

Two dimensional materials for wastewater treatment

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Abstract

Global population growth, economic expansion, and climate change have made water scarcity an increasingly complex challenge. There is a need for advanced waste water treatment or purification systems that can produce clean water in a scalable, dependable, cost-effective, and sustainable way. Because of their exceptional qualities and distinct structures, recent developments in 2D materials provide a new avenue for tackling the enormous problem of water purification. Emerging two-dimensional materials with unprecedented surface-to-volume ratios, including graphene, graphene oxide, MXenes, boron carbon nitride, g-C₃N₄, metal organic framework, and black phosphorus, offer extremely low material consumption, extremely fast processing times, and extremely high treatment efficiency for water cleaning and monitoring. This review will highlight the state-of-the-art account of 2D materials along with their uses in pollutant detection, separation, adsorption, and photocatalysis in waste water treatment. Due to the unique qualities of two-dimensional materials like their high conductivity, hydrophilicity, and catalytic activity, research interest in their potential uses in water treatment and environmental remediation. This review will also provide information about the synthesis and uses of two-dimensional materials as adsorbents, desalination, photodegradation, and catalytic activity in the field of water purification. The review ends by outlining novel avenues of research and a future outlook on the difficulties facing this developing area.

Keywords: Two dimensional materials, waste water treatment, adsorption, photocatalytic processes.

Full length article

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1. Introduction

The rapid industrial development and population growth around the world in recent decades have led to an increase in the degree of contamination in natural water streams. Due to the rapid speed of industrialization, hazardous wastes that are harmful to the environment and human health are being produced [1]. As a result, numerous inorganic pollutants are produced, such as biotoxins and dyes, pesticides, and pharmaceuticals, as well as organic pollutants including poisonous gases (NO_x, SO_x, CO, and NH₃) and hazardous heavy metals like arsenic, lead, mercury, and cobalt. Because most of the contaminants in water streams are hazardous and especially harmful to living things, they pose a threat to the environment on a worldwide scale. Examples of these pollutants are toxic metals, salts, medicines, aromatic molecules, and dyes used in textiles [2]. For the removal of various environmental pollutants, many biological and physicochemical techniques have been employed historically, including membrane filtration, adsorption, aerobic and anaerobic digestion, and biochar treatment. Furthermore, nanoparticles are showing promise as an economical and ecologically benign substitute for efficient environmental remediation in their roles as adsorbents, catalytic

antimicrobial agents and multifunctional membranes for effluent and water treatment. These advanced and practical nanomaterials include zeolites, carbon nanostructures, ceramics, and metal organic frameworks (MOFs). Engineering functional nanomaterial-based technology can provide us with new levels of sensitization, specificity, efficacy, and mechanical stability for environmental preservation [1].

Nanotechnology has recently become known as an intriguing approach to eliminate or decompose these contaminants in wastewater due to its unique structural, physicochemical, and electrochemical characteristics demonstrated by zero-dimensional (0D) nanoparticles, one-dimensional (1D) nanorods, two-dimensional (2D) nanosheets, and three-dimensional (3D) nanostructures, along with their functional composites [2]. The lateral dimensions of two-dimensional (2D) nanomaterials vary from tens of nanometers to a few micrometers in order to exhibit atomically thin structures. 2D nanomaterials are beneficial in a range of environmental contamination treatment applications, including adsorption, sensing, and catalysis, due to their great lateral dimensions and nanoscale thickness, which gives them a high specific

surface area [3]. Adsorption is a frequently employed technique for eliminating impurities from wastewater [1]. Recent studies have focused on 2D nanomaterials like graphene and MXenes as emergent adsorbents because of their distinct surface characteristics in comparison to traditional bulk adsorbents. For example, for medicines such as ciprofloxacin, doxycycline, and tetracycline, graphene and its nanocomposites have obtained removal efficiencies of approximately 100 mg of pollutants per gram of adsorbent. When used as adsorbents, membrane separators, photocatalytic compounds for waste disinfection, or sensing components for pollutant detection and/or removal, graphene-based materials exhibit remarkable performance in environmental remediation [2].

Moreover, graphene and its derivatives, such as graphene oxide (GO), were found to be excellent water purification membranes with unique characteristics like ultrahigh water flux, selective ion and molecule sifting, and excellent resistance to biofouling [1]. Graphene oxide (GO) is a novel material with a 2D laminar structure that has great promise for use in water treatment applications. GO materials have many oxygen-containing groups, such as carboxyl, hydroxyl and phenolic groups, which are found on the edges and basal planes of GO nanosheets. These oxygen-containing functional groups on GO nanosheets enhance GO dispersion in water and provide convenient sites for boosting interactions with transport components (water molecules and ions) during the water purification process [4]. MXenes are a new type of 2D nanomaterial derived from a large family of transition metal carbides, nitrides, and carbonitrides denoted by the general formula $M_{n+1}X_nT_x$ ($n = 1-3$), where M is an early transition metal group, X is carbon and/or nitrogen, and T_x are surface terminal groups (OH^- , O^{2-} , and/or F^-). Because of their large surface area, active metallic hydroxide sites, hydrophilicity, and environmental friendliness, MXenes have generated significant interest in expanding their uses for environmental remediation. MXenes are a type of 2D material that has several advantages. They are made up of abundant, non-toxic elements like Ti and C or N, and as they degrade naturally, they release carbon dioxide (CO_2), nitrogen gas (N_2), and Ti, which are all non-toxic byproducts. MXene research has thus identified a suitable niche in the primary field of environmental remediation applications [1]. This review provides an overview of two-dimensional materials for aqueous media applications, such as heavy metal removal, capacitive deionization, water purification, and antimicrobial applications. Different kinds of two-dimensional materials, their intriguing characteristics, and the ways in which their constituent elements affect them are also discussed. Recent developments in their synthesis, which is based on mechanical exfoliation of the bulk materials and chemical vapor deposition (CVD), are reviewed, along with the use of the resultant 2D materials for adsorption and catalysis [5].

2. Synthesis of two dimensional materials

It is crucial to establish simple, efficient, and trustworthy procedures for the synthesis of 2D nanomaterials. Numerous initiatives have been dedicated to exploring different synthetic methodologies for producing 2D nanomaterials in order to fully use their features, functions, *Perveen and Zahoor, 2024*

and applications. Different methods are explored to achieve atomic thickness. Two types of techniques can be distinguished for 2D materials: top-down and bottom-up. Bottom-up methods depend on using precursor atoms to directly assemble 2D nanomaterials. Chemical vapor deposition and electrochemical deposition are two examples of bottom-up synthesis techniques. Harsh reaction conditions, such as high temperature and high vacuum, are typically needed for these techniques. Top-down methods are specifically interesting due to the fact that they can produce dispersions of single- and few-layer flakes or sheets using either physical or chemical methods, as well as being scalable and feasible in ambient conditions. The exfoliation of layered bulk crystals into single- or few-layer sheets is typically the basis for these methods. Liquid phase and mechanical exfoliation are examples of top-down synthetic techniques [6]. The following section provides specifics on material categories and various synthesis pathways to produce 2D materials [7].

2.1. Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a popular bottom-up technique for creating 2D films of materials. Particularly for creating transition metal disulfide films, CVD forms solid sediments through chemical reactions that result in films on the substrate surface [8]. In the CVD process, by using the mass flow controller, a predetermined mixture of reactant and diluent inert gases is injected into the chamber at a predetermined flow rate. The gas species migrate to the surface. The reactants bind to the surface site. The NSMs are formed as a result of chemical reactions between the reactants and the substrate. The gaseous reaction products are desorbed, and the chamber is evacuated [9]. However, the vapor deposition method of preparing 2D materials has some risks, such as the preparation process being inefficient and the products being impure [8].

2.2. Liquid-Phase Exfoliation

Liquid-phase exfoliation is another technique for creating 2D materials. This process involves first adding the bulk layered material, which is usually in powder form, to a solution that contains either a pure solvent or a dispersant. Next, an exfoliation step is carried out using shear or ultrasonic energy. Subsequently, the resultant dispersion's partially-exfoliated thick layers and thinly-exfoliated nanosheets are separated, usually by centrifugation or slow, spontaneous sedimentation caused by gravity. Eventually, the well-dispersed, thin nanosheets-containing supernatant is extracted. Because the exfoliation of the 2D crystal nanosheets depends on the interfacial interaction between the exfoliated 2D crystal nanosheets and the liquid medium, it is crucial to choose the right liquid medium for exfoliation. Organic solvents usually offer high yields and stable graphene dispersions, making them the ideal solvents for LPE. In these solvent types, some of the most researched 2D materials, including h-BN, MoS_2 , and WS_2 , also exhibit remarkable exfoliation efficiency [10].

The liquid-phase exfoliation approach is comparatively easy to use compared to the redox and CVD

methods, and it can be used for commercial preparation of certain 2D materials. The addition of biomolecules as a stabilizer is typically beneficial for effective stripping and can improve preparation efficacy because certain 2D materials, like graphene, TMD, and h-BN, are more hydrophobic in nature than bulk materials. For instance, researchers can enhance outcomes in a conventional liquid-phase exfoliation experiment for two-dimensional material by utilizing the hydrophilicity of bovine serum protein [11]. However, it is important to note that liquid-phase exfoliation has a number of serious drawbacks. Above all, as-produced nanosheets often exhibit wide lateral size dispersion and thicknesses. Additional, smaller issues include the re-aggregation of nanosheets during film generation and deposition, as well as the challenge of fully eliminating dispersants like solvent, surfactant, or polymer molecules [12].

2.3. Mechanical Exfoliation Method

Micro-mechanical exfoliation (MME), first developed by Novoselov and Geim in 2004 for the synthesis of graphene, gained immense popularity for the synthesis of two-dimensional materials because of its affordability and adaptability, while preserving the crystal's structure and characteristics. In this procedure, an atomic layer of thick graphene is exfoliated from the bulk graphite mesas using basic scotch tape, and then the exfoliated layers of graphene are deposited on the substrate. AFM (atomic force microscopy) tips have been used by a number of different researchers to attempt micro-mechanical exfoliation by applying a lateral force. These efforts, however, failed to produce a single or a small number of graphene layers. Using micromechanical exfoliation, various non-carbonaceous 2-D-layered inorganic compounds, such as the MX_2 collection of substances, were successfully generated beyond graphene [13].

2.4. Electrochemical deposition

Electrochemical deposition is a technique that deposits a material containing a composite layer nanostructure onto a desired substrate by means of electrical current. Essentially, an electrochemical system with two or three electrodes is used in this procedure. Many researchers have recently turned to electrochemical deposition techniques for the 0D, 1D, 2D, and 3D NSMs. The 0D, 1D, 2D, and 3D NSMs were electrodeposited using pulse electrochemical deposition (PE) in an electrochemical deposition facility set up with three electrode cell systems. Saturated calomel electrode (SCE), sample, and thin Pt. wire were utilized as the working, reference, and counter electrodes, respectively. The depositing of nanoparticles on the substrate is influenced by four operation parameters in the PE. Higher potential, lower potential, on-time potential, and off-time potential. Using a time interval of precisely one second throughout the entire experiment, 0D, 1D, 2D, and 3D NSMs were applied to the working electrode. In contrast, we only used the counter electrode and working electrode in a two-electrode electrochemical system [9].

3. Importance of wastewater treatment:

The need for clean water has increased as a result of the rapid industrialization, urbanization, and population growth that have severely stressed and contaminated water resources. Water pollution has been connected to water as it is the liquid that can absorb the greatest number of things on Earth. The water supplies and the expanding economy are particularly vulnerable to pollution from wastewater from the textile industry. This characteristic makes it simple for waste, chemicals, plastics, and other dangerous things to poison water resources including streams, lakes, reservoirs, and the sea. According to the World Water Council, there will be about 3.9 billion individuals living in water-scarce places by 2030. Due to the current and impending scarcity of water, there is an increased need for wastewater treatment in order to make it fit for use in residences, commercial buildings, and agricultural operations [14].

Wastewater management and potable water purification are critical to sustaining human society's rapid development while reducing pollution and health risks. Reducing the amounts of solids, biodegradable organic matter, pathogens, and other hazardous chemicals in wastewater to comply with regulatory standards that safeguard the environment and public health are the primary goals of wastewater treatment. Wastewater pollution is commonly expressed in terms of suspended particles, total dissolved solids (TDS), dissolved oxygen (DO), chemical oxygen demand (COD), and biochemical oxygen demand (BOD). In order to accomplish the aforementioned goals, wastewater treatment systems use a combination of physical, chemical, and biological methods to remove pollutants from wastewater [15].

In this scenario, wastewater treatment becomes critical. The deliberate removal of microorganisms, inorganic matter, and organic matter from wastewater is known as wastewater treatment. To provide clean drinking water or to safeguard our water resources, contaminants must be eliminated. The environment and human dwellings must be secure when using the filtered water. To eliminate contaminants from water, a variety of wastewater treatment techniques have been created over time and are continuously being developed [16]. Based on research findings, treating wastewater with two-dimensional (2D) materials is a viable option that could save costs in comparison to conventional methods. The excellent ability to transfer electrons, mechanical properties, thermal and electrical conductivity, and chemical properties of 2D materials, like graphene, which was discovered in 2004 and has a single- or few-layer thickness, have made them suitable for wastewater treatment. In the areas of water purification and other environmental remediation applications, a wide variety of additional 2D nanomaterials, including Mxenes, metal organic frameworks, and graphitic carbon nitride, have been investigated and are the subject of intensive and extensive studies [15].

4. Traditional methods and its limitations used for wastewater treatment:

4.1. Coagulation

Coagulation is the process by which insoluble flocks are created in water through a series of physical and chemical processes involving the water's alkalinity, contaminants, and coagulant(s) introduced to the mixture. These are agglomerations of the colloidal and dissolved matter from the water that has been adsorbed by these reaction products and removed from the water, in addition to the suspended particles in the untreated water and the reaction products of the additional chemicals. Coagulants can be synthetic organic polymers, such as polyethylenimine and derivatives of polyacrylamide, or inorganic polymers, like aluminum sulfate and polyaluminum chloride. Natural coagulants, on the other hand, include chitosan and microbial coagulants [17]. The primary drawback is that it produces secondary pollutants that are detrimental to the environment and human health, necessitating additional secondary treatment in order to completely remove them. Its broad usage range is further limited by the massive sludge formation caused by the extensive use of chemicals. Cadmium, chromium, nickel, lead, and zinc were among the heavy metals found in the sludge formation that resulted from the coagulation process [18].

4.2. Ion Exchange

Another popular method for eliminating heavy metals from wastewater is the ion exchange process. This method uses an ion-exchange resin, synthetic or natural, that has the unique capacity to exchange its cations with the metals present in the wastewater. Ion-exchange resins are long-chain, cross-linked organic polymers that are microporous and contain exchangeable ions. It is found that synthetic resins are frequently employed due to their effectiveness and complete capacity to remove heavy metals from solutions [19]. Ion-exchange resins are simple to work with and recycle, making them ideal for repeated usage. On a commercial basis, obtainable ion-exchange resins are very costly, though; hence, a number of low-cost substitutes have been thoroughly investigated. These substitutes include processed and unprocessed cellulosic biomasses. Although ion-exchange resins are widely used, disposing of them can be problematic because synthetic ion-exchange resins do not biodegrade [20].

4.3. Membrane Filtration

In the field of water purification, the use of membranes technology is developing. Depending on the driving power and the ways of ionic and molecular transport via membrane, the membrane's structure can be dense or porous. Excellent results were obtained from the membrane filtering approach for removing toxic metals from wastewater. Reverse osmosis, ultrafiltration, microfiltration and nanofiltration are just a few of the membrane types that

have been effectively employed to extract harmful metal ions from wastewater. The main shortcomings of this approach are handling rejection, contamination of the membrane, and expensive power expenses. Generally speaking, this treatment technique has been successful in treating industrial wastewater effluent, creating drinking water, desalinating saltwater, recovering valuable components from industrial effluents, and producing salts [18].

4.4. Chemical Precipitation

Chemical precipitation is one of the methods most frequently employed in industry to remove heavy metals from inorganic wastewater due to its straightforward operation. The heavy metal hydroxide, sulfide, carbonate, and phosphate precipitates are insoluble and are created by these traditional chemical precipitation methods. This method produces insoluble metal precipitation by interacting dissolved metals in the solution with the precipitant. Chemical precipitant treatments are used to raise the size of the particle in order to eliminate extremely tiny particles created during the precipitation process as waste. The metals can be readily removed after they precipitate and solidify, and low metal concentrations can be released [21]. Due to their degree of effectiveness, moderate precipitant (lime) cost, and simplicity of automatic pH control, the most widely used precipitation techniques include both sulfur dioxide and hydroxide treatment. But there are a number of drawbacks to the chemical precipitation process. For instance, most heavy metal ions in the solution are acidic, and sulfide reagents in acidic solutions can produce toxic hydrogen sulfide gas, which is harmful for the environment and human health. The tiny particle size of the toxic metal sulfide makes it complicated to filter. Furthermore, when the pH goes above the ideal range, the insoluble hydroxide of amphoteric metals, including copper and chromium, tends to form water-soluble coordination complexes. The equipment is corroded by the potent alkaline precipitating agents [22].

4.5. Electrochemical Methods

The most efficient method for degrading various types of contaminants is the electrochemical process. The electrochemical processes are in a moderate state of repair. The method can be employed with different technologies and is dependent on the electrolytes in solution, pH, applied potential, and electrodes. Electrochemical processes are more appealing among the different methods suggested for the comprehensive degradation of a significant variety of contaminants pertaining to organic pollutants. This method has many benefits, including complete mineralization, minimal or no need for chemical reagents, the prevention of the emergence of new harmful species, and the lowest feasible energy expenditures. Additionally, there are two drawbacks, such as the large initial investment and the possibility of electrode fouling [23].

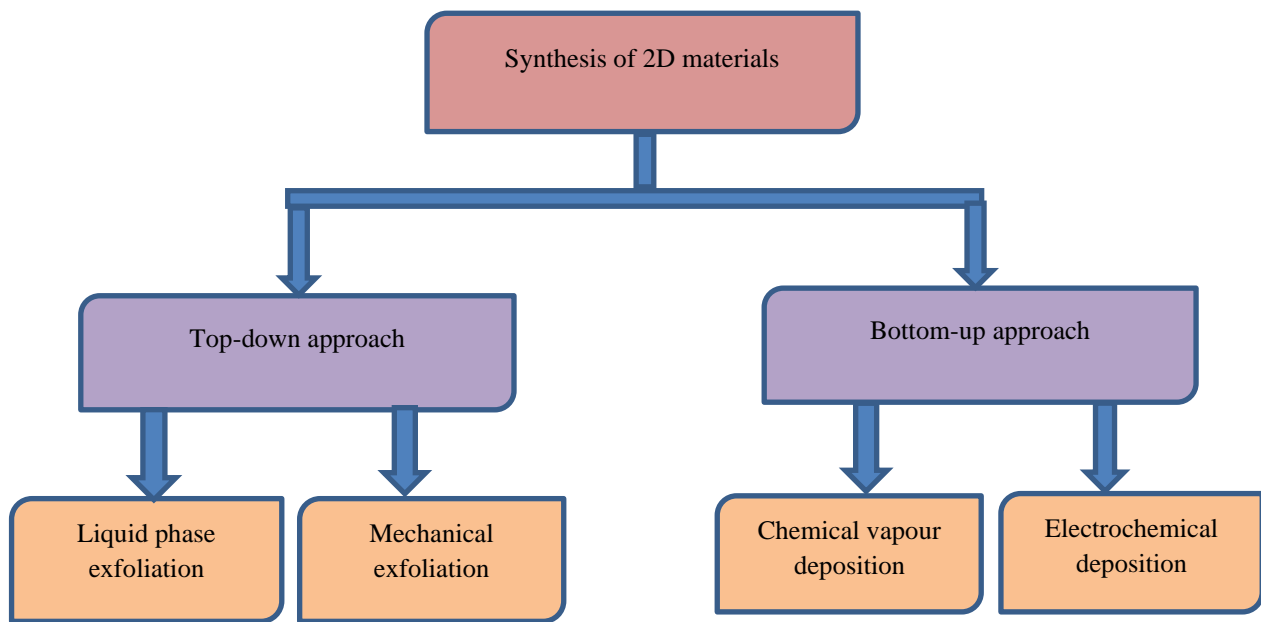


Figure 1. Fabrication methods of 2D materials

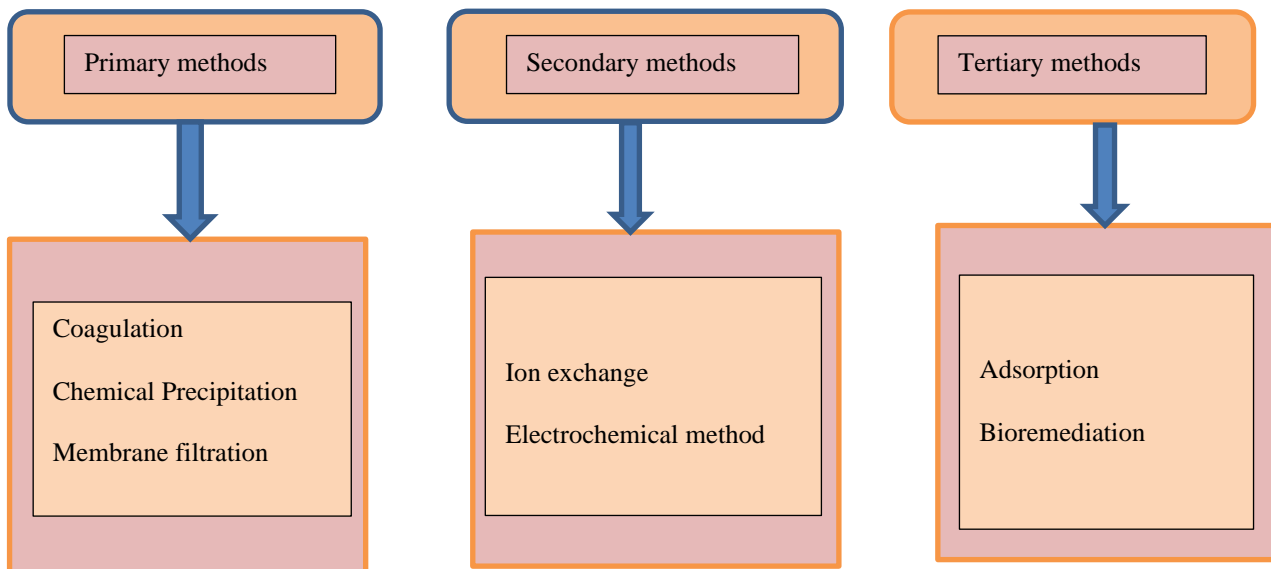


Figure 2. Some conventional waste water treatment methods

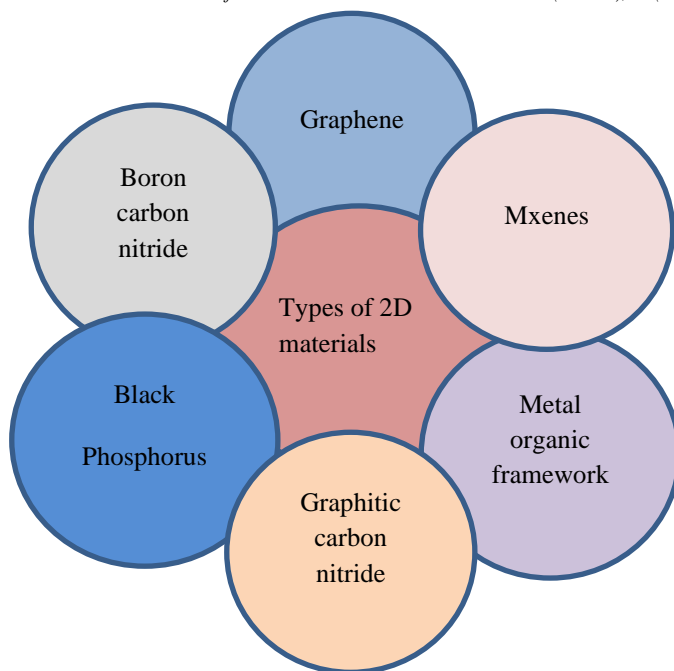


Figure 3. Different types of two dimensional materials

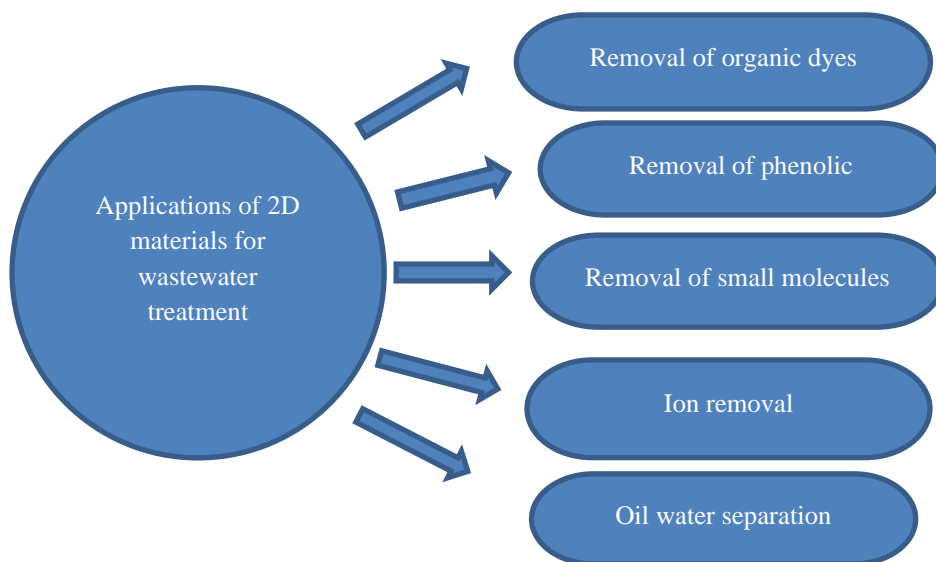


Figure 2. Applications of 2D materials

Table 1. Properties and applications of 2D materials for wastewater treatment

2D materials	Properties	Applications
Graphene	Great mechanical strength, high resistance	Heavy metal adsorption such Pb ₂ ,Cd ₂ etc.
Graphitic carbon nitride	High adsorption capacity, regeneration ability,	Removal of organic dyes such as rodamine B, methylene blue, Evans blue
MXenes	Superior electrical conductivity, high chemical stability	Desalination ,oil water separation, catalysis
Black phosphorous	Chemically inert, high thermal conductivity	Contaminant or pollutant adsorption
Metal organic framework	Large surface area ,high porosity, catalytic properties	Catalysis, removal of antibacterial from wastewater
Boron carbon nitride	Semiconductor, High thermal stability,	Removal of ions such as Li ⁺ ,K ⁺ Ca ²⁺ ,Mg ²⁺ etc

4.6. Bioremediation

The term "bioremediation" describes the biological process of contamination decomposition in the environment that uses the metabolic abilities of microorganisms to degrade a variety of organic materials. The primary advantage of bioremediation is its lower cost compared to conventional techniques. Not only is it an affordable permanent treatment, but it also has the potential to cause the contaminant to completely mineralize. It is also a non-invasive process that doesn't negatively impact the ecosystem. Lower toxin concentrations that would be hard to remove using physical or chemical methods can be eliminated by bioremediation [24]. One of the main drawbacks of using bioremediation as an approach to treating pharmaceutical wastewater is that, while there are a variety of bioremediation techniques available for industrial wastewater, not all of them have been thoroughly investigated for use in treating wastewater produced in the pharmaceutical industry. It is frequently noted that although microorganisms are present in water streams in large quantities, their activity is ineffective; this may be due to a deficiency in nutrients like phosphate or nitrogen. An additional constraint of bioremediation as a methodology is its often restrictive restriction to biodegradable contaminants and its highly selective nature, which may pose challenges in its application for treating a range of xenobiotic [25].

4.7. Adsorption

Adsorption is essentially a mass transfer process that involves moving solutes or detachable species from a flowing phase onto a solid phase's surface. Adsorbed species are confined to the solid surface via physiochemical interactions. Adsorption is regarded as an advanced method for eliminating colors from wastewater since it is less complicated and expensive compared with other techniques. Adsorption can have a removal effectiveness of up to 99.9%. Among other methods for treating wastewater, the United States Environmental Protection Agency (USEPA) named the adsorption process as one of the greatest and most effective. Conventional adsorbents such as clay, metal oxides, silica, alumina, activated carbon, titania, and bioadsorbents are the most often utilized for eliminating pollutants and dyes [26].

5. Types of two dimensional materials and their usage in wastewater treatment

5.1. Graphene

The thick sheet known as graphene is made up of single-atom, two-dimensional (2D) sp^2 hybridized carbon atoms that are assembled in a hexagonal structure via sigma and pi bonding. It is available in multiple forms, such as reduced graphene oxide, oxide of graphene, and original graphene [27]. Because of its special mechanical, chemical, and physical characteristics, graphene can be used to remove toxic metals from water. Graphene is a stronger adsorbent than activated carbon (AC) for treating polluted water because of its mostly delocalized p electrons and modifiable

chemical properties [28]. Functionalized graphene was created via the electrolysis process and subsequently employed as a sort of adsorbent to extract Pb_2 and Cd_2 from polluted water [29]. The highest absorption capacities were attained in 40 minutes for Pb_2 at pH 5.1 and Cd_2 at pH 6.2, respectively, at 406.6 mg/g and 73.42 mg/g. The scientists indicated that Pb_2 has a maximum adsorption capacity of 1308 mg/g. The sorbent is suited for use in large-scale water purification because it is recyclable and environmentally acceptable [30].

5.2. Graphitic carbon nitride ($g-C_3N_4$)

2D, or graphitic carbon nitride ($g-C_3N_4$), is a relatively novel material, having only recently been synthesized. The first graphitic carbon nitride ($g-C_3N_4$) nanosheets, which are extremely thin, were produced in 2012. The 2D nano-adsorbent known as graphitic carbon nitride has been found to be the strongest allotrope of carbon nitride. Guanidine hydrochloride produced in $g-C_3N_4$ was examined for its capacity to extract cadmium, lead, and chromium from water [31]. The majority of lead and cadmium adsorbed on the tri-s-triazine units occur through electrostatic interaction, while the majority of anionic chromium adsorbed on the $g-C_3N_4$ external surface. After 10 regeneration cycles, 80% of the $g-C_3N_4$ adsorption ability is still retained [32]. In contrast to graphene or graphite, $g-C_3N_4$ is easier to synthesize in large quantities and can be utilized as a material for composites. $g-C_3N_4$ was synthesized using the salt technique, which eliminated Cu_2 , Cd_2 , Pb_2 , and Ni_2 . The high efficiency of sorption and exceptional renewal ability of both graphene oxides and $g-C_3N_4$ allowed for their cost-effective usage in the removal of metallic substances from wastewater [33]. Even though $g-C_3N_4$ synthesis and application have experienced certain limits in managing environmental contamination, the material is still a promising adsorbent for removing heavy metal anions and cations from wastewater. Future reactor developments should focus on developing appropriate reactors in order to reach practical applications in wastewater treatment [30].

5.3. MXenes

One of the biggest families of two-dimensional materials, MXenes are ceramics made of transition metal carbide or nitride materials. These man-made substances have the general formula $M_{n+1}X_nT_x$. In this case, X stands for carbon or nitrogen, and M is an early transition metal. T stands for groups of surface termination. An integral number between 1 and 3 is denoted by the symbol x, which stands for the number of surface functional groups [34]. Their attributes include superior electrical conductivity, high chemical stability, and environmental friendliness. 2D nanomaterials are ideal for wastewater treatment applications because of their large specific surface area, large lateral size, and nanometer thickness [30]. The most extensively researched MXenes is titanium carbide ($Ti_3C_2T_x$). According to research by Peng and coworkers these 2-D $Ti_3C_2T_x$ nanosheets demonstrate a new promising function for environmental pollutant decontamination due to their substantial specific surface area (SSA), reducibility, and good dispersibility following the etching of the Al layer and exfoliation to 2-D

nanosheets. They reported on the unique adsorption activity of fluorine treated with alkalization intercalation and titanium carbide with hydroxyl-coated Ti surfaces for hazardous Pb (II) in the extremely neutral solution. The remarkable reductive elimination performance for hazardous Cr (VI) is also demonstrated by these 2-D $Ti_3C_2T_x$ nanosheets with fluorine and hydroxyl coated Ti surfaces. The WHO criterion for purified drinking water (0.05 ppm) may be met by treated water with a residual Cr (VI) content as low as 5 ppb. These two-dimensional $Ti_3C_2T_x$ nanosheets offer an all-purpose technique for the reductive elimination of hazardous oxidants from water [35].

5.4. Black phosphorus

BP was first discovered in 1914, and for the next 100 years, it received less and less attention. One bright spot in the single elemental 2D material space that may bridge the gap between graphene and 2D TMDs is black phosphorus. One of the elements that is most prevalent on Earth is phosphorus, which makes up around 0.1% of the planet's crust. There are four main forms of phosphorus: white phosphorus (WP), red phosphorus (RP), violet phosphorus (VP), and black phosphorus (BP). Of the four, BP is the most thermodynamically stable and is toxic. In the field of photocatalysis, semiconductor BP, an advanced two-dimensional material, has been identified as a formidable rival to post-graphene. An anionic dye called RB 5 and a cationic dye called Rho B were extracted from wastewater in 2014 by Lee's group using a novel hybrid material called BP@TiO₂. As a consequence, the apparent rate constants of BP@TiO₂ for Rho B and RB 5 under visible light illumination were 2.05 and 2.38 h⁻¹, respectively [36].

5.5. Metal organic framework

Coordination polymers called metal-organic frameworks (MOFs) are made up of extremely porous organic-inorganic hybrid frameworks. Their structures consist of natural ligands act serving as linkers and metal centers acting as connectors [37-38]. According to researchers, MOFs have an extensive range of designability with respect to shape and pore formation, [39-40]. These characteristics hold significant potential for tackling various issues, such as catalytic and adsorption processes used to remove emerging contaminants [41]. Very positive findings have been gained by studying the use of MOFs in photocatalytic and adsorption degradation processes to lower the concentration of both inorganic and organic contaminants [42].

5.6. Boron carbon nitride

BCN is a novel semiconductor material that possesses the outstanding chemical and thermal stability of h-BN. The conjugated sp² hybridized C atoms in the ternary BCN semiconductor are arranged in an electron system known as a honeycomb lattice, with C injected into the lattice. BCN materials have great thermal conductivity, excellent chemical resistance, exceptional strength, and flexible electrical properties that make them appropriate for a variety of harsh environmental applications [43]. The use of

BCN nanosheets in wastewater treatment, as well as information on their manufacturing processes, removal capabilities, adsorption capacities, readabilities, and ability to produce value-added materials. Peng and colleagues discovered that pyrolyzing melamine and boric acid was necessary for the one-pot production technique of BCN nanosheets in order to get rid of heavy metal ions. Furthermore, after six cycles of adsorption and desorption, the BCN nanosheets demonstrate remarkable chemical stability, holding onto more than 90% of their adsorption [44].

6. Mechanism of wastewater treatment by using 2D materials

6.1. Adsorption and catalytic activity of two dimensional materials:

6.1.1. Adsorption

Adsorption is a natural method wherein a few components of a fluid mixture are transported to the outermost layer of a solid substance through chemical or physical interaction, changing the level of concentration in relation to adjacent phases [45]. Adsorption techniques are frequently used in industrial settings to treat wastewater and separate compounds. Numerous appealing characteristics of this technology include its affordability, simplicity in design and use, and resistance to harmful substances. For the adsorbent to be used effectively for a long period of time, it also needs to have good mechanical properties like abrasion resistance. Adsorbents come in a variety of forms for a wide range of uses. Adsorbents such as silica, polymers, activated carbon, activated alumina, zeolites, and clay are frequently utilized in various applications [46].

6.1.1.1. MOFs as adsorbents

Due to their substantial surface areas, continuous porosity, and modifiable functional groups, MOFs are considered among the most promising adsorbents for controlling ecological contamination and effectively eliminating various pharmaceutical products [47]. As a result, MOFs are seen as a potentially useful material for effectively removing pharmaceutical contaminants from water. In an aqueous environment, for example, researchers have documented the adsorption of nonsteroidal anti-inflammatory medications using water-stable zirconium MOFs (UiO-66, MOF-802, and MOF-808). The sorption abilities were significantly enhanced by the synergistic influence of chemisorption by cationic Zr (Zirconium) and ligand-drug π - π (pi-pi) interactions [48].

6.1.1.2. MXenes as adsorbent

It is well known that MXenes use chemical and electrostatic interactions to adsorb metal ions, organic dyes, and other anionic pollutants. Electrostatic interactions may control the uptake of metals via MXenes. Researchers utilizing MXenes on Uranium (U (VI)), the most extensively researched radionuclide, have revealed that the surface area and interlayer space are critical for the electrostatic

adsorption of U (VI). In 6 hours of contact time, studies using hydrated $Ti_3C_2T_x$ intercalated with dimethyl sulfoxide (DMSO) demonstrated an adsorption capacity of 160 mg/g, larger interlayer spacing may therefore enhance metal ion sorption on MXenes. Graphene oxide, carbon nanotubes (CNT), and other materials exhibit much weaker adsorption capacities for metal ions, radionuclides, and non-ionic atoms than do traditional adsorbents. For example, Alk-MXene ($Ti_3C_2(OH/ONa)_xF_{2-x}$) exhibited an adsorption capacity of up to 140 mg/g, which is deemed high in comparison to traditional Pb adsorbents. What's more, the interlayer spacing and functional charge of Pb allowed Alk-MXene to react with it quickly, reaching equilibrium in about 2 minutes—eight times faster than sodium alginate-functionalized $Ti_3C_2T_x$ [49].

6.1.1.3. BCN based adsorbents

Adsorption is a straightforward process with high removal efficiency that is the most popular and promising approach in wastewater treatment operations. Wastewater contains high concentrations of pollutants and contaminants, which have been investigated using a variety of adsorbents. Considerable research has been done on the adsorption capabilities of BCN-based adsorbents for the removal of dyes, heavy metals, and antibiotics from water. With a large surface area of 890 m²/g, novel flower stamen-like BCN nanoscrolls were created using an easy method for water purification [50].

6.1.2. Catalytic activity

As a good adsorbent or active catalyst for wastewater treatment, MOFs are a promising option due to their structural flexibility. Organic linkers, metal centers, and functional groups determine the adsorptive or catalytic efficiency of MOFs. As per scientists, the MOF serves to stabilize the incorporated material and occasionally functions as a catalyst's size-selective support [51]. A number of studies have documented the successful use of MOFs as a catalyst to remove dangerous contaminants [49-52].

6.1.2.1. Photocatalytic processes

It is a relatively recent advancement to use MXenes for photocatalytic activities to remove pollutants from waste water [53]. Through photocatalytic degradation in the presence of ultraviolet (UV) radiation, MXenes can remove environmental pollutants [54]. TiO_2/TiC_2 and $In_2S_3/Ti_3C_2T_x$ are two examples of MXenes nanocomposites that show promise for photocatalytic applications. When $TiO_2/Ti_3C_2T_x$ nanocomposites are exposed to UV light, they outperform conventional TiO_2 photocatalysts in terms of organic pollutant adsorption and photocatalytic degradation, such as methyl orange (MO). The researcher reported that with $TiO_2/Ti_3C_2T_x$ nanocomposites, around 98% of MO was broken down after 30 minutes, as opposed to approximately 77% when using TiO_2 photocatalysts within the same circumstances [1-54]. Likewise, hybrid indium sulfide (In_2S_3) containing the additive $Ti_3C_2T_x$ demonstrated a MO degradation rate of 0.05 min⁻¹ from contaminated waters, roughly three times greater than that of pure In_2S_3

photocatalysts and approximately six times greater than that of pure $Ti_3C_2T_x$ [55].

6.2. Pollutants and their degradation by 2D materials

It is estimated that each year, 0.28 million tons of dyestuff from the food, pharmaceutical, and textile industries end up in rivers and other freshwater streams. These artificial dyes have a detrimental effect on people as well as inhibiting aquatic photosynthesis and depleting dissolved oxygen [56]. In the past, many reports in the literature have discussed the removal of congo red, methylene orange, and methylene blue from waste water. Numerous studies also employ graphene materials and composites in conjunction with the widely recognized photocatalysis technique to remove heavy metal ions from wastewater. g- C_3N_4 functions as a proficient electrocatalyst and photocatalyst. The use of g- C_3N_4 composites for photocatalytic degradation of industrial effluents has been demonstrated by a number of researchers. When g- C_3N_4 is photocatalytically active, it causes a wide range of organic pollutants to photodegrade and evolve into O_2 or H_2 [57]. The effectiveness of a few others recently developed 2D materials, including titanium carbide ($Ti_3C_2T_x$) sheets, 2D BN nanosheets, and molybdenum disulfide (MoS_2), has been investigated in recent years. Molybdenum disulfide (MoS_2) has antibacterial disinfecting qualities helps de-salt contaminant and pollutant adsorption, and acts as a co-catalyst for the degradation of hazardous pollutants. The hydrophilic 2D boron nitride nanosheets have a remarkable mechanical strength of 23.4 GPa. Excellent conductivity and strong structural and chemical stability make titanium carbide ($Ti_3C_2T_x$) a valuable material for the adsorption of pollutants and molecule separation [58]. Recent developments in nanotechnology have given rise to the creation of fresh plans and techniques for protecting the environment from pollution. Among the countless methods that have been developed, scientists are particularly interested in the adsorption technique. The found 2D materials such as graphene, MXenes, metal organic framework natural and other adsorbents have been used for water and wastewater treatment based on their molecular properties, porosity, topography, and thermal stability. The potential of the aforementioned 2D materials (g- C_3N_4 , TiO_2 , graphene, and other composites) as photocatalysts for wastewater purification has been examined [57]. Compared to adsorption, photodegradation is supposedly a better technique for treating wastewater because it eliminates the pollutant entirely rather than just transferring it through a phase change, negating the need for additional treatment. Researchers created a magnetic (M-) MIL-101 (Fe)/ TiO_2 composite to study the photodegradation of tetracycline under sun radiation [59]. The catalytic efficiencies of M-MIL-101 (Fe)/ TiO_2 (magnetic) and MIL-101 (Fe)/ TiO_2 (non-magnetic) were investigated under sunlight after tetracycline (TC) transformed over a period of three hours. The efficiencies that were achieved were 91.24 and 84.85%, in that order. Process optimization studies conducted under direct solar irradiation showed that 1 g/L of catalyst in a 20 mg/L aqueous solution of TC at an initial pH of 7 at 25°C could accomplish 92.76% TC conversion in 10 minutes. After being magnetically isolated from the solution, the material performed similarly after five catalytic cycles [42].

7. Applications of 2D materials for wastewater treatment

7.1. Removal of small molecule

Wastewater containing hazardous and toxic substances like antibiotics and color compounds is released by industries with excessive water consumption. Small-molecule pollutants may be effectively separated and removed from wastewater thanks to the unique physicochemical properties of MXene-based membranes, such as optimal layer spacing and excellent adsorption. The adsorption of organic dyes was described using a porous MXene/single-armed carbon nanotube membrane [60]. The researchers employed a commercially available hybrid cellulose filter that deposited the MXenes nanosheets, leading to an extremely thin, self-assembled composite membrane that showed higher permeability, eliminating almost 100% of methylene blue in comparison to the commercial UTC60 membrane. Their findings showed that the maximum amount of methylene blue that the p-MXenes/SWCNTs membrane could adsorb was 28403.7 mg/g and that it also does not cause secondary contamination when reused [61].

7.2. Removal of natural dyes

The primary global source of natural dyes is waste water dyeing, which was leading to alarms about potential effects on aquatic ecosystems. The natural components Rhoda Mine B, methyl blue, and methylene blue are frequently encountered in wastewater dyeing. These organic dyes are genetically toxic materials that may lead to birth abnormalities and issues with the food web [62]. Conventional membranes have a restriction on the removal of dye molecules shorter than the membrane's pore diameters. To address these problems, a variety of g-C₃N₄-based composite membranes have been studied to facilitate the purification of water and wastewater [63]. Scientists constructed synthetic nanopores and spacers to produce g-C₃N₄ nanosheets (CNNS), which were subsequently vacuum-filtered onto anodic aluminum oxide (AAO) membrane surfaces. Larger particles were discarded, and spacers might transmit water between the partially exfoliated g-C₃N₄ and the nanopores via nanochannels. Furthermore, the nanochannels were stable at pressures up to 6 bars and a pH range of 1–11. 87.2% of EB and 75.5% of RhB were rejected by the generated membrane more effectively than by pristine polyethersulfone (PES) membranes. Based on these discoveries, a unique Fe(OH)₃/g-C₃N₄ nanocomposite membrane was created by vacuum condensation and filtration. [64]. The Fe(OH)₃/g-C₃N₄ membrane could remove 99.9% of the EB molecules in 10 mg/L of solution [65]

7.3. Elimination of phenolic compounds

Phenols and their derived compounds are extremely harmful to both humans and the environment; hence they must be removed before being released. g-C₃N₄-based composite membranes have garnered a lot of attention because of their enhanced efficacy over conventional membrane filtration. When exposed to phenol molecules under UV light, the hybrid membrane degraded the phenol (10 mg/L) at a rate of 35.8%. This was mostly due to photo-

degradation rather than physical size sieving. For the phenol (10 mg/L), a degradation rate of 35.8% could be obtained when the hybrid membrane was exposed to phenol molecules under UV irradiation. Technology and membrane filtering were combined into one system. Phenol will eventually be eliminated by membrane filtration in conjunction with the PEC method and a visible-light reaction. When external voltages of 1.5 V and the exposure of visible light were implemented simultaneously, 94% of the detection of phenol disappeared; in contrast, the removal ratios for membrane filtering alone were only 7% and 26% with exposure to visible light, respectively [66].

7.4. Ion removal

Desalination is an important field that has to develop rapidly on a worldwide basis. When desalinating water, MXene nanosheets are an excellent material to utilize. Based on the principles of chemical screening and the charge impact, MXene-based membranes have the ability to substitute traditional nanofiltration technologies because of their selectiveness for low-valent ions of salt that are found in water. Its layer spacing of approximately 1 nm is predicted to create nanometer-scale penetration channels. Scientists announced the first attempt to perform cation-selective screening using micron-sized MXene membranes [67]. Their results showed that the charge size and hydration radius of an ion impact its penetration rate. When large-charge cations, such as Na⁺, were contrasted with single-charged cations, such as MXene nanosheets spacing, the former demonstrated noticeably reduced penetration rates. The modified membranes demonstrated a higher desalination performance than the unmodified MXene membranes, with refusal of K⁺, Na⁺, and Mg²⁺ continuing to be over 99% [68].

7.5. Separation of Oil from water

The unique wettability principle of 2D material makes it suitable for building an oil-water separation membrane. According to wettability theory, MXene nanosheets' unique wettability is attributed to their hydrophilic contact angle, which is less than 90°. A 2D MXene membrane's stacking and intercalation will create more textured and rough pores on its solid surface, hence boosting the quantity of transporters for liquid film development and penetration. This will enhance the oil-water separation performance of the MXene-based membrane. The first MXene/polyethersulfone composite membrane was created and demonstrated good oil-in-water emulsion separation performance. Moreover, it rejects oil more frequently in an environment with a high concentration of salt. The aforementioned research demonstrated the ability of an MXene-based membrane to separate water from oil [69].

8. Challenges and future perspectives

2D nanomaterials can be synthesized by several approaches for multiple purposes. However, multifunctional 2D nanomaterials are still needed in other fields, as they have uses in energy conservation, photocatalysis, antimicrobial, and wastewater treatment. A more comprehensive knowledge of the chemistry involved in a synthetic method would enable

one to alter reaction parameters, such as the amount of pressure, temperature, catalyst, quantity, amount of light, duration, and synthesis methodology, in order to produce application-specific 2D nanomaterials. When it comes to producing 2D nanomaterials, top-down and bottom-up methods offer benefits and drawbacks. Consequently, the development of an application-specific synthesis protocol is required to produce 2D nanomaterials in the lab with the required characteristics. With applications in solar panels, space exploration, medical, antimicrobials, textiles, detectors, agriculture, and environmental protection, 2D nanomaterials have a bright future awaiting them.

Compared to 0D and 1D nanomaterials, the main challenge in the synthesis of 2D nanomaterials is their isotropic crystal structure as well as their elevated surface energy. A relatively steady-state conductive polymer, graphene oxide sheet, metal-organic framework, and 2D nanomaterials based on dichalcogenides can all be used to solve this problem. Furthermore, an effective computational methodology is lacking in describing the mechanism of the creation of 2D nanomaterials, despite the existence of several ways for synthesizing them and multiple mechanisms postulated to explain the chemistry behind them. Furthermore, the control of 2D nanomaterials' thickness and lateral dimensions has received relatively little attention. To properly comprehend these materials for diverse applications, more study is necessary to manage the degree of thickness, lateral size, and morphology of 2D nanomaterials.

9. Conclusions

This review summarized and assessed the state-of-the-art research on novel 2D nanomaterials and their applications in water treatment, emphasizing the significant role of their 2D nanostructure and unique properties in membrane separation, photocatalysis, adsorption, and pollutant detection. The most popular synthetic 2D materials that have been employed for wastewater treatment were highlighted in the contribution, including MXenes, graphene family materials, metal-organic frameworks (MOF), and black phosphorus. A discussion was held regarding the properties of every 2D material, the standard synthesis and fabrication process, and the latest representative research. It is undeniable that the development of 2D materials has led to major advances in desalination and wastewater purification science and technology. Their many distinctive qualities, such as their uniform pore size, high porosity, and large specific surface area, could result in significantly lower treatment costs and less energy use for water purification. As of right now, research suggests that using 2D materials is one of the flexible separation technologies needed to meet water demand and facilitate water supply for businesses and cities. The review paper offers a thorough understanding of two-dimensional materials and their application in water desalination and purification.

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