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REVIEW

Remediation of wastewater using various nano-materials

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Abstract In the present era of scarcity of water resources, effective treatment of wastewater is a major prerequisite for growing economy. It is critical to develop and implement advanced wastewater treatment technologies with high efficiency and low capital requirement. Among various treatments, recent advanced processes in nano-material sciences have been attracting the attention of scientists. However, limited collective knowledge is available in this context. The present manuscript reviews the potential developments in nanotechnology with respect to wastewater treatment. The article reviewed and discussed utilization of various classes of nano-materials for wastewater treatment processes. This includes four main classes; First, nano-adsorbents such as activated carbon, carbon nanotubes, grapheme, manganese oxide, zinc oxide, titanium oxide, magnesium oxide and ferric oxides that are usually applied for removal of heavy metals from the wastewater. Second, nano-catalysts such as photocatalyst, electrocatalyst, Fenton based catalyst, and chemical oxidant have been shown the potential for removing both organic and inorganic contaminants. Third, nano-membranes have been used for effective removal of dyes, heavy metals and foulants using carbon nanotube membranes, electrospun nanofibers and hybrid nano-membranes. Finally, the integration of nanotechnology with biological processes such as algal membrane bioreactor, anaerobic digestion and microbial fuel cell is discussed with respect to its potential for wastewater purification.

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Contents

1. Introduction

Water on earth is one of the most abundant natural resources, but only about 1% of that resource is available for human consumption (Grey et al., 2013; Adeleye et al., 2016). It is estimated that over 1.1 billion people lack supply of adequate drinking water (WHO, 2015), due to the rising cost of potable water, growing populations, and variety of climatic and environmental concerns (Adeleye et al., 2016). The major challenge in water supply chain is continuous contamination of freshwater resources by a variety of organic and inorganic pollutants (Schwarzenbach et al., 2006). The treatment of wastewater and drinking water can reduce these concerns (Ferroudj et al., 2013); however, the traditional methods of treatment are not efficient enough to completely remove the emerging contaminants and meet the strict water quality standards (Qu et al., 2012). Moreover, the existing technologies of wastewater treatments have several drawbacks such as high-energy requirement, incomplete pollutant removal and generation of toxic sludge (Ferroudj et al., 2013).

The biological wastewater treatment is widely applied but these are usually slow, limited due to the presence of non-biodegradable contaminant, and sometime causes toxicity to microorganisms due to some toxic contaminants (Zelmanov and Semiat, 2008). The physical processes such as filtration can remove the contaminants by transforming one phase to another but producing a highly concentrated sludge (Catalkaya et al., 2003; Bali et al., 2003), which is toxic and difficult to dispose. In the above context, there is a real requirement for more efficient and powerful technologies for treatment of municipal and industrial wastewaters (Burkhard et al., 2000; Parsons and Jefferson, 2006; Crini and Badot, 2007; Ferroudj et al., 2013). This can be achieved either by development of completely new methods or by improving the existing methods through some interventions. Among the various emerging technologies, the advancement in nanotechnology has proved an incredible potential for the remediation of wastewater and various other environmental problems (Zare et al., 2013; Sadegh et al., 2014; Gupta et al., 2015).

Nanotechnology is the field of nanoscience, the phenomena applied on a nanometer scale level. Nano-materials are the smallest structures that humans have developed, having size of a few nanometers (Chaturvedi et al., 2012). More precisely, the nano-particles are those that have structure components with one dimension at least less than 100 nm (Amin et al., 2014). Nano-materials have been developed in variety of forms such as nanowires, nanotubes, films, particles, quantum dots and colloids (Edelstein and Cammaratra, 1998; Lubick and Betts, 2008). In wastewater treatment application, a variety of efficient, eco-friendly and cost-effective nano-materials have been developed having unique functionalities for potential decontamination of industrial effluents, surface water, ground water and drinking water (Brumfiel, 2003; Theron et al., 2008; Gupta et al., 2015).

Nanotechnology has been cited, in different literatures, as one of the most advanced processes for wastewater treatment. It may be classified based on the nano-materials nature into three main categories: nano-adsorbents, nano-catalysts and nano-membranes. In nano-adsorption technology, numerous and effective works have been published recently with the aim to investigate the removal of pollutants

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from wastewater using nano-adsorbent materials (Zhang et al., 2014a, b; Tang et al., 2014; Shamsizadeh et al., 2014; Kyzas and Matis, 2015). Nano-adsorbent can be produced using the atoms of those elements which are chemically active and have high adsorption capacity on the surface of the nano-material (Kyzas and Matis, 2015). The used materials for development of nano-adsorbents include activated carbon, silica, clay materials, metal oxides and modified compounds in the form of composites (El-Saliby et al., 2008).

The second class of the nanomaterials is nano-catalysts. The nanomaterials such as metal oxides and semiconductors have gained a considerable attention of the scientists in developing wastewater treatment technologies. Different types of nano-catalysts are employed for degradation of pollutants in wastewater, for instance, electrocatalysts (Dutta et al., 2014), Fenton based catalysts (Kurian and Nair, 2015) for improving chemical oxidation of organic pollutants (Ma et al., 2015) and catalysts having antimicrobial properties (Chaturvedi et al., 2012).

The third class of the nano-materials used in the wastewater treatment processes is using nano-membranes. In that technology, the pressure driven treatment of wastewater has been proved ideal for improving water quality of desire (Rao, 2014). Among various types of membrane filtration, (Lau and Ismail, 2009; Ouyang et al., 2013; Blanco et al., 2012) the nano-filtration (NF) is extensively applied for treatment of wastewater in industries because of small pore sizes, low cost, high efficiency and user friendliness (Petrinic et al., 2007; Hilal et al., 2004; Babursah et al., 2006; Rashidi et al., 2015). Nano-membranes can be developed from nano-materials such as nano metal particles, non-metal particles and nano-carbon tubes among others (El Saliby et al., 2008).

Numerous studies have been reviewed highlighting the efficiency of various newly developed nano-materials. The present review focused on four main categories of nano-materials in application of wastewater treatment. These include nano-adsorbents, nano-catalysts, nano-membranes, and the integration of aforementioned nano-technologies with biological methods.

2. Nano-adsorbents

In recent years, nano-particle materials have been studied for their potential as adsorbents. The smaller size of the nano-particles increases the surface area (Gubin et al., 2005) which enhances the chemical activity and adsorption capacity of nano-particles for the adsorption of metals on their surface (Kalfa et al., 2009; Gubin et al., 2005). Adsorption process depends on adsorption coefficient K_d and recitation partitioning of pollutant i.e. heavy metals or organic pollutants under equilibrium conditions (Hu et al., 2010; Mehrizad et al., 2011). Moreover, for persistent inorganic pollutants redox reaction is favored to start the ionic structure transformation (Gupta et al., 2015). However, some researchers strongly agree that changes in redox condition influence the toxicity of these pollutants (Chen and Mao, 2007; Ray, 2010). The frequently used nano-particles for the adsorption of heavy metals are activated carbon and carbon nanotubes, manganese oxide, grapheme, zinc oxide, magnesium oxide, titanium oxide and ferric oxides (Gupta et al., 2015).

Nano-adsorbents possess two main properties: innate surface and external functionalization. Their physical, chemical and material properties are also related to their extrinsic surface structure, apparent size and intrinsic composition (Mirkin et al., 1996). In the aqueous environment, the factors affecting the adsorption process are high surface area, adsorption activity, chemical activity, location of atoms on surface, lack of internal diffusion resistance and high surface binding energy (Khajeh et al., 2013). Nano-particles used as adsorbent for the removal of heavy metals should be nontoxic, high adsorption capacity, have the ability to adsorb pollutants in less concentration (ppb), adsorbed pollutants that can be easily removed from adsorbent surface and can be recycled for numerous times (Cloete, 2010).

2.1. Classification of nano-adsorbents

Nano-adsorbents are broadly classified into various groups based on their role in adsorption process. It includes metallic nano-particles, nanostructured mixed oxides, magnetic NPs and metallic oxide NPs. Besides that, a recent development on carbonaceous nano-materials (CNMs) included carbon nanotubes, carbon nano-particles and carbon nanosheets. Moreover, various types of silicon nano-material are also used as nano-adsorbents such as silicon nanotubes, silicon nano-particles and silicon nanosheets. In addition, nanoclays, polymer-based nano-materials, nanofibers, and aerogels are some of the nano-materials used for adsorption of heavy metals from wastewater.

Factors controlling the nano-adsorbents properties are size, surface chemistry, agglomeration state, shape and fractal dimension, chemical composition, crystal structure and solubility (OECD et al., 2010). Chemical activity and fine grain size are two key properties of nano-particles that make its prominent as compared to other substances such as normal scale titanium dioxide and alumina (Kalfa et al., 2009; Zhang et al., 2008). Moreover, modification in nano-particles can be carried out by some reagent to enhance its properties for metals ions pre concentration (Khajeh and Sanchooli, 2011; Khajeh, 2010).

2.1.1. Oxide based nano-particles

Oxide based nano-particles are inorganic nano-particles which are usually prepared by non-metals and metals. These nano-particles are extensively used for hazardous pollutants removal from wastewater. There include titanium oxides (Gao et al., 2008), Titanium oxide/dendrimers composites (Barakat et al., 2013a, 2013b) zinc oxides (Tuzen and Soylak, 2007), magnesium oxide (Gupta et al., 2011), manganese oxides (Feng et al., 2012) and ferric oxides (Xu et al., 2008a,b). Oxide based nano-particles are characterized by high BET surface area, minimum environmental impacts, less solubility, and no secondary pollutants (Gupta et al., 2015).

2.1.1.1. Iron based nano-particles. The natural occurrence of iron and its simple synthesis process make ferric oxide a low cost material for the adsorption of noxious metals. It is an eco-friendly material and can be used directly to a contaminated environment with less chance of secondary contamination (Li et al., 2003a, 2003b). Factors affecting the adsorption of different heavy metals on Fe_2O_3 nano-particles depend on the pH, temperature, adsorbent dose and incubation time (Gupta et al., 2015). To increase the adsorption capacity of Fe_2O_3 surface modification was carried out by different researchers (Wang et al., 2015; Ozmen et al., 2010). Palimi et al. (2014) reported the surface modification of Fe_2O_3 nano-particles with 3-aminopropyltrimethoxysilane. Gupta et al. (2015) reported that the modification of these nano-adsorbents shows high affinity for the removal of different pollutants such as Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+} and As^{3+} simultaneously from wastewater.

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2.1.1.2. Manganese oxides (MnO) nano-particles. A manganese oxide (MnOs) NPs show high adsorption ability due to their high BET surface area and polymorphic structure (Luo et al., 2010). It has been widely used for the removal of various heavy metals such as arsenic from wastewater (Wang et al., 2011). Most frequently used modified MnOs include nanoporous/nanotunnel manganese oxides and hydrous manganese oxide (HMO) (Gupta et al., 2015). Zaman et al. (2009), prepared HMO by adding $MnSO_4{\cdot}H_2O$ into NaClO solution. Modified HMO has around 100.5 $m^2\,g^{-1}$ BET surface areas. Adsorption of various heavy metals such as Pb (II), Cd (II) and Zn (II) on HMOs usually happens due to the inner-sphere formation mechanism that can be defined by ion-exchange process (Gupta et al., 2015). However, adsorption of divalent metals on the surface of HMOs occurred in two steps. At first, metal ions adsorb on the external surface of HMOs and then followed by intraparticle diffusion (Parida et al., 1981).

2.1.1.3. Zinc oxide (ZnO) nano-particles. Zinc Oxide (ZnO) has a porous micro/nanostructure with high BET surface area for the adsorption of heavy metals. Nano assemblies, nano-plates, microspheres with nano-sheets and hierarchical ZnO nano-rods are widely used as nano-adsorbent for the removal of heavy metals from wastewater (Ge et al., 2012; Kumar et al., 2013). The aforementioned modified forms of ZnO nano-adsorbent show high removal efficiency of heavy metals as compared to commercial ZnO. Wang et al. (2010) used ZnO nano-plates and porous nano-sheet for the removal of Cu (II) from wastewater. These modified ZnO nano-adsorbent shows high removal efficiency of Cu (II) due to their unique micro/nanostructure as compared to commercial ZnO. Moreover, nano-assemblies were used for the removal of different kinds of heavy metals which include Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+} and As^{3+} (Singh et al., 2013). Microporous nano-assemblies show high affinity for the adsorption of Pb^{2+}, Hg^{2+} and As^{3+} due to their electropositive nature (Gupta et al., 2015). Kumar et al. (2013) reported the high removal efficiency of Pb (II) and Cd (II) from wastewater by using mesoporous hierarchical ZnO nano-rods.

2.1.1.4. Magnesium oxide (MgO) nano-particles. Magnesium oxide (MgO) is used for the removal of different kinds of heavy metals from contaminated water. MgO microsphere are novel structure, which can improve the adsorption affinity for the removal of heavy metals (Gupta et al., 2015). To increase the adsorption capacity of MgO, different types of modification were carried out in NPs morphology. These include nanorods (Engates and Shipley, 2011), nanobelts (Zhu et al., 2001), fish-bone fractal nanostructures induced (Liang et al., 2004), by nanowires (Mo et al., 2005), nanotubes (Yin et al., 2002), nano-cubes (Li et al., 2002) and three-dimensional entities (Klug and Dravid, 2002). Li et al. (2003b) reported efficient adsorption of Pb (II) and Cd (II) on flowerlike mesoporous MgO.

2.1.2. Carbon nanotubes (CNTs)

Carbon nanotubes (CNTs) are extensively studied material having potential to remove heavy metals and a variety of organic contaminants from wastewater through adsorption (Ren et al., 2011). However, poor dispersion ability, difficulty in separation and small particles size are few problems exist for using CNT as adsorbent. To overcome these problems researcher modified the ordinary CNT into modified CNT such as multi-wall carbon nanotubes (MWCNT) (Tang et al., 2012; Tarigh and Shemirani, 2013). Modified magnetic CNTs have high dispersion ability and can be easily removed from wastewater or used medium by using magnet (Madrakian et al., 2011). Several studies reported the removal of heavy metals such as Pb(II) and Mn(II) (Tarigh and Shemirani, 2013), Cu(II) (Tang et al., 2012) by using MWCNTs. Gupta et al. (2011) have investigated the adsorption behavior of alumina supported on CNT for the treatment of lead aqueous solutions. They reported that the coated CNT exhibited better removal ability than the uncoated CNT.

Surface modification of CNT increases its overall adsorption activity. Various kinds of surface modification techniques are reported by different researchers which include acid treatment (Ren et al., 2011; Ihsanullah et al., 2015), metals impregnation (Tawabini et al., 2011; Zhang et al., 2012), and functional molecules/group grafting (Shao et al., 2010a,b; Chen et al., 2012). The aforementioned techniques alter the characteristics of CNTs surface like BET surface area, surface charge, dispersion and hydrophobicity. Acid treatment of CNTs was carried out by using different kinds of acids, which include HNO_3, $KMnO_4$, H_2O_2, H_2SO_4 and HCl (Ren et al., 2011; Fu and Wang, 2011). Acid treatment removes the impurities present on the surface of CNTs. Moreover, it also introduces new functional groups on the surface of CNTs, which resulted in increase in its adsorption capacity from wastewater (Gupta et al., 2015). In addition, oxygen-containing group can also be introduced by microwave-excited surface wave plasma (Chen et al., 2009).

Grafting functional molecules/groups on the surface of CNTs are another way to improve their surface characteristics. It can be carried out via different ways such as plasma technique, chemical modification and microwave (Shao et al., 2010a,b; Zhang et al., 2012; Chen et al., 2012). However among these techniques, plasma technique is one of the best due to less energy demand and environmental friendly process. Chen et al. (2012) reported the removal of heavy metals from wastewater by using modified CNTs grafted with various functional groups. Moreover CNTs modified with metal/metal oxide such as MnO_2 (Liang et al., 2015), Al_2O_3 (Gupta et al., 2011) and iron oxide (Tang et al., 2012; Tawabini, 2015) also show promising results for heavy metals removal from wastewater.

2.1.3. Graphene based nano-adsorbents

Graphene is one of allotropy of carbon having special features that make it highly favorable for several environmental applications. Graphene oxide (GO) is a carbon nano-material having two-dimensional structure produced by the oxidation of graphite layer via chemical method. The most common method used for the synthesis of GO is Hummers method (Lingamdinne et al., 2016b). The hydrophilic groups were induced in GO which required special oxidation process (Gopalakrishnan et al., 2015). The presence of these hydroxyl and carboxyl groups as functional groups in GO increases the adsorption of heavy metals (Li et al., 2009; Lingamdinne et al., 2016b). GO as adsorbent for the removal of heavy metals is getting more attention due to its high surface area, mechanical strength, light weight, flexibility and chemical stability

Table 1 Efficiency of various nano-adsorbents for the removal of heavy metals in wastewater.

Nano-adsorbent	Heavy metals	Experimental conditions			% Removal efficiency	Reference
		pH	Contact time (min)	Adsorbent dose (g/L)		
Magnetic multi-wall carbon nanotubes	Cr(VI)	3	600	0.1	100	Huang et al. (2015)
Magnetic zeolite-polymer composite	V	4–5	1440	0.15	73	Mthombeni et al. (2015)
ZIF-8 nanoparticles	As	7	240–420	0.20, 0.05	60.03	Jian et al. (2015)
ZnS nanocrystals	Hg (II)	1–6	5	10	99.99	Qu et al. (2014)
Modified magnetite Nanocomposite	Cu^{2+}	6.5	15	0.19	99	Neyaz and Siddiqui (2015)
Graphene nanosheets (GNS)/δ-MnO_2	Ni (II)	NR*	20	5	77.04	Varma et al. (2013)
Nanocrystalline titanium dioxide	As (III)	9.5	NR*	0.2	> 98	Pena et al. (2006)
NZVI	As (III)	7	10	1	99.9	Rahmani et al. (2011)
Magnetic nano-particles coated zeolite	As (III)	2.5	15	0.5	95.6	Attia et al. (2014)
Zeolite materials obtained from fly ash	Pb^{2+}	6–7.5	90	6	> 80	Visa (2016)
Magnetic nano-adsorbent	Pb^{2+}	6	10	20	80	Khani et al. (2016)
PMDA/TMSPEDA	Pb (II)	7	1440	0.01	79.60	Alsohaimi et al. (2015)
	Cu (II)				72.36	
	Zn (II)				66.80	
Magnetic nano-adsorbent	Zn (II)	5.5	90	2.5	95	Shirsath and Shirivastava (2015)

NR*: not reported.

(Gopalakrishnan et al., 2015; Taherian et al., 2013). Moreover the presence of functional group on the surface of GO also effects the adsorption process (Zare-Dorabei et al., 2016). GO has two main features as compared to other nano-materials such as CNTs. First, a single layer GO has two dimensional basal planes available for the maximum adsorption of heavy metals. Secondly, it has simple synthesis process, which can be carried out by chemical exfoliation of graphite without any metallic catalyst and complicated instrument (Santhosh et al., 2016). Moreover, GO did not require any further acid treatment to enhance its adsorption capacity as it already contains hydrophilic functional group (Zhao et al., 2011). Various researchers used graphene based nano-materials for the adsorption of heavy metals from wastewater (Azamat et al., 2015; Dong et al., 2015; Vu et al., 2016; Zare-Dorabei et al., 2016). Ding et al. (2014) studied the removal of heavy metals from wastewater by using GO enabled sand filter in column reactor as well. Lee and Yang (2012) modify the GO with TiO_2 and used hybrid composite for the adsorption of Pb^{2+}, Cd^{2+} and Zn^{2+} ions from the water. The adsorption capacity of hybrid composite reaches up to 65.6 mg/g, 72.8 mg/g and 88.9 mg/g for Pb^{2+}, Cd^{2+} and Zn^{2+} respectively. Graphene and its other composite show a very high efficiency for the removal of heavy metals from wastewater. Nevertheless, successful reduction in GO to pristine graphene material is still a big challenge because this reduction may decrease its mechanical and electronic properties (Santhosh et al., 2016).

2.2. Factors affecting adsorption processes

Adsorptions of heavy metals from wastewater by using the nano-adsorbents are affected by many factors such as temperature, pH, adsorbent dose and incubation/contact time. Srivastava et al. (2015) reported that pH plays a vital role on adsorption of heavy metals from wastewater. Maximum adsorption for Zn (II) on magnetic nano-adsorbent was observed at pH 5.5; however, it decreases with further increase in pH. Lingamdinne et al. (2016a) reported the maximum adsorption i.e. 93% and 99.6% for Pb(II) and Cr(III) at the pH of 6.0 and 4.0 respectively. Moreover, increase in contact time increases the adsorption of heavy metals from aqueous solution because it provides more time for the adsorption. Initially adsorption of heavy metals is high due to the high concentration of metals, which decreases as time increases due to blockage of active sites (Shirsath and Shirivastava, 2015). Lingamdinne et al. (2016a) reported that 120 min is the equilibrium time for maximum adsorption of Pb(II) and Cr(III) from wastewater. Nano-adsorbent characteristics also affect the adsorption of heavy metals, which include BET surface area, surface charge, hydrophobicity and addition of new functional groups. These modification techniques increase the adsorption capacity of nano-adsorbents (Tarigh and Shemirani, 2013; Wang et al., 2015). The efficiency of various nano-adsorbents for removal of heavy metal has been reported in various studies as described in Table 1.

3. Nano-catalysts

The nano-catalysts, especially those of inorganic materials such as semiconductors and metal oxides, are gaining considerable attention of the researchers in application of wastewater treatment. Various kinds of nano-catalysts are employed for wastewater treatment such as photocatalysts (Dutta et al., 2014), electrocatalysts (Dutta et al., 2014), and Fenton based catalysts (Kurian and Nair, 2015) for improving chemical oxidation of organic pollutants (Ma et al., 2015) and antimicrobial actions (Chaturvedi et al., 2012).

3.1. Nano-materials as photocatalysts

Nanoparticle photocatalytic reactions are based on interaction of light energy with metallic nano-particles and are of great interest due to their broad and high photocatalytic activities for various pollutants (Akhavan, 2009). Usually these photocatalysts are comprised of semiconductor metals that can degrade variety of persistent organic pollutants in wastewater

such as dyes, detergents, pesticides and volatile organic compound (Lin et al., 2014). Furthermore, semiconductor nano-catalysts are also highly effective for degradation of halogenated and non-halogenated organic compounds, PCPPs and also heavy metals in specific situation (Adeleye et al., 2016). Semiconductor nano-materials are required a mild operation conditions and very effective even at a small concentration. The simple mechanism of the working of photocatalysis is based on the photoexcitation of electron in the catalyst. The irradiation with light (UV in case of TiO_2) generates holes (h^+) and exited electrons (e^-) in the conduction band. In an aqueous media, the holes (h^+) are trapped by water molecules (H_2O) and generate hydroxyl radicals ($^{\cdot}OH$) (Anjum et al., 2016a). The radicals are indiscriminate and powerful oxidization agent. These hydroxyl radicals on reaction oxidize the organic pollutants into water and gaseous degradation products (Akhavan, 2009).

Among various nano photocatalysts developed up till now, TiO_2 is one of the most widely applied in photocatalysis due to its high reactivity under ultraviolet light (k < 390 nm) and chemical stability (Akhavan, 2009). Similarly, ZnO has also been extensively studied for its photocatalytic action, as it contains wide band gap just like TiO_2 (Lin et al., 2014). Numerous studies have shown the photocatalytic activity of various synthesized catalysts. Their efficiency depends on different factors such as band gap energy, particle size, dose, pollutant concentration and pH. For instance, Hayat et al. (2011) found that the photocatalytic degradation efficiency of ZnO decreased with high calcination temperature that increases the particle size due to agglomeration. CdS is also a well-known semiconductor having band gap of 2.42 eV and can be operated at wavelength < 495 nm (Khallaf et al., 2008). CdS nanoparticles have been attracted intensive interest as photocatalyst for treatment of industrial dyes in wastewater (Tristao et al., 2006; Zhu et al., 2009).

However, the above-mentioned catalysts are well known for their photocatalytic activity but they are active only under ultraviolet radiations (l < 387 nm). This is due to the wide band gap energy i.e. 3.2 eV as in case of TiO_2. Thus, further modifications for the catalysts have been studied to increase their activities under visible light source (sunlight) for degradation of organic pollutants (Dutta et al., 2014).

3.1.1. Doping/modification of photocatalysts

The use of visible light in photocatalytic treatment of wastewater is contemporary in research interest. To achieve this goal, the nano-material/semiconductor requires some modification to decrease the band gap energy form UV to visible region (Anjum et al., 2016b). There are number of available studies evaluating photocatalytic activity of modified nano-catalyst under visible light. The general methods used for modification of the catalyst include dye sensitization, doping metal impurities, hybrid nano-particles or composites using narrow band-gap semiconductors, or anions (Ni et al., 2007). The new metals and anions in the composite create a narrow band gap also called as impurity energy levels which upon exposure to visible light conducts electron into semiconductor for initiation of catalytic reaction (Qu et al., 2013).

ZnO and TiO_2 nano-materials have wide band gap of 3.2 eV and have been extensively investigated for their photocatalytic activity. However, in solar spectrum both catalysts can only absorb a small portion of the UV region, which decrease their efficiency (Chen and Zhou, 2004). However, modification in catalyst by loading metals on its surface can solve this problem. The modified composite material decreases the band gap energy and subsequently transfers the exited electron to semiconductor under illumination of solar radiation. Furthermore, not all conductive metals are effective for doping to improve photocatalaytic activity, e.g. Pt and Ru are ineffective for doping, while other metals such as Au, Ag and Pd showed excellent photocatalytic activities (Sathishkumar et al., 2011; Barakat et al., 2013a, 2013b). During recent years, various doped nano-catalysts have been developed such as ZnO:Co, Ni, ZnS:Mn, ZnS:Cu, CdS:Eu, CdS:Mn, ZnSe:Mn, ZnS:Pb, and Cu (Chandrakar et al., 2015). There are many dopants such as Cr, Si, Co, Mg, Mn, Fe, Fe, Al, In and Ga are used having capability to enhance the surface area of metal oxide nano-structure (Jamal et al., 2012). Among various dopants, anions such as nitrogen are also considered as most feasible and cost effective for industrial application (Fujishima et al., 2008; Qu et al., 2013). Doping of nano-materials alleviates the surface area of the catalyst and protects the nano-composite from size reduction, change in morphology and shape. Sathishkumar et al. (2011) synthesized CuO/ZnO photocatalyst to assist the degradation of a textile wastewater dye (Acid Red 88) under visible light. They achieved two times higher photocatalytic degradation with CuO/ZnO compared to that of unmodified ZnO. Eskizeybek et al. (2012) synthesized modified ZnO nano-composite using organic homopolymer polyaniline (PANI). The modified PANI/ZnO nano-catalyst showed 99% of removal of organic pollutants in wastewater such as methylene blue and malachite green dyes during photocatalysis, even with a little dose of catalyst i.e. 0.4 g/L of wastewater. Similarly, in another study, the modified CdS cross linked (CS/n-CdS) chitosan found to be highly effective for degradation of model organic pollutant CR Congo Red where 85.9% of degradation was observed in just 3 h of photocatalytic process under visible light (Zhu et al., 2009). Dutta et al. (2014) synthesized γ-Fe_2O_3 nanoparticles by thermal decomposition method and observed a high photocatalytic activity toward degradation of rose bengal and methylene blue dyes under irradiation of visible light. The use of grapheme for modification of catalyst has also getting attention of researcher due to its special characteristics. The composites of graphene with other semiconductor materials could significantly enhance the electron mobility through interfacial electron transfer process during photocatalysis. Moreover, graphene has capability to promote the separation efficiency of photo-induced electrons and holes in photocatalyst (Li et al., 2016). A comprehensive view on photocatalytic efficiency of various modified nano-catalysts for removal of organic pollutants from wastewater is summarized in Table 2.

3.2. Photocatalysts as antimicrobial agent

Photocatalysis has been proven as a promising technique for purification and treatment of various kinds of wastewater (Yu et al., 2001). In addition, it has an efficient ability to inactive the pathogenic organism such as bacteria, in the wastewater (Yu et al., 2003). As discussed in the above section, TiO_2 is extensively used photocatalyst and reported for its high antimicrobial power. The use of TiO_2 powder has some

Table 2 Photocatalytic efficiency of various nano-catalysts for removal of organic pollutants from wastewater.

Catalyst	Light region	Conditions	Pollutant	Results	Reference
$Y_2O_3:Eu^{3+}$	350–400 nm (UV)	Cat. Dose = 0.24 g/L, Duration = 120 min	Methylene blue	Up to 90% degradation efficiency of methylene blue was observed	Kumar et al. (2015)
Ti_2CO coatings	420 nm (Vis)	Duration = 3 h	Methylene blue	Removal of Methylene blue form 10 μ mol/L to around 8.5 μ mol/L was observed	Guan et al. (2016)
TiO_2/trititanate	UV–Vis region	Cat. Dose = 1 g/L, Duration = 2 h	Rhodamine B	The degradation efficiency of Rhodamine B of >91% was achieved	Chen et al. (2015)
AgBr/ZnO	410 nm (Vis)	Cat. Dose 1 g/L, pH = 6.86 Duration = 4 h	Methylene blue	Up to 87% of methylene blue was decomposed by AgBr/ZnO after 240 min	Dai et al. (2014)
3D SnO	365 nm (UV)	Cat. Dose = 2 g/L, Duration = 2.5 h	Methyl orange	Photocatalytic degradation of methyl orange was 83% after 150 min	Cui et al. (2015)
ZnO nanorods	365 nm (UV)	Cat. Dose = 1 g/L, Duration = 42 min	Rhodamine B	The quenched catalyzed greatly improved the photocatalytic degradation of Rhodamine B	Fang et al. (2015)
Zero-valent nano-copper	Visible region	Cat. Dose = 0.16 g/L, Duration = 80 min	Methyl orange	Up to 35% degradation of methyl orange was achieved with in 80 min.	Liu et al. (2016)
Biomorphic TiO_2 photonic crystal	>420 nm (Vis)	Cat. Dose = 1 g/L, Duration = 4 h	Methyl orange	Up to 30% degradation of methyl orange was achieved with in 4 h.	Wang et al. (2016)
$CuFe_2O_4@C_3N_4$	>420 nm (Vis)	Poll. Cone. 0.04 mM, Duration = 3.5 h	Orange II	Nearly 98% of Orange II is degraded within 210 min photocatalysis	Yao et al. (2015)
$Ag_3PO_4/BiPO_4$/Cu (tpa).grapheme	⩾420 nm (Vis)	Duration = 2 h	Atrazine herbicide	The nano composite showed more 80% photocatalytic degradation of Atrazine herbicide	Mohaghegh et al. (2015)
Carbon nanorods-TiO_2	⩾420 nm (Vis)	Cat. Dose = 0.2 g/L, Duration = 4 h	2,4-dichlorophenol	Up to 96% of photocatalytic degradation of 2,4-dichlorophenol was achieved with in 8 h	Ortega-Liebana et al. (2016)
Fe–TiO_2 coated with side-glowing optical fibers	Visible region	Duration = 8 h	Rhodamine B	Up to 90% of Rhodamine b removal can be achieved with in 8 h of photocatalysis	Lin et al. (2015)
Polyaniline/ZnO	Visible region	Catalyst dose = 0.4 g/L, Duration = 5 h	Methylene blue and malachite green dyes	Dyes removal with 99% efficiency was achieved under natural sunlight	Eskizeybek et al. (2012)
Immobilized TiO_2	300–800 nm	Duration = 96 h, Shaking = 75 rpm, Pollutant conc. = 5 mg/L	Pharmaceutically active compounds (propranolol, diclofenac, and carbamazepine)	Photocatalytic efficiency of 100% for propranolol, 100% for diclofenac, and 76% for carbamazepine was achieved	He et al. (2016)
ZnO/Zn	365 nm (UV)	pH = 6–8, Duration = 4.5 h	Methylene blue	Complete degradation of methylene blue was achieved (98%)	Lin et al. (2014)
ZnO–FeO-clinoptilolite	Solar light	pH = 8.3, Catalyst Dose = 0.1 g/L	Real Fish pond wastewater	More than 80% degradation efficiency was achieved	Bahrami and Nezamzadeh-Ejhieh (2014)
Ag–TiO_2/Ag/a-TiO_2	425 nm (Vis)	Duration = 90–110 min, *E. coli* population = 10^5 cfu	Escherichia coli bacteria	The relative rate of reduction in the bacteria was improved to 4.7×10^{-2}/min corresponding to 110 min in the visible	Akhavan (2009)
CuO/ZnO	Visible region	pH = 6.0, Duration = 1 h	Acid Red 88 dye	In the presence of external electron acceptors such as peroxomonosulfate, peroxodisulfate and H_2O_2, CuO-ZnO shows approximately 2 times higher photocatalytic degradation of Acid Red 88 compared to that ZnO	Sathishkumar et al. (2011)
Graphene-$Co_xZn_{1-x}Fe_2O_4$	Visible region	Duration = 1 h, Methylene blue conc. = 5 mg/L Catalyst dose = 100 mg/L	Methylene blue	The Graphene-$Co_xZn_{1-x}Fe_2O_4$ heterostructures showed more photocatalytic efficiency compared to $Co_xZn_{1-x}Fe_2O_4$ nano-particles (without graphene)	Nazim et al. (2016)

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drawback for instance; the post separation is these mobilized nano-particles is difficult. Thus, for efficient antimicrobial activity the nano-particles need to be immobilized and increase in surface area (Liu et al., 2008). For this concern, various studies have been conducted to increase the effectiveness of catalyst by modification with other materials.

Akhavan (2009) showed that the storage of Ag nano-particles on TiO_2 films achieved 6.9 times high antimicrobial activity against *E. coli* bacteria compared to that of TiO_2 under visible light. Similarly, in another study the mesoporous composite of Ag with TiO_2 films (Ag/TiO_2) showed high antibacterial actions as compared to the commercial P-25 TiO_2 spinning film. This is because the composite formation with other materials increased the surface area providing more active sites at mesoporous catalyst to degrade microorganisms (Liu et al., 2008). During antimicrobial action, the presence of extracellular polymeric substance (EPS) may decrease the antimicrobial efficiency of the catalyst. EPS is found to play a significant role in determining antibacterial kinetics as it increases the competition for reactive oxygen species between EPS and bacteria. Thus, it is important to remove EPS to achieve high efficiency of photocatalysis for wastewater disinfection (Chaturvedi et al., 2012).

3.3. Nano-materials as electro-catalysts

The process of electrocatalysis in microbial fuel cell is an emerging topic of discussion for wastewater treatment and direct electricity generation. In microbial fuel cell, electro-catalyst plays a detrimental role in working of a fuel cell (Chen et al., 2015). The use of nano-material as electrocatalyst can improve the performance of fuel cell by achieve larger surface area and uniform distribution of catalyst in the reaction media (Liu et al., 2005). Tremendous research has been conducted on development of carbon supported nano-electrocatalysts for application in fuel cells (Tang et al., 2005; Chaturvedi et al., 2012). It is reported the Pt nano-catalyst supported by carbon black XC72 showed a potential up to 6.2 mA cm^{-2} of current density in glucose oxidation electro-catalysis reaction (Chen et al., 2015). Moreover, Pt electrocatalysts also showed high potential for ethanol oxidation reaction in fuel cell in number of studies (Chen and Holt-Hindle, 2010; Kamarudin et al., 2013; Habibi and Mohammadyari, 2015).

Although Pt can be used as electro-catalyst, yet, it has various disadvantages which limit its application. For instance, Pt is a precious metal and it has limited availability, and high cost narrowed the interest to use it as catalyst. In addition, during electro-catalysis Pt may restrict the reaction due to poisoning of intermediate compounds (Zhou et al., 2003). However, these problems can be overcome by replacing Pt with Pd nano-particles. For instance in ethanol fuel cell Pd nano-catalyst can reduce the cost of anodes due its abundance in the earth i.e. fifty times more compared to Pt (Savadogo et al., 2004). Recently, Habibi and Mohammadyari (2015) have prepared the Pd nano-particles and functionalized carbon nano-materials by a facile spontaneous redox process. The PdNPs with functionalized single wall carbon nanotubes showed the high electro-catalytic activity, and thus could be used as supporting nanocarbon material for synthesis of nano-composite. Similarly, Pd can also form composites on six carbon nano-materials having different functionalities. These nano-materials include pristine multi-walled carbon nanotubes (pMWCNT), amine-modified MWCNT, carboxylated MWCNT, hydroxyl-modified pristine multi-walled carbon nanotubes carboxylated graphene and XC72 carbon black (Chen et al., 2015). Cai et al. (2013) demonstrated that MWCNT are ideal support material for Pd in glucose oxidation reaction that showed that MWCNT-supported Pd catalyst could be effectively catalyze GOR in alkaline medium and resulted in a catalytic current density of 2.7 mA cm^{-2}. The newly developed electro-catalyst Au supported on the imidazolium-type ionic liquids/Polypyrrole nanotubes surface was also evaluated for its activity in fuel cell for wastewater treatment. It was found that this hybrid electro-catalyst has smaller particle size and better dispersion, and thus showed high catalytic reduction in model pollutant 4-nitrophenol due to efficient electrocatalysis of dioxygen reduction and 4-nitrophenol (Qiu et al., 2012).

3.4. Nano-material based Fenton catalyst

Oxidation of organic pollutants by using Fenton's reaction has been widely applied in wastewater treatment (Neyens and Baeyens, 2003). The main drawback of Fenton's reaction is the continuous loss of catalyst material with effluent and requirement of acidic conditions (pH = 3) for optimum function (Kurian and Nair, 2015; Ferroudj et al., 2013). The use of nano-material based Fenton's reagent has been employed to overcome these problems. The nano-ferrites with controlled crystalline size, distribution and chemical structure can be obtained through sol-gel and auto combustion method (Kurian and Nair, 2013; Kurian et al., 2014). The spinel ferrites containing Ni, Zn, Co and Cu have significant importance as catalysts due to their special magnetic and electronic properties. The presence of these metals lattice modifies the stability and redox properties of ferrites, which further increases the catalysis efficiency. It is reported that the heterogeneous MFe_2O_4 is extensively used as catalyst due to its high chemical and thermal stability (Kurian and Nair, 2015)

Magnetically separable nano-particles of iron oxide can be used as Fenton catalysts for removal of several types of pollutants (Shahwan et al., 2011; Sun and Lemley, 2011). The magnetic divided materials containing iron oxide phase such as carbonaceous materials, ferrite with Ba, Co and Mn, and maghemite have high capability to recover from water through magnetic field. Magnetic separation is more quick and efficient compared to the decantation and filtration methods (Ambashta and Sillanpaa, 2010). Ferroudj et al. (2013) found that maghemite nano-particles (Fe_2O_3) and maghemite/silica nano-composite (Fe_2O_3/SiO_2) have controlled mineralization rates during Fenton reaction. This indicates that these nano-catalysts have stability toward uncontrolled oxidation of pollutant and organic intermediate products. Similarly, in another study nano nickel-zinc ferrite catalysts were evaluated for the degradation of 4-chlorophenol. Experimental results revealed the complete degradation of the target pollutant with considerable reduction of COD in just 75 min of reaction (Kurian and Nair, 2015).

3.5. The role of nano-catalysts for oxidation of pollutants

In wastewater treatment, nano-material catalyst can be used in chemical oxidation of organic pollutants. Nano-particles

developed from noble metals such as Au, Pt and Pd have efficient catalytic potential for degradation of variety of organic and inorganic contaminants (Liu et al., 2013; Wang et al., 2013a,b). Compared to conventional treatment methods, the use of nano-catalyst in chemical oxidation provides some advantages such as target recalcitrant compounds, shorten treatment time, ability to transform wastes into valuable by-products (Wigginton et al., 2012; Hering et al., 2013). Hildebrand et al. (2009) reported that Pd could provide selective removal of pollutants like chloro hydrocarbons from the wastewater with commercial application. The synthesized Pd based nano-catalyst (Pd/Fe_3O_4) showed high hydro dechlorination and easy recovery of nano-catalyst through magnetic separation from wastewater.

Although the use of nano-catalyst has many positive aspects, it may have limitations of high cost of metal nano-particles (Pt) and difficulties in recovery for reuse. Thus, the challenge is how to reduce the high capital investment and replenishment of catalysts for continuing the treatment process. Recent researches showed that, the effective strategy for making catalytic process cost effective is by improving the reactivity of noble metal nano-particles by forming bimetallic alloy through blending with other metals (Ma et al., 2015). Blending of noble metal catalysts with other cheap transition metals can decrease the overall cost of catalytic water treatment. Not all the nano-metal alloys have same capability to treat all kinds of pollutants, and there is need to synthesize a series of nano-particle alloys considering varied compositions, so that the treatment of pollutant of interest can be performed efficiently. Ma et al. (2015) used Pt with Ni as promoter element and successfully prepared Pt/Ni nanoparticles having size 2.9–4 nm. In another study Pd nano-catalyst with Fe_3O_4 (Pd/Fe_3O_4) has been prepared which have ability of magnetically re-extractable Pd-on-magnetite catalyst and high activity for treatment of halogenated organic pollutants (Hildebrand et al., 2009). The wastewater may contain a variety of organic and inorganic materials, where the presence of inorganic anions such as HCO_3, SO_4, Cl, Na, Ca and Mg plays an important role in increasing nano catalyst activity. According to study by Zelmanov and Semiat (2008), iron (III)-oxide catalyst showed strong effect of HCO_3, $PO_4/HPO_4/H_2PO_4$ and H_2O_2 on the phenol oxidation rate in wastewater. However, other ions such as Cl, Na, SO_4, Ca, and Mg did not show significant effect on phenol oxidation kinetics.

4. Nano-membranes

Among the current advanced wastewater treatment techniques, membrane filtration technology fabricated by nano-materials is one of the most effective strategies (Ho et al., 2012; Zhang et al., 2013a,b). Nanotechnology concepts go beyond state-of-the-art performance of water treatment membranes and enable new functionality, such as catalytic reactivity, high permeability, and fouling resistance (Pendergast and Hoek, 2011). The main reasons for adoption of this technology are their benefits in terms of quality treated water, effective disinfection and low space requirement for plant (Jang et al., 2015). Moreover, it is highly economical, efficient and simple in design compared to other treatment techniques (Zhou et al., 2014; Zhang et al., 2015; Guo et al., 2016). For wastewater treatment, nano-membrane separation technology is used for effective removal of dyes, heavy metals and other contaminants (Jie et al., 2015). Beside particle separation from wastewater, nano-materials in novel membrane also play an integral role in the chemical decomposition of organic foulants separation (Volodymyr, 2009; Yang et al., 2015). The compositions of these types of membrane are one-dimensional nano-materials (comprising organic and inorganic materials) such as nanotubes, nanoribbons, and nanofibers (Liu et al., 2014). For selective filtration and nano-particle removals, a membrane fabricated with carbonaceous nanofibers (CNFs) showed outstanding selective filtration/removal efficiency under high pressure (Liang et al., 2010). Furthermore, assembling beta-cyclodextrins in CNF membranes through simple filtration process possess remarkable potential for removal of phenolphthalein and fuchsin acid (Chen et al., 2012). For aqueous osmotic separation, zeolite based nano-membranes can be employed. The common zeolite materials used in membranes include sodalite, MFI-type and Linde Type A. The most commonly applied zeolite in nano-membranes is Zeolite ZSM-5 (MFI) which has a chemical composition as $Na_nAl_nSi_{96-n}O_{192} \approx 16H_2O$ ($n \approx 3$) for a unit cell (Pendergast and Hoek, 2011). In addition, the capturing potential of nano-particles and other small molecules can be positively enhanced by interconnection nano-particles and negatively charged bodies on macroscopic disk-like titanate-nanoribbon membrane (Cao et al., 2013; Liu et al., 2014).

4.1. Fouling and membrane modification

The membranes are commercially available and fit for many applications; however, the drive to produce new water resources from wastewater needs membranes with improved productivity and fouling resistance at lower cost (Pendergast and Hoek, 2011). Membrane fouling is caused by interaction of organic compounds in water with hydrophobic membrane. Fouling can be attributed to the deposition of particles on the membrane surface or within the pores of membrane (Baker, 2004; Judd, 2006; Yang et al., 2015). The results are low quality treated water; and reduce reliability of membrane filtration equipment and limitation in further development (Gu et al., 2013). Under low pressure the flux of nano-filtration membrane is very low (Guo et al., 2016). For reducing flux resulting from membrane fouling, it is required to clean the membrane chemically or mechanically or even some time the complete replacement of membrane is also required (Yang et al., 2015). In order to minimize the problem of membrane fouling, various techniques have been developed in the last few decades like membrane modification, changing feed solution properties and operational conditions (Altaee et al., 2010; Su et al., 2011). Among these, main focus has been exerted on modification of membrane by coating with a hydrophilic polymer layer such as poly-vinyl alcohol and chitosan but the main drawbacks of these methods are their high cost, complexity and pollutant production (Jie et al., 2015). The investigations on preparation of mixed matrix membranes (MMMs) with carbon nanotubes (CNTs) as membrane filler showed that the resulted CNT-MMMs exhibit significant potential in making high flux (Ismail et al., 2009; Rajabi et al., 2013). The study by Deng et al. (2007) on polyether urethane (PEU) membranes filled with isophorone diisocyanate grafted with multi wall carbon nanotubes (MWCNT-IPDI) showed significant improvement

in glass-transition temperature and mechanical properties in PEU by incorporating less amount of MWCNT-IPDI.

4.2. Carbon nanotube membranes

Carbon nanotubes are getting more importance as nanomaterials for synthesis of polymer composite membranes with maximum performance. These composites have various features such as low mass density, extremely high strength and tensile modulus, high flexibility and large aspect ratio, which enhance its performance (Liu et al., 2016). On the basis of its synthesis structure it may be called as single-walled carbon nanotubes (SWCNTs) or multi walled tubes carbon nanotubes (MWCNTs) consist of singular and multi-walled tubes respectively (Popov, 2004; Rajabi et al., 2013).

Various studies have been conducted for synthesis of modified nanotube membranes. Jie et al. (2015) reported the synthesis of Carboxyl multi-walled carbon nanotubes/calcium alginate (CMWCNT/CA) composite by using polyethylene glycol 400 as pore-forming agent with hydrogel nanofiltration membrane. CMWCNT/CA membrane had a high strength around 1.83 MPa. Moreover, membrane has good anti-fouling property, as 96.87% was bovine serum albumin (BSA) solution flux of pure waterflux (PWF). In addition, the study on rejection of Congo red showed up to 98.62% of removal efficiency. In study by Guo, 2016, nanofibrous filtration membranes were developed composed of Polyhydroxybutyrate-calcium alginate/carboxyl multi-walled carbon nanotube composite. The composite membrane increases the hydrophilic and tensile mechanical property, which increase the removal of selected pollutant. It was observed the 32.95 L/m^2h and 98.20% of flux and rejection rate respectively of composite membrane for the dye Brilliant blue. Liu et al. (2016) prepared chitosan/Silica-coated carbon nanotubes (CS/SCNTs) composite membranes by utilizing the chitosan and SCNTs which was prepared by adopting a simple sol-gel method. The CS/SCNTs composite membrane showed enhanced mechanical properties, oxidative and thermal stability and proton conductivity.

4.3. Electrospun nano-fiber membranes

Electrospun nanofiber membranes (ENMs) are the recently emerging membranes which give birth to a novel way to treat wastewater (Matsuura et al., 2010; Botes and Eugene Cloete, 2010; Qu et al., 2013). The key features of this new emerging technique include less energy consumption, less expensive and lighter process as compared to the existing conventional techniques. Moreover, higher porosity and surface to volume ratio are the major advantages of this technique (Balamurugan et al., 2011; Tabe, 2014). Electrospinning is advantageous over conventional nanofiber spinning techniques in being capable of producing fibers that are orders of magnitude thinner. The fiber diameter governs the surface area to volume ratio and affects membrane porosity. In electrospinning, fiber diameter can be adjusted by varying the process parameters such as solution concentration, applied voltage, surface tension, and spinning distance (Theron et al., 2004; Tabe, 2014). Various types of natural and synthetic polymers have been electrospun into nanofibers. The reported number of these polymers has been more than 100. These include natural and synthetic polymers such as polystyrene (PS), poly (vinyl chloride) (PVC), polyvinylidene fluoride (PVDF), polybenzimidazole (PBI), poly(vinyl phenol) (PVP), Kevlar (poly (p-phenylene terephthalamide), or PPTA), polyurethanes (PUS), Nylon-6, poly(vinyl alcohol) (PVA), polycarbonates, poly(e-capro-lactone) (PCL), polysulfones, poly(ethylene terephthalate) (PET), and many others (Souhaimi and Matsuura, 2011; Feng et al., 2013). In recent years, various studies have shown that electrospun nano-fibers can be applied to proton exchange membrane fuel cell catalysts. The nanofiber polymer supports the catalyst particles and assists in access to reactant, proton transfer and electronic continuity for fuel cells (Wang et al., 2014). Graphene has gained a widespread attention in this regard to be used as catalyst with electrospun nano-fibers because of its unique two dimensional single layer structure, extraordinary electronic properties and high surface area. Wei et al. (2016) prepared a graphene doped polyacrylonitrile/polyvinylidene fluoride electrospun nanofiber having improved porosity and electrical conductivity.

Nanofiber membranes have wide applied in wastewater treatment containing heavy metals, particulate microbes and salts (desalination). In study by Xu et al. (2008) electrospun polysulfone fiber membrane was used to remove the particles from biotreated wastewater. The ultimate goal was to decrease the COD, ammonia and suspended solids from wastewater. Another type of electrospun nanofibrous membrane prepared from polyvinylidene fluoride was used for separation of particles from wastewater and achieved up to 90% of micro-particles rejection. These membranes have potential application as pretreatment prior to reverse osmosis or ultra-filtration step in wastewater treatment plant (Gopal et al., 2006).

The electrospun membranes have also been reported for removal of toxic heavy metals such as nickel, cadmium, copper and chromium among others (Nasreen et al., 2013). Taha et al. (2012) successfully synthesized amine cellulose acetate/silica nanofiber membranes that showed an efficient removal of chromium(VI) from wastewater. Another study conducted by Lin et al. (2011) found not only removal of Cr from wastewater but also achieved conversion of Cr(IV) to Cr(III) by using PAN/$FeCl_3$ composite membranes. The removal of other toxic metals such as lead and copper has also been reported by using chitosan nanofiber mats (Teng et al., 2011).

In case of removal of salts from water in desalination process, the use of nano-fiber membranes has been proved an effective way for salt removal due lower operational pressure, improved flux, and low energy requirement (Nasreen et al., 2013). Shih (2011) prepared composite nanofibrous membranes of polyvinylidene fluoride-co-hexafluoropropene having an average fiber diameter of 170 nm. They achieved almost 100% salt rejection at flow rate of 210 ml/min and high temperature of 55 °C. Similarly, Prince et al. (2012) attained greater than 99.95% salt removal using clay nano-particles PVFD composite membranes in distillation process.

The electrospun nano-fibrous membranes have been observed for its antimicrobial activity for both bacteria and viruses. Sato et al. (2011) developed a new nanofibrous membrane consists of ultra-fine cellulose fibers infused with PAN ENM. Using this membrane, the virus having slightly negative surface charge was trapped due to the presence of electrostatic positive change on membrane. Similarly, membrane also showed the capability of removing almost 100% *Escherichia coli* bacteria from water. In

another study, the electrospun membrane composed of Ag nano-particle doped PAN nanofiber was found to be efficient for its antimicrobial action against gram-negative *Escherichia coli* and gram-positive *Basillus cereus* (Shi et al., 2011).

4.4. Hybrid nano-membranes

The hybrid membranes were developed to introduce additional functionalities such as adsorptions, photocatalysis, or antimicrobial activities. This can be achieved by simply tuning the hydrophilicity of membranes, their porosity, pore size, mechanical stability and charge density. Yurekli (2016) coupled the filtration and adsorption process by using impregnated polysulfone (PSf) with zeolite nano-particle membrane for removal of lead and nickel form wastewater. They found that both the sorption capacity and hydraulic permeability of membrane could be improved by simple modification in the membrane fabricating conditions such as NaX loading and period of evaporation of the casting film. This hybrid membrane showed the efficient adsorption capacity for nickel and lead ions that is up to 122 and 682 mg/g respectively, during 60 min of filtration transmembrane pressure of one bar. Recently, Wen et al. (2016) applied the hybrid mechanism of adsorption for treatment of radiations tainted water and oil uptake. Using sodium titanate nanobelt membrane (Na-TNB) for Sr^{2+}-removal highest adsorption coefficient value (Kd) was observed up to 107 ml/l. The basic mechanism of Na-TNB adsorption is based on the formation of radioactive cation stable solid that was permanently trapped inside the membrane. In addition, this multi-functional membrane has capability to adsorb oils up to 23 times of weight of adsorbent. The removal of oil from wastewater has also been found by El Naggar et al. (2015) using a nano-structured polymer-based (styrene, divinyl benzene, potassium persulfate, sorbitan monooleate) membrane/sorbent. This polymer material was used in the form of sheets (membrane) and showed the efficiency up to 99.75% of oil removal from wastewater in just 75 min. The idea of using hybrid membranes is also to remove target pollutants from wastewater through process of adsorption (Tabe, 2014). For instance, Singh et al. (2010) prepared the membrane based adsorbent i.e. carbonized PAN ENMs and multi-walled carbon nanotubes embedded membranes for application in removal of target contaminants. A comprehensive view on efficiency of various types of nano-membranes for treatment of wastewater is described in Table 3.

5. Combination of biological-nano technology processes

Nanoscale science and engineering technologies suggested that many of the current problems involving water quality could be resolved by using nano-catalysts, nanoabsorbent, nanotubes, nanostructured catalytic membranes, nanopowder and micro-molecules (Gupta et al., 2006). All these nano-particles and colloids had a momentous impact on water quality in treatment process (Diallo and Savage, 2005). Research studies showed that integration of biological wastewater treatment process with advance nanotechnology resulted in efficient water purification system (Yin et al., 2013). The reviews on integration of nanotechnology with biological process for wastewater treatment are described below:

5.1. Algal membrane bioreactor (A-MBR) with nano-particles

Algae cultivation in wastewater is one of the promising techniques in terms of energy production and water purification. Many algae species effectively grow in wastewater due to the availability of micronutrients (trace metals and vitamins like cyanocobalamin, thiamin) and macronutrients (salts of NO^{-3}, PO_3^4 with Ca, Na, K and NH^{4+}) essential for their growth (Abou-Shanab et al., 2013; Chong et al., 2000). Solutions are made up as a result of mixture of these chemical salts (Nutrients) and water. Nutrient solutions (along with light and carbon dioxide) provide the materials required for algal growth. The result is nutrients removal from wastewater and algal biomass for energy production (Grima et al., 2003). For algal biomass harvesting there are various techniques like sedimentation, air flotation, and centrifugation in support with chemical flocculation but these techniques are unaffordable on large scale due to high cost (Brennan and Owende, 2010). Among advance techniques, the most advantageous approach for algae cultivation and biomass harvesting is membrane technology in which high-density algae cultivation is simply done through membrane bioreactor (Hu et al., 2015). The benefits of membrane technology are that no addition chemicals such as coagulants are required for membrane filtration, thus facilitate the water reuse after filtration and simplify the algal biomass separation (Ríos et al., 2012). Moreover better algal biomass recovery can be achieved without cell damage and low energy required for algae harvesting as compared to conventional methods (Hu et al., 2015). Membranes made of polysulfone (PSF), polyvinylidene fluoride (PVDF) and polyethersulfone (PES) are largely used due to their chemical and physical stability but the only problem is the membrane fouling due to hydrophobic mechanism between membrane materials and microbial cells (Maximous et al., 2009). For increasing hydrophilicity and diminishing membrane fouling there are many techniques like plasma treatment (Kim et al., 2011), surface coating (Madaeni and Ghaemi, 2007) and incorporation of nano-materials (Yin et al., 2013). Research studies revealed that nano-particles improve the hydrophilicity and reduce membrane fouling. For example blending of carbon nanotubes and TiO_2 nano-particles with PSF hollow fiber membranes (HFMs) resultsin improvement in surface modification (hydrophilicity) and antifouling (Yin et al., 2013). Madaeni and Ghaemi (2007) modified the polyvinyl top layer of the reverse osmosis membrane through coating with TiO_2 nano-particles and minimize fouling through self-cleaning mechanism under ultraviolet radiation. Beside self-cleaning, TiO_2 particle photocatalysis has also been studied for pollution control due to their high surface area and hydrophilic properties (Martínez et al., 2013). Due to these characteristics, the hydrophobicity and fouling can be reduced through the incorporation of these nano-particles with membranes (Moghimifar et al., 2014). An investigation was conducted by Hu et al. (2015) in which they fabricate the PVDF hollow fiber membranes with TiO_2 by phase inversion method on a custom designed single head spinning machine. The fabricated PVDF/TiO_2 nanocomposite membranes were then tested on algal membrane bioreactor (A-MBR) for wastewater treatment. Results showed that maximum nutrient removal was achieved and up to 75% of phosphorus and nitrogen was removed by A-MBRs. In addition, the PVDF/TiO_2 mem-

Table 3 Efficiency of various types of nano-membranes for treatment of wastewater.

Technology	Contaminant	Efficiency	Comments	Reference
Nano-filtration	Remazol fiber reactive dyes from cottage textile industry	⩾80%	• Efficient and economical technique as compared to conventional technique • Good quality permeates water for reuse process	Rashidi et al. (2012)
Photocatalysis using nano fiber membrane	Dairy effluents	75–95%	• Nano-materials ($AgTiO_2$) within nano-fiber membrane play a vital role in photocatalytic degradation of dairy effluents	Kanjwal et al. (2010)
Nano-membrane combined with biodegradable poly-gamma-glutamic acid (γ-PGA)	Removal of lead (Pb) ions from aqueous solution	99.8%	• Biodegradable γ-PGA binds with Pb^{2+} ions and can be filter fast • Efficient combination of nano-membrane and fast filtration using linear or cross linked γ-PGA biopolymer technology with optimal Pb^{2+} removal • The permeate water meets WHO standard	Hajdu et al. (2012)
Nano-filtration membrane bioreactor	Removal of COD, NH_3-N, NO_3-N, and PO_4-P from hospital wastewater	COD (92%), NH_3-N (88%), NO_3-N (80%) PO_4-P (68%)	• Simple in operation and cleaning system with sufficient removal capacity • No chemical required for cleaning and flux rate recovery • Effluents can be reused and discharged to natural water	Kootenaei and Rad (2013)
Nano-filtration with forward osmosis	COD, Paracetamol and Nebivolol compounds from industrial wastewater	COD (97%), Paracetamol and Nebivolol compounds (100%)	• The level of treated water is of reusable criteria • Problem of drop in flux and membrane fouling can be overcome	Thakura et al. (2015)
Nano-filtration membranes	Reactive dye Black 5 removal from textile effluent	99%	• The negatively charged hollow fiber composite NF membrane could effectively remove the dye from textile effluent through submerged filtration • Less amount of electrolytes in the effluents • Excellent antifouling property and high water cleaning efficiency	Zhu et al. (2013)
Nano-membrane prepared from coating γ-alumina and titania nanocrystallites	Microorganisms and ions rejection from wastewater	Microbes (100%), ions (25%)	• Successful removal of microorganisms • Ion rejection can be enhanced by proper pH adjustment	Shayesteh et al. (2016)
Nanoporous membrane filtration	TSS, TDS, oil, grease, COD, BOD from oil wastewater	TSS (100%), TDS (44%), oil (99%), Grease (80%), BOD (76%)	• The optimum conditions for efficient water purification were; feed temperature of 45 °C, cross flow velocity of 1.3 m/s, trans-membrane pressure of 4 bar, salt concentration of 11.2 g/L and pH of 10. • Treated water can be used for agricultural purpose	Salahi et al. (2015)
Nano-structured polymer based membrane	Oil removal	99.75%	• Achieved a new methodology for combining nano-filtration and floatation for oil in water demulsification • The increased sorbent surface area and concentration (weight) enhanced system efficiency • High adsorption capacity of the sorbent was due to its porous structure	Ahmed et al. (2015)
Sodium titanate nanobelt membrane (Na-TNB)	Removal of oil and radioactive Cs^+ ions and Sr^{2+}	Sr^{2+} (97.5%), Cs^+ (57.7)	• The developed membrane posses high adsorption capacity and rapid ions exchange kinetics • Membrane can be used for large area deposition of different materials • Significant ions exchange behavior of TNB at room temperature	Wen et al. (2016)
Integrated carbon nanotube (CNT) polymer composite membrane with polyvinyl alcohol layer	Treatment of oil contaminated water	Over 95%	• Integration of CNT with polymer composite increases suitability of membrane for practical application due to ultimate tensile strength, toughness and young's modulus • Increasing CNT concentration increases membrane flux	Maphutha et al. (2013)
Hydrophilic electrospun nanofiber membrane	Suspended particles		• Efficient turbidity and total dissolved solids removal • Overcoming on membrane fouling and blocking problems • Efficient particle removals by membrane due to coagulation process	Asmatulu et al. (2013)
Carbon nanofiber membrane	Metal and metal oxide nano-particles	Up to 95%	• Mechanically strong and bendable membrane • Withstand filtration under high pressure or vacuum • Capability to produce easy and cost efficient nanofiber by electrospinning	Faccini et al. (2015)
ZrO_2 microfiltration membrane	Pretreatment of dimethylformamide (DMF) wastewater	Turbidity removal (99.6%), suspended solids (99.9%)	• Effective removal of suspended fine particles from DMF wastewater • Effective flux recovery by combined ultrasonic, chemical cleaning and flushing	Zhang et al. (2014)

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branes in the A-MBR also increase hydrophilic characteristic of PVDF and reduce membrane fouling. Their findings also demonstrated that PVDF/TiO_2 nanocomposite membranes were promising for lowering membrane fouling in A-MBRs for nutrient removal, wastewater treatment and algal biomass production.

5.2. Pretreatment of aerobic digestion with nano-particles

Traditionally municipal wastewater has been treated with biological process (activated sludge process) but industrial wastewater is more challenging due to the presence of toxic and less biodegradable pollutants (Rittmann and McCarty, 2001). The demand for high quality, less toxic and nutrients proportion in treated water resultsin intensive assessment of the emerging technologies. One of these technologies includes zero valent iron (ZVI) nano-particles, which have not been used on large scale for water treatment. This nano-particle can degrade organic contaminants and has been used for the remediation of chlorinated organic compounds from ground water (Metcalf and Eddy, 2003). Integration of biological processes (aerobic degradation) with ZVI nano-particle treatment is promising in efficient biodegradation of the organic pollutants from wastewater on large scale. In the combination, half of the contaminants are degraded by nano-particles, which are further easy for biodegradation under aerobic conditions (Ma and Zhang, 2008). Partial degradation and reduction in organic compounds occurred due to bimetallic structures form micro and nanoscale cells as electron donor with metallic iron. Further, the products from ZVI reactor are then more biodegradable by aerobic microorganisms. For example in case of degradation of petroleum hydrocarbons and chlorinated solvents, the first section consists of granular iron in which chlorinated ethenes reduced through dechlorination while in second part the aerobic biodegradation of remaining chlorinated compounds and any other hydrocarbons is promoted by the addition of dissolved oxygen (Bell et al., 2003; Morkin et al., 2000). Similarly, it has also been reported by Oh et al. (2001) and Saxe et al. (2006) that azo dye and nitroaromatic compounds were treated through coupling of biological process with ZVI nano-particles. A bench scale experiment was conducted by Ma and Zhang (2008) to examine the impact of ZVI on biological treatment. Experimental setup was comprised of pretreatment by ZVI reactor followed by a sequencing batch bioreactor. The influent water to the reactor was comprised of large amounts of persistent organics like halogenated hydrocarbons, petroleum hydrocarbons, nitroaromatic compounds, heavy metals and dyes. Their findings showed that BOD was reduced from 235 to 7.7 mg/l (96.5% removal) while COD removal efficiency was 86%. Likewise ammonia removal efficiency was 92% whereas nitrogen removal efficiency was increased from 35 to 52.2%. From the study they concluded that ZVI pretreatment followed by biological treatment is the promising potential for industrial wastewater purification.

5.3. Improvement of microbial fuel cells efficiency through nanotechnology

The attraction toward microbial fuel cell (MFC) technology increased due to double benefits of treating water as well as energy production from inorganic and organic compounds in wastewater by using microbes as biocatalysts (Ghasemi et al., 2013a; Logan and Regan, 2006). The power generated by MFCs can potentially cut down the electricity requirement for a conventional treatment process (Ghangrekar and Shinde, 2007) while complex organic molecules such as butyrate, acetate and propionate are broken down to H_2O and CO_2 by bacteria (Logan et al., 2008). However, major barriers in commercialization of this technology are the overall low performance as compared to other fuel cell technologies and high costs of its components (Ghasemi et al., 2013b). In order to make it economically feasible it is required either to cut down the cost of membrane maintenance or to use cheaper membrane and cathode catalyst (Di Lorenzo et al., 2010). Moreover, it is also necessary to select an appropriate material to improve the performance of MFCs (Jafri et al., 2009). This includes modification of electrode surface to increase its conductivity, as cathode surface must have high catalytic activity for oxygen reduction reaction (Zhuang et al., 2009). The best option to increase certain prosperities is the use of nanoparticles (Vaddiraju et al., 2010) as these particles are biologically more active than other particles with similar composition due to its high surface area that effectively interact with biological system (Uskokovic, 2007). Currently the performance of MFCs has been improved by using cheap nanocomposite materials like nanostructured carbon in electrodes. These electrodes are mechanically stabile with larger surface area, high conductive and better electrochemical catalytic activity (Yuan et al., 2010). Ghasemi et al. (2011) examine carbon nanotubes (CNT) as electrode and Pt as catalyst cathode in MFC in various COD media i.e. 100, 500, 1000 and 2000 mg/l and compare the results with Pt as common cathode catalysis. The results showed that the highest power generation was produced by CNT/Pt in all COD media followed by CNT and Pt respectively. From the study they concluded that the catalytic activity of Pt enhanced by CNT whereas the ORR was improved due to high surface area of the electrode. The significant results from CNTs electrodes were due to its unique structural characteristics and high electrical conductivity (Wang et al., 2006). Hence, in MFCs the commercial cathode catalyst to Pt can be replaced by CNT/Pt due to all its unique properties (Ghasemi et al., 2013b). Furthermore, to increase the microbial attachment and reduce toxicity, CNTs have been coated with various weak polymers like polyaniline (PA) and polypyrrole (PPy) to form nanocomposite. These nanocomposites contain negatively charged carbon nanotubes bound to positively charged polycationic polymer through electrostatic interaction as MFC anodes (Sun et al., 2010). These electrodes have large surface area with more active sites for electrochemical reactions and microbial attachment. Hence, bacteria can easily attach in PPy–CNTs composites forming a biofilm essential for electron transportation toward anode surface (Zou et al., 2008).

5.4. Integration of microbes with electrospun nanofibrous webs (NFW) for water purification

Electrospinning is a recent technology for the production of nanoweb/nanofiber due to its unique properties and cost effectiveness (Wendorff et al., 2012). Environmental application of electrospun nanofibrous webs is its large surface area along with nanoscale porosity that makes them capable for mem-

brane and filter materials (Mahanta and Valiyaveettil, 2013). The electrospun nanofiber integration with microbes can increase the potential of purification and filtration. Research has been conducted on the integration of microbe-electrospun nanofibers containing algae or bacteria showed momentous impacts for environmental applications (San et al., 2014). Eroglu et al. (2012) generated a hybrid system in which algal cells were immobilized on electrospun chitosan nanofiber mats (ECNMs) for the removal of nitrates from wastewater. From the study they summarized that immobilization of the microbial cells is advantageous than free cells due to less space occupancy, easy to handle and low volume required for growth medium. Moreover they also found that ECNMs are water insoluble, non-toxic to algal growth and effectively immobilized the microbial cells. For wastewater treatment they found that 87% of nitrates were removed due to physiochemical adsorption by chitosan and nutrient consumption by algae. In other study the immobilization of ammonium oxidizing bacteria *Acinetobacter calcoaceticus* STB1 cells was performed on electrospun cellulose acetate nanofibrous webs (CA-NFW) for removal of ammonium from wastewater (Sarioglu et al., 2013). The study findings revealed that STB1/CA-NFW effectively removed the ammonium ions (98.5%) by converting them to nitrogen form that accumulated as bacterial biomass without loss of their reusability potential. Likewise San et al. (2014) also carried out an experiment for decolorization of methylene blue (MB) dye by selecting electrospun CA-NFW for immobilization of dye decolorization bacteria species i.e. *Pseudomonas aeruginosa*, *Clavibacter michiganensis*, *Aeromonas eucrenophila* in wastewater. From the study, they noted that efficient decolorization of MB (95%) was attained in 24 h. The fact behind decolorization of MB dye was the biodegradation carried out by bacteria. Moreover the reusability of the nanofibrous biocomposite was also examined and it was found that bacteria immobilized NFW possess the capacity to decolorized dye at the end of 4th cycle. Consequently due to its reusability, simple and porous characteristics this nanofibrous biocomposite can be utilized for treating industrial wastewater. As immobilized bacteria NFW require less space and volume for growth medium compared to free bacteria and hence it is more economical whereas the biofilm formed also possesses high resistance to metal toxicity, salinity and harsh environmental conditions.

6. Evaluation of nano-particles in wastewater treatment

In the present review, three main categories of various nanomaterials, i.e. nano-adsorbents, nano-catalysts, and nano-membranes, have been discussed. Each category has its own merits and limitations with respect to their efficiency, applicability and risk to the environment and health.

6.1. Nano-adsorbents

Nano-adsorbent is widely used adsorbents for the removal of heavy metals from wastewater. CNTs and metal oxides are the most commonly used nano-particles for the removal of heavy metals from aqueous solution (Ray and Shipley, 2015). These nano-particles have some key features such as high BET surface area, microporous structure, high dispersion ability, economically and environmental friendly (Gupta et al., 2015; Li et al., 2003a, 2003b). However, smaller size of particles and difficulties in separation from aqueous solution will lead to secondary pollution (Ray and Shipley, 2015). This further effects the bioavailability and mobility of the heavy metals and causes toxicity in the environment (Wang et al., 2013a,b). In addition, economical reuse and regeneration is one of another challenge for these nano-particles (Pan et al., 2009). However modification was carried out by different researchers such as Hydrous Manganese Oxide (HMO) (Gupta et al., 2015)and multi-wall carbon nanotubes (MWCNT) (Tang et al., 2012; Tarigh and Shemirani, 2013), to overcome these challenges. Nevertheless, new trends in nano-adsorbents such as organic-inorganic hybrids are sustainable option to overcome the associated limitations of nano-adsorption process (Ray and Shipley, 2015).

6.2. Nano-catalysts

The use of nano-particles would be a great value for advancements in catalytic wastewater purification such as photocatalysis, electrocatalysis and Fenton catalysis. In photocatalysis the widely used ZnO and TiO_2 catalysts faced limitation of requirement of ultraviolet radiation for their activity due to wide band gap energy. The industrial application of these materials may cause exposure to UV light to the workers, thus causing serious risk to health such as skin cancers and mutation in DNA (Lim et al., 2011). Moreover, TiO_2 is a potential carcinogenic material and may cause adenocarcinoma of the lung and pneumoconiosis in humans (NIOSH, 2011). Since it is requisite for industry to produce water of high quality either for drinking or safe disposal, there is an obvious requirement to develop the stable materials and methods to overcome these challenges.

The use of nano-catalysts has also various process limitations. The use of catalysts requiring UV light in photocatalysis is inadequate because electron-holes pair recombines easily because of high density of trap states (Guan et al., 2016). Another limitation that hinders the photocatalytic activity is instability of various types of nano-catalysts such as AgBr, which if dispersed in the solution then cannot be recycled for reuse (Dai et al., 2014). Currently, the focus is on synthesizing new photocatalysts using metal oxide or composite with metals and semiconductor oxide to overcome the associated problems with conventional catalysts (Rashid et al., 2014; Mohaghegh et al., 2015). In case of electrocatalyst (fuel cell), Pt is widely applied catalyst, but its application has some disadvantages, which affect the electrocatalysis process. These include, the limited availability, high cost of precious Pt and poisoning of intermediates may restrict the reaction rates (Zhou et al., 2003). This limitation can be overcome by replacing Pt with abundantly available Pd catalyst. In basic reaction of Fenton-catalysis, the main drawbacks are continuous loss of catalyst material and acidic conditions for optimum functioning (Kurian and Nair, 2015; Ferroudj et al., 2013). To overcome these problems, the use of nano-material based Fenton's reagent has been employed in various studies as mentioned in previous sections.

6.3. Nano-membranes

The main reasons for adoption of membranes filtration technology are their benefits in terms of quality water treatment, effective disinfection and low space requirement for plant

(Jang et al., 2015). Moreover, it is highly economical and simple in design compared to other treatment techniques (Zhou et al., 2014; Zhang et al., 2015; Guo et al., 2016). Nano-membrane separation technology can be efficiently applied for removal of dyes and heavy metals (Jie et al., 2015). In terms of environmental concerns, the nano-membranes have large ecological footprint during their manufacturing process. Khanna et al. (2008) found that the life cycle of carbon nanofiber contributes 100 times more per unit weight to toxicity, global warming and ozone depletion than conventional materials. Another disadvantage is the problem of membrane fouling which is caused by interaction of organic compounds in water with hydrophobic membrane. The deposition of particles on the membrane surface or within the pores of membrane increases the chance of membrane fouling (Baker, 2004; Judd, 2006; Yang et al., 2015) which results in low quality treated water and reduces reliability and life of membrane equipment (Gu et al., 2013). Membrane fouling reduces the water flux and thus needs a membrane cleanup process by chemical or mechanical means or even some time the complete replacement of membrane (Yang et al., 2015). To lower these problems, the researchers are focusing on modification of membrane by coating with a hydrophilic polymer layer such as poly-vinyl alcohol and chitosan (Jie et al., 2015). Moreover, the nano-particles such as TiO_2 may be incorporated to increase the hydrophilicity of membranes, thus reducing fouling and increasing the permeate flux (Hu et al., 2015).

6.4. Integrated nano-particles and biological process

Integration of biological process with advance nanotechnology for wastewater treatment resulted in efficient water purification (Ma and Zhang, 2008). Different nano-particles like CNT (Ghasemi et al., 2011), TiO_2 (Yin et al., 2013), nanofibers and ZVI (Metcalf and Eddy, 2003) have been successfully studied for wastewater polishing. It has been studied that through nano-particles integration the efficiency of each biological process i.e. A-MBR (Abou-Shanab et al., 2013), MFC (Ghasemi et al., 2013a), activated sludge process (Bell et al., 2003) has been positively enhanced than the process alone. In literatures, it has also been reported that process efficiency in terms of pollutants removal like nutrients removal has been increased up to 98.5% (Sarioglu et al., 2013), dye decolorization up to 95%, and BOD and COD reduction up to 96 and 86% respectively (Ma and Zhang, 2008). Hence, this area of research can provide efficient and ecofriendly ways for wastewater reclamation but there are limitations in adopting these technologies. Among major constrains is the requirement of high level of technical approach, specific biological agents for treating each pollutants (nutrients, dyes, organic compounds) and equilibrium level of each microbial and nano-particles assembling in each technology on large scale. Likewise, these processes are also time consuming like pretreatment with nano-particles fallowed by biological process, algae cultivation for wastewater reclamation, and microbial immobilization on nanofiber mats.

7. Conclusions and future perspective

In a current scenario, there is a significant need for advanced water technologies to ensure a high quality of water, eliminate chemical and biological pollutants, and intensify industrial production processes of wastewater. In this regard, nanotechnology is one of the ideal options for advance wastewater treatment processes. Various nano-materials have been developed and investigated successfully for wastewater treatment. These include nano-adsorbents (based on oxides, Fe, MnO, ZnO, MgO, CNT), photocatalysts (ZnO, TiO_2, CdS, ZnS:Cu, CdS:Eu, CdS:Mn), electrocatalysts (Pt, Pd), and nano-membranes (multi walled CNTs, electrospun PVDF, PVC, Na-TNB). Furthermore, these nano-particles can be integrated with biological processes (algal membrane, anaerobic digestion, microbial fuel cell) to improve in water purification. Each technology has its own merits and specific pollutant removal efficiency. The nano-adsorbents have efficient potential to remove heavy metals such as Cr, As, Hg, Zn, Cu, Ni, Pb and Vd from wastewater. Nano-particle photocatalysts can be used for treatment of both toxic pollutants and heavy metals, where the modification in catalyst material can provide the capability of using visible region of solar light instead of high cost artificial ultraviolet radiation. In electrocatalytic treatment of wastewater, the process could be improved by using nano-particles to achieve larger surface area and uniform distribution of catalyst in the reaction media. In filtration of wastewater, nano-membranes have been proven highly effective for reducing foulants, heavy metal and dyes. Furthermore, in case of biological treatment processes, nano-technologies have been efficiently integrated, as the use of nano-membranes in algal wastewater treatment facilitates in efficient harvesting of algal biomass, reducing the membrane fouling and use of coagulants.

There is no doubt of efficiency of utilization nano-materials in wastewater treatment; however, this technology has some serious downsides that need to be negotiated,since nano-particles might release into the environment during preparation and treatment processes, where they can accumulate for long time and cause serious risks. In order to reduce the health risk there is need a future research to prepare such catalysts having least toxicity to the environment. More work is required to re-evaluate the ecotoxicity potential for each new modification in catalyst and for existing materials. In addition, life cycle assessment of nano-materials is crucially required to address their overall benefits and risks. Nano-technology is rarely adopted to mass processes. Given that up until now, most of the nano-materials have not been cost-competitive when compared with conventional materials such as activated carbon, and thus future applications will focus on efficient processes where only small quantities of nano-materials are required. Moreover, further work is required on developing a cost effective methods of synthesizing nano-materials and testing the efficiency at large scale for successful field application.

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