WASTE WATER TREATMENT: A PERSPECTIVE OF NANOTECHNOLOGY

DHANAJI M. MOHITE[1], PANDURANG M. CHAVHAN[2,*], RAMESH D. MOHITE[3], T.R. MUDGAL[4,*]

[1]Research and Development, Excel Industries Ltd, MIDC, Roha-402116, Raigad, Maharashtra, India.

[2]Department of Chemistry, Amity School of Applied Sciences, Amity University Mumbai, India.

[3]Department of Chemistry, Karmaveer Bhaurao Patil College Vashi, Navi Mumbai, India.

[4]Department of Physics, State Institute of Engineering and Technology, Nilokheri, Karnal, Haryana, India.

ABSTRACT

Pure and fresh drinking water is the one of the most important material for life. Availability of water on the earth is essential for all living species. Unambiguously, this world is facing a serious problem of availability of fresh drinking water. As we know maximum consumption of water seen in industries in different processes and generated contaminated water called water waste in terms of aqueous effluents. Industrial waste water treatments have been aroused a great concern due to growing problems in many ways. Waste water coming out of industries is loaded with inorganic salts, metals and organic compounds. Nanoparticles like metallic nanoparticles, carbonaceous nanomaterials and zeolites having unique characteristic properties, such as high surface to volume ratio play a catalytic role to remove disease causing microbes, organic and inorganic solutes, and toxic metal ions from water efficiently. This critical review article describes up to date progress in development of various waste water treatments using nanomaterial form industrial waste water effluents. Different types of nanomaterial, its properties, applications, advantages and limitations are discussed meticulously for its possible uses in industrial waste water treatments. New modern technology and equipment applicable for treatment of waste water should be low cost, flexible, and efficient for the industrial purpose.

Keywords: Microbes, Nanomaterial, Nanoparticles, Waste Water.

1. INTRODUCTION

Water pollution and contamination is a serious problem around the globe due to several reasons like marine dumping issues, industrial wastes, agricultural perspectives, man-made activities, inadequate sewage treatment, radioactive waste material, (Ahmad et al., 2015). Figure 1 represents flow chart of use of nanotechnology for the treatment of polluted and contaminated and polluted water. Waste water is contaminated by pathogenic viruses, bacteria, harmful chemicals, organophosphorous compounds, polyhalogenated aromatic hydrocarbons (PHAH), pesticides, insecticides, inorganic salts and metals like arsenic, mercury etc. (Karishma and Chorawalaa, 2015). Many available traditional treatment methods like chemical adsorption reaction, extraction and absorption are generally useful but quite expensive. Nanotechnology is relatively a new technology that provides an opportunity to treat waste water with high working efficiency at low expense, in removing pollutants (Baruah et al., 2016). Nanotechnology has paved to different ways which are proving to be the best alternative, innovative and advanced techniques for industrial waste water treatment. Nanomaterials have observed as superior absorbents, catalysts, sensors materials due to their large surface to volume ratio leading to increased reactivates. The nanosorbents, catalytic membranes, metal nanoparticles (Karishma and Chorawalaa, 2015) can be employed for degradation of organic pollutants, removal disease causing microbes, toxic metal ions etc. from waste water. In the competition of development novel, low cost alternative methods, nanomaterials plays a significant role in handling large volumes of waste water to make a place in the market (Crane and Scott, 2012).

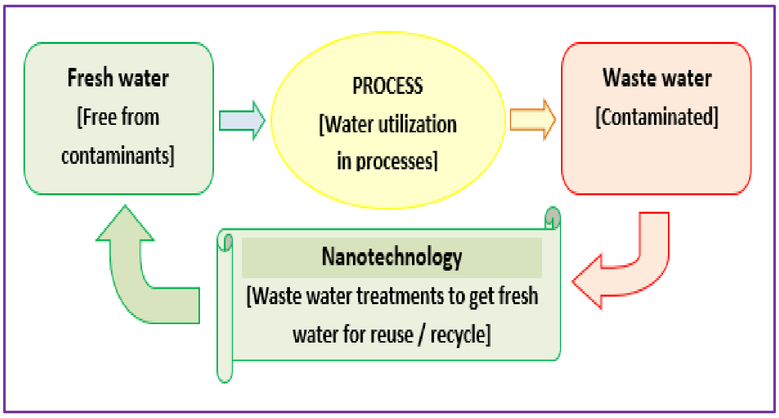

Fig.1- Schematic figure showing process waste water treatments

In recent times nanotechnology came in a big way for identification and detection of various pollutants. Heavy metal and non-biodegradable organic pollutants poses serious threats to environment and society because it is toxic effects on living organism, including humans. Different processes like adsorption and electrochemical oxidation, photo-catalysis, nanofiltration uses titanium dioxide, Zinc oxide (ZnO) metal oxides. Further, ceramic membranes, polymer membranes, carbon nanotubes, nanowire membranes, magnetic nanoparticles submicron nanopowder, etc. also found increasingly important in waste water treatment. Boron doped diamond nanostructures are used for water quality improvement to diminish the pollutants in water and environment (Karishma and Chorawalaa, 2015). Researchers and scientists are continuously exploring on development of nanoscale materials, which can act as functional material for waste water purification for better process efficiency.

Waste water from industries is highly contaminated with organic compounds like poly halogenated hydrocarbons (PHH), insecticides, pesticides and inorganic salts like phosphates, nitrates, nitrites from chemical, agrochemical industrial processes (Okereke et al., 2016). So in this context, advanced nanotechnology plays important role to treat industrial processes sludge with highly contaminated toxic compounds (Sayan et al., 2013). In this review article an attempt is made to reveal clearly different nanomaterials platforms, nanocatalysts, their general synthesis methods and their different classes of nanomaterials have been effectively used for waste water treatments generated out of chemical and allied industries.

2. METHODOLOGY

Wet-chemical technique such as sol-gel process is known to develop kind of novel nanomaterials possessing unrealized properties finding application in the field of materials science and ceramics. The process is simple and low cost as compared to physical methods which uses the vacuum units in many times. In this process precursor can be converted to inorganic solids by polymerization using water hydrolysis and acid as catalyst. Hydrolysis leads to formation of colloidal suspension of solid particles which upon condensation and polycondesation repeatedly results in to skeleton of solid particles in liquid state termed as gel. The sol-gel method has many advantages like low temperature of drying, annealing and can offer coating on substrates. Thus, compared to other the methods (Dongfang, 2018), synthesis of inorganic and organic-inorganic hybrid nanomaterials, nanocomposites are very promising. Moreover, at low processing temperatures (<100°C) molecular level particle shape and size, composition homogeneity can be controlled easily. The synthesis of catalyst like TiO_2 having uniform shape, size and distribution powder as well as coating can be achieved using titanium (IV) alkoxides precursor sol solution via an acid-catalysis (Pardon et al., 2018). The process also offer tailoring of various parameters like temperature and time to have control over hydrolysis and condensation processes involved thereby possibility to develop fascinating nanomaterials of varying dimensions (Mehrotra and Singh, 1997). Figure 2 represents diagram of various steps to control the final morphology of the nanomaterials and sol-gel process.

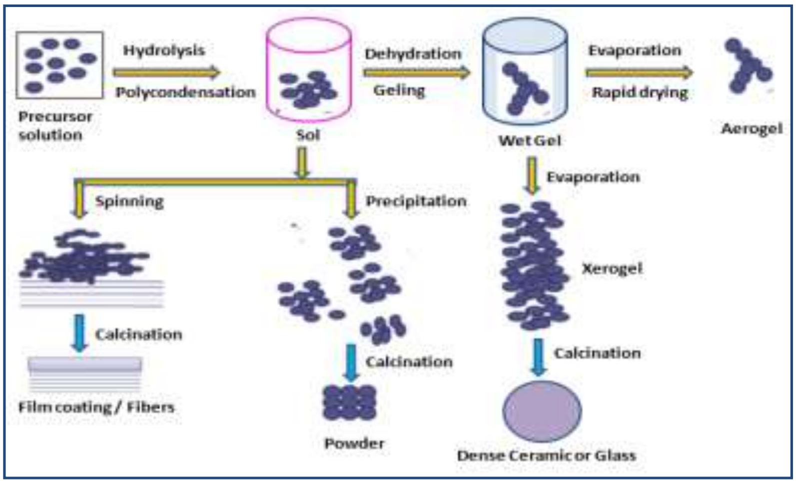

Fig.2- Diagram showing sol-gel process to control the final morphology of the nanomaterials.

The metal alkoxide has M─O─R bonding and highly reactive to hydrolysis using water, replaces the –OR (alkoxy) group easily. The addition of acid leads to condensation of hydroxyl groups making a M-O-M linkages as inorganic polymers. The general hydrolysis and polycondensation reactions using titanium alkoxide precursor are mentioned below to get the corresponding sol and nanoparticles.

$$TiOR + mH_2O \rightarrow Ti\,(OR)_{4-n}\,(OH)_n + nROH \quad (1)$$

$$Ti{-}OH + OR{-}Ti \longrightarrow Ti{-}O{-}Ti + ROH \quad (2)$$

$$Ti{-}OH + OH{-}Ti \longrightarrow Ti{-}O{-}Ti + H_2O \quad (3)$$

Chelating ligands like carboxylic acids, β-diketones, or other complex ligands are used as modifiers for obtaining the desire properties of solution. Monomers on further condensation turn to oligomers followed by polymers (Dongfang, 2018). Thus processed precursor can have reduced reactivity and functionality, controlling condensation leading to materials of smaller size and dimensions (Mehrotra and Singh, 1997). Effective and easy control of particle shape and size, low processing temperature, better homogeneity from raw materials is main advantage of sol-gel process .

3. NANOMATERIALS PLATFORMS FOR WASTE WATER TREATMENTS

3.1 Nanosorbents

Nanosorbents materials have very high surface to volume ratio offering a higher sorption capacity and hence find wide applications in waste water treatment and purifications.

S.No.	Nanosorbents	Applications for specific contaminants
1.	Carbon-based nanosorbents (lee *et al*., 2012).	Water containing nickel ions (Ni^{2+}). Excellent chemical resistance and high specific surface area, good adsorption capacity and mechanical strength.
2.	Captymer TM (Dunwell, 2011).	Contaminants (nitrate, perchlorate, uranium and bromide).
3.	Regenerable polymeric nanosorbent	Many organic and inorganic contaminants in waste water.
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 (Dongqing *et al*., 2010).	Complex three-dimensional networks caused by the iron beam providing better efficiency.

Table 1- Nanosorbents and its applications for specific contaminants.

The commercial grade nanosorbents have high cost and are nonspecific to contaminants in water (Chen and Mao, 2007). Applications of nanosorbents for specific contaminants are listed in Table 1.

The contaminants are generally nonmagnetic in nature and hence using separation aids and/or kits are reported to be useful adsorb the contaminants waste and the remaining magnetic pollutants can then be easily separated by applying magnetic field. The nanosorbents used in separation of contaminates sometime it adds the toxicity to water. In order to remove such nanosorbents, ion exchangers, cleaning agents and magnetic forces are used to avoid unnecessary toxicity. The separated nanosorbents are further reemployed which makes the process cost effective and viable for possible exploitation and use for commercialization.

3.2 Nanocatalysts

Nanocatalysts have increased surface area, high catalytic activity due to which is responsible for its wide use and application for waste water treatment from different sources. The nanoconfinement of catalytic particles has increased reactivity towards the particularly organic pollutants from dye and agricultural industrial waste effluents. It enhances the reactivity and degradation of contaminants. The degradation of contaminants of such industrial pollutants can be achieved by catalytic nanoparticles. The nanoparticles which are reported to be found useful for degradation are semiconducting metal oxides (TiO_2, ZnO, SiO_2), zero valence metals (Ag, Pt, Pd, Au) and bimetallic nanoparticles etc. Azo dyes, halogenated herbicides, halogenated aliphatic, polychlorinated biphenyls (PCBs), organochlorine pesticides, and nitro aromatics are major industrial waste contaminates (Chen et al. 2007), which are allowed to go in the other surface water reserves.

Silver (Ag) nanocatalyst, N-doped TiO_2 and ZrO_2 nanoparticles are found to be catalytically more active for its possible applications in degradation of waste water with microbial contaminants. TiO_2-AGS (Anchored Graphene Sheets) composite was revealed to be very efficient for Cr (VI) toxic ions present in water for conversion to less toxic form. TiO_2-AGS composite catalyst absorb UV as well as natural visible light due to shift of band in visible region and the modified TiO_2-AGS composite catalyst have more degradation ability than single pristine TiO_2 nanoparticles. Halogenated organic compounds (HOCs) are considered to have serious toxic effect, H_2/Pd nanoparticles due to quantum size effect of Pd nanoparticles attributes the selectively for biological microbes in waste waters with improved catalytic activity (Mehrotra and Singh, 1997). Hildebrand et al., (2008) have reported that palladium (Pd) and ZnO composite nanoparticles have been found to be having high photocatalytic activity. Furthermore a study done on silver-amidoxime fibers for waste water treatment containing organic dyes is also effective (Okereke et al., 2016).

3.3 Nanophotocatalysts

To enhance the reactivity of catalyst due to a greater surface ratio and shape dependent features nanophotocatalysts are used (Chen et al., 2019, Gomes et al., 2019). Presence of dyes, metal ions, complex organic compounds, and hazardous organic and inorganic pollutants in waste water can be treated by nano-sized photocatalysts in the presence of light (Tahir et al., 2019). At temperature 25-30°C nanophotocatalys is found significant for the degradation of dangerous organic materials. This method is effective and efficient for detoxification of water (Tahir et al., 2020). In a study made by Gomez-Pastora et al., 2017 it is shown that the oxidation ability can be expanded by nanophotocatalysts for effective production of oxidizing species by degradation of pollutants from the polluted water effectively. Different composites of TiO_2/H-ZSM5 may be used for the photocatalytic degradation of polychlorinated phenols under ultraviolet (UV) irradiation at ambient temperature in aqueous waste effluent generated from chemical processes. The degradation efficiency of the catalyst/ adsorbent TiO2/H-ZSM5 composites (20%, 40%, 60% and 80% TiO_2) was compared with zeolite adsorbent.

CdS/TiO2 composite nanomaterial catalyst under the irradiation of visible light has been used for photocatalytic performance for the degradation of dimethyl sulfoxide in water treatment (Li et al. 2014). Pd incorporated ZnO nanomaterial may be used to remove of Escherichia coli from polluted water due to its high high photocatalytic reacting property (Berekaa, 2016). Radhika et al., 2019 have shown that due to inexpensive usage of chemicals heterogeneous nanophotocatalyst is achieving the pre-industrial scale.

3.4 Photocatalytic Degradation and Mineralization Mechanism

In recent past, photocatalysis has come out as an alternative technique to remove organic pollutants (Sajjad et al. 2010). Degradation and mineralization of organic pollutants are two processes that occur in photocatalysis (Umar et al., 2013). TiO_2 is a semiconductor and it absorbs the light which is greater or equal to its band gap width. h^+_{vb} reacts with H_2O (surface-bound) to generate the OH radicals and at the same time excited electrons e^-_{cb} reduce as oxygen molecule to produce the radical anion to degrade phenol to small molecules as shown below in equations

$TiO_2 + h\nu \longrightarrow e^-_{cb} + h^+_{vb}$ (1)

$O_2 + e^-_{cb} \longrightarrow O_2^-$ (2)

$H_2O + h^+_{vb} \longrightarrow {}^-OH + H^+$ (3)

Where, *cb* - covalent band, *vb* - conduction band.

Figure 3 represents possible mechanism of pollutant degradation in presence of visible radiations. Figure 4 shows the degradation of chlorinated phenols in polluted water against irradiation time by using by various composites (commercial TiO_2, ZSM-5, TiO_2/H-ZSM-5). The degradation by H-ZSM-5 zeolite due to its adsorption effect, was around 80% up to 60 min. and then decreased to 0% because of saturated adsorption. On the other hand due to photocatalytic effect the degradation by catalyst TiO_2 was around 80% initially then gradually decreased to approx70%. While for the TiO_2/zeolite composites the degradation efficiency is found 20 wt% and 40 wt % which is less in comparison with those of 60 wt% and 80 wt % TiO2- supported zeolite and comm. TiO_2 catalyst.

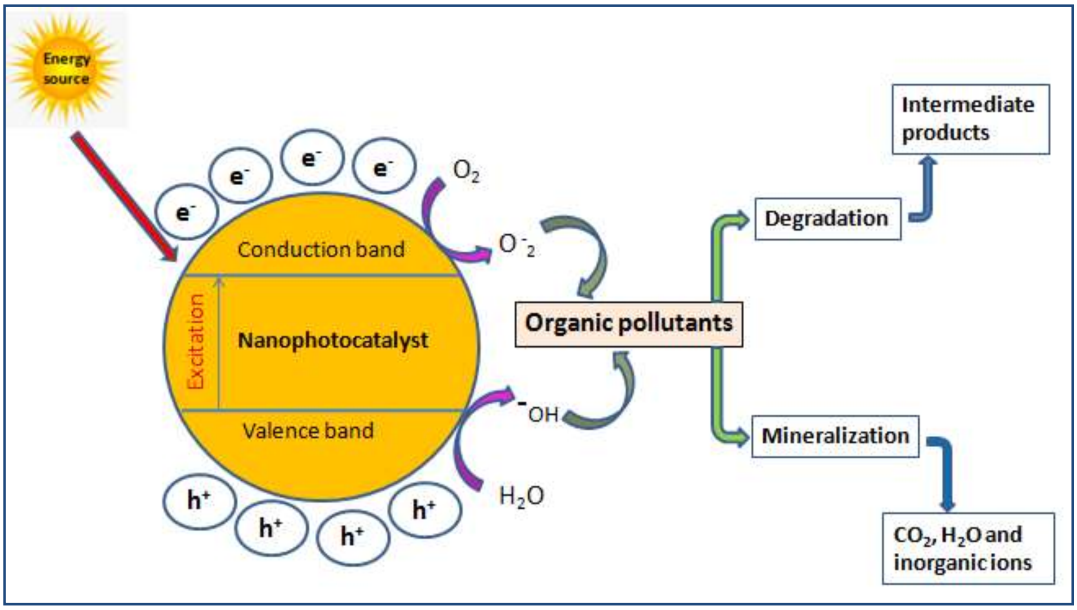

Fig.3- Schematic diagram of mechanism of toxic organic compound degradation.

The results indicate that the optimal composite ratio seems to be 60 wt% to 80 wt % TiO_2/ZSM-5 composites. Therefore, it can be predicted that combination of a small amount of TiO_2 photocatalyst and H-ZSM-5 zeolite catalyst can help to enhance degradation of chlorinated phenols in aqueous waste.

3.5 Titanium Dioxide

A well-known photocatalyst is Titanium dioxide. This is low cost, non-toxic in nature, highly stable in aqueous medium, biocompatible, having tunable electrical and optical properties.

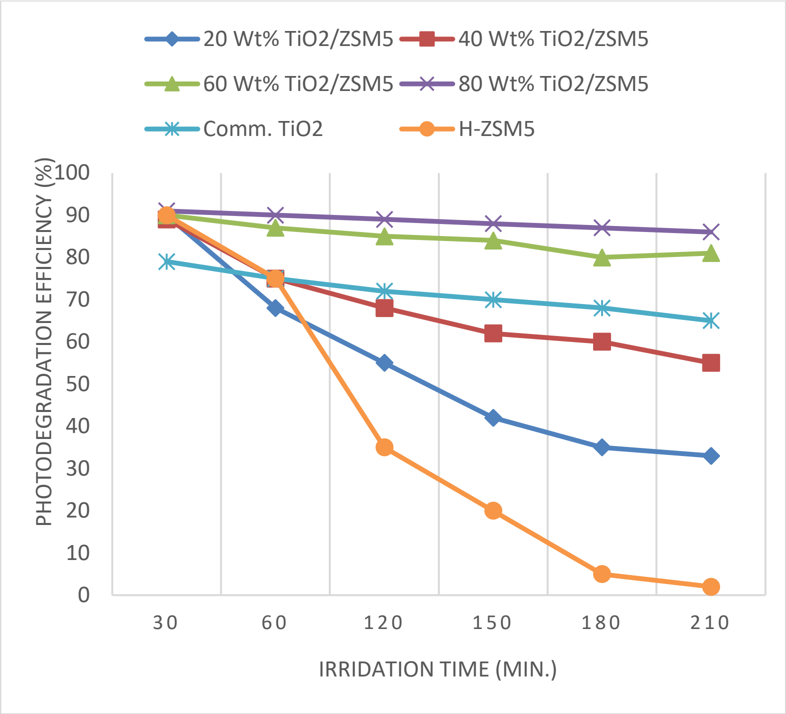

Fig.4- Effect of TiO_2 content in the TiO_2/zeolite composites on the photodegradation efficiency of chlorinated phenols in aq. waste water under a flow residence time.

Antase, rutile and brookite are three main crystalline phases of TiO_2. Out of these anatase is considered good nanophotocatalyst material.

Band gap (3.2 eV) of TiO_2 can further widen to visible range making nanosize rutile and anatase phases. The large band gap energy (3.2 eV) of TiO_2 requires UV excitation to induce charge separation within the particles. Different impurities from surface water can be removed with the help of photocatalysit TiO_2 as shown in Figure 5. Reactive oxygen species are generated under UV irradiation by TiO_2 to complete degrade impurities in very short reaction time.

The nano sized TiO_2 can act as visible light photocatalyst when doped to shift absorption edge in visible region and thus revealed as highly efficient catalyst under light exposure for waste water organic pollutants. The nano dimension size and shape with increased surface area is applicable for degradation of herbicides, carboxylic acids, alcohols to carbon dioxide and water completely (Dongfang, 2018). Sol-gel process, reverse micelles and metal organic chemical vapor deposition are popular methods of preparation of nano TiO_2 photocatalysts (Will, 2013, Lee et al., 2012).

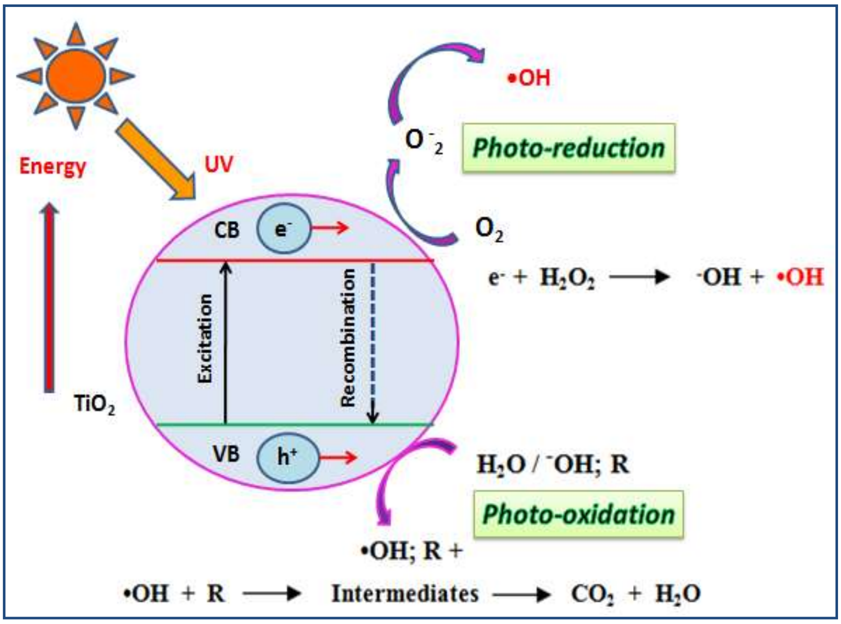

Fig.5- Schematic representation of TiO2 photocatalytic process

3.6 Membrane Filtration

Nano-filtration (NF) membrane process is becoming an efficient method for water treatment due to higher rejection compared to ultrafiltration and lower energy consumption compared to reverse osmosis (Mulyanti and Susanto, 2018). Nano-filtration is capable to separate the solutes of size in the ~ 0.001 micron range, while reverse osmosis (RO) is useful method to remove the solute molecules of size of ~ 0.0001 micron range. With the use of NF technologies it is also possible to remove bacteria, viruses, suspended particles, colloids as well as organic dyes (Fig.6). Nano-filtration removes nearly all bacteria, viruses, suspended particles, most organic matter, divalent ions and up to 90% of monovalent ions.

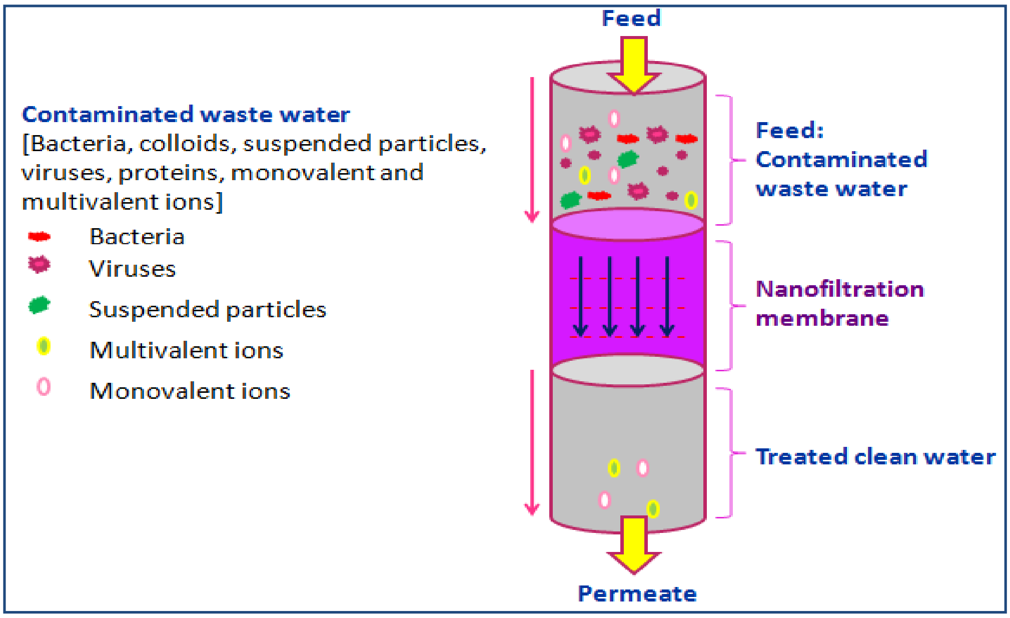

Fig.6- Schematic outlook of nanofiltration membrane technology

Nqombolo et al. (2018) used composite nano-filtration membranes for treatment of waste water. The prepared composite membrane had greater hydrophilic surface. This high hydrophilic surface gave rise to high pure water flux compared to that of the pure polymer. The results obtained showed enhanced fouling resistance and high dye rejection to bovine serum albumin. In a study Xu et al., (2016) reported NF membrane for treatment of textile wastewater, the prepared membrane displayed removal of common salts and dyes, heavy metal ions, showing high removal efficiency toward cationic dyes and metal ions.

Nano-filtration is a very useful method and widely utilized especially pesticides and organic contaminants removal from surface and ground waters. Thus NF processed water actually helps to insure the safety of public drinking water as we are losing the confidence in quality of drinking water supplies. This technology may have great potentials for future for waste water treatment.

3.7 Catalytic Wet Air Oxidation using Nanoparticles

The treatment of phenolic compounds using catalytic wet air oxidation platinum nanoparticles with hyper cross-linked polystyrene impregnated leads to high phenol conversion (Sayan et al., 2013). To design highly selective nanocatalyst is a major challenge. It is advantageous for nanocatalysts particularly; kind of organic functional polymers to tailor the structure using variation of the polymer source have high catalytic activity, selectivity and stability. Use of platinum nanocatalysts in bubble column reactor for wet air oxidation of oxalic acid is found as an efficient method at lower temperature.

4. RETENTION AND REUSE OF NANOMATERIALS

For low cost and public health issues the design of devices enabled with nanotechnology is a key step for the retention and reuse of nanomaterials. Ceramic membranes are more resistant to chemical oxidants and ultra violet radiations. But, the suspended particles retained by the membrane reduce significantly the reaction efficiency (Sayan et al., 2013). On the other hand in immobilization techniques there is a significant loss of treatment efficiency. Therefore, it gives scope for development of novel membranes to immobilize nanomaterials which cost effective without significantly impacting its performance. Magnetic separation method provides an alternate and low cost option for magnetic nanoparticles or nanocomposites (Vikas and Akhilesh, 2012). The main problem is the detection of release of nanomaterial for risk assessment (Volodymyr and Tarabara, 2014). However, in complex aqueous matrices the detection of nanomaterial is expensive with available techniques.

5. IMPLICATIONS OF NANOTECHNOLOGY

Nanotechnology has both positive as well as adverse implications depending on the treatment methods of waste water used, which are highlighted below:

5.1 Positive Implications

Large sample testing can be done simultaneously using small sample size with more efficiency. Utilizing advanced nanotechnology, a detector can made to detect a nuclear leak faster and more accurate (Fukushima Daiichi Nuclear Power Plant) that can identify radiation faster. With the help of nanotechnology ultra-small probes can be developed to detect and control water, soil and air contamination for the purpose of agriculture. Biomedical applications include the medical diagnostic kits and tools for early detection of diseases in healthcare. Use of nanomaterials in industrial processes enables to treat industrial waste in cleaner and more efficient way.

5.2 Adverse Environmental Effects

The nanomaterials vary by shape and size and it is now a days important to determine their toxicity as nanotechnology improves, new and novel nanomaterials are gradually developed, the analysis method are also not realized. To use nanomaterials for waste treatments it becomes important for full risk assessment, human health safety needs to be evaluated at all stages of usage. The critical risk factors which needs immediate attentions but not limited are exposure time, probability of exposure, toxicological analysis etc. The nanomaterials based processes and technologies needs to be relooked with many other concern factors are; life cycle risk assessment, experimental design, persistent nanosubstances, dissemination of toxic materials, lack of trained engineers and workers, etc needs to be assesses to predict the environmental impacts (Mehrotra and Singh, 1997).

6. CONCLUSIONS

Nanotechnology has made substantial progressive development for waste water treatments from surface reserved water, industrial effluents, sewages and different sources for handling water contamination problems. Nanotechnology based treatment methods particularly metal, metal oxide and its nanocomposites at nanoconfinements have been utilized for waste water treatment in an efficient manner in comparison with conventional treatment methods.

In order to make further advancements in future the applications of nanotechnology for treating waste water, the major concerns needs to undertake for study. This papers explains review on different nanomaterials platforms i.e. nanosorbents, nanocatalysts, nanophotocatalysts, photocatalytic degradation and mineralization pathways, nanoparticles, membrane filtration, nanofibers, metal nanoparticles and their synthetic methods have made substantial improvement in dealing the waste water treatments. However, as per standards laid down by regulatory authorities further progress is still needed in order to validate the performance analysis, testing and evaluation of nanotechnology in of waste water treatment. Long-term efficacy of these nanotechnologies is need of hours to understand the feasibility of such nanoenabled technologies for more practical applications for problems of today's time. However, research addressing solutions are still not applicable for waste water in large volumes and remain challenging. Studies related to long term performance of high volumes of waste water treatment still have scope for future advancement. It is a challenge to mitigate the issues of commercialization of nanotechnology for treatment of waste water at low cost.

Conflict of Interest

Authors declare no conflict of interest.

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