCLAP is that the particles are easily accumulated, releasing excess phosphorus that contributes to eutrophication. Thus, the stabilizer needs to combine with nCLAP as it could decrease the grouping of the nCLAP particles and enhanced the efficiency in restraining the movement of heavy metal (loids) (Cai et al., 2019).

2.7 Silver Nanoparticles (Ag NPs)

Silver nanoparticles possess good electrical conductivity that is beneficial in eliminating some heavy metal contaminants attributed to the active sites and nano size of Ag NPs (Sultan and Mohammad, 2017). Sumesh et al. (2011) have conducted a study using Ag NPs to remove mercury ions through the usage of activated alumina as a carrier. They found that under the condition of 1:6 Ag@MSA, per gram of Ag@MSA achieved to remove 0.8 g of mercury ions. The high affinity of mercury for iodine has led the Ag NPs to be fixed on the cellulose acetate membrane thereby effectively remove the radioactive iodine. Another study by (Rtimi et al., 2019) concluded that the methylene blue could be removed effectively through the combination of Ag NPs and activated carbon. This attributed to the absorption process of silver nanoparticles mechanism as the particles combined with metabolic active sites of a medium or enzyme of a bacteria are filtered out or let the bacteria dry out completely.

Table 1 Several common nanomaterials applied for the remediation of water pollution

Nanomaterials	Remediation	Common preparation methods	Advantages	Disadvantages	Reference
nZVI	Azo dyes, chlorinated solvents, zinc, cadmium, arsenic, nitroaromatics	Reduction-oxidation	Controllable particle size, high specific surface area, abundant reactive surface sites, high reactivity and strong reducibility to heavy metal (loid)s	Easily agglomeration, may have possible toxic effects on living organisms	(Yirsaw et al., 2016), (Crane and Scott, 2012), (Zhu et al., 2019), (Huang et al., 2018), (Cai et al., 2019)
SWCNTs	Various pollutants in eutrophicated landscape water	Molecular techniques, electrospinning, solution blowing, centrifugal jet spinning, electrohydraulic dynamic direct writing, etc	A superior adsorbent with high adsorption capacity for heavy metal (loid)s	May accumulate in the food chain and has high persistence, exerting possible risks to human health and environment and affecting the adsorption of P on aquatic sediments	(Cai et al., 2019), (Zhu et al., 2019)

Nanomaterials	Remediation	Common preparation methods	Advantages	Disadvantages	Reference
nHAP	Heavy metals, contaminated soil	Phytoextraction, coprecipitation	Large specific surface area, excellent sorption and stability capacity for heavy metal (loid)s, good cytocompatibility, environmental risk is negligible	-	(Cai et al., 2019), (Wang et al., 2011), (Jin et al., 2016)
TiO ₂ NPs	Various organic substances such as formaldehyde and some inorganic substances	Gas phase method, liquid phase method	High reactivity, large specific surface area	Have a toxic effect on organisms	(Zhu et al., 2019), (Cai et al., 2019)
GNMs	Heavy metals and dyes	Mechanical stripping, chemical oxidation-reduction, carbon nanotube conversion, photocatalytic reduction	High surface area, extraordinary electrical and thermal conductivity, and strong mechanical strength	In vitro toxicity of GNMs in bacterial, adherent mammalian, cancerous cells or suspended cells.	(Farré et al., 2009), (Zhu et al., 2019), (Chatterjee et al., 2014), (Guo and Mei, 2014)
nCLAP	Heavy metals	Sequential extraction method,	Excellent ability to stabilize heavy metal (loid)s, such as Pb ²⁺ , Cd ²⁺ , Zn ²⁺ , Cu ²⁺	Easy agglomeration, may produce excess phosphorus, causing eutrophication (Cai et al., 2019), (Wan et al., 2018)	
Ag NPs	As water antibacterial agent, photocatalyst	Chemical reduction, photoreduction, electrochemical laser cauterization, electroplating, radiation and seed	Large surface area, high antimicrobial activity	Bioaccumulation and toxic effects in living organisms	(Zhu et al., 2019), (Rtimi et al., 2019), (Priya et al., 2020)

2.8 Hematite (-Fe₂O₃)

Hematite is considered the most stable in the iron oxide group and proven to have high corrosion resistance (Park et al., 2019). The Hematite nanoparticles consist of different morphologies which include hexagonal, plate-like, nano-cubes, sub-rounded and spherical. As such, this has contributed to the numerous physicochemical properties of hematite nanoparticles depending on the crystallinity, sub particle structure, size of particles, active sites and cation doping (Abdel Maksoud et al., 2020). These parameters act as the deciding factor for the absorption efficiency of hematite. Shipley et al. (2013) have studied the absorption rate of nano hematite towards Pb(II), Cd (II), Cu (II), and Zn (II). The results stated the affinity between the heavy metals and absorbent follow the sequence of Pb (II) > Zn (II) > Cd (II) > Cu (II). The advantages of hematite nanoparticles include low cost, small dimension and ease of operation. Besides, hematite nanoparticles are capable to remove multiple heavy metals from water sediment simultaneously. However, hematite is limited to its photocatalytic activity causing poor separation effectiveness and conductivity (Shipley et al., 2013). Thus, hematite is usually cooperating with different semiconductor materials to form a heterostructure to enhance the materials photocatalytic activity. Kang et al. (2019) reported a case study on the synthesis of hematite with graphitic carbon nitride-based Z-scheme heterojunction via simple solid-state reactions. The results showed that the efficiency of rhodamine B photocatalytic degradation was improved by double as compared to pristine hematite.

2.9 Maghemite (-Fe₂O₃)

The structure of maghemite is defined as a cubic structure whereas the Fe⁽³⁺⁾ ions are allocated over the A-sites and B-Sites (Al-Rashdi et al., 2017). As such, this signifies that maghemite nanoparticles consist of high chemical stability without any reducing agents. The mechanism of maghemite nanoparticles is through electrostatic interactions which have proved promising absorbance for heavy metal pollutants (J. Yang et al., 2019). The advantages of utilizing maghemite nanoparticles are that it consists of a large surface area which contributes to high absorption capability. Also, maghemite nanoparticles are recyclable as the nanoparticles could easily be separated from wastewater after the treatment (Abdel Maksoud et al., 2020). Maksoud et al. (2020) stated that the saturated magnetization of maghemite nanoparticles provides high efficiency of separation between the particles and the wastewater. The maghemite was recorded to provide good flexibility as the inclusion whereas maghemite nanoparticles undergo modification with poly (1-vinylimidazole), polyrhodanine, polypyrene, polyaniline etc, have proven to enhance the absorption capacity and selectivity towards heavy metal ions (J. Yang et al., 2019). Besides, the formation of maghemite nanoparticles are environmentally friendly and does not produce secondary pollution (Etale et al., 2016).

2.10 Hydrous Iron Oxides (HFO)

Hydrous Iron oxide (HFO) has been used widely as one of the most promising heavy metal adsorbents. The HFO nanoparticles perform through adsorption, ion exchange and co-precipitation to remove heavy metals in wastewater.

The advantages of HFO possess include large surface area, strong electron-interaction towards metal (loids) and low production cost. According to Zhang and Li, (2017) the particles are chemically stable and environmental-friendly. They also have reported that the hydrous iron oxide cannot be utilized directly into stationary bed or open-flow systems as the nanoparticles shows poor mechanical rigidity, low hydraulic permeability, and inconsistent pressure drop. Henceforth, hydrous iron oxides are often merged with porous nanomaterials such as activated carbon, diatomite and polymeric absorbents to form a composite to counteract the weakness HFO possessed.

2.11 Polymer-Supported Nanocomposites

Polymer Nanocomposite contains two strains of properties and synthesis traits which are synthetic organic polymer-supported nanocomposite and biopolymer-supported nanocomposite. Both nanocomposites could be obtained through two different methods which are direct compounding and in situ synthesis (Nasir et al., 2019). The polymer nanocomposite holds many beneficial properties which proved to have good mechanical strength, superior flexibility, film forming capability, good penetrability, selectivity to chemical species and high removal capacity. Its applications are also environmentally friendly and low production cost (J. Yang et al., 2019). Both the natural and synthetic polymer nanocomposites can be used in various membrane treatment sys-

tem for wastewater due to the superior feasible function group of the polymer. Therefore, various membrane technologies have been developed through these nanocomposites such as nanofiltration, membrane distillation, membrane bioreactor and separation by liquid membranes in regard to the separation methods and properties of the membrane (Nasir et al., 2019). In term of biopolymer such as cellulose, chitosan is usually utilized as a supporting agent for nanocomposite due to abundant coordination sites for heavy metal ions contained numerous hydroxyl groups on its glucose ring (J. Yang et al., 2019).

Another biopolymer known as chitosan shows a great absorption capacity for heavy metal due to the coexistence of $-NH_2$ and $-OH$ in its structure (J. Yang et al., 2019). The synthesized ZnO/chitosan core-shell nanocomposite (ZOCS) a hybrid polymer nanocomposite is proven to produce less toxicity and improvement in production cost and absorption capabilities in removing Pb (II), Cd (II) and Cu (II) (Saad et al., 2018). Table 3 illustrated the common polymers used in nanocomposite membranes. The mechanism is through absorption and exchange of fractions. Suman et al. (2015) reported on the removal of dye, heavy metal ions and microbes in water through the water column method using nanocellulose (NC)-Ag nanoparticles (AgNPs) embedded pebbles-based composite material. The result showed that 99.48 % of Pb (II) and 98.30% of Cr (III) were removed from the water as well as a 99% decontamination efficiency for the microbial load.

Table 2 The advantages and disadvantages of polymers in nanocomposite membranes

Polymer	Advantages	Disadvantages	Reference
Cellulose acetate	High toughness, low cost, non-toxic nature, biodegradability, excellent biocompatibility, high mechanical strength, easy processability, relatively low cost, fabrication flexibility	High crystalline nature, poor chlorine resistance, poor thermal resistance, poor chemical resistance	(Nasir et al., 2019), (S. Yang et al., 2019), (Mahalakshmi et al., 2019)
Polystyrene polyethersulfone	Superior thermal resistance, wide pH range, superior chlorine resistance, high mechanical properties	Hydrophobicity, less operating pressure limit	(Nasir et al., 2019)
Polyvinylidene fluoride	High crystallinity, high mechanical strength, sufficient chemical stability, high thermal stability	Hydrophobicity	(Nasir et al., 2019), (Mai et al., 2011)
Polyamide	High mechanical properties, wide pH range, good thermal stability, excellent physical properties, good separation efficiency, higher salt resistance	Poor chlorine resistance, poor miscibility between inorganic nanoparticles and polyamide layers	(Nasir et al., 2019), (Jung et al., 2021), (Zhang et al., 2017), (Wang et al., 2020)
Polyvinyl alcohol	Good mechanical properties, low thermal properties and strength for few applications, fabrication flexibility, low cost, chemical stability, transparency and good film-forming properties	Dissolve in aqueous solutions	(Nasir et al., 2019), (Zhuang et al., 2018)

3 Factor Affecting Nanoparticles-Pollutant Interaction

3.1 pH

The pH value act as an important factor in deciding the absorption rate of the nanoparticles on heavy metal and inorganic pollutants. At a low pH value, the absorption ability and bioavailability of metal ions decrease while increasing the mobility of heavy metal (loid) (Esfandiyari et al., 2017) (Shahraki et al., 2020). It could also affect the reaction process between the contaminant and nanoparticles (Cai et al., 2019). This is because alteration on the pH value will cause drastic changes to the surface charge den-

sity, ionization of functional group presents and chemical properties of adsorbent in the aqueous phase (Daneshfozoun et al., 2017).

3.2 Organic Matter (OM)

Organic matter (OM) affects the function and properties of some nanomaterials. It is mainly made up of humid and fulvic substances which have the potential to affect the absorption process of nanoparticles (Abdel Maksoud et al., 2020). The absorption process could be disrupted in between nZVI particles and heavy metal (loid)s as the organic matter compete for reactive surface sites, and thus decrease the reaction rate of the nZVI (Cai et al., 2019). Besides, the reaction of organic matter and heavy metal formed a complex compound that altered the original properties

of the heavy metal (loid) ions as well as affects the metal (loid) adsorption capacity. The presence of organic matter also leads to the increased of the particle size and lowering the stability of the nanoparticles. While the degradation of organic matter would reduce the pH value of sediments.

3.3 Oxidation-Reduction Potential (ORP)

The oxidation-reduction potential in sediment plays an important role in regulating the movement and the toxicity of numerous elements such as Cr, Se (Marefat et al., 2019). This is because it has a potential effect to alter the reactivity of nanomaterials on absorbing or immobilizing pollutants. There are some nanomaterials such as nZVI nanoparticles that could react with common environmentally relevant electron acceptors and is not restricted to only redox-amenable pollutants. The oxidation-reduction may trigger to release of H⁺ ions into the sediment or wastewater and resulted in the decrease of pH value (Cai et al., 2019). Thus, causing the release of secondary heavy metal (loid)s contamination.

4 Conclusion

The unique chemical and physical properties of nanomaterials proved to be promising adsorbent for inorganic pollutant remediation. Despite the limitation and weaknesses, the advantages that nanomaterials provide far exceed its limitation and should be considered to be widely integrated as common treatment practices in various fields. Nanomaterials such as nano zero-valent iron (nZVI) can be modified with a stabilizer or supporting agents that aid in counteracting the limitation of the materials which aid in decreasing the aggregation of nanoparticles and increase the reaction rate and the longevity of the materials. Other nanomaterials, such as nano apatite-based materials are other promising adsorbance materials that are cost-efficient, more environmentally friendly and readily available. Therefore, this technology could be established following the improvement from the previous explored studies to date for sufficient outcome in dealing with heavy metal (loids).

Declaration of competing interest

The authors declare no known competing interests that could have influenced the work reported in this paper.

Acknowledgements

The authors thank Curtin University Malaysia for facilitating this work. Collaboration from Universiti Teknologi Malaysia and Geo TriTech Malaysia is highly appreciated.

References

- Abdel Maksoud, M.I.A., Elgarahy, A.M., Farrell, C., Al-Muhtaseb, A.H., Rooney, D.W., Osman, A.I., 2020. Insight on water remediation application using magnetic nanomaterials and biosorbents. *Coord. Chem. Rev.* <https://doi.org/10.1016/j.ccr.2019.213096>
- Adeleye, A.S., Keller, A.A., 2014. Long-term colloidal stability and metal leaching of single wall carbon nanotubes: Effect of temperature and extracellular polymeric substances. *Water Res.* 49, 236–250. <https://doi.org/10.1016/j.watres.2013.11.032>
- Al-Rashdi, K.S., Widatallah, H.M., Al Ma'Mari, F., Cespedes, O., Elzain, M., Al-Rawas, A., Gismelseed, A., Yousif, A., 2017. Structural and Mössbauer studies of nanocrystalline Mn²⁺-doped Fe₃O₄ particles. *Hyperfine Interact.* 239, 3. <https://doi.org/10.1007/s10751-017-1476-9>
- Ali, I., Basheer, A.A., Mbianda, X.Y., Burakov, A., Galunin, E., Burakova, I., Mkrtychyan, E., Tkachev, A., Grachev, V., 2019. Graphene based adsorbents for remediation of noxious pollutants from wastewater. *Environ. Int.* <https://doi.org/10.1016/j.envint.2019.03.029>
- Awad, A.M., Jalab, R., Benamor, A., Nasser, M.S., Ba-Abbad, M.M., El-Naas, M., Mohammad, A.W., 2020. Adsorption of organic pollutants by nanomaterial-based adsorbents: An overview. *J. Mol. Liq.* <https://doi.org/10.1016/j.molliq.2019.112335>
- Cai, C., Zhao, M., Yu, Z., Rong, H., Zhang, C., 2019. Utilization of nanomaterials for in-situ remediation of heavy metal(loid) contaminated sediments: A review. *Sci. Total Environ.* <https://doi.org/10.1016/j.scitotenv.2019.01.180>
- Calderon, B., Fullana, A., 2015. Heavy metal release due to aging effect during zero valent iron nanoparticles remediation. *Water Res.* 83, 1–9. <https://doi.org/10.1016/j.watres.2015.06.004>
- Chatterjee, N., Eom, H.J., Choi, J., 2014. A systems toxicology approach to the surface functionality control of graphene-cell interactions. *Biomaterials* 35, 1109–1127. <https://doi.org/10.1016/j.biomaterials.2013.09.108>
- Chen, L., Zhou, L., Liu, Y., Deng, S., Wu, H., Wang, G., 2012. Toxicological effects of nanometer titanium dioxide (nano-TiO₂) on *Chlamydomonas reinhardtii*. *Ecotoxicol. Environ. Saf.* 84, 155–162. <https://doi.org/10.1016/j.ecoenv.2012.07.019>
- Crane, R.A., Scott, T.B., 2012. Nanoscale zero-valent iron: Future prospects for an emerging water treatment technology. *J. Hazard. Mater.* <https://doi.org/10.1016/j.jhazmat.2011.11.073>
- Cumbal, L., Greenleaf, J., Leun, D., SenGupta, A.K., 2003. Polymer supported inorganic nanoparticles: Characterization and environmental applications. *React. Funct. Polym.* 54, 167–180. [https://doi.org/10.1016/S1381-5148\(02\)00192-X](https://doi.org/10.1016/S1381-5148(02)00192-X)
- Dai, H., 2002. Carbon nanotubes: Opportunities and challenges. *Surf. Sci.* 500, 218–241. [https://doi.org/10.1016/S0039-6028\(01\)01558-8](https://doi.org/10.1016/S0039-6028(01)01558-8)
- Daneshfozoun, S., Abdullah, M.A., Abdullah, B., 2017. Preparation and characterization of magnetic biosorbent based on oil palm empty fruit bunch fibers, cellulose and Ceiba pentandra for heavy metal ions removal. *Ind. Crops Prod.* 105, 93–103. <https://doi.org/10.1016/j.indcrop.2017.05.011>
- Esfandiyari, T., Nasirizadeh, N., Dehghani, M., Ehrampoosh, M.H., 2017. Graphene oxide based carbon composite as adsorbent for Hg removal: Preparation, characterization, kinetics and isotherm studies. *Chinese J. Chem. Eng.* 25, 1170–1175. <https://doi.org/10.1016/j.cjche.2017.02.006>
- Etale, A., Tutu, H., Drake, D.C., 2016. The effect of silica and maghemite nanoparticles on remediation of Cu(II)-, Mn(II)- and U(VI)-contaminated water by *Acutodesmus* sp. *J. Appl. Phycol.* 28, 251–260. <https://doi.org/10.1007/s10811-015-0555-z>
- Fan, X., Wang, P., Wang, C., Hu, B., Wang, X., 2017. Lead accumulation (adsorption and absorption) by the freshwater bivalve *Corbicula fluminea* in sediments contaminated by TiO₂ nanoparticles. *Environ. Pollut.* 231, 712–721. <https://doi.org/10.1016/j.envpol.2017.08.080>
- Farré, M., Gajda-Schrantz, K., Kantiani, L., Barceló, D., 2009.

- Ecotoxicity and analysis of nanomaterials in the aquatic environment. *Anal. Bioanal. Chem.* 393, 81–95. <https://doi.org/10.1007/s00216-008-2458-1>
- Gopalakrishnan, A., Krishnan, R., Thangavel, S., Venugopal, G., Kim, S.J., 2015. Removal of heavy metal ions from pharmaceutical effluents using graphene-oxide nanosorbents and study of their adsorption kinetics. *J. Ind. Eng. Chem.* 30, 14–19. <https://doi.org/10.1016/j.jiec.2015.06.005>
- Guo, X., Mei, N., 2014. Assessment of the toxic potential of graphene family nanomaterials. *J. Food Drug Anal.* <https://doi.org/10.1016/j.jfda.2014.01.009>
- He, M., Shi, H., Zhao, X., Yu, Y., Qu, B., 2013. Immobilization of Pb and Cd in Contaminated Soil Using Nano-Crystallite Hydroxyapatite. *Procedia Environ. Sci.* 18, 657–665. <https://doi.org/10.1016/j.proenv.2013.04.090>
- Huang, X. yue, Ling, L., Zhang, W. xian, 2018. Nanoencapsulation of hexavalent chromium with nanoscale zero-valent iron: High resolution chemical mapping of the passivation layer. *J. Environ. Sci. (China)* 67, 4–13. <https://doi.org/10.1016/j.jes.2018.01.029>
- Ihsanullah, Abbas, A., Al-Amer, A.M., Laoui, T., Al-Marri, M.J., Nasser, M.S., Khraisheh, M., Atieh, M.A., 2016. Heavy metal removal from aqueous solution by advanced carbon nanotubes: Critical review of adsorption applications. *Sep. Purif. Technol.* <https://doi.org/10.1016/j.seppur.2015.11.039>
- Jin, Y., Liu, W., Li, X. liang, Shen, S. gang, Liang, S. xuan, Liu, C., Shan, L., 2016. Nano-hydroxyapatite immobilized lead and enhanced plant growth of ryegrass in a contaminated soil. *Ecol. Eng.* 95, 25–29. <https://doi.org/10.1016/j.ecoleng.2016.06.071>
- Jung, K.H., Kim, H.J., Kim, M.H., Seo, H., Lee, J.C., 2021. Superamphiphilic zwitterionic block copolymer surfactant-assisted fabrication of polyamide thin-film composite membrane with highly enhanced desalination performance. *J. Memb. Sci.* 618, 118677. <https://doi.org/10.1016/j.memsci.2020.118677>
- Kang, M., Lee, S.M., Kim, W., Lee, K.H., Kim, D.Y., 2019. Fubp1 supports the lactate-Akt-mTOR axis through the upregulation of Hk1 and Hk2. *Biochem. Biophys. Res. Commun.* 512, 93–99. <https://doi.org/10.1016/j.bbrc.2019.03.005>
- Karthick Kannan, P., Shankar, P., Blackman, C., Chung, C.-H., 2019. Recent Advances in 2D Inorganic Nanomaterials for SERS Sensing. *Adv. Mater.* 31, 1803432. <https://doi.org/https://doi.org/10.1002/adma.201803432>
- Lal, S., Singhal, A., Kumari, P., 2020. Exploring carbonaceous nanomaterials for arsenic and chromium removal from wastewater. *J. Water Process Eng.* <https://doi.org/10.1016/j.jwpe.2020.101276>
- Li, Y.H., Ding, J., Luan, Z., Di, Z., Zhu, Y., Xu, C., Wu, D., Wei, B., 2003. Competitive adsorption of Pb²⁺, Cu²⁺ and Cd²⁺ ions from aqueous solutions by multiwalled carbon nanotubes, in: *Carbon*. Pergamon, pp. 2787–2792. [https://doi.org/10.1016/S0008-6223\(03\)00392-0](https://doi.org/10.1016/S0008-6223(03)00392-0)
- Liu, R., Zhao, D., 2007. Reducing leachability and bioaccessibility of lead in soils using a new class of stabilized iron phosphate nanoparticles. *Water Res.* 41, 2491–2502. <https://doi.org/10.1016/j.watres.2007.03.026>
- Lu, C., Huang, Z., Liu, B., Liu, Y., Ying, Y., Liu, J., 2017. Poly-cytosine DNA as a High-Affinity Ligand for Inorganic Nanomaterials. *Angew. Chemie Int. Ed.* 56, 6208–6212. <https://doi.org/https://doi.org/10.1002/anie.201702998>
- Mahalakshmi, M., Selvanayagam, S., Selvasekarapandian, S., Moniha, V., Manjuladevi, R., Sangeetha, P., 2019. Characterization of biopolymer electrolytes based on cellulose acetate with magnesium perchlorate (Mg(ClO₄)₂) for energy storage devices. *J. Sci. Adv. Mater. Devices* 4, 276–284. <https://doi.org/10.1016/j.jsamd.2019.04.006>
- Mai, Z., Zhang, Huamin, Li, X., Xiao, S., Zhang, Hongzhang, 2011. Nafion/polyvinylidene fluoride blend membranes with improved ion selectivity for vanadium redox flow battery application. *J. Power Sources* 196, 5737–5741. <https://doi.org/10.1016/j.jpowsour.2011.02.048>
- Marefat, A., Karbassi, A., Nasrabadi, T., 2019. The role of the estuarine zone on the river particulate toxicity. *Environ. Sci. Pollut. Res.* 26, 5038–5053. <https://doi.org/10.1007/s11356-018-3932-8>
- Mobasherpour, I., Salahi, E., Pazouki, M., 2011. Removal of nickel (II) from aqueous solutions by using nano-crystalline calcium hydroxyapatite. *J. Saudi Chem. Soc.* 15, 105–112. <https://doi.org/10.1016/j.jscs.2010.06.003>
- Nasir, A., Masood, F., Yasin, T., Hameed, A., 2019. Progress in polymeric nanocomposite membranes for wastewater treatment: Preparation, properties and applications. *J. Ind. Eng. Chem.* <https://doi.org/10.1016/j.jiec.2019.06.052>
- Nizamuddin, S., Siddiqui, M.T.H., Mubarak, N.M., Baloch, H.A., Abdullah, E.C., Mazari, S.A., Griffin, G.J., Srinivasan, M.P., Tanksale, A., 2018. Iron Oxide Nanomaterials for the Removal of Heavy Metals and Dyes From Wastewater, in: *Nanoscale Materials in Water Purification*. Elsevier, pp. 447–472. <https://doi.org/10.1016/B978-0-12-813926-4.00023-9>
- Pang, H., Wu, Y., Huang, S., Ding, C., Li, S., Wang, Xiangxue, Yu, S., Chen, Z., Song, G., Wang, Xiangke, 2018. Macroscopic and microscopic investigation of uranium elimination by Ca–Mg–Al-layered double hydroxide supported nanoscale zero valent iron. *Inorg. Chem. Front.* 5, 2657–2665. <https://doi.org/10.1039/C8QI00779A>
- Park, H.J., Hong, S.Y., Chun, D.H., Kang, S.W., Park, J.C., Lee, D.S., 2019. A highly susceptible mesoporous hematite microcube architecture for sustainable P-type formaldehyde gas sensors. *Sensors Actuators, B Chem.* 287, 437–444. <https://doi.org/10.1016/j.snb.2019.01.153>
- Patra, S., Roy, E., Madhuri, R., Sharma, P.K., 2017. A technique comes to life for security of life: the food contaminant sensors, in: *Nanobiosensors*. Elsevier, pp. 713–772. <https://doi.org/10.1016/b978-0-12-804301-1.00017-5>
- Priya, K., Vijayakumar, M., Janani, B., 2020. Chitosan-mediated synthesis of biogenic silver nanoparticles (AgNPs), nanoparticle characterisation and in vitro assessment of anticancer activity in human hepatocellular carcinoma HepG2 cells. *Int. J. Biol. Macromol.* 149, 844–852. <https://doi.org/10.1016/j.jbiomac.2020.02.007>
- Rtimi, S., Dionysiou, D.D., Pillai, S.C., Kiwi, J., 2019. Advances in catalytic/photocatalytic bacterial inactivation by nano Ag and Cu coated surfaces and medical devices. *Appl. Catal. B Environ.* <https://doi.org/10.1016/j.apcatb.2018.07.025>
- Saad, A.H.A., Azzam, A.M., El-Wakeel, S.T., Mostafa, B.B., Abd El-latif, M.B., 2018. Removal of toxic metal ions from wastewater using ZnO@Chitosan core-shell nanocomposite. *Environ. Nanotechnology, Monit. Manag.* 9, 67–75. <https://doi.org/10.1016/j.enmm.2017.12.004>
- Shahraki, S., Delarami, H.S., Khosravi, F., Nejat, R., 2020. Improving the adsorption potential of chitosan for heavy metal ions using aromatic ring-rich derivatives. *J. Colloid Interface Sci.* 576, 79–89. <https://doi.org/10.1016/j.jcis.2020.05.006>
- Sheng, G., Alsaedi, A., Shammakh, W., Monaque, S., Sheng, J., Wang, X., Li, H., Huang, Y., 2016. Enhanced sequestration of selenite in water by nanoscale zero valent iron immobilization on carbon nanotubes by a combined batch, XPS and XAFS investigation. *Carbon N. Y.* 99, 123–130. <https://doi.org/10.1016/j.carbon.2015.12.013>
- Shingley, H.J., Engates, K.E., Grover, V.A., 2013. 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.* 20, 1727–1736. <https://doi.org/10.1007/s11356-012-0984-z>
- Sierra, I., Morante-Zarcelero, S., 2018. New advances in food sample

- preparation with nanomaterials for organic contaminants analysis by liquid chromatography, in: *Nanomaterials in Chromatography: Current Trends in Chromatographic Research Technology and Techniques*. Elsevier, pp. 118–154. <https://doi.org/10.1016/B978-0-12-812792-6.00005-4>
- Silva, M.M., Pérez, D.V., Wasserman, J.C., Santos-Oliveira, R., Wasserman, M.A.V., 2017. The effect of nanohydroxyapatite on the behavior of metals in a microcosm simulating a lentic environment. *Environ. Nanotechnology, Monit. Manag.* 8, 219–227. <https://doi.org/10.1016/j.enmm.2017.08.002>
- Sultan, A., Mohammad, E., 2017. Chemical sensing, thermal stability, electrochemistry and electrical conductivity of silver nanoparticles decorated and polypyrrole enwrapped boron nitride nanocomposite. *Polymer (Guildf)*. 113, 221–232. <https://doi.org/10.1016/j.polymer.2017.02.074>
- Suman, Kardam, A., Gera, M., Jain, V.K., 2015. A novel reusable nanocomposite for complete removal of dyes, heavy metals and microbial load from water based on nanocellulose and silver nano-embedded pebbles. *Environ. Technol.* 36, 706–714. <https://doi.org/10.1080/09593330.2014.959066>
- Sumesh, E., Bootharaju, M.S., Anshup, Pradeep, T., 2011. A practical silver nanoparticle-based adsorbent for the removal of Hg²⁺ from water. *J. Hazard. Mater.* 189, 450–457. <https://doi.org/10.1016/j.jhazmat.2011.02.061>
- Sundararajan, M., K Ghosh, S., 2011. Designing Novel Materials through Functionalization of Carbon Nanotubes for Application in Nuclear Waste Management: Speciation of Uranyl. *J. Phys. Chem. A* 115, 6732–6737. <https://doi.org/10.1021/jp203723t>
- Vilardi, G., Ochando-Pulido, J.M., Verdone, N., Stoller, M., Di Palma, L., 2018. On the removal of hexavalent chromium by olive stones coated by iron-based nanoparticles: Equilibrium study and chromium recovery. *J. Clean. Prod.* 190, 200–210. <https://doi.org/10.1016/j.jclepro.2018.04.151>
- Wan, J., Zeng, G., Huang, D., Hu, L., Xu, P., Huang, C., Deng, R., Xue, W., Lai, C., Zhou, C., Zheng, K., Ren, X., Gong, X., 2018. Rhamnolipid stabilized nano-chlorapatite: Synthesis and enhancement effect on Pb- and Cd-immobilization in polluted sediment. *J. Hazard. Mater.* 343, 332–339. <https://doi.org/10.1016/j.jhazmat.2017.09.053>
- Wang, D., Chu, L., Paradelo, M., Peijnenburg, W.J.G.M., Wang, Y., Zhou, D., 2011. Transport behavior of humic acid-modified nano-hydroxyapatite in saturated packed column: Effects of Cu, ionic strength, and ionic composition. *J. Colloid Interface Sci.* 360, 398–407. <https://doi.org/10.1016/j.jcis.2011.04.064>
- Wang, Y., Zhang, H., Song, C., Gao, C., Zhu, G., 2020. Effect of aminophend/formaldehyde resin polymeric nanospheres as nanofiller on polyamide thin film nanocomposite membranes for reverse osmosis application. *J. Memb. Sci.* 614, 118496. <https://doi.org/10.1016/j.memsci.2020.118496>
- Yang, J., Hou, B., Wang, J., Tian, B., Bi, J., Wang, N., Li, X., Huang, X., 2019. Nanomaterials for the Removal of Heavy Metals from Wastewater. *Nanomaterials* 9. <https://doi.org/10.3390/nano9030424>
- Yang, L., Wei, Z., Zhong, W., Cui, J., Wei, W., 2016. Modifying hydroxyapatite nanoparticles with humic acid for highly efficient removal of Cu(II) from aqueous solution. *Colloids Surfaces A Physicochem. Eng. Asp.* 490, 9–21. <https://doi.org/10.1016/j.colsurfa.2015.11.039>
- Yang, S., Zou, Q., Wang, T., Zhang, L., 2019. Effects of GO and MOF@GO on the permeation and antifouling properties of cellulose acetate ultrafiltration membrane. *J. Memb. Sci.* 569, 48–59. <https://doi.org/10.1016/j.memsci.2018.09.068>
- Yirsaw, B.D., Megharaj, M., Chen, Z., Naidu, R., 2016. Environmental application and ecological significance of nano-zero valent iron. *J. Environ. Sci. (China)*. <https://doi.org/10.1016/j.jes.2015.07.016>
- Zhang, R., Yu, S., Shi, W., Wang, W., Wang, X., Zhang, Z., Li, L., Zhang, B., Bao, X., 2017. A novel polyesteramide thin film composite nanofiltration membrane prepared by interfacial polymerization of serinol and trimesoyl chloride (TMC) catalyzed by 4-dimethylaminopyridine (DMAP). *J. Memb. Sci.* 542, 68–80. <https://doi.org/10.1016/j.memsci.2017.07.054>
- Zhang, X., Sun, H., Zhang, Z., Niu, Q., Chen, Y., Crittenden, J.C., 2007. Enhanced bioaccumulation of cadmium in carp in the presence of titanium dioxide nanoparticles. *Chemosphere* 67, 160–166. <https://doi.org/10.1016/j.chemosphere.2006.09.003>
- Zhang, Y., Li, Z., 2017. Heavy metals removal using hydrogel-supported nanosized hydrous ferric oxide: Synthesis, characterization, and mechanism. *Sci. Total Environ.* 580, 776–786. <https://doi.org/10.1016/j.scitotenv.2016.12.024>
- Zhang, Y., Wu, B., Xu, H., Liu, H., Wang, M., He, Y., Pan, B., 2016. Nanomaterials-enabled water and wastewater treatment. *NanoImpact*. <https://doi.org/10.1016/j.impact.2016.09.004>
- Zhu, Y., Liu, X., Hu, Y., Wang, R., Chen, M., Wu, J., Wang, Y., Kang, S., Sun, Y., Zhu, M., 2019. Behavior, remediation effect and toxicity of nanomaterials in water environments. *Environ. Res.* <https://doi.org/10.1016/j.envres.2019.04.014>
- Zhuang, C., Jiang, Y., Zhong, Y., Zhao, Y., Deng, Y., Yue, J., Wang, D., Jiao, S., Gao, H., Chen, H., Mu, H., 2018. Development and characterization of nano-bilayer films composed of polyvinyl alcohol, chitosan and alginate. *Food Control* 86, 191–199. <https://doi.org/10.1016/j.foodcont.2017.11.024>