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A Review of Application of Nanotechnology in Wastewater Treatment in Oil, Gas and Petrochemical Industries

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ABSTRACT

The increase in population and the expansion of industries have led to the pollution and reduction of many natural resources, including water resources. Widespread use of these resources in domestic, agricultural and industrial uses has led to the entry of pollutants and limited water resources. One of these industries is the oil and gas industry and related sectors, such as petrochemicals, which introduce many pollutants such as heavy metals, aromatics, etc. into water sources. Therefore, it is necessary to pay attention to the correct use of these resources and strategies for treatment and reuse of wastewater. Various methods are used for wastewater treatment such as flocculation, adsorption, filtration, etc., but each of them has some limitations such as low efficiency or high cost. The use of nanotechnology is one of the solutions that has recently been considered. This method improves performance by reducing the dimension of material to nanometers. There are different types of nanomaterials that due to their unique properties such as larger surface area, ability to work at low concentrations, etc., have great potential for treating contaminated water very effectively. Studies show they can be used in various forms such as nano-adsorbents, nano-membranes, nano-filters and nano-photocatalysts to remove or reduce contaminants specially from oil, gas and petrochemical wastewater. In this review, the importance and application of nanotechnology has been discussed in wastewater treatment in oil, gas and petrochemical.

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1. Introduction

Oil is of great importance as a national strategic resource. Oil and petrochemical production processes include various segments including exploration, development and production such as drilling, processing of hydrocarbons in refineries and petrochemicals, storage, transportation and distribution of petroleum products. Water is used in different sectors of the oil and gas industry and the resulting wastewater contains contaminants that need to be treated for release or reuse. Lack of proper treatment causes destructive effects on the environment and human health(Ahmad et al., 2020; Jafarinejad & Esfahani, 2021; Liu et al., 2021) for example oily wastewater affects on human health, drinking water and groundwater resources, air, crop production, and aquatic life (Varjani et al., 2017; Zafra et al., 2015). Also, due to the increasing shortage of usable water resources, effective wastewater treatment with safer and more efficient methods is a key priority. One promising approach that has shown growing potential, according to the results of several studies, is the use of nanotechnology(Cheriyamundath & Vavilala, 2021). Nanotechnology has been used in various industries. One of these industries is the oil and gas industry, which its applications covered different areas in upstream and downstream(Alsaba et al., 2020).

A lot of research has been done on the fabrication of nanoparticles with specific properties and applications. Nanoparticles are nanoscale versions of their bulky counterparts(Kumari et al., 2019). Nanomaterials criteria include well-organized structure, filtration capability, small in size, and high surface to volume ratio. Some special properties of materials under the nanoscale are the effects on the surface region, large quantum tunnel effects and small size effects. These properties add to their adsorption capacity and reactivity, which are unprecedented and are great for heavy metal ions removal(Basu & Ghosh, 2013; Rivero-Huguet & Marshall, 2009). The chemical, physical, optical, electrical, magnetic and biological properties of nanoparticles make them suitable tools for removing wastewater contaminants(Kefeni & Mamba, 2020; Kumari et al., 2019; Mustapha et al., 2020).

A brief look at the recent publication related to nanomaterial reveals the application of wide range of them such as nanoadsorbent for removal of crude oil and diesel oil from wastewater(Vlaev et al., 2011), nanomembrane in water and wastewater treatment(Folio et al., 2018; Khamforoush et al., 2015), nanofilters to remove biochemical oxygen demand (BOD) and total dissolved solids (TDS)(Salahi et al., 2013) and nanophotocatalyst for chemical oxygen demand (COD) removal from refinery wastewater(Saien & Nejati, 2007). Using this technology to treat and reuse effluents can be more efficient and cost-effective than conventional methods(Kumari et al., 2019).

Since the oil industry is so important and it is rapidly expanding, protecting the environment and preventing the pollution of natural resources, in particular water resources, are becoming a more prevalent topics than ever. In this review, we discuss a summary of the recent progress of nanotechnology and its successful application, especially in oil and gas wastewater treatment.

2. Nanotechnology in oil and gas wastewater treatment

Hundreds of compounds can be present in the oil and natural gas. Every crude oil type contains 200-300 different compounds. About 50-98% of the oil composition corresponds to hydrocarbons (Sayed et al., 2021), which are primarily alkanes (paraffins); 5-6 atom-per-cycle cycloalkanes (naphthenes); aromatic compounds (20-40% of the oil) such as volatile compounds (benzene, toluene, xylene), bicyclic compounds (naphthalene), tricyclic compounds (anthracene, phenanthrene) and polycyclic compounds (pyrene). In addition to hydrocarbons there are sulfur compounds reaching up to 10%, and fatty acids and nitrogen compounds, as well as vanadium and nickel(Kharisov et al., 2014). Wastewater from the oil, gas and petrochemical industries contains many complex organic compounds such as polycyclic aromatic hydrocarbons (PAHs), aromatic hydrocarbons, oils, heavy metals, phenol, bacteria and various inorganic chemicals(Li et al., 2019; Liu et al., 2021). In addition, oily wastewater is one of the major type of wastewater discharged by different industries. The oil and gas industry produces a significant amount of oily wastewater during the exploration, production, transportation, storage, and refining of crude oils as well as the synthesis of petrochemical products. The majority of oil mixed in water is coming from petrochemical and metal processing industries, in terms of fats, hydrocarbons, and petroleum fractions like diesel oil, gasoline, and kerosene. These constituents exist in the form of oil-in-water emulsions(Abuhasel et al., 2021; Ahmad et al., 2020; Cai et al., 2020).

Nanotechnology is a science employing nanoparticle for various engineering applications including environmental remediation(Khan et al., 2019). It can be used to eliminate or reduce the pollutants. Contaminants removal from the wastewater of the oil and gas industries can be done through physical, chemical and biological methods such as adsorption, flocculation, chemical deposition, chemical oxidation and membrane filtration(Peng et al., 2020). The application of nanotechnology in these methods is effective for improving the water purification process.

2.1. Nanoadsorbent

The use of adsorbents is one of the wastewater treatment methods that has been considered due to its ease and high efficiency. Pollutants are adsorbed on the adsorbent surface, and the pores on the adsorbent surface play a key role in this process(Han et al., 2019). Therefore, specific surface area and high porosity are of special importance. The use of nanotechnology and synthesis of nanoadsorbents can increase their performance and efficiency. In addition, nanoadsorbents can be regenerated and reused(Kumari et al., 2019). Adsorbent processes can be classified into two mechanisms of physical adsorption (physisorption) and chemical adsorption (chemisorption) according to the nature of interactions between the adsorbate and the adsorbent(Queiroz et al., 2022). Various adsorbents have been used to eliminate oil from wastewater such as activated carbon(Liang & Esmaeili, 2021), lipophilic activated carbons(de Tuesta et al., 2020),etc. Recently, the use of nano-adsorbents to remove oil from emulsion has received much attention. Nano-adsorbents are broadly categorized into various groups, including metallic NPs, magnetic NPs, metallic oxide NPs ,and nanostructured mixed oxides. Also, carbonaceous nano-materials include carbon nano-sheets, carbon nano-tubes, and carbon nano-particles(Khoshkerdar & Esmaeili, 2019).

Oilfield wastewater can cause several environmental problems if it is directly discharged because it contains high salinity metal ions, such as Ca^{2+} and Mg^{2+}(Imran et al., 2019; Johnston et al., 2019) Therefore, the high salinity of metal ions in oilfield wastewater, which is reinjected down to oil wells as the oil-displacing solution, can have an adverse affect on oil recovery(He, Yang, et al., 2021). Hence, effective removal of metal ions is necessary before reinjection. Graphene oxide (GO) is one of the adsorbents that are used for rapid removal of some metal ions such as Cu^{2+} due to its high adsorption capacity(He, Yang, et al., 2021). He et al.(He, Yang, et al., 2021) prepared a PEG/Fe_3O_4/GO-NH_2 nanoadsorbent by amination of GO, incorporating magnetic Fe_3O_4 nanoparticles, and PEG coating. The synthesized nanosorbents effectively remove Ca^{2+} and Mg^{2+} from the oilfield wastewater and displayed relatively high reusability. Also, in the core displacement experiments using oilfield wastewater treated with the nanoadsorbent, the oil recovery efficiency (11.8%) increased compared to the untreated oilfield wastewater.

In another study, He et al.(He, Wang, et al., 2021) prepared Fe_3O_4/GO-COOH nanoadsorbents by magnetization and carboxylation of graphene oxide (GO) to remove Ca^{2+} and Cu^{2+} metal ions from oilfield wastewater. After 30 minutes, the Fe_3O_4/GO-COOH adsorption capacity for Ca^{2+} and Cu^{2+} reached 69.3% and 49.3%, respectively, and at 60 minutes reached 78.4% and 51%, respectively. In addition, after five adsorption/desorption cycles, the nanoadosorbent maintained a high recovery rate and removal percentage.

In order to remove PAHs, Ruiz et al.(Patiño-Ruiz et al., 2020) synthesized composites from chitosan beads modified with iron oxide (FeO) and titanium dioxide (TiO_2) nanoparticles via ionic cross-linking (Ch-FeO/TiO_2). The enhanced adsorption mechanism of Ch-FeO/TiO_2 was determined by the removal of naphthalene from water and seawater samples. The Ch-FeO/TiO_2 showed a higher adsorption capacity of 33.1 mg/g compared to 29.8 mg/g of unmodified chitosan beads (un-Ch). Due to its cheapness and environmental friendliness, this adsorbent can be a good option for remediation of water sources contaminated with complex compounds.

Magnetic nanoparticles have properties such as extremely large surface area per volume substance and strong magnetic response and these properties make them exciting candidates for separation applications in oil and gas production and processing. Most of the attention in application of magnetic nanoparticles has been given to the removal of dispersed oil (Lü et al., 2016; Sabouri et al., 2019). In a method to remove oil droplets from water by cationic surface-coated magnetic nanoparticles has been developed by Ko et al., Adsorption experiments were performed on a batch scale with 5 wt % decane-in-water emulsions. The reported removal efficiency of the decane droplets was in the range between 85 and 99.99 %(Ko et al., 2014; Simonsen et al., 2018).

Table 1. Nanoadsorbents samples

Nanoadsorbents	Studied Points	Results	Reference
PEG/Fe_3O_4/GO-NH_2	To remove Ca^{2+} and Mg^{2+} from the oilfield wastewater	The oil recovery efficiency (11.8%) increased compared to the untreated oilfield wastewater	(He, Yang, et al., 2021)
Fe_3O_4/GO-COOH	To remove ca^{2+} and cu^{2+} metal ions from oilfield wastewater	After 30 minutes, the adsorption capacity for Ca^{2+} and Cu^{2+} reached 69.3% and 49.3%, respectively, and at 60 minutes reached 78.4% and 51%, respectively	(He, Wang, et al., 2021)
Ch-FeO/TiO_2	The removal of naphthalene from water and seawater samples	A higher adsorption capacity of 33.1 mg/g compared to 29.8 mg/g of unmodified chitosan beads (un-Ch).	(Patiño-Ruiz et al., 2020)
Sodium salt of oleoyl carboxymethyl chitosan (NaO-CMCS) adsorbent	Enhancing the removal of oil from the creamy emulsion	75-85% oil in deionized water; 19-49% oil in seawater were recovered	(Doshi et al., 2018)
MIL-101 and MIL-101@ nanoporous graphene (NPG) adsorbent	oil adsorption	The proposed composite was used successfully for adsorption of crude oil (14 g/g) in water samples	(Rahmani et al., 2018)

2.2. Nanomembrane

Membrane technology is one of the most commonly used methods for the separation of oil-water wastewater or emulsions, in food processing, pharmaceutical, desalination, and fuel cell industries(Ma et al., 2016). In recent decades, membrane technology has grown significantly due to advantages such as the possibilities of low or no usage of chemicals and environmental friendliness for use in water and wastewater treatment. With a significant reduction in the size of equipment, energy requirements and low capital costs can be a more desirable option in wastewater treatment processes.

Membrane is a barrier that separates the two phases by restricting the movement of components in a selective manner. Membrane materials are classified into two categories: organic or inorganic. Organic membranes are made from synthetic organic polymers including polyethylene (PE), polytetrafluoroethylene (PTFE), polypropylene and cellulose acetate. Mineral membranes are made from materials such as ceramics and zeolites(Aliyu et al., 2018; Obotey Ezugbe & Rathilal, 2020). Membranes seperation technique used in water and wastewater treatment systems classified based on the membrane pore sizes include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). MF and UF are commonly used to remove solids and/or microbes. NF and RO are used in desalination and are regularly applied for multi-valent ions (such as calcium, magnesium, sulfate, etc.) and TDS removal, respectively(Adham et al., 2018). Descriptions of membrane types with corresponding pore diameters and preserved species are shown in Figure 1. According to this figure, microfiltration can reject colloids or bacteria larger than 100 nm, ultrafiltration can reject macromolecules and proteins larger than 2 nm, nanofiltration can reject multivalent salts, and reverse osmosis can reject monovalent salts but the main advantage of nanofiltration is that they are able to work in lower pressure (between 20-4bar) and it causes the treatment process more economical (Adham et al., 2018; Ali et al., 2019; Jafarinejad & Esfahani, 2021; Yang et al., 2019).

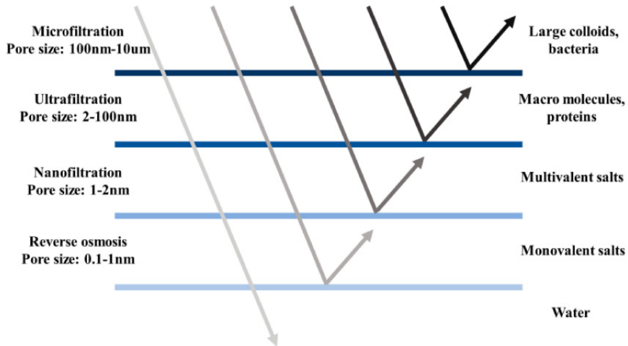

Figure 1. Classification of membranes for water purification in terms of pore size and retained species(Yang et al., 2019).

Zhang et al. (Zhang et al., 2021) prepared a new nanofiber and micro/nanospheres coated with PVDF/graphene (GE) composite membrane (TPGCM) through a simple simultaneous electrospinning/electrospray strategy. By examining the relationship between different concentrations of GE in the electrospray precursor and morphology, microstructure, wettability and performance of the composite membrane showed high permeability and excellent separation efficiency of 99.8% for the separation of different types of Span-80-stabilized water-in-oil emulsions. Velayi et al.(Velayi & Norouzbeigi, 2020) fabricated micro/nano hierarchical structured ZnO coated mesh via a simple chemical bath deposition method. The coated meshes were used for chloroformwater and n-hexane-water separations showing high efficiencies in a dead-end system. Also, the prepared meshes can selectively separate mixtures of various corrosive solutions without significant changes in flux and efficiency values. In addition, the heat-induced switchable wetting characteristics were applied to creation ZnO-mesh membranes for oil/water isolation continuously with a high permeation flux and excellent durability which is more affordable and efficient for practical applications.

Fang et al.(Fang et al., 2019) have developed a route for fabrication of catalytic-ultrafiltration (UF) membrane via blending the natural polyphenol tannic acid (TA)-Fe complexes in UF membrane matrix to in situ form Ag nanoparticles on inner pore walls of the polymeric membrane. The evenly-distributed TA provides a convenient platform for forming and immobilizing catalytic nanoparticles in the membrane matrix. As a result, most of the nanoparticles were distributed on the surface of inner pores and protected with membrane separation layer from the macromolecular pollutants. Naseem et al.(Naseem et al., 2018) prepared asymmetric composite fiber membranes of three-layered graphene oxide (GO), titanium dioxide (TiO_2) and recycled waste industrial cellulose triacetate(rTAC) to separate oil from water. GO and TiO_2 coated by electrophoretic deposition method increased water permeability on rTAC membranes.This coating can effectively repel oil and has self-cleaning and anti-fouling properties. Hu et al.(Hu et al., 2015) fabricated GO-modified MF membranes via the vacuum filtration method by using commercially alumina (Al_2O_3) as substrates. The permeate flux values of unmodified and GO-modified membranes were compared with each other, which showed 28% improvement after GO modification. Due to high electrical and thermal conductivity, as well as excellent chemical stability and mechanical strength, graphene is an excellent candidate for developing water treatment membranes(Aghigh et al., 2015). Graphene oxide has similar properties to graphene, but is more hydrophilic due to the variety of oxygen functional groups, and this property makes it better dispersible in water and other organic solvents(Noamani et al., 2019).

Nanofiltration membrane (NF) is one of the most important types of membranes used in wastewater treatment. This membrane can be aqueous or non-aqueous. The main task of NF is the selective removal of ions and organic matter(Abdel-Fatah, 2018). The characteristics of NF which are 1- 5 nm pore size and 7- 30 bar operating pressure(Shon et al., 2013) are used to separate solutes with low molecular weight like lactose, glucose, salt, and it's effective in rejecting hardness, dye and heavy metal(Mulyanti & Susanto, 2018). In comparison with MF and UF processes, this process has higher efficiencies in the reduction of COD and TDS and also operates under low pressure (i.e., low energy usage) conditions compared to RO process(Abadikhah et al., 2015). Low energy consumption, enhanced capacity for the removal of contaminants, excellent lifetime, and cost-effectiveness have led to great popularity and wide acceptance of NF membranes worldwide(Tul Muntha et al., 2017). Nezhad et al.(Nezhad et al., 2022) investigated the performance of NF and RO membrane processes for treatment of wastewater containing ethylene glycol (EG) from South Pars Gas Complex (SPGC) and compared them. For the RO process, the EG removal from synthesized and industrial wastewaters at different pressures are 80% and 99%, respectively, and for the NF process, these are 60% and 80%, respectively, which indicates membrane technologies are suitable choices to treat industrial wastewater containing EG. In addition, it has been observed RO has better performance than NF and RO membrane has less fouling than the NF membrane, which means the RO process has more lifetime and fewer operational costs. However, it should be noticed the flux of the NF membrane is higher than RO due to less compression of the NF membrane.

Nanofiltration is increasingly used in various applications such as textile industry for separation of dyes, wastewater treatment of olive factory, removal of sulfate acid from mine water, oily wastewater treatment and etc(Mulyanti & Susanto, 2018). In Table 2, a number of studies on nanofiltration membranes are summarized.

Table 2. Nanofiltration membranes samples.

Nanofiltration membranes	Preparation method	Performance	Filteration Capacity	Reference
Zirconia nanofilter	Aqueous sol-gel process modified by glycerol	Treatment of wastewater with high salinity	At the high NaCl mass fraction varying from 0% to 24.92%, the ZrO_2 NF membrane displays much better retention performance at about 68% while only 36% for polymeric NF membrane.	(Da et al., 2016)
Zeolite nano-particles impregnated polysulfone membranes	Nanoparticles fabricated via conventional and microwave heating methods and then incorporated into a polysulfone	Removal of nickel and lead cations	The maximum sorption capacity of the hybrid membrane for the lead and nickel ions was measured as 682 and 122 mg/g respectively at the end of 60 min of filtration.	(Yurekli, 2016)
PSf/pebax/F-MWCNTs nanocomposite membrane	The porous PSf support was prepared and then a thin layer of pebax as selective layer was coated on it	Nanofiltration of oil/ water emulsion	PSf/Pebax/2%F-MWCNT membrane oil filteration value reported 99.26%.	(Saadati & Pakizeh, 2017)
Combined UF and NF/ RO	The integrated membrane systems based on ultrafiltration (UF) coupled with nanofiltration(NF) or reverse osmosis (RO)	Treatment of phenolic wastewater from a paper mill	Rejections of 95.5% for COD and 94.9% for phenol	(Sun et al., 2015)
A commercial titania ceramic nanofiltration membrane	Titania Nanofiltration membrane Unit(TNU)	Reduce ion concentration, Total Suspended Solids (TSS) and Total Organic Carbon (TOC) in recycle water from a Canadian oil sands mine	High rejection of divalent cations, 75-90% TOC rejection, and almost 100% TSS rejection	(Cabrera et al., 2021)
Nanofiltration membrane (JCM-1812-50N, USA)	Thaguchi method	Removing Ba, Ni, Cr, NaCl and TDS from produced wastewater by dewatering unit of an oil and gas well drilling industry	85.3% removal of Ba, 77.4% removal of Ni, 58.5% removal of Cr, 79.6% removal of NaCl and 56.3% removal of TDS	(Hedayatipour et al., 2017)
A superwetting and robust PES-PAA-ZrO_2 nanofiltration membrane	A ZrO_2 coating was formed on polyethersulfone (PES) membrane surface through chemicalbonding.	Polycyclic aromatic hydrocarbon removal(PAH)	More than 90% of PAH rejection rate	(Chen et al., 2022)

2.3. Nanophotocatalyst

Among the various processes available for water and wastewater treatment, the use of heterogeneous photocatalysts is more cost-effective than other Activated Oxidation Processes (AOPs) such as ozonation or the Fenton process because of no need to addition of expensive chemicals for complete mineralization of the target compound. AOPs can completely destroy organic pollutants into carbon dioxide and water that used in the additional treatment stage, which is an optional stage known as AOPs(Gómez-Pastora et al., 2017; Hassan & Al-zobai, 2019). Some of the most widely used photocatalytic nanomaterials are Fe_3O_4, TiO_2, ZnO, and graphitic carbon nitride (g-C_3N_4). These nanomaterials and their combinations carry an enormous potential for water and wastewater treatment(Ahmed & Haider, 2018). It has been proven that the use of TiO_2-induced semiconductor photocatalysis technology can be a suitable method for oil and gas wastewater treatment(Liu et al., 2021). since titanium dioxide has a large energy band gap (3.2 eV) which exceeds the REDOX potential of most organic compounds(Fujisawa et al., 2017), and can effectively excite oxygen and OH· radicals in water. Finally, organic matter can be completely mineralized and transformed into a carbonaceous gas, which eliminates the need of subsequent biomass treatment(Ng, 2021).

Ghasemi et al.(Ghasemi et al., 2016) synthesized a new nano-TiO_2/Fe-ZSM-5 photocatalyst by immobilization TiO_2 in the Fe-ZSM-5 structure synthesized by sol-gel method. The aim of this study was to photocatalytically decompose organic pollutants in oil refinery wastewater under UV and sunlight. The maximum reduction of COD was 80% at pH 4, the photocatalyst concentration was 2.1 g/L, the temperature was 45 °C and the UV exposure time was 240 minutes. In addition, the results showed that various petroleum compounds decomposed under UV and visible light and the removal of COD degradation was not reduced by increasing the photocatalyst reuse cycle.

Ethyl benzene (EB) is one of the solvents used in various fields such as organic synthesis and cleaning equipment, in addition to being used as a chemical raw material in chemical productions. Therefore, this material exists in petroleum products refinery and chemical industry wastewater. Due to improper waste disposal practices, accidental fuel spills, and leaks in underground storage tanks and pipelines may happen, EB is among the most common organic contaminants(Cui et al., 2017; Shirzad Taghanaki et al., 2021). Taghanaki et al.(Shirzad Taghanaki et al., 2021) synthesized Cu-TiO_2@SiO_2 and Cu-N-TiO_2@SiO_2 photocatalytic powders using three different concentrations of copper and nitrogen by sol-gel method via ambient pressure drying and the optical decomposition efficiency of ethyl benzene in aqueous media was tested under visible light. 3Cu-3N-TiO_2 @ SiO_2 had the highest photocatalytic activity in EB degradation under visible light (90%).

Phenols in wastewater arise from a large number of industrial processes such as refineries, manufacturing of paints, pharmaceuticals, and petroleum production, are highly soluble in water, acutely toxic, and biologically recalcitrant (Maszenan et al., 2011). Phenol and its derivatives Chlorophenol and nitrophenol are broken down by photocatalytic process. The main by-products detected during its photocatalytic degradation are 4-nitrocatechol, benzoquinone, hydroquinone, and some organic acids(Maszenan et al., 2011; Ren et al., 2021). Darabdhara et al.(Darabdhara & Das, 2019) reported the colorimetric detection and photocatalytic degradation of toxic phenolic compounds using Au@Ni loaded reduced graphene oxide (rGO) nanostructures. Core-shell nanoparticles of Au and Ni are successfully designed on rGO with size < 8 nm by a solvothermal route . Additionally, the Au@Ni/rGO nanocomposite exhibits excellent photo responsive behaviour towards degradation of phenol, 2-chlorophenol (2-CP) and 2-nitrophenol (2-NP) under natural sunlight irradiation with more than 87% degradation. Khaksar et al.(Khaksar et al., 2017) developed a novel cascade photocatalytic backlight reactor to remove phenol from petrochemical wastewater and the effect of five factors including initial phenol concentration, TiO_2 concentration, turbidity, and pH on phenol removal efficiency was investigated using full factorial design. The best removal efficiency was 88% obtained after three hours when pH is 9, initial phenol concentration equals 50mg/L, and TiO_2 concentration equals 80g/m^2. The significance of reaction parameters is shown as follows: time> initial phenol concentration> TiO_2 concentration> pH.The analysis also reveals that turbidity has no effect on phenol removal efficiency.

Ammonia is a common water contaminant that contains nitrogen and a source of nutrients that may accelerate the eutrophication and cause algal growth in natural water(Shavisi, Sharifnia, Zendehzaban, et al., 2014). Shavisi et al.(Shavisi, Sharifnia, Zendehzaban, et al., 2014) investigated the influence of solar light irradiation on ammonia degradation from petrochemical industry wastewater using TiO_2/LECA photocatalyst. The photodegradation of ammonia was performing by two methods of aeration, using air diffuser and stirring with a blender. The results showed that the ammonia removal efficiency increased with increasing the pH value. The optimal efficiency of the photocatalytic degradation process reached to 96.5%, at pH = 11. The optimum dosage of catalyst was 25 g/L which the maximum efficiency achieved with this amount of catalyst. The catalyst efficiency after three times regeneration was reduced by only about 41%. Two types of industrial aeration methods were applied in photoreactors which this comparison shows systems have almost a same efficiency on degradation of ammonia. In another study, Shavisi et al.(Shavisi, Sharifnia, Hosseini, et al., 2014) used TiO_2/perlite photocatalysis for degradation of ammonia from synthetic wastewater, under UV light irradiation. Results showed that the TiO_2/perlite photocatalyst after 120 min of starting irradiation removed about 64.3% of ammonia at 170 mg/L of ammonia concentration, pH = 11 and 125 W Hg lamp as UV source.

Table 3. Nanophotocatalysts samples

Nanophotocatalyst	Studied Points	Results	Reference
Vertically aligned zinc oxide nanorods (ZnO NRs) photocatalyst	Degradation of hydrolyzed polyacrylamide (HPAM) and reduction in TOC from oil and gas produced water	Reduction 51% of HPAM within 6 h, almost 20 % and 37% reduction in TOC after 7h and 14hr	(Al-Sabahi et al., 2018)
Silver/titanium dioxide/ graphene ternary nanoparticles (PU-Ag/P25/G) photocatalyst	Diesel-polluted surface water	76% degradation of diesel in a period of 16 h	(Ni et al., 2016)
Ni-N-TiO_2 floating photocatalyst	Diesel oil removal from wastewater	Diesel oil removal efficiency was 95.9% in 5 h	(Wang et al., 2017)

3. Conclusions

According to studies, nanotechnology has many applications for oil, gas and petrochemical industry wastewater treatment. The small size of nanomaterials to their bulk counterparts has created unique properties in them. The contact surface and porosity in these materials is higher, which is an advantage in processes such as adsorption and membrane filtration.

Therefore, the separation of pollutants is done better and the effluent is treated with higher efficiency However, it is important to mention that some of these nanomaterials are still in the stage of experimental research and there are many attempts to find a balance between economic and environmental benefits. It is also worth mentioning this point that each of these nanostructures is fitted to a specific mechanism for treating wastewater. For nanoadsorbents, pollutants are adsorbed on the adsorbent surface, and the adsorbent surface plays a key role in this process. Therefore, specific surface area and high porosity are of special importance. The use of nanotechnology and the synthesis of nano adsorbents can increase their performance and efficiency. Nanomembrane plays the role of barrier that separates the two phases by restricting the movement of components in a selective manner. So nanoporous in the membrane can help to reject smaller particle sizes. Nanophotocatalysts, can completely destroy organic pollutants into carbon dioxide and water that are used in the additional treatment stage, and also nanostructures should cause more activate sites for these reactions. As a result, nanotechnology can be a promising solution for having improvement wastewater treatment.

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مروری بر کاربرد فناوری نانو در تصفیه آب و پساب صنایع نفت، گاز و پتروشیمی

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چکیـــــده

افزایش جمعیت و گسترش صنایع منجر به آلودگی و کاهش بسیاری از منابع طبیعی از جمله منابع آب شده است. استفاده گسترده از این منابع در مصارف خانگی، کشاورزی و صنعتی منجر به ورود آلاینده‌ها و محدودیت منابع آبی شده است. یکی از این صنایع، صنعت نفت و گاز و بخش‌های مرتبط با آن مانند پتروشیمی است که آلاینده‌های زیادی مانند فلزات سنگین، آروماتیک و غیره را وارد منابع آبی می‌کند. بنابراین توجه به استفاده صحیح از این منابع و راهکارهای تصفیه و استفاده مجدد از پساب ضروری است. روش‌های مختلفی برای تصفیه پساب از جمله لخته سازی، جذب سطحی، فیلتراسیون و غیره استفاده می‌شود که هر کدام دارای محدودیت‌هایی مانند راندمان کم و یا هزینه بالا هستند. استفاده از فناوری نانو یکی از راهکارهایی است که اخیراً مورد توجه قرارگرفته است. این روش با کاهش ابعاد مواد به نانومتر، عملکرد را بهبود می‌بخشد. انواع مختلفی از نانومواد وجود دارد که به دلیل خواص منحصر به فرد خود مانند سطح تماس بزرگ‌تر، توانایی کار در غلظت‌های پایین و غیره، پتانسیل بالایی برای تصفیه مؤثر آب‌های آلوده دارند. مطالعات نشان می‌دهد که می‌توان از آن‌ها در اشکال مختلف مانند نانوجاذب‌ها، نانوغشاها، نانوفیلترها و نانوفوتوکاتالیست‌ها برای حذف یا کاهش آلاینده‌ها به‌ویژه از پساب نفت، گاز و پتروشیمی استفاده کرد. در این بررسی به اهمیت و کاربرد فناوری نانو در تصفیه پساب نفت، گاز و پتروشیمی می‌پردازیم.

واژگان کلیدی: فناوری نانو، صنایع نفت و گاز، تصفیه پساب، نانوغشا، نانوجاذب، نانوفوتوکاتالیست