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## ROLE OF DIFFERENT NANOMATERIALS FOR WASTE WATER TREATMENT - A REVIEW

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### Abstract

Worldwide, the pervasive issue of water pollution caused by diverse toxic contaminants has reached alarming levels. To address this concern, a range of technologies has been employed for the treatment of water and wastewater, including flotation, ion-exchange, chemical precipitation, membrane filtration, coagulation-flocculation, adsorption, and electrochemical techniques. In recent decades, nanotechnology has garnered significant attention, leading to the creation of numerous nanomaterials designed for water purification. This review article focuses on the evaluation of various nanomaterials utilized in the decontamination of water, with particular emphasis on the adsorption of dyes.

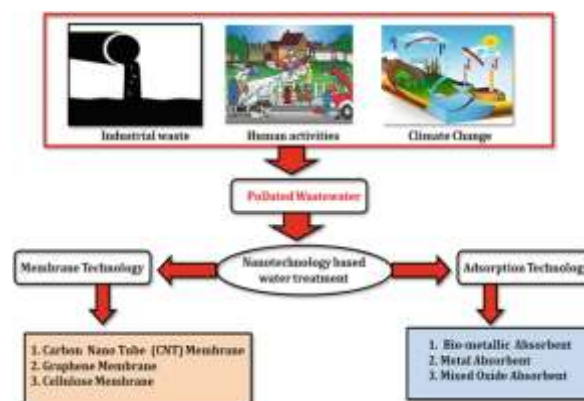
**Keywords:** Nanomaterials; water treatment; adsorption and carbon nanotubes.

### 1. Introduction

Clean water is one of the most important elements for all living organisms to sustain life. However, due to the rapid pace of industrialization and tremendous increase in the population, the contamination of water resources has occurred globally [1, 2]. Besides other needs, the demand for water has increased tremendously in agricultural, industrial and domestic sectors consuming 70, 22 and 8% of the available fresh water, respectively and this has resulted in the generation of large amounts of wastewater [3] containing a number of 'pollutants'. Some of the important classes of aquatic pollutants are heavy metal ions and dyes, and once these enter into the water, water is no longer safe for drinking purpose and sometimes it is very difficult to completely treat the contaminated water. Aquatic pollutants are often very dangerous for living beings, and also affect the ecosystem. Therefore, the removal of these pollutants from contaminated water is an urgent need in order to prevent the negative effects on the human health and to the environment. From past few decades, various techniques have been developed for treating the waste water [4]. Among them, most important methods are solvent extraction, micro and ultra-filtration, sedimentation and gravity separation, flotation, precipitation, coagulation, oxidation, evaporation, distillation, reverse osmosis, adsorption, ion exchange, electrodialysis, electrolysis, etc. From above mentioned

techniques, adsorption is one of the considerable techniques for treating the waste water, because of its easy operation, low cost and the availability of a wide range of adsorbents. Besides, adsorption can also be applied for the removal of soluble and insoluble organic, inorganic, and biological pollutants. Additionally, adsorption can also be used for source reduction and reclamation for potable, industrial, and other water purposes. In spite of these facts, adsorption has certain limitations such as it could not achieve a good status at commercial levels. Probably, it is due to the lack of suitable adsorbents with high adsorption capacity and limited use of adsorbents on commercial scale columns. Besides, a single adsorbent cannot be used for removing all kind of pollutants. Different adsorbents are used for different pollutants based on their properties [5].

In spite of some limitations, adsorption will be considered a good water treatment technology in the near future. Much work has been conducted on the removal of different pollutants from water by using adsorption in batch mode process. Initially, activated carbon was used for the removal of pollutants from water, which has been replaced by some cost-effective adsorbents [6].



**Fig 1: Waste water Treatment**

In the last two decades, nanotechnology has emerged significantly with its applications in almost all branches of

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science and technology. As a matter of fact, various nanomaterials have been prepared and used for the removal of aquatic pollutants. In view of the importance of water quality and emerging utilities of nanotechnology, attempts have been made to discuss various aspects of water treatment by adsorption using nanomaterials. In this regard, promoting nanomaterials presents opportunities to develop local and practical solutions for tackling global water pollution [7]. This review article presents a brief overview of the technical applicability of different nanomaterials for removing various aquatic pollutants. (Fig.1)

## 2. Nanomaterials as adsorbents for water treatment

Nano adsorbents are nanoscale particles from organic or inorganic materials that have a high affinity to adsorb substances. Because of their high porosity, small size, and active surface, nanoadsorbents not only are capable of sequestering contaminants with varying molecular size, hydrophobicity, and speciation behavior, but also enable manufacturing process to consume raw materials efficiently without releasing its toxic payload. Nanoadsorbents not only work rapidly, but also have considerable pollutant-binding capacities. They can also be chemically regenerated after being exhausted. For these reasons, scholarly interests of nanotechnology have been growing rapidly worldwide. At the nanoscale, materials show unique characteristics and, because of their small size, they possess a large surface area and 'surface area to volume' ratio [8]. These characteristics improve the adsorption capacity of the nanoparticles. In addition to the large surface area, these particles show unique characteristics, such as catalytic potential and high reactivity, which make them as better adsorbing materials than conventional materials. Because of their high surface area, nanoparticles have a greater number of active sites for interaction with different chemical species. To get better results for the removal of pollutants from wastewater, nanoparticles are becoming new alternatives for the treatment of wastewater (Fig.2) [9].

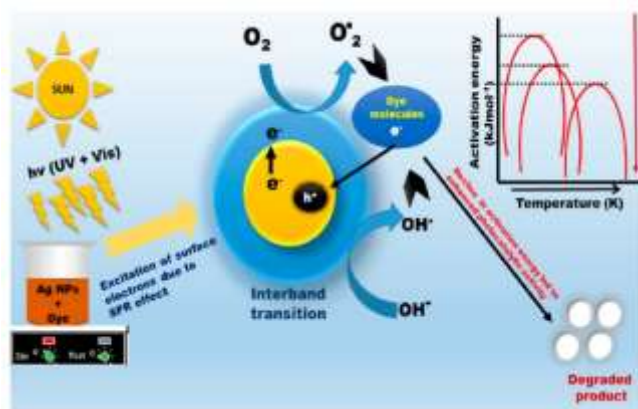


Fig 2: Nanomaterials in water Treatment

### 2.1. Carbon based materials

For any adsorption process, an adsorbent having large surface area, pore volume, and proper functionalities is the key to success. Currently, many different porous

materials have been developed, such as activated carbon, pillared clays, zeolites, mesoporous oxides, polymers and metal-organic frameworks, showing varying extent of effectiveness in removing the toxic pollutants from air, water and soil. Among them, carbon-based adsorbents including activated carbon, carbon nanotubes, fullerenes and graphene, usually show high adsorption capacity and thermal stability. Of the various nanomaterials based adsorbents, carbon based materials have been probed as superior adsorbents for the removal of inorganic and organic pollutants. Since the discovery of carbon nanotubes (CNTs) and fullerene, these materials have been extensively used as effective adsorbents but its large scale application is limited on economic grounds and hence, designing the adsorbents at a lower cost is a great challenge. Multiwalled carbon nanotube shows considerable removal efficiency of inorganic metal ions with the help of magnetic nanomaterials [10].

#### 2.1.1. Carbon nanotubes (CNTs)

Carbon nanotubes are one of the allotropes of carbon and these can be considered as various structural forms of carbon element. Basically CNTs are composed of cylindrical shape rolled up in a tube like structure. CNTs are of two types, single walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs), where single walled carbon nanotubes are composed of single graphene sheet with a roll up and multiwalled carbon CNTs, with their high surface active site to volume ratio and controlled pore size distribution, have an exceptional sorption capability and high sorption efficiency compared to conventional granular and powder activated carbon, which have intrinsic limitations like surface active sites and the activation energy of sorption. Extensive studies have found that the adsorption capacity of CNTs depends on both the surface functional groups and the nature of the sorbate. For instance, the amounts of surface acidity (carboxylic, lactonic and phenolic groups) favor the adsorption of polar compounds. On the other hand, unfunctionalized CNT surface is proved to have higher adsorption capacity towards non-polar compounds such as polycyclic aromatic hydrocarbons. The sorption behaviors of CNTs mainly involve chemical interaction for polar compounds and physical interaction for non-polar compounds [11].

Sorption capacity of CNTs is effective over a broad pH range. Particularly, optimum performance was reported in the pH range of 7 to 10. Other than this pH range, ionization and in another study, resorcinol was taken as a model phenolic derivative and the efficiency of MWCNTs was assessed for the adsorption of resorcinol. The kinetics of resorcinol onto MWCNTs was fast. The experiments were not performed at pH values greater than 8.0 as in basic condition resorcinol is oxidized. Resorcinol uptake increased with the decrease in solution pH since its solubility decreases with the lowering of pH. A reduction in the uptake capacity of resorcinol was observed due to the electrostatic repulsion between negatively charged resorcinol and acid-treated MWCNTs. Also the carboxylic groups, those were present on the surface of MWCNTs,

acted as electrons withdrawing groups localizing electron from  $\pi$  system of MWCNTs interfering and weakening the forces between aromatic ring of resorcinol and graphite structure of MWCNTs. The hydroxyl group (located in meta-position) present in the structure of resorcinol also positively influenced its adsorption. The potential of MWCNTs for herbicide adsorption has also been tested by the researchers [12]. Carbon nanotubes have also been tested for the removal of Natural organic matter (NOM) from aqueous solution and the results have been found promising. Hyung et al. investigated the role of MWCNTs in the removal of NOM. CNT in particular, in the natural aquatic environment might occur to a higher extent than predicted based only on the hydrophobicity of these materials. The NOM had anionic character across the pH range 3.0-9.0. The effect of NOM characteristics and water quality parameters on adsorptive interaction between MWCNT and NOM in aqueous phase was examined. Freundlich isotherm studies have been employed and were compared with the adsorption onto activated carbon.

Finally, the amount of stable MWCNT suspension formed in water as a result of NOM adsorption under varying conditions was quantitatively analyzed. A wide range of NOM concentrations (2.5-50 mg C/L) was investigated, and it was noted that NOM concentrations in some natural surface and ground waters were lower than concentration levels used. Joseph et al. [13] investigated NOM removal from a variety of potential drinking water sources through a combination of coagulation and adsorption with CNTs. Both SWCNTs and MWCNTs were examined for their removal efficiencies for NOM parallel to coagulation process in the presence of alum and ferric chloride metal coagulants. Synthetic seawater (SW) and brackish water (BW) (contained humic acid as its representative NOM), synthetic (old and young) landfill leachates (OL, YL) (contained glucose as its representative NOM), and natural river water (BRW) were chosen to obtain a detailed knowledge of NOM and its behavior towards adsorption and coagulation. Humic acid used in the study contained ~40% DOC. The isotherm data of BW, SW and BRW fitted well with the Freundlich model and SWCNTs consistently had a higher adsorption capacity than MWCNTs for NOM. The higher specific surface area of SWCNTs (407 m<sup>2</sup>/g) as compared to that of MWCNTs (60 m<sup>2</sup>/g) was attributed to be responsible for the greater NOM uptake capacity of former. Adsorption of trihalomethanes (THMs) from water using MWCNTs has also been investigated. Multiwalled carbon nanotubes (MWCNTs) were purified by mixed HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> solution and were employed as adsorbents. CNTs from a pure solution was found to be quite different from a mixed solution. As the temperature increased from 5 to 35 °C, the maximum adsorption capacity of CHCl<sub>3</sub> calculated by the Langmuir model decreased from 3.158 to 2.826 mg/g. These values were two to three times more than that of commercially available PAC (1.32 mg/g) measured at 25 °C in the study, reflecting that CNTs are efficient adsorbents. The kinetics of adsorption process was found to follow the first order rate law. Morawski et al. [68]

indicated that the adsorption of CHCl<sub>3</sub> onto carbon sphere from a mixed solution was strongly depressed, about 40% of adsorption capacity from a solution of pure CHCl<sub>3</sub>. Besides these, several other reports are available where carbon nanomaterials have been used for the removal of aquatic pollutants. There is no doubt that CNTs possess great potential as superior adsorbents for removing divalent metal ions, dyes, NOMs and THMs from aqueous solution, but their relatively high unit cost restricts their practical use. In addition to it, raw CNTs may possess some degree of toxicity due to the presence of metal catalysts while chemically functionalized CNTs have not demonstrated any toxicity so far [14]. As a result, the practical use of CNTs as sorbents in water and wastewater treatment depends on the continuation of research into the development of a cost effective way of CNTs production and the no or low toxicity of CNTs and CNT related materials such as carbon nanocrystals (CNCs).

Besides metals removal, CNTs have also been used for the removal of various organic pollutants from water and wastewater and a brief discussion is presented here. Most of the organic dyes will have high levels of toxicity at their lower level of concentration in water and will affect the potential carcinogenic effects in the living organisms. Due to these reason, most of the researchers are working on the treatment of organic dyes using various adsorbents, before leaving them into the environment. For treating the organic dyes from wastewaters, there are wide range of adsorbents has been used, such as zeolites, clays, polymers and activated carbon, etc., Dyes are important water pollutants which are generally present in the effluents of the textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries. The colored dye effluents are generally considered to be highly toxic to the aquatic biota and affect the symbiotic process by disturbing the natural equilibrium through reduced photosynthetic activity due to the coloration of the water in streams. Carbon nanotubes are one of the promising adsorbent for treating the organic dyes, because of their large surface area and their unique properties [15]. Other than dyes, some other organic pollutants such as pharmaceuticals, phenols, pesticides, aromatic amines, and other toxic organics have shown the potential negative impact on the environment, mainly onto the water sources. For example, olaquinox (OLA) is a well-known food additive that is highly phototoxic, mutagenic, genotoxic, and carcinogenic. Tetracycline (TC) is one of the most widely used antibiotics in the world and has serious side effects on human health and potential negative effects on the environment when it accumulates in water systems. Thus, effective removal of organic pollutants from contaminated water is of great importance. The current priority is to develop novel adsorbent materials with high adsorption capacities and removal efficiencies to realize effective control of these environmental pollutants.

### 2.1.2. Graphene based materials

Research has also been focused on another allotropy of carbon, which is graphene. From the past decade, there is a huge growth in the use of graphene and

graphene based materials for environmental remediation, due their unique properties which helps to new possibilities to improve the performance of numerous environmental processes. There is a choice of whether to use graphene as a carbon-based nanocomposite will be determined by the cost, process ability, and environmental implications of each material. In this regard, environmental applications based on GO offer more realistic possibilities compared to pristine graphene due to GO's lower production costs. In addition to economic considerations, environmental implications of graphene-based materials will represent an important factor in the development of graphene based technologies. Graphene is a substitute for CNT and an ideal material for water treatment. Compared to CNTs, the utilization of graphene-based materials as adsorbents may offer several advantages. First, single-layered graphene materials possess two basal planes available for pollutant adsorption. In contrast, the inner walls in CNTs are not accessible by the adsorbates. Second, graphene oxide (GO) and reduced graphene oxide (rGO) can be easily synthesized through chemical exfoliation of graphite, without using complex apparatus or metallic catalysts. The resulting graphene material is free of catalyst residues, and no further purification steps are needed. In the specific case of GO, the as-prepared material already possesses a large number of oxygen-containing functional groups and no additional acid treatments are required to impart a hydrophilic character and reactivity to GO [16]. This is a significant advantage, since those functional groups are likely responsible for the adsorption of metal ions by GO sheets.

Graphene based materials serve as efficient adsorbent, due to their large specific surface area and electron rich environment. Due to the strong functional groups on graphene oxide (GO) surface, GO will be a potential adsorbent for metal ion complexation through both electrostatic and coordinate approaches. A variety of studies have described the application of graphene based materials as adsorbents for the removal of inorganic species from aqueous solutions. Most of these studies have employed GO as a model adsorbent for remediation of metal ions in water. GO is preferable to pristine graphene for metal ion adsorption due to GO's high content of oxygen groups available to interact with metal ions. The importance of these oxygen containing functional groups was demonstrated by comparing the Pb(II) adsorption performance of pristine and oxidized graphene sheets. GO and graphene nanosheets (GNs) can also be incorporated with metal oxides to form composite materials. A composite with GO and metal oxide usually has specific features and has been used as effective adsorbents for the removal of different pollutants. Detailed ecotoxicological assessments and life-cycle analyses still need to be performed, in order to identify the forms of graphene-based nanomaterials that will allow us to utilize the properties of graphene, while minimizing the associated health and environmental impacts. Until these economic and environmental considerations are known and better

understood, it would be hard to determine the most promising areas of research for graphene based materials. One of the most important challenges will be to reduce GO successfully to a pristine graphene material in order to restore its exceptional electronic and mechanical properties. Reduction of GO for the production of graphene certainly appears a most promising approach to produce low cost graphene on a large scale (Table 1).

**Table 1: Specialization of Nanosorbent**

St. No.	Nanosorbent	Specialization/Treatment
1.	Carbon-based nanosorbents	Water containing nickel ions ( $Ni^{2+}$ ), (high specific surface area, excellent chemical resistance, mechanical strength, and good adsorption capacity)
2.	Captymer™	Contaminants (perchlorate, nitrate, bromide and uranium) branched macromolecules forming globular micro particles
3.	Regenerable polymeric nanosorbent	Many organic and inorganic contaminants in wastewater
4.	Nanoclays	Hydrocarbons dyes and phosphorus
5.	Carbo-Iron	The activated carbon for sorption while the elementary iron is reactive and can reduce different contaminants
6.	Nano networks	Complex three-dimensional networks caused by the ion beam providing better efficiency

## 2.2. Metal oxide based nanomaterials

### 2.2.1. Nano metal oxides

Among the available adsorbents, nanosized metal oxides (NMOs), including nanosized ferric oxides, manganese oxides, aluminum oxides, titanium oxides, magnesium oxides and cerium oxides, are classified as the promising ones for removal of pollutants from aqueous systems. This is partly because of their large surface areas and high activities caused by the size quantization effect. Recent studies suggested that many NMOs exhibit favorable sorption to heavy metals in terms of high capacity and selectivity, which would result in high removal of toxic metals to meet increasingly strict regulations. However, as the size of the metal oxides reduces from micrometer to nanometer levels, the increased surface energy inevitably leads to their poor stability. Consequently, NMOs are prone to agglomeration due to van der Waals forces or other interactions, and the high capacity and selectivity of NMOs would be greatly decreased or even lost. Moreover, NMOs are unusable in fixed beds or any other flow through systems because of the excessive pressure drops (or the difficult separation from aqueous systems) and poor mechanical strength. To improve the applicability of NMOs in real wastewater treatment, these were impregnated into porous supports of large size to obtain composite adsorbents. The widely used porous supports include activated carbon, natural materials, synthetic polymeric hosts, etc. Besides traditional NMOs, magnetic NMOs attract increasing attentions as they can be easily separated from water under a magnetic field. Also, magnetic NMOs-based composite adsorbents allowed easy isolation from aqueous solutions for recycling or regeneration. Such facile separation is essential to improve the operation efficiency and reduce the cost during water/wastewater

treatment. Since there are so many types of NMOs employed for heavy metals removal, comparison of their capacity is necessary. However, the experimental conditions in the related references varied greatly and thus, a direct comparison of the reported data seems a little meaningless. For example, due to the different synthetic methods of a given NMO, it is difficult to keep constant its size and surface chemistry. In addition, the operating conditions, like the solution chemistry (pH, ionic strength and ion types), temperature, experimental form (batch or column runs) are quite different from each other. Here, a simple comparison on some typical NMOs for metals removal has been made [17].

### 2.3. Miscellaneous nanoadsorbents

Besides the above categorized nanoadsorbents, there are some other nanoadsorbents which have been prepared and applied in water treatment by different researchers. A brief discussion is presented here. Chitosan-Fe(0) nanoparticles (chitosan-Fe(0)) were prepared using biodegradable chitosan as a stabilizer and batch experiments were conducted to evaluate the influences of initial Cr(VI) concentration and other factors on Cr(VI) reduction on the surface of the chitosan-Fe(0). The authors suggested that the overall disappearance of Cr(VI) might include both physical adsorption of Cr(VI) onto the chitosan-Fe(0) surface and subsequent reduction of Cr(VI) to Cr(III). Characterization with high-resolution X-ray photoelectron spectroscopy revealed that after the reaction, relative to Cr(VI) and Fe(0), Cr(III) and Fe(III) were the predominant species on the surface of chitosan-Fe(0). Chitosan also inhibited the formation of Fe(III)-Cr(III) precipitation due to its high efficiency in chelating the Fe(III) ions. The adsorption of eosin Y, as a model anionic dye, from aqueous solution using chitosan nanoparticles, prepared by the ionic gelation between chitosan and tripolyphosphate, was examined by Du et al. The adsorption capacity was found to be 3.33 g/g. The adsorption process was endothermic in nature with an enthalpy change ( $\Delta H$ ) of 16.7 kJ/mol at 20–50 °C. The optimum pH value for eosin Y removal was found to be 2–6. The dye was desorbed from the chitosan nanoparticles by increasing the pH of the solution. The desorption percentage was about 60% within 60 min at pH 11.0, whereas 98.5% of the dye could be eluted at pH 12 in 150 min. The potential of nanochitosan to remove acid dyes from aqueous solution has also been explored by the researchers. The monolayer adsorption capacities were determined to be 1.77, 4.33, 1.37 and 2.13 mmol/g for acid orange 10, acid orange 12, acid red 18 and acid red 73 dyes, respectively.

The differences in capacities might be due to the differences in the size of dye molecules and the number of sulfonate groups on each dye molecule. The results have demonstrated that monovalent and smaller dye molecular sizes have superior capacities due to the increase in dye/chitosan surface ratio in the system and deeper penetration of dye molecules into the internal pore structure of nano-chitosan. The mechanism of the

adsorption process of acid dye on nano-chitosan was proposed to be the ionic interactions of the colored dye ions with the amino groups on the chitosan. By encapsulating zirconium phosphate (ZrP) nanoparticles into three macroporous polystyrene resins with various surface groups, from the three nanocomposite adsorbents (denoted as ZrP-Cl, ZrP-S, and ZrP-N) were fabricated, respectively for lead removal from water. Effect of functional groups on nano ZrP dispersion and effect of ZrP immobilization on the mechanical strength of the resulting nanocomposites were investigated. As compared to ZrP-N, ZrP-S exhibited higher preference toward lead ion at high calcium levels as a result of the potential Donnan membrane effect. On the other hand, nano-ZrP immobilization would simultaneously reinforce both the compressive strength and the wear performance of the resulting nanocomposites with the ZrP loadings up to 5 wt%. The organic-inorganic hybrid of poly(acrylic acid-acrylonitrile)/attapulgitite, P(A-N)/AT nanocomposites, were prepared by using in situ polymerization and composition of acrylic acid (AA) and acrylonitrile (AN) onto modified attapulgitite (AT) nanoparticles. The resulting P(A-N)/AT nanocomposites were transformed into novel nano-adsorbent of poly(acrylic acid acrylamidoxime)/attapulgitite by further functionalization, i.e. P(A-O)/AT nano-adsorbent. The adsorption properties of P(A-O)/AT toward metal ions were determined, and the results indicated that the adsorbents with nanocomposite structure held a good of selectivity to Pb(II) among numerous metal ions. The maximum removal capacity of Pb(II) was up to 109.9 mg/g and it was notable to see that the adsorption removal of P(A-O)/AT nano-adsorbent for Pb(II) could achieve more than 96.6% when the initial concentration of Pb(II) was 120.0 mg/L. Besides the above mentioned nanoadsorbents, several other materials have also been examined as nano-adsorbents for the removal of different aquatic pollutants. Raveendra et al. have synthesized nanocrystalline meta-zinc titanate ( $ZnTiO_3$ ) ceramic using a self-propagating solution combustion synthesis (SCS) using urea as fuel. The preparation and characterization of ilmenite type nanocrystalline  $ZnTiO_3$  ceramic were discussed in detail and studied its effectiveness in the adsorption of hazardous malachite green (MG) dye. Mechanism of adsorption of MG onto the nanocrystalline  $ZnTiO_3$  ceramic was explained on the basis of pH effect. Under acidic conditions, it was difficult for cationic MG dye to adsorb onto the nanocrystalline  $ZnTiO_3$  surface.

This is because, as initial pH of dye solution decreased, the number of negatively charged adsorbent sites decreased and positively charged sites increased which did not favor the adsorption since the MG is a cationic dye resulting in electrostatic repulsion. This decrease in the adsorption at lower pH was also due to the fact that the presence of excess  $H^+$  released from the MG dye at acidic condition which opposed with dye cations for the adsorption. In turn, at higher pH, the negatively charged sites on adsorbent molecule increased which

attracted the positively charged sites of cationic MG dye resulting in higher adsorption. The results showed that the parameters such as effect of pH and contact time played a very important role on the adsorption. Adsorption kinetics results show that adsorption of MG over ZnTiO<sub>3</sub> followed first order kinetics. They have synthesized nickel nanoparticles (Ni-NP) and zinc selenide nanoparticles (Zn-Se-NP) which were loaded on activated carbon and used for the removal of Arsenazo (III) dye from aqueous medium. The results show that Langmuir plot for Arsenazo (III) adsorption on both adsorbents is linear over the whole concentration range studies and the correlation coefficients were extremely high ( $R^2 > 0.99$ ). Heat of adsorption and the adsorbent-adsorbate interaction were studied by Tempkin and Pyzhev models. Adsorption equilibrium data were also fitted with Dubinin and Radushkevich isotherm models. From the correlation coefficient it was concluded that the adsorption was not fitted well with Dubinin and Radushkevich isotherm model. The high Arsenazo (III) removal using both adsorbents showed their applicability to remove the dye in short equilibrium time (less than 25 min). Adsorption kinetics was found to follow a second-order rate expression and equilibrium adsorption data for both adsorbents were best represented by the Langmuir isotherms. Higher inhibition field of nickel nanoparticle (120–205 Oe) in comparison to respective value for bulk nickel may be attributed to decrease in the size of produced nickel and formation of nanoparticle. The Ni-NP-AC was efficient for quantitative removal of Arsenazo (III) (98% within 20 min). It was found that the dye removal efficiency of Ni-NP-AC was superior to that of Zn-Se-NP-AC. The maximum adsorption capacity of Ni-NP-AC and Zn-Se-NP-AC was found as 168 and 162.74 mg/g, respectively.

#### 2.4. Silsesquioxane based materials

A silsesquioxane is an organosilicon compound with the chemical formula [RSiO<sub>3/2</sub>]<sub>n</sub> (R = H, alkyl, aryl or alkoxy). Silsesquioxanes are members of polyoctahedral silsesquioxanes ("POSS"), which have attracted attention as precursors to ceramic materials and nanocomposites. The potential applications of silsesquioxane based materials lie in the fields of catalysis, separation and storage, opto-electronics and environmental field. These materials are extensively used for the synthesis of nano structured hybrid polymer materials, having nanometer sized inorganic cores surrounded with organic functional groups. There are diverse POSS based nanocomposites which have been developed, and generally, there are mainly three approaches for integrating POSS into nanocomposites: first is the core as a POSS function and the microinitiator to initiate polymerization from the surface of the POSS, giving a star-like macromolecules; second is multi-functional POSS compounds which can function as nano fillers or monomers to polymerize with organic monomers or polymers, forming crosslinked nanocomposites and the third is monofunctional POSS compounds as tethering macromolecules to graft onto a

polymer backbone, forming polymers with pedant POSS cages. Star-like nanocomposites with POSS as the core are generally prepared using functional POSS as the micro-initiator. For example, by reacting octa(aminophenyl) silsesquioxane (OAPS) with 2-bromo-isobutyryl bromide, octa-butyrylbromide POSS can be obtained and it can subsequently initiate atom transfer radical polymerization (ATRP) of 2,2,3,4,4,4-hexafluorobutyl methacrylate (HFBMA) or methyl methacrylate (MMA). Due to the incorporation of a thermally stable inorganic Si-O core, the star-like POSS-g-HFBMA exhibits improved thermal properties. These hybrid porous polymers possessed high surface areas, unique bimodal pores with uniform micropores and mesopores centered at 1.5 nm and 3.7 nm, respectively, and an excellent size-selective adsorption for dyes. They displayed an outstanding adsorption ability for rhodamine B (RhB) with maximum adsorption capacities of 828.6 mg/g, and could rapidly remove more than 90% RhB within 3 minutes when the initial concentration of the RhB solution was 50 ppm. Liu et al. reported the removal of Pb<sup>2+</sup> ions from aqueous solutions by using synthetic polymer P(AO/AN/MA) which achieved an adsorption capacity of 4.28 mmol/g at 25 °C. Polymers which could selectively adsorb metal ions should consist of two monomer groups, each having a different role. One functional group forms a complex with the target and the other allows the polymers to stretch and shrink reversibly in response to environmental change [18, 19]. Generally, amidoxime (AO) and carboxylic groups (AA) were chosen as the functional groups. Based on the discussion above, it can be concluded that these materials are very promising to be industrialized and be of great use in the field of wastewater treatment. A future direction for the development of POSS-containing materials is also proposed for applications in organic photovoltaic and other high-performance materials [20].

#### 3. Conclusion

The current review article examines a number of nanomaterials that have been applied to waste water purification. The literature analysis makes clear that a variety of nanomaterials have been investigated for their potential to remove organic and/or inorganic contaminants. Moreover, because of their enhanced adsorption, nanoparticles ultimately offer a strong substitute for traditional therapeutic approaches. It has become crucial in recent decades to treat water for environmental values.

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