#### **REVIEW ARTICLE**



# A state-of-the-art review on wastewater treatment techniques: the effectiveness of adsorption method

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## Abstract

The world's water supplies have been contaminated due to large effluents containing toxic pollutants such as dyes, heavy metals, surfactants, personal care products, pesticides, and pharmaceuticals from agricultural, industrial, and municipal resources into water streams. Water contamination and its treatment have emerged out as an escalating challenge globally. Extraordinary efforts have been made to overcome the challenges of wastewater treatment in recent years. Various techniques such as chemical methods like Fenton oxidation and electrochemical oxidation, physical procedures like adsorption and membrane filtration, and several biological techniques have been recognized for the treatment of wastewater. This review communicates insights into recent research developments in different treatment techniques and their applications to eradicate various water contaminants. Research gaps have also been identified regarding multiple strategies for understanding key aspects that are important to pilot-scale or large-scale systems. Based on this review, it can be determined that adsorption is a simple, sustainable, cost-effective, and environmental-friendly technique for wastewater treatment, among all other existing technologies. However, there is a need for further research and development, optimization, and practical implementation of the integrated process for a wide range of applications.

Keywords Recent developments · Wastewater treatment techniques · Adsorption · Efficient adsorbents · Industrial effluents · Pollutants

# Introduction

A hygienic living environment and safe drinking water are the basic requirements to support healthy living. Clean water is an essential element for domestic usage and is required for industrial and agricultural applications. The increased water usage would ultimately generate larger effluents of wastewater. Although more than 70% of the earth is covered with water,

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only 3% is suitable for human consumption, and the remaining 97% is salty water (Ahmad et al. 2019). Around four billion people worldwide face water scarcity for at least 1 month annually (Dongare et al. 2017). This life-sustaining asset is continuously being strained by the use of toxic chemicals in agricultural and industrial developments and population growth, which has led to the depletion of aquifers (Foster 2017; Shafiq 2018; Shafiq et al. 2019). Suitable water sources are required for human consumption, industry, agriculture, and recreation. Usually, a range of contaminations deprives us of this natural gift and forces us to set down to tackle a more challenging environment (Kannaujiya et al. 2019). There are several sources of water pollution: mining, industrial waste, sewage, pesticides, agricultural fertilizers, etc. (Crini and Lichtfouse 2019). Halogenated hydrocarbons, heavy metals, dyes, surfactants, organic compounds, salts, soluble bases, etc. are the key contaminants in wastewater effluents (Chauhan et al. 2019; Saravanan et al. 2019).

Due to the environmental concerns instigated by water pollution, several researchers have dedicated their efforts towards establishing novel wastewater treatment techniques (Nassar et al. 2017). To date, several strategies have been developed to minimize the wastewater discharges and mitigate the hazards of pollutants, including adsorption, membrane filtration, coagulation/flocculation, oxidation, biological treatment, etc. (Xu et al. 2018). The treatment of wastewater typically demands high costs because it is mandatory to effectively remove the pollutants present in the wastewater to make water clean and reusable. However, these wastewater treatment techniques are designed considering effluents' characterization and purification requirements, ignoring their impact on overall treatment performance and the environment (Khan et al. 2020). The conventional treatment methods available nowadays do not entirely remove the pollutants; instead, pollutants are concentrated or degraded into another phase (Yahya et al. 2018). Among all other techniques, adsorption is considered one of the most efficient techniques for wastewater treatment due to several characteristics, which are less efficient in the different comparable methods (Slatni et al. 2020).

Several researchers have recently devoted their struggles to search out the adsorbents with large surface areas, low-cost, and friendliness to the environment. The researchers found their way for efficient adsorbents in nano-sized materials, which have been observed as an essential material for removing dyes, heavy metals, organic compounds, etc., from the wastewater (Nassar et al. 2017). This review will critically analyze the techniques used for wastewater treatment and conclude with the most efficient method used for water purification with wide-ranging applications. Furthermore, the challenges encountered during this technique's application will be discussed and future perspectives will be outlined.

# Techniques used for wastewater treatment

Progressively developmental achievements are being accomplished in order to develop new strategies for wastewater treatment and fulfill the requirements of clean water (Ahmed and Haider 2018). However, it has been challenging to treat discharged water containing pollutants thoroughly with available methods (Nguyen and Juang 2019). Several techniques have been reported for wastewater treatment in the literature. They typically include physical, chemical, and biological processes that are considered effective enough for water treatment in many ways, as shown in Fig. 1. Their selection depends on various factors like dye concentration, sewage composition, cost of the process, or the additional impurities present in wastewater (Wawrzkiewicz et al. 2019). The distinctive features of each treatment method can be beneficial in one way but restricted in another. Treatment techniques that require high installation and running costs, increased processing time, low output, and produce toxic byproducts after treatment are often less considerable for industrial applications (Wong et al.

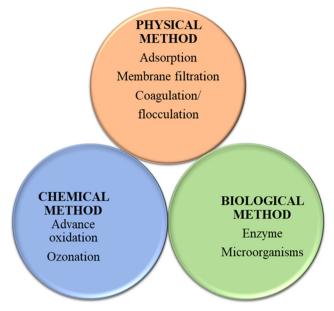


Fig. 1 Conventional and advanced techniques used for wastewater treatment

2019). Hence, it is crucial to find an alternative treatment system that can completely degrade or remove contaminants (Yahya et al. 2018).

# **Physical method**

Mass transfer strategy is the base of the physical pollutant removal methods (Samsami et al. 2020). It is more likely to be used due to its simplicity, flexibility, high efficiency, and pollutant recyclability (Foroutan et al. 2019; Wong et al. 2019). The fewer chemical requirement is another advantage of this approach. Physical treatment seems highly reliable than the other treatments because it does not depend on living organisms (Samsami et al. 2020). Among physical methods, adsorption has been used by researchers in recent years because of its high efficiency and low operational cost (Foroutan et al. 2019).

#### Adsorption

Adsorption is usually considered a cost-effective and reliable method for wastewater treatment (Liu et al. 2020). Adsorption is basically a process of mass transfer in which solute or removable species are transported from a runny phase onto the surface of a solid phase. By physiochemical interactions, adsorbed species are bounded to the solid surface, as shown in Fig. 2 (Manchisi et al. 2020). The removal efficiency of adsorption can range up to 99.9%. The United States Environmental Protection Agency (USEPA) declared the adsorption process as one of the most excellent and best wastewater treatment techniques, among others (Anil et al. 2020).

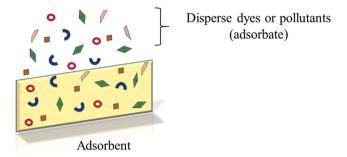


Fig. 2 General mechanism of adsorption to remove contaminants

Adsorption is considered a well-developed process for removing dyes from wastewater due to its simplicity and costeffectiveness compared with the other approaches. In this process, generally, adsorbate migration occurs in three sequential steps: (1) migration of adsorbate to the border shell of the adsorbent, (2) intraparticle diffusion into pores, and (3) adsorption and desorption of solute. The characteristics of adsorbate, adsorbent, and matrix control the rate of all these steps. In order to determine the maximum adsorption capacity of the material, adsorption isotherms are utilized. Adsorption isotherms are structured by plotting the adsorbed molecules per unit area of the interface versus the gas pressure or the liquid solution's concentration in equilibrium. Langmuir and Freundlich's isotherms are the most commonly used models to assess pollutant adsorption (Wong et al. 2020).

Preferably, an adsorbent should be provided with enough binding sites that can perform appropriate adsorption for dyes and other pollutants. The most commonly used conventional adsorbents for pollutants and dye elimination are bio-adsorbents, silica, alumina, activated carbon, clay, metal oxides, titania, etc. (Wadhawan et al. 2020; Prajapati et al. 2020; Prajapati and Mondal 2019). Activated carbon (AC) is considered the most efficient adsorbent material for removing many types of pollutants from wastewater (Azam et al. 2020; Liu et al. 2020). AC is non-toxic and low-cost material with high efficiency because of the porous structure and large surface area (Kamaraj et al. 2020). In the exploration of practical and economic adsorbents, bio-adsorbents (agriculturebased) have shown significant competency in dye removal and other wastes. Still, they possess the drawbacks like enhancing total organic carbon (TOC), biological oxygen demand (BOD), and chemical oxygen demand (COD) in wastewater (Chatterjee et al. 2020). Silica is an efficient adsorbent material due to the large surface area, uniform pore size, and potential catalysis applications (Slatni et al. 2020). Mesoporous silica is also considered a support material due to its large surface area and good accessibility for metals and metal oxides (Hussain et al. 2012). Nano silica has effectively been used in wastewater treatment as its efficiency relies on hydroxyl (OH) groups in numerous situations. Nano alumina is also one of the excellent materials for wide-ranging applications in wastewater treatment (Ahmed et al. 2020). But alumina has the limitation of compromised adsorption capacity. Thus, its modifications are still under the stage of development to overcome the deficiency (Kumari et al. 2020). Titania (TiO<sub>2</sub>)-based nanocomposite materials attract researchers' attention in materials science because of the broad possibilities of property modification (Tatarchuk et al. 2020). Mostly adsorption carried out by titania and its composites are based on electrostatic interactions of sulphonic groups of dyes (SO<sup>3</sup><sup>-</sup>) and protonate hydroxyl group (-OH<sup>2+</sup>) in acidic media. The proficiency of dye adsorption is determined by the presence of sulphonic groups in dyes' structure (Wawrzkiewicz et al. 2019). In recent years, nano-porous particles, especially titanium oxide (TiO<sub>2</sub>), Fe<sub>3</sub>O<sub>4</sub>, ZnO, and their composites have generated considerable interest due to their non-toxicity, physical and chemical stability, regular pore structure, uniquely large specific surface area, and exhibiting high catalytic efficiency. TiO<sub>2</sub> possesses high adsorption capacity and its modifications further enhance the surface area by controlling the growth of crystallites and gives higher porosity leading to high adsorption efficiency (Jaseela et al. 2019). Comparison of porosity and surface area of some of the commercially available adsorbents are listed in Table 1.

Nanomaterials have gained considerable interest nowadays as adsorbents in wastewater decontamination due to their large specific surface area, lower flocculent formation, and excessive accessible active sites for species binding. Moreover, these adsorbents can also be recycled and reused, making them highly attractive and cost-effective [12].

## **Membrane Filtration**

Separation or removal of dyes and organic matter by membrane filtration is among the most efficient and economically effective wastewater treatment techniques from different industries. However, membrane development with sufficient thermal stability and improved performance is still a challenging task. Hydrophilicity and surface charge of the membrane can help determine its rejection, permeability & antifouling performance (Yang et al. 2020). The general mechanism of membrane filtration is shown in Fig. 3.

(a) Nanofiltration

Nanofiltration (NF) technology has been revealed as a successful purification and separation method in treating wastewater. However, the performance of the NF membrane may severely be restricted by concentration polymerization and fouling. Fouling declines the membrane's permeability as it causes membrane pore blocking by forming a layer of organic compounds. Additionally, high salinity plays a negative role in the flux of membrane, as the osmotic pressure is high due to

Adsorbent	Nature	Particle density (g cm $^{-3}$ )	Surface area $(m^2 g^{-1})$	Reference
Activated carbon	Hydrophobic	0.5–0.9	400–1200	(Manchisi et al. 2020)
Silica gel	Hydrophilic/hydrophobic	1.09	750-850	(Manchisi et al. 2020)
Activated alumina	Hydrophilic	1.25	320	(Manchisi et al. 2020)
Titania	Hydrophilic	_	405	(Mironyuk et al. 2019)

 Table 1
 Properties of commercially available adsorbents for wastewater treatment

salt rejection. Hence, the NF membrane with the hydrophilic surface is desired under large throughputs for textile wastewater treatment (Zhu et al. 2020). Usually, commercial NF membranes at an industrial level have close-fitting surface morphologies, subsequent in high rejection of salts and organics (dyes); thus, the occurrence of permeation flux declines (Ye et al. 2020).

## (b) Ultrafiltration

The ultrafiltration (UF) method is of growing interest in dyeing and salt fractionation as it enables high salt penetration with improved permeation flux. Comparative studies reveal that UF membranes have high separation efficiency as it provides better salt permeation and maintains high throughputs due to low osmotic pressure. To prepare efficient UF membranes, a large number of polymeric materials containing polyacrylonitrile (PAN), polysulfone (PSf), cellulose acetate (CA), polyethersulfone (PES), and poly(vinylidene fluoride) (PVDF) have been used extensively explored (Yang et al. 2020).



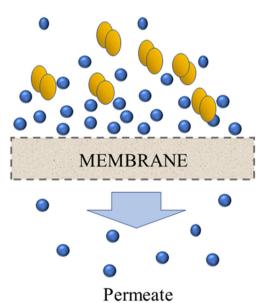


Fig. 3 General mechanism of membrane filtration to remove contaminants

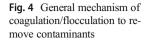
## Coagulation/flocculation

Coagulation-flocculation methods are sufficient for the decolorization of dispersing dye-containing wastewater. They have low decolorization efficiency for reactive and vat dye wastewater. Such techniques often limit their application due to poor decolorization performance and a significant generation of resulting sludge (Liang et al. 2014). Coagulation is a process in which dye solution systems are destabilized to form flocs and agglomerates. Flocculation is a method of destabilizing the suspended particles and joining aggregated flocs into larger agglomerates that settle down under gravity's influence (Lee et al. 2012; Zahrim et al. 2011), shown in Fig. 4.

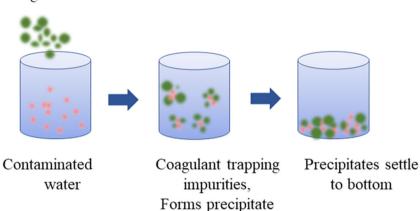
The coagulation-flocculation process is performed to counterbalance charges by bridging or trapping the suspended particles organized to form gelatinous agglomerates, large enough to be restricted in the filter or settle down. Coagulationflocculation is generally employed in textile industries to treat the wastewater as this is an economically feasible process, having low detection time and simple operation. In these techniques, coagulants like lime (Ca(OH)<sub>2</sub>), ferric chloride (FeCl<sub>3</sub>·7H<sub>2</sub>O), ferric sulfate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O), and aluminum sulfate  $(Al_2(SO_4)_3 \cdot 18H_2O)$  bind with the pollutants and other dispersed dyes to remove through the action of sorption, electrostatic force and bridging. The sorption and bridging help coagulate-flocculating dyes and pollutants from wastewater due to the protonated amine groups and polymer (high molecular weight), respectively. Coagulation-flocculation reduces the dissolved substances, suspended matter, colloidal particles, non-settable particles, and coloring agents from the wastewater effluent (Yogalakshmi et al. 2020).

#### **Chemical method**

Several chemical oxidation processes are reported for a range of catalysis applications (Shafiq et al. 2020, 2021). However, the advanced oxidation process is considered an essential technique for wastewater treatment. AOPs is an acronym that indicates all methods used in wastewater treatment that have common principles in generating oxidizing species, such as hydroxyl radicals (•OH) (Sicardi 2020). Oxidation may involve electrochemical oxidation, photo-electrochemical



## Coagulant added



oxidation and UV assisted Fenton's oxidation and ozonation. Generally, catalysts and pH play an essential role in the oxidation process (Ahmad et al. 2015). Advanced oxidation processes used for the treatment of textile wastewater are shown in Fig. 5.

## **Electrochemical oxidation**

The electrochemical advanced oxidation processes (EAOPs) has appeared as a promising technique for wastewater treatment (dye removal). EAOPs are environment friendly, as the electrons are inherently clean species, and no supplementary procedure is mandatory for removing dye sludge. Other benefits comprise high efficiency for the removal of pollutants, simple equipment, and easy handling. The main challenge that obstructs applications of EAOPs is increased energy costs with comparatively lower oxidation efficiencies. Attention has recently been paid to electrode materials' stabilities and catalytic activity improvement by the fabrication of different metal oxides on electrodes and doping.

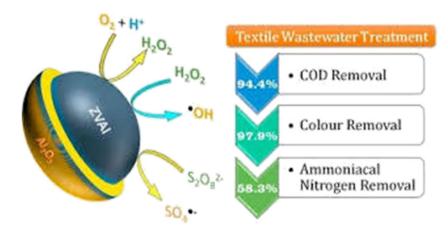
Electrochemical oxidation with pulse current supply is considered an exemplary method for energy efficiencies than traditional ones. Generally, Pulse electrolysis is accompanied by

Fig. 5 Textile wastewater treatment by advanced oxidation process (Khatri et al. 2018)

a stream of square-wave pulse current, in which the pulse cycle (T) involves a turn-off period (Toff) and a turn-on period (Ton). Current is provided as constant amplitude and intermitted at the turn-on period and the turn-off period, respectively. For this study, Methyl Orange (MO), Alizarin Red S (ARS), and Indigo Carmine (IC) were selected as descriptive azo dyes, anthraquinone dyes, and indigo, respectively, and they all were treated by electrochemical oxidation one by one with the anode (PbO<sub>2</sub>/Ti) under pulse mode. After treatment, it was concluded that with the optimized operating parameters, current density and pulse electrolysis have evident influence with dye degradation and the electrochemical oxidation process can save energy needs up to 47.9%, 41.0%, and 25.5% for MO, ARS, and IC, respectively (Wang et al. 2020).

## Photo-electrochemical oxidation

In order to achieve high removal efficiencies and degradation of pollutants, advanced oxidation processes (AOPs), based on the active and strong oxidizing agents like hydroxyl (•OH) radicals, are desired to retain the level of pollution under legal limits. Among AOPs, •OH-based electrochemical processes are becoming increasingly important (Geng et al. 2018; Mais



et al. 2020). In the photo-electrocatalysis process, a chemical reaction occurs at the semiconductor anode to increase light efficiency in response to the electric current. A photoanode semiconductor is irradiated with solar light for removing a dye such as a methyl orange (MO) photo-electrochemically. •OH radicals, which are generated by water oxidation, mediate the oxidation of MO. They are reactive enough to produce small molecules, aromatic ring-opening, and azo bond breakdown. When interest is just dye removal of wastewater, a high rate can be attained at high current and low primary concentrations, and the high yield can be achieved by operating at low concentrations and low current. Photo-electrocatalysis reduces the concentration of dyes and degrades them (Mais et al. 2020).

## Fenton's oxidation

Advanced oxidation processes (AOPs) can help achieve complete or partial degradation of organics or dyes in textile wastewater. Oxidation processes generate free radicals like hydroxyl radicals with more significant oxidation potential. Among all other oxidations, Fenton's oxidation is considered the practical and advanced water treatment method (Sözen et al. 2020) as it employs ferrous sulfate (FeSO<sub>4</sub>) and hydrogen peroxide  $(H_2O_2)$  to generate strong oxidizing agent, i.e., hydroxyl radicals. •OH has been recognized to have a high oxidation potential. Fenton oxidation has been employed effectively to treat industrial wastewaters in previous investigations. During Fenton oxidation, the development of a large amount of various sizes flocs is observed. These small flocs are ferric hydroxo-complexes generated by chain reactions of hydroxide ions and ferrous ions. It is not easy to settle down these small flocs in wastewater as they are smaller in size (Lin and Leu 1999).

The reactions that involve Fenton's reagent with any organic compound (RH) are shown below:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + OH^-$$
(1)

$$\mathbf{R}\mathbf{H} + \mathbf{O}\mathbf{H} \cdot \rightarrow \mathbf{H}_2\mathbf{O} + \mathbf{R} \cdot \tag{2}$$

$$\mathbf{R} \cdot + \mathbf{F} \mathbf{e}^{3+} \rightarrow \mathbf{R}^{+} + \mathbf{F} \mathbf{e}^{2+} \tag{3}$$

$$R^{+} + H_2 O \rightarrow ROH + H^{+}$$
(4)

Hydrogen peroxide  $(H_2O_2)$  generates hydroxyl radicals upon interaction with the iron ions, as hydrogen peroxide is not good enough for dye decolorization alone at normal conditions (Sicardi 2020).

#### Ozonation

Ozone is involved in several chemical reactions with organic and inorganic compounds as it is a strong oxidizing agent. Ozonation process can be considered an advanced oxidation process (AOP) at a particular pH. Hydroxyl radicals are created from the ozone decomposition. In ozonation, under the influence of pH, two reactions are considered:

**Direct pathway** pH < 4 reaction occurs between dissolved compounds in water and molecular ozone.

**Indirect pathway** pH > 10 reactions occur between hydroxyl radicals produced by ozone breakdown and dissolved compounds.

Catalytic ozonation of pollutants is shown in Fig. 6. Ozone can generate hydroxyl radicals in water; therefore, it is considered an advanced oxidation process itself. Ozone can be used with other technologies like  $H_2O_2$ , ultraviolet (UV), ultrasound (US), and others, to increase the color or organic matter removal efficiency (Sicardi 2020).

## **Biological method**

Microorganisms decompose or degrade organic colorants in biological treatment via aerobic or anaerobic cycle (Saxena and Bharagava 2017). Microbes use organics as an energy source by degrading them. Biofilms are developed for the removal of contaminants from sewage water, as shown in Fig. 7. Various dyes used in textile industries are harmful to aerobic organisms and create sludge rising, flocculation, and sludge bulking. Therefore, the biological process that proceeds through the aerobic route is testified to be insufficient to decompose textile dyes, specifically azo dyes (Ibrahim et al. 2009). Furthermore, it also requires a more prominent space and more significant hydraulic retention time. Aeration is mandatory for producing the unknown oxidation compounds that can add color intensity to the effluent. Anaerobic microorganisms are slow growers and so require a longer time to acclimatize. The treatment of textile dyes in anaerobic conditions generates more toxic aromatic amines during azo dye break down by azoreductase. Aromatic amine produced in

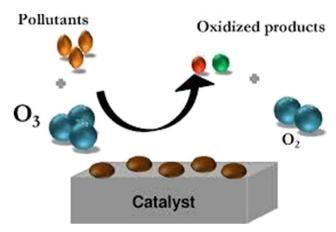
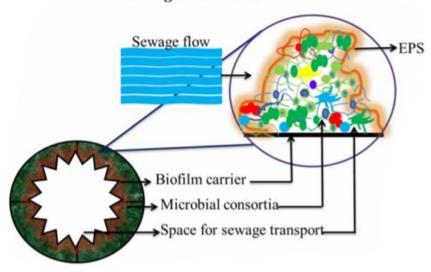


Fig. 6 Schematic illustration of catalytic ozonation (Lina 2016)

**Fig. 7** Biofilm for sewage water treatment (Machineni 2019)

**Biofilm growth mode** 



an anaerobic environment mineralizes into the environmentfriendly compound when exposed to air; hence, an anaerobic system integrated with the aerobic system can be used to achieve effective treatment (Yogalakshmi et al. 2020). The biological methods for the complete degradation of textile wastewater have benefits such as (a) eco-friendly, (b) costcompetitive, (c) less sludge production, (d) giving nonhazardous metabolites or complete mineralization, and (e) less consumption of water (higher concentration or less dilution requirement) compared with the physical/oxidation method. The efficiency of biological processes for degradation depends on the selected microbes' adaptability and enzymes' activity. Therefore, many microorganisms and enzymes have been isolated and tried for the degradation of several dyes. The isolation of potent microbes and their use of degradation is an interesting biological aspect of textile wastewater treatment. A wide range of microorganisms such as bacteria, fungi, and algae can degrade a wide variety of dyes present in the textile wastewater (Holkar et al. 2016).

# Limitations of different techniques

Chemical methods are simple, rapid, efficient processes and have multiple approaches concerning oxidants. Besides all these properties, chemical methods are generally laboratoryscale techniques and economically not feasible for small industries to fulfill their energy requirements.

Physical methods like membrane filtration are rapid and straightforward techniques, even at high concentrations. They are considered suitable for almost all types of pollutants like dyes, mineral ions, suspended particles, etc. Contrary to this, they require high energy, maintenance, and operation cost and are not feasible for small industries as rapid membrane clogging occurs at high concentrations. Coagulation and flocculation are a simple physiochemical process, but it is challenging to handle sludge volume generation (large size flocs), which alternatively increases this process's cost.

The public wells accept biological treatment as it is a simple and economically attractive technique. Still, it is a slow process, has low biodegradability, and requires an optimally favorable environment and proper maintenance of microorganisms.

After reviewing different wastewater treatment techniques, it is observed that adsorption is a technologically simple, efficient, cost-effective, and non-destructive technique. It has an excellent ability to remove various pollutants, including dyes, metal ions, minerals, and other contaminants from water and wastewater (Crini and Lichtfouse 2019).

# An efficient treatment method: adsorption

Several water purification techniques have been reported, but adsorption is considered one of the easiest, simple, flexible, operative, insensitive to noxious materials, and economically feasible methods for wastewater treatment (Azam et al. 2020; Singh et al. 2018). It is a separation method through which the constituents of a liquid(fluid) or gas stick or bind to solid material's external and internal surfaces named as the adsorbent (Crini et al. 2019). Many adsorbents and their mechanisms have been reported in literature like natural materials, industrial and agricultural byproducts and wastes, biomass material, etc., to remove contaminants from wastewater. The selection of adsorbent for removing contaminants mainly depends on the concentration and pollutant nature present in water, adsorption capacity, and effectiveness for the pollutant. Moreover, adsorbents should be readily available, cost-effective, and non-toxic and can be regenerated easily (Singh et al. 2018).

The characteristics of adsorbents and adsorbates are relatively specific and usually depend on their constituents. Physical interactions between the solid surface of the adsorbent and the adsorbed molecules are called physisorption. These interactions are due to van der Waals forces, as they are weak forces, which results in a reversible process. If the adsorbent and adsorbate interactions are due to the chemical bonding, it is called chemisorption. Divergent to the physisorption, chemisorption is a monolayer process, challenging to break chemical bonding to make it reversible (Cooney 1998). Different types of adsorbents used in wastewater treatment are categorized in Fig. 8.

# **Types of adsorbents**

## Low-cost adsorbents

A large number of low-cost adsorbents can purify or remove contaminants from water and wastewater. They are considered advantageous due to economic feasibility and reduced byproducts and waste (De Gisi et al. 2016). Table 2 summarizes the commonly used low-cost adsorbents with the removal efficiency for different contaminants.

## Natural adsorbents

There are a large number of materials present naturally that have properties similar to that of an adsorbent. Though they are large in numbers, such as chitin, clay, zeolite, peat moss, coal, and wood, they have effectively been employed to eliminate pollutants, heavy metal ions, organic compounds, and dyes from wastewater [45].

Zeolites are naturally occurring crystal-like aluminosilicates comprising tetrahedral framework structure, linked together by oxygen atoms (Lin and Juang 2009). Surfactantmodified zeolites can be utilized to absorb different pollutants and organics (Li et al. 2000). Natural zeolites may show effective adsorption ranging from 45 to 64% for contaminants in 4 h (Kuleyin 2007).

Chitin and chitosan are the biopolymers, which led to fiber production. These fibers have better removal efficiency and have more strength than activated carbon (Wei et al. 1992; Yoshida et al. 1993) and have attracted much attention due to their unique properties and biodegradability. Chitin is a naturally occurring renewable resource and offers potential applications as an adsorbent in wastewater treatment and other fields (Agboh and Qin 1997).

Clay minerals are alternative inorganic adsorbent that offers several advantages that may include its abundant availability, low-cost, non-toxicity, and more significant pollutant adsorption. The negative charge layers and colloidal properties improve their capacity of adsorbing the organic molecules and cations (Abidi et al. 2015). However, they have little adsorption capacity for anions under natural conditions, but different surfactants can improve adsorption as these modifications change the surface charge from negative to positive (Duc et al. 2006). Earlier studies showed that raw clay is capable of adsorbing anionic dyes, but it follows a complicated process. Furthermore, the untreated natural clay competently removes the colors of ionic dyes and multiple additives (Errais et al. 2010).

Wood is considered a non-regeneratable, low-cost natural adsorbent that can be discarded by burning (Poots et al. 1976). The timber consists of cellulose microfibrils embedded in the

Low cost Nano Bio sorbents adsorbents adsorbents Carbon based Enzyme based Metal oxide based Natural Agricultural waste Nanocomposites Microorganism Industrial waste based **Boron** nitride material

Fig 8 Different types of adsorbents for wastewater treatment

Sr. no.	Adsorbents	Pollutants	Adsorption capacity (mg/g)	Maximum removal efficiency	Reference
1	Modified sawdust	Heavy metal (Cr)	8.84	100%	(Chakraborty et al. 2019)
2	Wheat straw	Cu Cd	7.05 14.56	99.8%	(Wu et al. 2009)
		Pb	599.1		(He et al. 2014) (Chakraborty et al. 2020)
3	Red mud	Cr Pb	35.66 64.79	_	(Gupta et al. 2001)
4	Coal fly ash	Cd Zn	18.98 6.5–13.3	100%	(Chakraborty et al. 2020)
5	Coffee residue	Pb Zn	9.7 4.4	96% 44%	(Wu et al. 2015)
6	Waste tea leaves	Pb	73	96%	(Gavrilescu 2004)
7	Sugarcane bagasse	Hg Cd	35.71 74	97.58	(Chakraborty et al. 2020)
8	Eggshell waste	Cd Cu	111.1 142.86	94 93.17	(Zheng et al. 2007)
9	Fly ash (geopolymer)	Anionic surfactant	714.3	_	(Siyal et al. 2019)

Table 2 The adsorption capacity of Low-cost adsorbents for wastewater treatment

porous lignin matrix, taking benefits of the hierarchical and porous structure; wood recently has been explored to develop its applications in different areas of energy storage, solar stream generation, and wastewater treatment (Guan et al. 2018). Many plants with wood and bark have been used for pollutant adsorption from wastewater, like *Eucalyptus* bark, without any pre-treatment used to remove dye (Morais et al. 1999).

### Agricultural wastes

Agricultural deposits and vegetable and fruit peels are the waste material that cannot be used anywhere. Hence, they can easily be used as low-cost adsorbents after pre-treatment (Anastopoulos and Kyzas 2014). Agricultural wastes are mainly composed of cellulose and lignin, due to which they possess versatile structure and chemical properties and can act as attractive alternative adsorbents. They exist in polymer chains with specific functional groups like alcohol, aldehyde, phenol, ketone, and carboxyl, which help remove various contaminants from water (Singh et al. 2018). A variety of agricultural wastes, i.e., orange peel, lemon peel, banana peel, wheat bran, rice husk, coconut, pulse seed coat, etc., have already been reported in wastewater treatment (Tasaso 2014). Agricultural waste materials are useful in natural as well as in modified form. In the natural system, the waste product is washed adequately, grounded, and sieved until it reaches the desired particle size and is later used as an adsorbent to purify water. The material is pre-treated into a modified form through different modification techniques (Bhatnagar and Sillanpää 2010). Aygun et al. studied the use of hazelnut shells, almond shells, walnut shells, and apricot shells as raw material to produce granular activated carbon (GAC). GACs are assessed for their physical, chemical, surface area, and adsorption properties (Aygün et al. 2003). An experimental study stated that the rice husk was dedicated by potassium carbonate and chemically activated to urea modified activated carbon to remove nitrate ions from wastewater (Hossain et al. 2020). Diverse plant parts such as plant bark, coconut fiber, coconut shell, pine needles, neem leave powder, and cactus leaves have been examined to remove chromium, showing efficiency greater than 90% at optimum pH (Dakiky et al. 2002). Sugarcane bagasse is used in both natural and modified forms to remove chromium from wastewater (Sud et al. 2008). Soybean hulls, rice straws, and rice bran are modified with citric acid and efficiently used for metal ion removal from wastewater, specifically copper ions (Khan et al. 2004). Lotus leaves are used for the removal of commonly discharged dye., i.e., methylene blue. The adsorption isotherm represents the maximum adsorption capability of the lotus leaf. Pumpkin seeds were also subjected to methylene blue removal from aqueous solutions (Rangabhashiyam et al. 2013).

#### Industrial wastes

Industrial activities produce solid waste materials; some of the byproducts are reused while others are disposed of in landfills. Therefore, the opportunity to reuse material in the adsorption process is an exciting solution because these waste materials cause major environmental problems (De Gisi et al. 2016). The byproducts of industries are used as low-cost adsorbents to remove heavy metals, organic compounds, and dyes from wastewater. They are inexpensive and locally available in large quantities, including fly ash, palm oil ash, red mud, bagasse ash, coffee waste, etc. (Zaini et al. 2014). These waste materials can cause serious environmental problems if left untreated (Anastopoulos et al. 2017). A variety of treatment methods are employed but they are complicated, expensive, and easily cause secondary pollutants. If these wastes are transformed into reused material, it will reduce pollution to a great extent (Mo et al. 2018).

It is observed that fly ash possesses a porous surface with small, glassy spherical, and irregular-shaped particles. The modification on fly ash surface makes it more suitable for adsorption (Tiadi et al. 2018). Fly ash originates in the combustion process and is mainly used in road construction, cement, bricks, etc. Fly ash is an inexpensive adsorbent as it contains high alumina and silica percentage making it suitable for adsorption (Bhatnagar and Sillanpää 2010).

Red mud has a porous, smooth, and dense surface texture (Tiadi et al. 2020). Red mud is an aluminum industry effluent and has received attention as an active adsorbent to control pollution by significantly removing various aquatic contaminants. Red mud is alkaline with a pH range of 10–12 as it contains sodium hydroxide solution (used in the refining process) (Kumar et al. 2006). It can be a hazardous waste because of its alkaline nature; therefore, it needs to be neutralized before using it as an adsorbent (Zhou and Haynes 2010). Neutralization results in a pH of 8–8.5 of red mud (Bhatnagar and Sillanpää 2010). The adsorption by red mud has widely been applied for arsenic and removing dyes from wastewater (Mohan and Pittman 2007).

Bagasse fly ash is a waste product of sugar industries, always creates a disposal problem. It is presently used as a filler in building materials, but now bagasse fly ash has been converted into an active and efficient adsorbent to remove toxic substances (Gupta and Ali 2001). Recently, bagasse has shown its applications in removing zinc and other metals from aqueous solutions (Gupta and Sharma 2003).

#### Nano-adsorbents

Nanotechnology has successful applications in various fields, but its application in wastewater treatment has appeared as a fascinating area of attention. Nanotechnology is concerned with the preparation and study of constituents at the nanoscale. These nanomaterials have versatile properties because of their petite size and large surface to volume ratio (Mamalis 2007). Recently, nanomaterials, nano-adsorbents, or nanoparticles have shown successful applications in many areas of interest, mainly in removing the metallic pollutants from industrial wastewater (Sharma et al. 2009). Nanomaterials, primarily as nano-adsorbents and their modifications, have been used to separate and purify various analytes (Khajeh et al. 2013). Materials are categorized at the nanoscale by different biological, physical, and chemical properties than the usual or actual material size. Hence, materials such as metal oxides, ceramics, polymers, and carbon derivatives have a large surface area and high surface to volume ratio at the nanoscale. Shortly, the surface area of materials increases with decreasing the particle size and alternatively properties are shown by materials at the macroscopic level are also changed at the nanoscale (Kyzas and Matis 2015). The maximum reported removal efficiencies of some of the nano-adsorbents are listed in Table 3.

## Carbon-based nanomaterials

With the increasing demand for nanotechnology, various carbon-based nanomaterials have been developed (Smith and Rodrigues 2015). Activated carbon exhibit excellent adsorption capacity because of the large surface area and tunable porosity (Hassan et al. 2020). Carbon and graphene-based nanomaterials, such as nanotubes, are available in functionalized and non-functionalized forms (Kuila et al. 2012). The organic functional groups present on carbon-based nanomaterials, improved by surface modification, help achieve higher adsorption activities (Upadhyayula et al. 2009). The advances in carbon-based nanomaterials provide two significant benefits: (1) improves hydrophilicity, which increases dispersion in an aqueous medium. The more excellent distribution offers more surface area for exposure to pollutants or other unwanted species (Ahmed et al. 2012; Saleh et al. 2008) and (2) increases electrostatic interactions between adsorbent and adsorbate to maximize adsorption capacity. The electrostatic interactions are the key driving force for adsorption of specifically positively charged species such as heavy metals if the surface is functionalized by a negative charge (Wang et al. 2013).

Carbon nanotubes (CNTs) have proven to be an excellent adsorbent for removing pollutants from water, contributing to a healthy environment (Yang et al. 2009). CNTs discovered by Iijima in 1991 have been widely adopted to study display potential in water treatment by several researchers. CNTs are cylindrical-shaped macromolecules composed of hexagonal carbon atoms, having a radius of few nanometers, and are about 20 cm in length (Thines et al. 2017). The layered and cylindrical structures of CNTs provide a large surface area, making them suitable for contaminants' adsorption in wastewater treatment (AlSaadi et al. 2016; Mubarak et al. 2016).

Three-dimensional (3D) graphene has a uniform structure, high surface area, chemical stability, structural sustainability, and highly oleophilic and hydrophobic surfaces, making graphene a feasible candidate for the adsorption process. Graphene has significant development in the loading ability of organic liquids and oils and can be reused compared with existing adsorbents (Wan et al. 2016). Graphene and CNTs-

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Sr. no.	Adsorbents	Pollutants	Adsorption capacity (mg/g)	Maximum removal efficiency	Reference	
1	Activated carbon	Crystal violet dye	84.11	85–90%	(Sarabadan et al. 2019)	
2	Natural zeolite	Dye	177.75	60%	(Pan et al. 2020)	
3	Fe <sub>3</sub> O <sub>4</sub> nanoparticles	Pd Cd	369.0-523.6	98%	(Xin et al. 2012)	
		Cu				
4	SiO <sub>2</sub>	Cu Pb	6.35 5.20	-	(Manyangadze et al. 2020)	
5	Anionic surfactant (SDS)	Cationic dyes	18	_	(Pham et al. 2020)	
6	DS-Zn/Al LDHs	Organic pollutant	87–149.3	-	(Grover et al. 2019)	
7	Fe <sub>3</sub> O <sub>4</sub> -silica	Pb Hg	-	97.34% 90%	(Xu et al. 2012)	
8	Montmorillonite-supported MNPs	Cr	15.3	_	(Xu et al. 2012)	
9	MWCNTs	Reactive dyes	95-352.1	-	(Machado et al. 2011)	
10	Graphene	Cd Co	106.3 68.2	_	(Zhao et al. 2011)	
11	TiO <sub>2</sub> nanotubes/CNT	Cu Pb	83–124 192–588	-	(Sadegh et al. 2017)	

 Table 3
 The adsorption capacity of different nano-adsorbents for wastewater treatment

based nano-adsorbents have widely been used to remove heavy metal ions and organic contaminants (Ngah et al. 2011).

#### Metal oxide-based nanomaterials

A significant number of metal oxides nanomaterials such as  $Fe_3O_4$ , CuO, ZnO, and their composites have already been used to remove toxic metal ions, inorganic and organic pollutants from wastewater and raw water (Singh et al. 2018). Metal nanoparticles are considered the best material for removing toxic dyes, especially azo dyes, because of their large surface area and good catalytic activity (Iqbal et al. 2020). Iron and its compounds, such as iron oxide-coated materials, hematite, granular ferric hydroxide (GFH), and goethite, are the ultimate materials for the adsorption of arsenic and other ions (Lata and Samadder 2016).

Cupric oxide (CuO) can perform well in the presence of other competing species. Hence, CuO is an effective nanoadsorbent for the removal of arsenic in water purification. These nano-adsorbents can be regenerated quickly and reused for arsenic removal from water (Reddy et al. 2013).

ZnO is a very stable and non-toxic material. The durable pH range for the effective working of zinc oxide is 5.8 to 6.8, making it user-friendly. Zinc oxide with its nanocomposites shows a high capacity of adsorption rather than the individual metal oxides. These composites may include Fe-Mn, Fe-Ce, Fe-Ti, Fe-Zr, Ce-Ti, Fe-Cu, Fe-Cr, and Mn-Co (Lata and Samadder 2016).

## Nanocomposites

Adsorption has widely been used to decontaminate various unwanted species and pollutants from numerous contaminated water effluents. A single type of adsorbent is not considered adequate for different pollutants (Liu et al. 2019). Multiple nano-sized adsorbents have been synthesized and utilized for water purification applications (Wang et al. 2015). Such nanosized adsorbents have several limitations with pollutants removal from wastewater. Hence, the development of novel nano-adsorbents with practical separation features is still grasping a significant consideration (Nadagouda et al. 2012). To accomplish this objective, nanomaterials are extensively explored to develop an adsorbent for water treatment with versatile separation characteristics such as large surface area and more binding sites for the superlative pollutants removal application (Liu et al. 2011). Spinal ferrite nanoparticles (SFNPs), as well as their nanocomposites, are using for the purification of water. Numerous research studies reveal that SFNPs based nanocomposites have better photodegradation capacities; thus, they are useful for completely removing contaminants (Kefeni and Mamba 2020).

#### Boron nitride material

Inorganic oxides containing porous materials have attracted attention due to their potential for water and air purification (Shafiq et al. 2020, 2021; Wu and Bein 1994). Boron nitride (BN) is a chemical material constructed from equal numbers of nitrogen (N) and boron (B) atoms. Balmain first synthesizes BN in 1842 by the reaction of molten boric acid (H<sub>3</sub>BO<sub>3</sub>) with potassium cyanide (KCN) (Balmain 1842a, b). Since then, various investigations have been assembled on the preparation of different BN nanostructures such as nanotubes, nanofibers, nanoparticles, nanoflowers, nanosheets, etc. (Yu et al. 2018). Hexagonal boron nitride in porous structure shows unique chemical and physical properties like large surface area, oxidation resistance, and chemical durability (Li et al. 2013). These characteristics make BN auspicious material for applications in many fields such as hydrogen storage, adsorption of inorganic and organic pollutants, and catalysis in severe environments (Meng et al. 2011; Weng et al. 2013).

# **Bio-sorbents**

Bio-sorption is an adsorptive method for potentially removing pollutants, metal ions, and organic dyes present in aqueous solutions. The name suggests, bio-sorbents are derivative of biological sources or biological means. These bio-sorbents tend to attract or bind to pollutants due to particular functional groups present on their surface (Chojnacka 2010). It involves a liquid phase containing suspended or dissolved species that have to be adsorbed on the solid-phase surfaces (bio-sorbent) (Saha et al. 2019). This process competently removes diverse organic and inorganic species through passive binding to the bio-sorbents depending on the functional group polarity they contain (Pacheco et al. 2011). Table 4 Categorize the removal efficiency of the number of bio-sorbents used for the removal of pollutants.

To eliminate toxic dyes and heavy metals, extensive studies have been reported on algal biochar as bio-sorbent (Davis et al. 2003). Algal biochar is gifted with better bio-sorption properties. Hence, it is considered appropriate for the wastewater treatment applications, such as removing various inorganic, ammonium-N, and organic pollutants from waste effluents (Hina 2013). Jung in 2016 has used biochar for sorption of phosphate ions, while Cole in 2017 has used biochar for isolation of dissolved phosphorous and nitrogen from the municipal wastewater (Michalak et al. 2019). Walnuts shells modification has demonstrated a promising method for obtaining bio-sorbents with useful sorption properties. Modifications with a high concentration of inorganic acid improve the sorption capacity. Such bio-sorbents can also be used in the low wastewater demineralization system (Halysh et al. 2020).

# Conclusion

This literature review revealed that due to the limited resources of clean water and growing pollution levels, many techniques have been explored, exhibiting their superlative applications in removing the pollutants from wastewater. Among all of them, adsorption is an extensively used method of removing a diverse range of contaminants. Contrary to the earlier times, the nature of the adsorbents used is considerably changed. Now low-cost adsorbents are seeking attention for their applications in wastewater treatment. Significant attention has been paid to porosity enhancement, modifying the textural properties and improving the adsorbents' specific surface area to introduce a new class of nanomaterials with improved adsorption efficiency. However, besides all these, this technology's key drawback is that the applications are still confined to the laboratory stage. The assets and liabilities of this concept are still unknown for applications on the industrial scale. Despite the progress, there is a need to develop such adsorbent whose performance covers versatile pollutants, particularly on a large scale. Wastewater treatment industries should be proactive and assess the waste materials' potential to synthesize low-cost adsorbents and utilize them on an industrial scale in real practice. Suppose the target mentioned above will be accomplished. In that case, the industries will play a key role in waste management globally and initiate a new horizon for an economically feasible wastewater treatment era. Specific policy-making from the government and proper implementation for water industries can make this successful and carry long-term

 Table 4
 The adsorption capacity of different bio-sorbents for wastewater treatment

Sr. no.	Adsorbents	Pollutants	Adsorption capacity (mg/g)	Maximum removal efficiency	Reference
1	Citrus limetta residue	_	12.6	80-86%	(Ibrahim et al. 2019)
2	Modified biogas residue	Nitrate Phosphate	64.12 34.40	82%	(Pan et al. 2020)
3	Waste-based bio-sorbent	Fluoxetine	21.86-233.5	-	(Silva et al. 2020)
4	ZrO2-modified diatoms	_	15.53	90%	
5	Modified lemon leaf	Cationic dye	36.10	70%	(Putri et al. 2020)
6	Fungal and bacterial biomass	VOCs	374–620	_	(Cheng et al. 2020)

benefits not only for the environment but also for society and the economy.

# **Future prospects**

The grouping of adsorbents based on different contaminants' adsorption nature is another impression to synthesize a single adsorbent for multiple applications. Therefore, more experimental work has become a need to develop an improved classification method. A practical approach is required to prepare adsorbents from waste products for wastewater treatment and their applications on the pilot-scale plant or commercial scale in the future. The review of various techniques reveals that even though a bundle of methods has been developed and tested, challenges are still related to the objective evaluation of techniques, limited validation, lack of guidelines and collaborative methods, and limited active optimization options for data information and quality. Furthermore, efforts are required to develop knowledge generation and application techniques. Only a few previous studies have discussed the cost of the treatment methods and improved available technologies at commercial levels. Researchers should concentrate on the complexity of treatment techniques and cost analysis in the coming future.

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Muhammad Javid Iqbal: co-supervision, editing, conceptualization, data analysis

Murid Hussain: idea for the article, organization, critical feedback and revision, supervision, conceptualization, data analysis

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# **Compliance with ethical standards**

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**Abbreviations** USEPA, United States Environmental Protection Agency; AC, Activated carbon; TOC, Total organic carbon; BOD, Biological oxygen demand; COD, Chemical oxygen demand; NF, Nanofiltration; UF, Ultrafiltration; PAN, Polyacrylonitrile; PSf, Polysulfone; CA, Cellulose acetate; PES, Polyethersulfone; PVDF, Poly (vinylidene fluoride); AOP, Advanced oxidation process; EAOP, Electrochemical advanced oxidation process; MO, Methyl Orange; ARS, Alizarin Red S; IC, Indigo Carmine; UV, Ultraviolet; US, Ultrasound; GAC, Granular activated carbon; CNTs, Carbon nanotubes; GFH, Granular ferric hydroxide; SPNPs, Spinal ferrite nanoparticles; BN, Boron nitride; KCN, Potassium cyanide

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