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Use of Nano-Sized Adsorbents for Wastewater Treatment: A Review

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Abstract: There is an increased demand for high-quality drinking water, which requires the removal of hazardous contaminants emerging from municipal, agricultural, and industrial effluents. An approach towards safe drinking water requires the implementation of various treatment processes for water emerging from natural resources as well as coming in the form of industrial wastewater. Pollutants in water bodies may be present in multiple states, including large suspended particles, dissolved chemical substances, in the form of microorganisms or suspended solids. Over the last few years, researchers have concentrated on developing a practical methodology for extracting pollutants from wastewater. During the course of time, although many advanced and complex wastewater treatment processes have evolved, yet adsorption has its own importance. Owing to its simple operation process, low cost, and less sludge formation, adsorption is being considered the most promising technique for wastewater treatment. In this regard, nanomaterial adsorbents have become a topic of great interest owing to their exceptional properties such as high adsorption strength, greater surface area, and chemical stability. Keeping in view, key features of nanoparticles, researchers have explored the applications of various adsorbents at the nanoscale in addressing wastewater treatment issues. The present review focuses on the use of nano-adsorbents in treating various industrial effluents and also provides a comparative assay in terms of the advantages and drawbacks of these nano-adsorbents, employed in removing hazardous contaminants from industrial effluents.

Keywords: Wastewater, nanoparticles, adsorbents, polymer adsorbents.

Introduction

An existence of life without water is not possible on earth. It is the most fundamental asset for human and animal life. Drinking water is not safe for use without proper treatment and it is the most basic element of life. A considerable number of dangerous pollutants and waste is accumulated in freshwater bodies through various anthropogenic activities including an increased expulsion of poisonous materials containing heavy metals. This day-to-day increase in water pollution is dangerous to human wellbeing which needs a proper legitimate and financial-based treatment for removing harmful pollutants. Over the past few years, an increase in the urbanization of population demands a bigger measure of mechanical units to overcome the water scarcity issues. World Health Organization reported that around seven hundred and eighty million individuals have no access to shelter and clean drinking water (Tarras and Benjelloun, 2012). Keeping in mind this water scarcity issue, scientists have put forth a few strategies that ought to be considered quite effective for the treatment of wastewater to ensure a healthy life. Some of the conventional procedures reported in the literature for wastewater treatment includes tertiary treatment evaluation, season variability, nitrogen content variability, polysaccharide-based treatment etc. (Meneses et al., 2010, Crini, 2005). Nanotechnology plays a vital role in the treatment of wastewater bodies due to properties like high adsorption rates and enhanced surface activity. All these properties lie under the umbrella of Green Nanotechnology, which aims to lessen the ecological issues using safer methods. Adsorption via nanoparticles has a wide range of applications in wastewater management owing to their extraordinary properties like large surface area which will help in agglomeration of the required material during the adsorption process. In this context, an assortment of nanoparticles adsorbents for treating wastewater bodies was put forward towards the end of the twentieth century. Dye is the primary hotspot for the increased water contamination emerging from the fabric industry, affecting water bodies by utilizing dissolved oxygen and ruining marine life. Magnetic nanoparticle adsorbents are mostly utilized for eliminating dye contents as reported in various literature (Gupta et al., 2015; Chen and Liao, 2002, Liao and Chen, 2002, Mak and Chen, 2004, Sheela et al., 2012, Tuutijärvi et al., 2009, Pieters, et al., 1992).

Apart from dyes, wastewater also contains hazardous heavy metals like arsenic, cadmium, antimony, zinc, nickel-chromium, and many others which may cause severe health disorders like cancer, asthma, etc. Nowadays, the main problem is to eliminate pollutants like heavy metals, herbicides, agrarian, and industrial waste from the water assets that are adversely affecting human life. Among various heavy metals, arsenic causes most water pollution making water dangerous for drinking and other activities. Majority of the countries using ground water are facing arsenic contamination in water reservoirs (Hua et al., 2012, Huang et al., 2011, Lin et al., 2011, Tuutijärvi et al., 2009).

Keeping in view the effectiveness of nano adsorbents, present review study comprises a detailed overview of various nano adsorbents employed for treating industrial effluents.

Carbon Nanotubes Adsorbents (CNTs)

For the removal of organic content from wastewater, carbon nanotubes are often used. Carbon nanotubes have unique properties like high porous structure, the large surface area, low density, and high interacting properties that could be used for the treatment of wastewater. Two types of carbon Nanotube are used for this purpose (Fig. 1). Due to its best adsorption sites found in the structure, carbon nanotubes show high surface activity resulting in increased percentage removal (Fig. 2). In wastewater containing Pb^{+2} as a major contaminant, carbon nanotubes provide high solute uptake speed which is the most unique and attractive feature of carbon nanotubes for its potential application for removal of lead ions. In one of the studies reported it has been found that the adsorption rate of Pb^{+2} ions increase instantly in the first ten minutes and with a linear increase in adsorption as time lapses. Some vital parameters of Pb^{+2} ions adsorbed on CNTs extracted from various studies have been summarized in Table I.

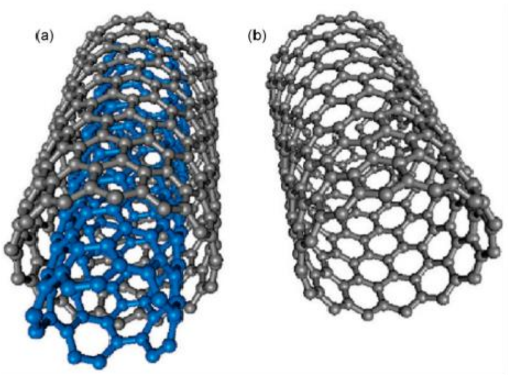

Fig. 1: (a) MWCNTs (b) SWCNTs (Structural representation)

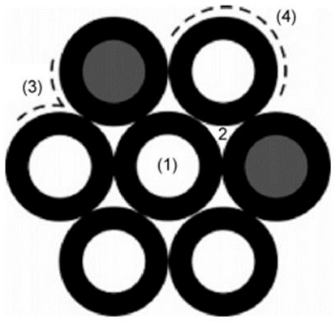

Fig. 2 The image of SWCNTs that have certain adsorption sites (1) represents the internal, (2) interstitial channel, (3) external groove site (4) and external surface (Ren et al.,2011)

Nanofiber Membranes as Adsorbent

Carbon nanofibers have a variety of specific characteristics such as organic dyes elimination due to C=O and OH groups working with CNFs, imparting them enhanced adsorption ability. Due to these specific features, carbon nanofiber possesses a rapid adsorption rate and high adsorption capacity leading to effective treatment of heavy metal assisted dyes such as chromium, methylene blue, and lead. These properties impart mechanical strength to nanofiber membranes where filtration under pressure up to thirty-kilo Pascal is required (Liang et al., 2011). Literature reveals that most of these carbon nanofibers are synthesized by a directed hydrothermal carbonization process. Moreover, membrane pore size can easily be controlled from ten to a hundred nanometers during hydrothermal treatment. In this study, we have reported the effectiveness of different types of carbon nanofibers/membranes namely Carbon Nano Fiber CNF (50), CNF (100), and CNF (280) nm for treating wastewater bodies (Liang et al., 2011). It has been found that the Polyether-sulfone membrane is the most commonly used membrane for commercial purposes. However, the Nanofiber membrane is found much more advantageous over this commercially used membrane.

Clay-polymer Nanocomposites Adsorbents

Increased progress in nanocomposite polymers contributes to the development of fundamental characteristics and new technologies for their different applications in everyday life. The introduction of nanofillers is responsible for substantial improvements in the characetristics of polymer nanocomposites such as graphene, nano clay, metal oxides, carbon nanotubes, and double layered hydroxides (Azzam, 2014, Banks-Sills et al., 2016, Cailloux et al., 2016, Ensafi et al., 2014, Mallakpour and Barati, 2014, Mallakpour and Dinari, 2016, Mallakpour and Jarahiyan, 2016, Mallakpour and Javadpour, 2016, Mallakpour and Khani, 2015, Mallakpour and Khani, 2016, Mallakpour and Soltanian, 2016).

Over the past few years, engineers and scientists have shown keen interest in the use of new class of materials called polymer-clay nanocomposites (PCN) due to unique characteristics of heat deflection, high dimensional stabilization, gas barrier output, optical clarification, the permeability of reduced gas and flame retardance resulting in effective removal of pollutants from various industrial effluents (Agag and Takeichi, 2000, Fu and Qutubuddin, 2001, Galgali et al., 2001, Hasegawa et al., 1998, Huang et al., 2001, Kawasumi et al., 1997, Kojima et al., 1993, Lan et al., 2002, LeBaron et al., 1999, Manias et al., 2001, Messersmith and Giannelis, 1995, Okamoto et al., 2000, Tien and Wei, 2001, Usuki et al., 1993).

The use of PCN's to extract organic contaminants from water in recent years has been intensively carried out, because of lesser toxicity of clay, large surface area, rapid cation exchange mechanism, and low operational cost. Studies indicate that organic molecules' adsorption to the specific minerals is affected by exchangeable cations, existence of water molecules present among layers and spaces among clay mineral layers etc. (Mishra, 2014, Unuabonah and Taubert, 2014).

Lead is a toxic material, present in freshwater that could be removed by using a blend of polymer with iron oxide nanoparticles to form polymer nanocomposites to increase efficiency (Gholami et al., 2014). Another nanocomposite named carboxymethyl cellulose with acrylic acid by grafting with silica gel is reported to have an adsorption capacity of 546 mg g^{-1} and 781 mg g^{-1} nearly equal to that of clay polymer nanocomposites used for the removal of crystal violet dye and cadmium (II) ions from wastewater (Saber-Samandari et al., 2016). Improvised adsorption of Pb^{+2} and methylene blue (MB) has been reported using monolithic rectorite /starch composites (PRSs), giving adsorption capacity for lead (II) ion 180.8 mg g^{-1} and for methylene blue (MB) 277.0 mg g^{-1}, respectively (Wang et al., 2015).

Iron oxide Nanoparticles Adsorbents

Iron oxide nanoparticles have also been reported in the literature for an effective removal of contaminants from water resources effectively. In one of the reported studies, it has been found that iron oxide has greater efficiency in the removal of lead ions showing an adsorption capacity of up to 36.0 mg g^{-1}. This seems to be less than the adsorption capacity as has been reported for Clay Polymer Nanocomposites (Table 1). In one of the research works conducted by a group of workers , iron-oxide nanoparticles are combined with chitosan, resulting in adsorption capacity for Nickel up to 58 mg g^{-1} and for Chromium up to 202 mg g^{-1}. (Keshvardoo Stchokami et al., 2017, Xu et al., 2012). In another study, pectin-coated iron-oxide magnetic nanocomposites have been reported as efficient adsorbents for copper ions from wastewater giving adsorption capacity up to 48.99 mg g^{-1} following the pseudo-second order. This value seems to be less than the adsorption capacity of clay polymer nanocomposites for the removal of Cu (II) ions (Gong et al., 2012). Lunge et al. have reported the removal of arsenic (III) and arsenic (V) is carried out using magnetic iron oxide nanoparticles with tea waste having adsorption capacities as 188.69 mg g^{-1} for arsenic (III) and 153.8 mg g^{-1} for arsenic (V) (Lunge et al., 2014).

Zinc oxide Nanoparticles Adsorbents

ZnO nanoparticles have extensive use in paints, packaging, plastics, cosmetics and sunscreen formulation, and thus indirectly released into the environment. Studies indicate that ZnO nanocomposites serve as efficient adsorbents for the treatment of industrial wastewater. Water containing Zn (II), Cd (II) or Hg (II) ions can be removed more efficiently using ZnO nanoparticles. The literature reveals that ZnO nanoparticles are more efficient than silver, titania (TiO_2), and aluminium nanoparticles for wastewater treatment (Lombi et al., 2012). In one of the studies conducted by (Rafiq et al. 2014), it was found that ZnO nanoparticles show greater adsorption capacity which is >1600 mg g^{-1} for Cu (II) ions in wastewater (Rafiq et al., 2014). The maximum adsorption capacity shown by Zinc-oxide nanoparticles for Zn (II), Cd (II), and Hg (II) ions are 357 mg g^{-1} for Zn (II), 384 mg g^{-1} for Cd (II), and 714 mg g^{-1} for Hg (II) ions (Sheela et al., 2012).

Table 1 A comparative assay of removal efficiency of various nano adsorbents in treating waste water effluent.

Nano adsorbent used	Contaminant	Removal efficiency	References
Iron Oxide nanoparticles	Pb^{+2}	36.0	(Keshvardoostchokami et al., 2017; Xu et al., 2012)
	Ni ions	58	
	Cr ions	202	
	Cu ions	48.99	(Gong et al., 2012)
	As (III)	188.69	(Lunge et al., 2014)
	As (V)	153.8	
ZnO Nanoparticles	Zn (II)	357	(Sheela et al., 2012)
	Cd (II)	384	
	Hg (II)	714	
	Cu (II)	>1600	(Rafeeq et al., 2014)
Ag-Nanoparticles	crystal violet	87.20	(AbdEl-Salam et al., 2017)
	Cu (II) ions	16.21	(Venkata et al., 2013)
	Cd (II) ions	16.94	
Nickel Nanoparticles	Cr (VI)	4.73	(Behnajady and Bimeghdar, 2014)
	As (III)	23.4	(Çiftçi and Henden2015)
	As (V)	17.8	
monolithic rectorite/starch composites (PRSs)	MB	277.0 mg g^{-1}	(Wang et al., 2015)
	Pb^{+2}	180.8 mg g^{-1}	
MWCNTs	Cu (II)(l)	175 mg/g (For tap water)	(Tang et al., 2012)
MWCNTs	Pb(II)(l)	~13.3 mg/g	(Shao et al., 2012)
MWCNTs	Ni (II)(l)	49.261 mg/g	(Kandah and Meunier, 2007)
SWCNTs	CO_2 (g)	2 mg/g	(Long and Yang, 2001)
CNFs	Hexane(g)	3.95 mmol/g	(Hsieh and Wen Chou, 2006)
SWCNTs	Synthetic organic compounds(l)	66.6 mg/g	(Apul et al., 2013)
MWCNTs	Atrazine(l)	18.83 mg/g	(Tang et al., 2012)

Silver Nanoparticle Adsorbents

For the removal of crystal violet dye and other pigments from wastewater bodies, studies reveal that Ag-nanoparticles serve as good candidates among the various classes of adsorbents. This is because in most of silver-based adsorbents, the Ag-nanoparticles are immobilized on activated carbon, resulting in an effective increase in adsorption capacity for the removal of crystal violet from water. The adsorption capacity recorded for crystal violet is 87.20 mg g^{-1}. (AbdEl-Salam et al., 2017). In the case of Ag-nanoparticles deposited on multi-walled carbon nanotubes, the adsorption capacity was found to be is 16.21 mg g^{-1} for Cu (II) and 16.94 mg g^{-1} for Cd (II) ions at 50 mg L^{-1}, respectively (Venkata et al. 2013).

Nickel Nanoparticles as Adsorbents

Chromium (VI) is one the most hazardous heavy metals found in wastewater causing serious diseases like cancer etc. The adsorption capacity shown by mesoporous Ni-oxide nanoparticles to remove chromium (VI) is 4.73 mg g^{-1}. (Behnajady and Bimeghdar, 2014). For the removal of Arsenic (III) and Arsenic (V) from the wastewater most of the studies reported have used either nickel or nickel bromide nanoparticles showing adsorption capacity for Arsenic (III), 23.4 mg g^{-1} and for Arsenic (V) 17.8 mg g^{-1}, respectively (Çiftçi and Henden, 2015). Table 1 gives an overall comparison of various nano adsorbents employed for treating wastewater.

Nevertheless, the extremely fine nature of NPS has greatly hampered its use in optimized-up water treatment because NPs faced some difficulties, such as propensity to combine, organizational complexity, and potential risk when unleashed into the environment (Zhao et al., 2011). A number of polymer-based nanocomposites have been developed in the last decade by encapsulation of inorganic nanoparticles (NPs) that are used inside the polymer host of porous nature to integrate NPS of high reactivity, and the host of bulky polymer is easy to operate (Bargar et al., 1997, Fan et al., 2005, Jang and Dempsey, 2008, Kawashima et al., 1986, Kinniburgh et al., 1976, Swallow et al., 1980, Trivedi et al., 2001).

Conclusion

It is concluded that wastewater is the main risk for human life that needs proper treatment. For this purpose, at an early stage, some traditional techniques were used. The literature utilized in the present review reveals that Nanoparticles have a wide range of adsorption properties like large surface area greater or larger adsorption capacity. The present study reveals that clay-based polymer nanocomposites are the best adsorbents for the treatment of wastewater owing to their wide range of adsorption capacity for almost all kinds of contaminants.

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