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# The Future of Nanomaterial in Wastewater Treatment: A Review

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# Abstract

The shortage of having clean water for drinking combined with many environmental factors compels for developing novel technology for purification of wastewater. The use of nano materials is an advanced approach which do not generate toxic side products and also decontaminate the wastewater at a very low cost. This review focuses on different nano-based approaches towards wastewater treatments and the most recent advancements made in each aspect. It will also highlight the challenges associated with synthesis of nanomaterials. Furthermore, nanomaterials in recent times have become the hot spot because they are sustainable as they are recyclable making the nanotechnology economically a promising approach. One of the encouraging materials among nanomaterials are the nano-photocatalysts. This article will comprehensively review diverse applications of various nanomaterials employed in decontamination of water. This study will bring up great future possibilities for the researchers in the field of nanotechnology.

Keywords: Wastewater; Wastewater treatment; Nanomaterial; Photocatalyst; TiO<sub>2</sub>; Nanocatalyst; nanoadsorption

Full length review article \*Corresponding Author, e-mail: <u>fareehaasghar49@gmail.com</u>

# 1. Introduction

The presence of heavy metals and dyes in industrial wastewater poses serious threat, therefore, demands for an effective water treatment procedure [1]. It is obvious that such contaminants will ultimately become a part of human food chain and enters in our body. Already many methods such as flocculation, filtration, adsorption; being cost effective, versatile and efficient have been employed for pollutant removal from wastewater [2]. However, the widespread use of nanomaterials for treating wastewater owes to its features of being biodegradeable, non-toxic and having excellent water purification capabilities [3]. Adsorption has been the most employed, cost effective conventionally used technique for treating harmful pollutants. But, increase influx of more hazardous chemical pollutants like pesticides, phthalates, PAHs, and many heavy metal ions lately demands for a more novel, advanced method [4]. Nanomaterials are hence incorporated in adsorption process making it super effective against pollutants owing to its enhanced surface properties [5-6].

Nanoscale synthesis and processing has become a prime focus of researchers in the last two decades. The researchers has bring polymeric nanomaterials into attention owing to its novelty and considerably increased physiochemical features [7-8]. These polymers used as membranes have proven valuable as they are comparatively inexpensive, are highly selective thus gives greater membrane performance. No doubt that enormous polymeric materials are being used as nanofibrous membranes but only few of its classes are employed in wastewater treatment applications [9-10]. Moreover, there are remarkable advances made in the field of nanotechnology by utilizing sustainable natural resources to extract nanomaterials, which are employed in removing pollutants from industrial wastewater [11]. Cellulose is considered the most environmental friendly, superabundant among the natural material, which is also bio-resorbable, and sustainable material [3].

Photocatalytic technology is among the emerging trend in the field of nanotechnology with much higher efficiency and less energy utilization. It has gained limelight due to the prevailing condition of energy crisis across the world [12]. Photo-catalytic phenomenon is based on conversion of energy in light form into chemical form of energy by using visible or ultraviolet rays, thereby, favors either synthesis or degradation of organic materials [13].

# 2. Properties of nanomaterial

Class of nanomaterials with their large surface areas having special ability to generate super active various adsorption sites, small diffusion distance among the particles, larger surface energies, and tunable pore size makes the excellent naoadsorbents [14]. These outstanding features at a nano scale aids in providing high adsorption capacity comparable to the bulk counterpart of the material [15-16]. Surface engineering has its broad application by aiding in the site-specific particular adsorption of pollutants in water over to surface of nanoadsorbents. Further via desorption technique, the contaminants can be removed and nanoadsorbent is recycled. In this manner the overall operational cost of this remediation process is reduced [1].

Nanofibres are the nanostructures with two of its external dimension in the scale of nano with specifically larger, unrestricted third dimension. Membrane filtration using nanofibers is gaining importance in remediation of wastewater [17]. It has gained broad attention comparable to other conventional methods of using fibrous structures due to features like high surface-to-volume ratio, being lighter in weight and having unique interconnected porous structure (as high as 90%) along the possibility of associating large chemical functional groups [18]. The unique parameters for altering nano-fibre features usually includes: diameter of fiber, shape and surface morphology. The diameter and the unique surface area of fiber are the interdependent attributes. Similarly, the greater flexibility in manufacturing fiber characteristics is provided by morphology of fiber. For instance, morphology may be wrinkled, hollow, grooved, cactus, porous, core-shell or mesoporous (Zaarour et al., 2020). The characteristic morphology of nano-scale fiber allows for free faction of holes and electron to unrestricted site of structure [19]. This property of nanostructure provides amazing feature of electrical and optical properties to nano-fibres [9].

Cellulose is considered as most sustainable, abundant, environment friendly and bioresorbable polymer. Although, nanocellulose shows additional features of high surface area and more strength than their bulk counterparts creating it to be an extremely promising material for forming high-performance membranes and manufacturing filters. On account of these properties, it is employed in pollutant removal from drinking and commercial waters to make them sustainable for use. Other than this, nanaocellulose is a worth employing material in highpressure treatments of water purification due to its excellent stiffness and mechanical strength [3].

 Table 1: Properties of nanomaterial towards wastewater

 treatment

Class	example	Properties
Nanoadsorbent		Large surface
		area, Small
		diffusion
		distance
Nanofiber	PAN	High surface-
		to-volume
		ratio, Lighter
		in weight,
		interconnected
		porous
		structure
Natural	Cellulose	Sustainable
nanomaterial		Bioresorbable,
		Excellent
		stifness
Photocatalyst	Doped TiO <sub>2</sub>	Enhanced
		mobility rate

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# **3.** Approaches of nanotechnology towards wastewater treatment

# 3.1 Nano-adsorption

The most effective method to eliminate POPs in order to meet discharge standard is the highly promising technique adsorption. Nanomaterials as adsorbents are found to be very effective against eliminating POPs from the wastewater. In general, >70% removal efficiency is depicted by nanomaterial in order to remove persistent organic pollutants, however, has ability to sustain >90% of POPs removal via adsorption even about for 3 cycles. The hydrophobic interactions like van der Waals, electron donoracceptor, and  $\pi$ - $\pi$  interactions or electrostatic interaction or last but not least the hydrogen bonding are the major mechanisms through which the nanoadsorbents so easily take up POPs and remove them [20].

## 3.1.1 Carbon based nanoadsorbents

Nanomaterials made up of carbon and having adsorptive nature are the carbonaceous nanoadsobents. They includes CNTs, carbon NPs, fullerenes, graphenes and nanosheets. They are having high adsorption capacity than their bulk counterparts and many other macroadsorbent. Carbon atoms with  $sp^2$  hybridization forms a two dimensional sheet like structure graphene. G aerogel (GA) and GO hydrogel are the examples of nanoadsorbents that are graphene based [21]. SPE columns are employed for direct synthesis of GA adsorbent, which shows outstanding removal efficiency when practically used, nevertheless the issue stands with its inherent hydrophobicity due to which its application is limited and is unable to eliminate pollutants from water soluble materials. On the other hand, is 3dimensional GO hydrogel which shows excellent removal efficiency, have high adsorption capacity and is highly selective due to its unique pore-like structure, larger surface area and increased number of active sites [4-18].

Nanocomposites made up of activated carbon show effective antibacterial activity against the *Staphylococcus aureus*, a grampositive bacteria and Pseudomonas aeruginosa, a gramnegative bacteria [22]. Au-Fe<sub>3</sub>O<sub>4</sub> is one of another activated carbon modified nanostructure which founds its application in efficient removal of dye rhodamine 123 and disulfine blue with increased capacity for adsorbing toxins from wastewater [23]. The poor dispersion ability and such small particle size are certain drawbacks of using carbonaceous nanomaterial, however, certain modifications are suggested to attain the desired efficiency [1].

#### 3.1.2 Oxide-based nanomaterial as adsorbents

Metal oxides are the nanoadsorbents with an advantage of having small intraparticle diffusion distance due to which they are able to compress without modifying surface area hence enhancing further the kinetics of adsorption [24]. The use of iron oxide nanoparticles has become the hotspot in the recent years due to their easy availability and simplicity of its use. They are particularly employed for the removal of heavy metals from wastewater. Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ - Fe<sub>2</sub>O<sub>4</sub>) are the magnetic iron ores used as nanoadsorbents. They are

successfully employed as they are easy to separate and get recovered by aiding external magnetic field [25]. While hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), a non-magnetic form of iron is another common nanoparticle considered as an efficient adsorbent for eliminating ions of heavy metal from spiked tap water.

## 3.1.3 Nano zero valent iron as adsorbents

Zero valent nanoparticles has grabbed the attention of researchers due to their great potential for application in wastewater treatments. One of the most extensively studied and employed nano particle is nano zero valent iron due to its promising features including outstanding adsorption ability, precipitation, and a potential to act as reducing agent against the contaminants that are labile to redox reactions [26]. Nano zero valent Fe covers the broad spectrum of contaminants for removal from wastewater. However, they too have few limitations like their aggregation which further aids in separation difficulty from the water system. In spite of that, there are modification techniques to increase the activity of nano zero valent Fe in wastewater treatment. The approaches includes doping, surface coating with other metals, conjugation, encapsulation and emulsification [25-27].

# 3.2. Nanofiltration

The permeability and selectivity of membrane technology makes this method highly efficient and effective in wastewater treatment. The use of CNTs in association with other polymers or nanocomposites makes it more beneficial and help determines its saturation effectiveness and capacity for antifouling. This integration of CNTs with thin membranes is the major reason for the exceptional antifouling property [28]. It is due to this coupling of CNTs with polymeric membranes that has made the separation of TiO<sub>2</sub> NPs so easily through the process of simple filtration rather than photocatalysis [29].

# 3.2.1. PAN nanofiber

PAN are popularly used polymers that are hydrophilic and act as precursors for the production of nanofibres membranes used in wastewater treatment. Such membranes either act as the support system in order to build pressure-driven membrane or becomes the media to filter pollutants like bacteria and other nanoparticles. These membranes due to their smaller size outclass their bulk counterparts in their antifouling feature. El-Aswar et al. made a modification in PAN nanofibre by surface coating it with a co polymer named polyethylenimine (PEI)-diepoxy (EGdGE) for eliminating viruses. Modifying it resulted in making amino group on the nanofibres turn to positive charge which ultimately will adsorb negatively charged viruses in a neutral environment. This modification made this membrane phenomenon more efficient and highly practical [9-30]. Methaapanon et al. prepares sheath like structure of PAN coated with ZnO-PVP mix using sol-gel and electrospinning method. A thick, stable coaxial PAN nanofibres structure was obtained as a result of calcination. The results prove its efficacy by entirely depleting the organic material from wastewater [31]. Bahmani et al. uses  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles to modify the PAN nanofibres membrane through electrospinning for removal of As(V) Asghar and Mushtaq, 2023

(Bahmani et al., 2019). The hydrophilicity of membrane doubled and the active adsorption sites were created which otherwise the unmodified form lacks [32].

# 3.2.2. Nano silver

Nanoparticles of silver are natural defense against micro-organisms as they are proven toxic against them. They act by adhering to the wall of bacterial cell, and when reaches inside produces free radicals that subsequently cause the cell death of bacteria. The use of Ag NPs in wastewater disinfection is due to their promising antibacterial activity. Moreover, they are cost-friendly. Zahmatkesh et al. have studied the anti-bacterial activity of Ag NPs sheets against the Escherichia coli and Enterococcus faecalis suspensions. Silver loss predicted was found to be according to safe drinking water standards but the aggregation tendency of silver NPs makes it problematic to use for the long term [6]. Ag NPs are also used in the construction of ceramic filters along with clay and dust. Their use highly improves the removal efficiency of specie Escherichia coli. Higher the porosity of a filter, better will be the removal efficiency [28].

# 3.3. Photocatalysis

Photocatalysis is an advanced and highly promising process involving oxidation. The phenomenon occurs when light energy equal or exceeds than band gap of semiconductor stimulates electron. This photoexcited electron transfers to the conduction type band while leaving behind the hole in valence band. As a consequence, electron hole pairs are generated in a matter of femtoseconds. Moving on, the photoexcited charge carriers get trapped. Commonly used semiconductors materials in photocatalysis oxidation are TiO<sub>2</sub>, ZnO, WO<sub>3</sub>, ZnS, and CdS [33].

# 3.3.1. Native photocatalyst

Photocatalytic oxidation is a favorable method for removal of VOCs [33]. TiO<sub>2</sub> is strongly employed in this field as catalyst due to outclass catalytic activity, stable chemical activity, non-toxic nature, and longer service life. TiO<sub>2</sub> in nature has three crystal structures: rutile, anatase, and brookite. The anatase  $TiO_2$  with 3.2 eV energy gap is best among them because of its excellent catalytic activity [34-35]. Ultraviolet lamp is used to induce TiO<sub>2</sub> activation but the use of artificial light along with sunlight is also permitted [29]. The use of native  $TiO_2$  has its repercussions associated such as there is decreased quantum yield due to faster electron hole recombination, lower measure of adsorption and most of all is the reduced degradation of contaminants because of exposed surface of photocatalyst. Another emerging candidate for efficient water purification treatment are the ZnO NPs due to their peculiar features of having large band width in spectra, excellent ability for oxidation. Despite these features, its application is not very common as photo-corrosion impedes its performance causing faster recombination of charges resulting in reduced photocatalytic efficiency.

# 3.3.2. Metal doped photocatalyst

Doping the metal is a well-known method of improving the activity of native photocatalysts. Use of noble metals to modify TiO2 can highly accelerate the process of photogenerated  $e^{-}/h^{+}$  pairs separation and eventually enhances the activity of photocatalyst. Noble metals also increase absorption activity of TiO2 in visible light but as their use is proven uneconomical, the non-noble metals (such as Mn, Fe, Cu, Ce) are employed as an alternative. A study employed Ag or Pd metal deposition over TiO<sub>2</sub> to study the photocatalytic removal of diclofenac (DCF). This results in enhanced mobility rate of electron hole pair as there are now more than one metals available now to capture the photogenerated electrons [36]. Another study reported Au deposition on nanotubes made of TiO<sub>2</sub> and observe the increase in the separation frequency of e<sup>-</sup>/h<sup>+</sup> pairs making it simple for the formation of OH· radicals over the Au/TiO<sub>2</sub> surface results in enhancement of photo-degradation activity [37-38]. Taghipour et al., 2021 reported the Cd-1,4-BDOAH<sub>2</sub> synthesis photocatalyst. By loading it with Ag metal, the band gap decreases and the efficiency of Ag:Cd-1,4-BDOAH<sub>2</sub> increases exponentially for removal of brilliant green dye using blue LED irradiation [34].Different categories based on their mode of action are described below with examples;

**Table 2:** Approaches of nanotechnology towardswastewater treatment

Process	Examples	
Nanoadsorption	<ul> <li>Carbon based: fullerenes, CNTs.</li> <li>Graphene based: G aerogel (GA) and GO hydrogel</li> <li>Oxide-based: Magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite (γ- Fe<sub>2</sub>O<sub>4</sub>), hematite (α- Fe<sub>2</sub>O<sub>3</sub>),</li> <li>Nano zerovalent iron</li> </ul>	
Nanofiltration	<ul><li>PAN nanofiber</li><li>Nano silver</li></ul>	
Photocatalysis	<ul> <li>Native photocatalyst: TiO2</li> <li>Metal doped photocatalyst: Ag or Pd metal deposition over TiO2</li> </ul>	
Integrated nanotechnology	• Aerobic degradation coupled with nano zero valent Fe (nZVI)	

## 3.4. Integrated nanotechnology

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Incorporation of biological methods into advanced nanotechnology is an environment friendly and a practical approach in wastewater purification. Such integrated technologies comes up with the noteworthy outcomes such as better dye decolourization, highly effective in removal of pollutants, BOD, and COD. Sahu et al. reported that coupling the process of arerobic degradation with nano zero valent Fe (nZVI) has offered a better method for large scale bioremediation of organic compounds present in wastewater. nZVI in its granular form degrades the chlorinated solvents and other hydrocarbons in the first step resulting in reduction of chlorinated ethenes via dechlorination. Adding dissolved oxygen in the second step had facilitated the process of aerobic degradation of rest of chlorinated compounds and other hydrocarbons [39]. Gottinger et al. has also investigated the nZVI effect in integration with biological method revealing the high removal efficiency of contaminant to be 96.5% for BOD and 86% for COD [40-41]. Nonetheless, this technology does have drawbacks like requisition of expensive instruments, particular reagents for contaminant handling and the significant of all is the specific process condition required for each different microbe. However, its significance supersedes the related issues and is considered as a promising technology in order to meet the challenges associated in water treatment in coming future [39].

#### 4. Recent trends in nanomaterials synthesis

The surface engineering of nanomaterials is a popular and recent development with its broad applications in site-specific selective adsorption of water pollutants. Huang et al. conducted a study in 2021 and found that the modification of graphene surface with suitable magnetic nanoparticles (NPs) increased its separation convenience and adsorption efficiency[4]. Li et al. created G@Fe<sub>3</sub>O<sub>4</sub> through chemical precipitation method, which showed better magnetic property of dispersion and high capability for adsorbing bisphenol A from water. Fe<sub>3</sub>O<sub>4</sub> quantum dots (QDs) are highly valued magnetic nanoparticles due to having peculiar magnetic properties, are biocompatible, and effective selectivity for target molecules [42]. Cao et al. successfully synthesized Fe<sub>3</sub>O<sub>4</sub> QDs-G nanocomposite through a one-step hydrothermal process for extracting dyes from aqueous solution. The material demonstrated excellent adsorption and magnetic separation abilities for water treatment [43]. Gu et al. suggested that coating G-grafted silica with Fe<sub>3</sub>O<sub>4</sub> nanoparticles in order to separate and trace the material of target in the water body have highly enhances the adsorption ability and selectivity towards target material [44]. Ye et al. developed the effective method to produce mats of composite that doesnot shrink and are nano-fibrous, which act as self-standing and is also recyclable when heated for removing organic pollutants from water [45]. Shayegan et al. explored the recent advancements in modified-TiO<sub>2</sub> for removing gas-phase pollutants under ambient conditions. They evaluated various modification techniques, such as doping with metals and non-metals, co-doping, and heterojunction with other semiconductors, and found that the heterostructure photocatalysts have better prospects for applications due to their small band widths and improved separation of electron and holes [33].

# 5. Challenges in NMs synthesis

Agglomeration is an inherent concern associated with particles at nanoscale, consequently, impacts their synthesis and the performance in related fields. On encounter with each other, the particles begin to agglomerate. This is due to various reasons like developing electrostatic interactions, increase in the surface energy of particles or may be simple physical entanglement can cause agglomeration. Baig et al.2021 reported that  $\pi$ - $\pi$  type of interactions and the presence of van der Waals forces are the basic cause that triggers agglomeration of the basal graphene sheet planes [46-47]. Method to be cost effective is a major aim of nanotechnology, but, for a nanomaterial to be best in its activity requires high end instrumentation for synthesis, which otherwise will result in formation of poor quality nanomaterial with defects. Pure nanomaterials in terms of structure with keenly calculated theoretical features is achieved by controlled synthesis and for the nanomaterial synthesis to be highly controlled is a challenging job. The stability of nanomaterial specifically 2D ultrathin material is a potential concern which needs to be anticipated for the practical utilization of nanoparticles [46-48].

# 6. The mechanism study and Application in wastewater treatment

# 6.1. Removal of BTEX compounds

Benzene, toluene, ethylbenzene and xylenes are the mono-aromatic hydrocarbons termed as BTEX, commonly found in plumes in ground water and many other water sources. Variety of techniques including adsorption, ozonation, natural attenuation, phytoremediation, and bioremediation are being reported for the purification of BTEX contaminated water.

Natural attenuation is a process of diluting the compound concentration during source-to-source travel therefore does not necessarily employed as a removal method for BTEX. Similarly, bioremediation despite being harmless and cost effective is undesirable process due to duration problem. If it is performed in-situ, then rate of process is unpredictable because cannot be ascertained. In spite of these erroneous methods, the use of modified TiO<sub>2</sub> to perform photodegradation of these highly overlooked compounds is the most suitable method. Research found that the oxidation of BTEX compounds leads to the transformation of the compounds into aldehydes and organic acids, followed by mineralization into compounds like CO<sub>2</sub> and H<sub>2</sub>O. The various pathway for degrading BTEX compounds are influenced by the number and position of methyl and ethyl groups. Combination techniques are commonly employed for the removal of BTEX due to practical application complexities. Heating of catalyst or UV cleaning are employed to prevent inactivation of catalyst. The integration of technologies such as coupling adsorption with photocatalysis, combining plasma with photocatalysis, and temperature driven thermo-photocatalysis results in a more effective and cost-friendly approach for BTEX degradation[13]. Modified with Ag, ZnO has been found to be highly effective in removing benzene. Solimmobilization of Carbon doped ZnO with Pd improved the catalytic activity during oxidation of benzene [46].

# 6.2. Removal of heavy metals, dyes, pesticides

Heavy metals are the highly threatening pollutants to the human health present in great concentration in water. Adsorption of ions of heavy metal by employing CNTs via electrostatic interaction is one of many successful removal method [49]. According to Puri et al. (2021), the use of SWNTs as well as MWNTs for removing hazardous ions of Cr(VI) is efficient and have shown good adsorption efficiency. The use of carbon nanotubes has offered a more reliable alternative even though there may occur the competitive inhibition of active sites due to SO<sub>4</sub><sup>2-</sup> ions. It is because it took only few minutes for adsorption to occur on surface and ion diffusion into the pores of CNT so is better to use nano tubes. Mura et al. (2018) reported the use of of graphene oxide (GO)/FeO-Fe(VI) in mixture decontaminating the water. It covers the removal of an organic synthetic rhodamine B dve, an organic non-ionic diethyl 4-nitrobenzyl phosphonate (DNBP) pesticide, and also a pharmaceutical drug named diclofenac (DCF) from actual samples of water. Almost 99% efficiency was achieved for remediation of aforementioned compounds from water using graphene oxide nanomaterial [50].

# 7. Reusability of nano-adsorbent

Ability of nano-adsorbents to be reused is crucial in wastewater treatment, as it enables their use on an industrial level. There are two key factors for the determination of application of nanotechnology in practical. Their cost effectiveness to synthesize nano scale particles and the foremost is their reusability which makes it economical [51] . However, because of the small size, their separation during the sorption is a challenging aspect for the researchers. To make nano-adsorbents reusable, different reagents have been employed, including alkalis like NaOH, acids such as CH<sub>3</sub>COOH, and EDTA [52]. Research has shown that by employing even low amount of acids or bases, the nanoadsorbents loaded with contaminants are easily be desorbed hence recovered. Nano adsorbents that are magnetic in nature are peculiarly the best in term of reusability. Nano-adsorbents such as Fe<sub>3</sub>O<sub>4</sub> is magnetic and can be easily separated from wastewater by employing a magnet [26-53].

Lu et al. (2016) investigated use of poly(Nisopropylacrylamide) which is coated with nanoparticles which is magnetic in order to treat oily type of wastewater, and found that nanoparticles gives good removal efficiency and are also recycled. Magnet is used for the purpose of separating the nano composite which is paramagnetic in nature [50]. To maintain the performance of photocatalysts, various regeneration techniques are utilized. In order to renew a catalyst, nanomaterial can be thermally heated or cleaned via UV radiation. Another study reported the regeneration of catalyst by heating at 200 degree for half hour in the 20 vol% H<sub>2</sub>/He. Meanwhile, Wu's group applied a different method for regenerating the catalytic property by irradiating the catalyst with UV light for 1 whole hour in clean air. Additionally, the fouling on the catalyst can also be removed through coupled technique of non-thermal plasma with process of photocatalysis that even without UV [46].

# 8. Key challenges, gaps and issues of nanomaterials

Nanotechnology have made a huge progress in the field of wastewater purification for removal of contaminants but there exist certain concerns that should be resolved to meet the strict standards in cost-effective manner. The small size of the nanoadsorbents poses a major challenge of their recovery and separation after the purification of water [25]. In addition to it, the nanofibres in spite of having unique characteristics have problem of fouling and shrinkage associated with them. They exhibit poor mechanical properties and even deforms after treating wastewater [54]. Surface engineering is a good modification over the surface of photocatalyst like TiO<sub>2</sub> but use of transition material for this purpose might cause blockage of porous sites at surface partially, which subsequently reduce the particular surface area and impacts the overall performance of the [33]. Experiments conducted photocatalyst using nanomaterials are generally the lab experiment having simple composition and significant concentration. Their mechanism and activity will surely be different from the real working conditions in industry. Toxicity of nanomaterials is the potential risk that must not be overlooked, however, it is the most poorly understood and highly unclear phenomenon since now. Scientific community need to spend time and do effort in order to overcome this knowledge gap. Hence, in order to commercialize the nanotechnology, a proper and systematic knowledge of in vitro toxicity and its relation to nanotechnology is a pre-requisite [46-55].

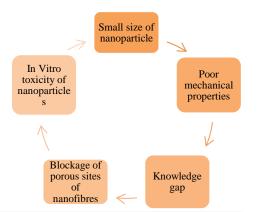


Figure 1. Challenges associated with nanomaterials

#### 9. Conclusions and future perspectives

There are remarkable advances made in the field of nantechnology by utilizing recyclable, cost-effective and sustainable resources to extract nanomaterials for the degradation of pollutants from industrial wastewater. Incorporation of biological methods into advanced nanotechnology is also an environmentally friendly and a practical approach in wastewater purification. Developing such coupled technologies will greatly improve the contaminant degradation in a most efficient manner. The ability of nanomaterials to be recycled and reused is a prime feature in wastewater treatment, as it enables their use on an industrial level. Future efforts should be focused on discovering novel way of immobilization and separation method such as magnetic separation. Moreover, nanoparticle *Asghar and Mushtaq*, 2023 surface modification has a great potential therefore efforts should be put through in order to minimize the associated concerns. In short, nano-based research has broad horizon therefore more nanomaterials with charming features will continue to be explored and discovered in the coming future.

# References

- [1] N. Puri, A. Gupta, A. Mishra. (2021). Recent advances on nano-adsorbents and nanomembranes for the remediation of water. Journal of Cleaner Production. 322: 129051.
- [2] R. Kant. (2011). Textile dyeing industry an environmental hazard.
- [3] A.J. Sayyed, D.V. Pinjari, S.H. Sonawane, B.A. Bhanvase, J. Sheikh, M. Sillanpää. (2021). Cellulose-based nanomaterials for water and wastewater treatments: A review. Journal of Environmental Chemical Engineering. 9(6): 106626.
- [4] T. Huang, X. Tang, K. Luo, Y. Wu, X. Hou, S. Tang. (2021). An overview of graphene-based nanoadsorbent materials for environmental contaminants detection. TrAC Trends in Analytical Chemistry. 139: 116255.
- [5] R. Paliwal, J.P.N. Rai, Nanomaterials for the Removal of Inorganic Contaminants from Industrial Wastewater. In *Nano-biotechnology for Waste Water Treatment: Theory and Practices*, Springer: 2022; pp 171-189.
- [6] I. Akbar, M.A. Hanif, U. Rashid, I.A. Bhatti, R.A. Khan, E.A. Kazerooni. (2022). Green Nanocomposite for the Adsorption of Toxic Dyes Removal from Colored Waters. Coatings. 12(12): 1955.
- [7] S. Kumar, M. Shandilya, P. Uniyal, S. Thakur, N. Parihar. (2022). Efficacy of polymeric nanofibrous membranes for proficient wastewater treatment. Polymer Bulletin. 1-56.
- [8] Y. Chauhdary, M.A. Hanif, U. Rashid, I.A. Bhatti, H. Anwar, Y. Jamil, F.A. Alharthi, E.A. Kazerooni. (2022). Effective removal of reactive and direct dyes from colored wastewater using low-cost novel bentonite nanocomposites. Water. 14(22): 3604.
- [9] E.I. El-Aswar, H. Ramadan, H. Elkik, A.G. Taha. (2022). A comprehensive review on preparation, functionalization and recent applications of nanofiber membranes in wastewater treatment. Journal of Environmental Management. 301: 113908.
- [10] A. Enesca, C. Cazan. (2022). Polymer Composite-Based Materials with Photocatalytic Applications in Wastewater Organic Pollutant Removal: A Mini Review. Polymers. 14(16): 3291.
- [11] B. Barik, B. Maji, D. Sarkar, A.K. Mishra, P. Dash, Cellulose-based nanomaterials for textile applications. In *Bio-Based Nanomaterials*, Elsevier: 2022; pp 1-19.
- [12] E. Gong, S. Ali, C.B. Hiragond, H.S. Kim, N.S. Powar, D. Kim, H. Kim, S.-I. In. (2022). Solar fuels: research and development strategies to accelerate photocatalytic CO 2 conversion into

hydrocarbon fuels. Energy & Environmental Science. 15(3): 880-937.

- [13] C. Liang, C. Li, Y. Zhu, X. Du, C. Yao, Y. Ma, J. Zhao. (2022). Recent Advances of Photocatalytic Degradation for BTEX: Materials, Operation, and Mechanism. Chemical Engineering Journal. 140461.
- [14] A.B. Albadarin, J. Mo, Y. Glocheux, S. Allen, G. Walker, C. Mangwandi. (2014). Preliminary investigation of mixed adsorbents for the removal of copper and methylene blue from aqueous solutions. Chemical Engineering Journal. 255: 525-534.
- [15] S. Dwivedi, S. Mishra, R.D. Tripathi. (2018). Ganga water pollution: a potential health threat to inhabitants of Ganga basin. Environment international. 117: 327-338.
- [16] A. Ashfaq, R. Nadeem, S. Bibi, U. Rashid, M.A. Hanif, N. Jahan, Z. Ashfaq, Z. Ahmed, M. Adil, M. Naz. (2021). Efficient Adsorption of Lead Ions from Synthetic Wastewater Using Agrowaste-Based Mixed Biomass (Potato Peels and Banana Peels). Water. 13(23): 3344.
- [17] M.O. Akharame, O.S. Fatoki, B.O. Opeolu, D.I. Olorunfemi, O.U. Oputu. (2018). Polymeric nanocomposites (PNCs) for wastewater remediation: an overview. Polymer-Plastics Technology and Engineering. 57(17): 1801-1827.
- [18] A. Hanif, S. Ali, M.A. Hanif, U. Rashid, H.N. Bhatti, M. Asghar, A. Alsalme, D.A. Giannakoudakis. (2021). A novel combined treatment process of hybrid biosorbent– nanofiltration for effective Pb (II) removal from wastewater. Water. 13(23): 3316.
- [19] H.R. Pant, H.J. Kim, M.K. Joshi, B. Pant, C.H. Park, J.I. Kim, K. Hui, C.S. Kim. (2014). One-step fabrication of multifunctional composite polyurethane spider-web-like nanofibrous membrane for water purification. Journal of hazardous materials. 264: 25-33.
- [20] J.O. Ighalo, P.-S. Yap, K.O. Iwuozor, C.O. Aniagor, T. Liu, K. Dulta, F.U. Iwuchukwu, S. Rangabhashiyam. (2022). Adsorption of persistent organic pollutants (POPs) from the aqueous environment by nano-adsorbents: A review. Environmental Research. 212: 113123.
- [21] M. Riaz, M. Hanif, S. Noureen, M. Khan, T. Ansari, H. Bhatti, Q. Imran. (2012). Coagulation/flocculation of tannery wastewater using immobilised natural coagulants. Journal of Environmental Protection and Ecology. 13(3A): 1948-1957.
- [22] A.A. Bazrafshan, S. Hajati, M. Ghaedi, A. Asfaram. (2018). Synthesis and characterization of antibacterial chromium iron oxide nanoparticleloaded activated carbon for ultrasound-assisted wastewater treatment. Applied Organometallic Chemistry. 32(1): e3981.
- [23] S. Bagheri, H. Aghaei, M. Ghaedi, A. Asfaram, M. Monajemi, A.A. Bazrafshan. (2018). Synthesis of nanocomposites of iron oxide/gold (Fe3O4/Au) loaded on activated carbon and their application in water treatment by using sonochemistry:

Optimization study. Ultrasonics sonochemistry. 41: 279-287.

- [24] M.E. El-Sayed. (2020). Nanoadsorbents for water and wastewater remediation. Science of the Total Environment. 739: 139903.
- [25] H. Lu, J. Wang, M. Stoller, T. Wang, Y. Bao, H. Hao. (2016). An overview of nanomaterials for water and wastewater treatment. Advances in Materials Science and Engineering. 2016.
- [26] N.N. Nassar. (2012). Iron oxide nanoadsorbents for removal of various pollutants from wastewater: an overview. Application of adsorbents for water pollution control. 81-118.
- [27] M.I. Jilani, R. Nadeem, M.A. Hanif, T. Mahmood Ansari, A. Majeed. (2015). Utilization of immobilized distillation sludges for bioremoval of Pb (II) and Zn (II) from hazardous aqueous streams. Desalination and Water Treatment. 55(1): 163-172.
- [28] S. Zahmatkesh, M. Hajiaghaei-Keshteli, A. Bokhari, S. Sundaramurthy, B. Panneerselvam, Y. Rezakhani. (2022). Wastewater treatment with nanomaterials for the future: A state-of-the-art review. Environmental Research. 114652.
- [29] W. Kangwansupamonkon, W. Jitbunpot, S. Kiatkamjornwong. (2010). Photocatalytic efficiency of TiO2/poly [acrylamide-co-(acrylic acid)] composite for textile dye degradation. Polymer Degradation and Stability. 95(9): 1894-1902.
- [30] M.A. Hanif, R. Nadeem, M.N. Zafar, H. Bhatti, R. Nawaz. (2008). Physico-chemical treatment of textile wastewater using natural coagulant cassia. J. Chem. Soc. Pak. 30(3): 385.
- [31] R. Methaapanon, K. Chutchakul, V. Pavarajarn. (2020). Photocatalytic zinc oxide on flexible polyacrylonitrile nanofibers via sol-gel coaxial electrospinning. Ceramics International. 46(6): 8287-8292.
- [32] P. Bahmani, A. Maleki, H. Daraei, R. Rezaee, M. Khamforoush, S. Dehestani Athar, F. Gharibi, A.H. Ziaee, G. McKay. (2019). Application of modified electrospun nanofiber membranes with  $\alpha$ -Fe2O3 nanoparticles in arsenate removal from aqueous media. Environmental Science and Pollution Research. 26(21): 21993-22009.
- [33] Z. Shayegan, C.-S. Lee, F. Haghighat. (2018). TiO2 photocatalyst for removal of volatile organic compounds in gas phase–A review. Chemical Engineering Journal. 334: 2408-2439.
- [34] T. Taghipour, G. Karimipour, M. Ghaedi, A. Asfaram, H. Javadian, M.M. Sabzehmeidani, H. Karimi. (2021). Photoelectro-Fenton/photocatalytic process for decolorization of an organic compound by Ag: Cd-1, 4-BDOAH2 nano-photocatalyst: Response surface modeling and central composite design optimization. Journal of Molecular Liquids. 335: 113689.
- [35] M.A. Hanif, M. Touqeer, M. Usman, M. Zahid. Wastewater treatment by biological processes.
- [36] M. Espino-Estévez, C. Fernández-Rodríguez, O.M. González-Díaz, J. Araña, J. Espinós, J.A. Ortega-Méndez, J.M. Doña-Rodríguez. (2016). Effect of

TiO2–Pd and TiO2–Ag on the photocatalytic oxidation of diclofenac, isoproturon and phenol. Chemical Engineering Journal. 298: 82-95.

- [37] C. Fu, M. Li, H. Li, C. Li, X. guo Wu, B. Yang. (2017). Fabrication of Au nanoparticle/TiO2 hybrid films for photoelectrocatalytic degradation of methyl orange. Journal of alloys and compounds. 692: 727-733.
- [38] M.A. Hanif, H.N. Bhatti. (2012). Bioremediation of nickel from wastewater using immobilized Phanerochaete chyrsosporium biomass. Int. J. Chem. Biochem. Sci. 2(1): 54-59.
- [39] J. Sahu, R.R. Karri, H.M. Zabed, S. Shams, X. Qi. (2021). Current perspectives and future prospects of nano-biotechnology in wastewater treatment. Separation & Purification Reviews. 50(2): 139-158.
- [40] A. Gottinger, D. McMartin, D. Wild, B. Moldovan. (2013). Integration of zero valent iron sand beds into biological treatment systems for uranium removal from drinking water wells in rural Canada. Canadian Journal of Civil Engineering. 40(10): 945-950.
- [41] M. Khalil, M.A. Hanif, U. Rashid, J. Ahmad, A. Alsalme, T. Tsubota. (2022). Low-cost novel nanoconstructed granite composites for removal of hazardous Terasil dye from wastewater. Environmental Science and Pollution Research. 1-19.
- [42] X. Li, S. Li, J. Bai, Y. Peng, B. Ning, H. Shi, W. Kang, H. Zhou, Z. Gao. (2020). Determination of bisphenol A by high-performance liquid chromatography based on graphene magnetic dispersion solid phase extraction. Journal of Chromatographic Science. 58(3): 280-286.
- [43] J. Cao, Q. Liu, J. Du, L. Yang, M. Wei, M. Gao, J. Yang. (2017). Facile one-step hydrothermal method to fabricate Fe3O4 quantum dots–graphene nanocomposites for extraction of dye from aqueous solution. Journal of Materials Science: Materials in Electronics. 28(2): 2267-2271.
- [44] W. Gu, X. Zhu. (2018). Graphene-grafted silicacoated Fe3O4 nanoparticles as a magnetic solidphase extraction material coupled with inductively coupled plasma optical emission spectroscopy for the separation and analysis of heavy metal ions. Separation Science Plus. 1(3): 209-216.
- [45] H.-M. Ye, W.-Y. Zhu, P. Liu, X.-W. Wei, H. Li, L. Cai, X. Meng, G. Huang, Q. Zhou. (2020). Fabrication of shrinkage-free poly (ether ether ketone) nanofibrous mat and its use for flexible and thermally-recycled MOF composites. Materials Today Communications. 23: 100862.
- [46] N. Baig, I. Kammakakam, W. Falath. (2021). Nanomaterials: A review of synthesis methods, properties, recent progress, and challenges. Materials Advances. 2(6): 1821-1871.
- [47] A. Akhtar, M.A. Hanif, U. Rashid, I.A. Bhatti, F.A. Alharthi, E.A. Kazerooni. (2022). Advanced Treatment of Direct Dye Wastewater Using Novel Composites Produced from Hoshanar and Sunny Grey Waste. Separations. 9(12): 425.

- [48] Q. Imran, M. Hanif, M. Riaz, S. Noureen, T. Ansari, H. Bhatti. (2012). Coagulation/flocculation of tannery wastewater using immobilized chemical coagulants. Journal of applied research and technology. 10(2): 79-86.
- [49] S. Rajendran, A. Priya, P.S. Kumar, T.K. Hoang, K. Sekar, K.Y. Chong, K.S. Khoo, H.S. Ng, P.L. Show. (2022). A critical and recent developments on adsorption technique for removal of heavy metals from wastewater-A review. Chemosphere. 135146.
- [50] S. Mura, Y. Jiang, I. Vassalini, A. Gianoncelli, I. Alessandri, G. Granozzi, L. Calvillo, N. Senes, S. Enzo, P. Innocenzi. (2018). Graphene oxide/iron oxide nanocomposites for water remediation. ACS Applied Nano Materials. 1(12): 6724-6732.
- [51] I. Jagodić, I. Guth, S. Lukić-Petrović, D. Tamindžija, D. Šojić Merkulov, N. Finčur, S. Bognár, P. Putnik, N. Banić. (2023). Reusable Fe2O3/TiO2/PVC Photocatalysts for the Removal of Methylene Blue in the Presence of Simulated Solar Radiation. Nanomaterials. 13(3): 460.
- [52] S. Lata, P. Singh, S. Samadder. (2015). Regeneration of adsorbents and recovery of heavy metals: a review. International journal of environmental science and technology. 12(4): 1461-1478.
- [53] T. Zhang, X. Wu, X. Fan, D.C. Tsang, G. Li, Y. Shen. (2019). Corn waste valorization to generate activated hydrochar to recover ammonium nitrogen from compost leachate by hydrothermal assisted pretreatment. Journal of Environmental Management. 236: 108-117.
- [54] A. Qayoom, I. Ashraf, A. Rashid, M. Ayoub, D. Kumar. (2022). Synthesis and Characterization of NiS and Zn doped NiS Quantum Dots and their application in methylene blue degradation in aqueous solution.
- [55] A. Bendre, M.P. Bhat, K.-H. Lee, T. Altalhi, M.A. Alruqi, M. Kurkuri. (2022). Recent developments in microfluidic technology for synthesis and toxicity-efficiency studies of biomedical nanomaterials. Materials Today Advances. 13: 100205.