Nanomaterials in Advanced Oxidation Processes (AOPs) in Anionic Dye Removal

Aiswarya Thekkedath, Samuel Sugaraj, and Karthiyayini Sridharan

Abstract Water, popularly known as Universal Solvent, plays a vital role for surviving in this environment. Over a decade, water bodies are being polluted in several ways (wastewaters, chemicals, dyes, papers, etc.). Out of these pollutants, dyes are relatively more toxic. Dyes are the pigment used in textile industries. The dye waste from the industries is likely to pollute the water. For the degradation of dyes from water, different methods were introduced. Advanced oxidation processes are one of the prominent methods. In this process, there are physical, chemical as well as biological methods involved. This chapter coveys a detailed description of water pollution, how dyes are affecting the quality of the water, advanced oxidation process, and the nanomaterials used in the advanced oxidation process.

1 Water Pollution—Introduction

In this era, the most challenging situation is freshwater access, a major issue faced by every region. In rural parts the major cause for drinking water are pollution and scarcity. Interpreting the causes of pollution, we can say the major reason will be over population, and besides the increasing demand in agriculture and industry. When the strange particles enter into the water, the quality is being disturbed resulting in a change in the environment and human health hazard [1].

Major issues for human health as well as surroundings is the sewage or effluents disposed to the water as well as environment. It will destroy the common natural resources, thereby resulting in severe diseases like typhoid like fever, diarrhea, vomiting, etc. There is another possibility for the quickest destruction of animals and plants. The pollutants from the water will kill marine life and our ecosystem also. In our normal food processes some insecticides also influencing more [2].

A. Thekkedath · K. Sridharan (✉)
Department of General Sciences, BITS Pilani Dubai Campus, Dubai, UAE
e-mail: rajkar6761@gmail.com

S. Sugaraj
Department of Physics, The New College, Chennai, India

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2 Hazards of Water Pollution

Factories discharge a huge amount of toxic waste, colors, and organic chemicals. Heavy metals like copper, arsenic, lead, cadmium, mercury, nickel, and cobalt and certain auxiliary chemicals and acids, dyes, soaps, chromium compounds, etc., make the water highly toxic. Some formaldehyde-based dyes, hydrocarbons, non-biodegradable dyeing chemicals are other kinds of toxic materials. Some factories dispose of water having high temperature and pH, which may affect the system. Other forms which make water appear bad with a foul smell are the colloidal matter present along with colors and oily scum. This prevents the light penetration into the water that is necessary for photosynthesis, resulting in refraining the oxygen transfer mechanism at the air interface. Another issue is the depletion of dissolved oxygen in water causing hindrance to marine life which will stop the self-purification of water.

In addition, when this effluent is allowed to flow in the fields, it clogs the pores of the soil resulting in loss of soil productivity. The texture of soil gets hardened and penetration of roots is prevented. The wastewater that flows in the drains corrodes and incrustates the sewerage pipes. If allowed to flow in drains and rivers, it affects the quality of drinking water in hand pumps making it unfit for human consumption. It also leads to leakage in drains increasing their maintenance cost. Such polluted water can be a breeding ground for bacteria and viruses. Impurities in water affect textile processing in many ways. In scouring and bleaching, they impart a yellow tinge to the white fabric. In the dyeing stage, metallic ions present in water sometimes combine with the dyes causing dullness in shades. Textile effluent is the cause of a significant amount of environmental degradation and human illnesses. About 40% of globally used colorants contain organically bound chlorine a known carcinogen. All the organic materials present in the wastewater from the textile industry are of great concern in water treatment because they react with many disinfectants, especially chlorine. Chemicals evaporate into the air we breathe or are absorbed through our skin and show up as allergic reactions and may cause harm to children even before birth.

2.1 *Effects of Water Pollution on Human Health*

Bonding between human health and pollution is much higher. The spreading will be through microorganisms commonly known as pathogens and they will spread diseases easily [2]. Most of the diseases which we commonly know are waterborne diseases [3]. Floods and heavy rainfall also favor the spreading in developing as well as developed nations [4]. Only a few percent of the whole population, say 10%, depends on veggies and others grown from this wastewater [5]. Diseases caused through water were linked with waste excreted toward the water sources and their resultants [6]. Human health became high risk with this contaminated water as it results in cancer, nervous disorder, etc. [7]. Chemicals excreted into the water will cause blue baby syndrome and cancer [8]. Both urban and rural areas' mortality rates are increased due to this sewage water. People who are poor will be more at risk of unhygienic and improper water supply [9]. Women are also affected because of effluents, as it will cause a lower fetal birth rate [10]. Lower the quality of water, lesser the production of crops and will affect the marine as well as human life [11]. Whenever the pollutants are heavier, it will enter into fish's body which will be directly eaten by the humans thereby results the entering the pollutants inside the human body as the pollutants effects the respiratory system of fishes [12]. Water contamination due to metals will result in liver cirrhosis, hair fall, nervous system failure [13] http://www.alliedacademies.org/environmental-risk-assessment-and-remediation/. ISSN: 2529–8046.

2.2 Categories of Water Pollution

The two main sources for water pollution can be generally concluded as point sources and non-point sources.

Point sources

The directly identifiable sources that are causing pollution are popularly known as point sources. For example, pipe attached to a factory, oil spill from a tanker, effluents coming out from industries. Point sources of pollution include storm sewer discharge and wastewater effluent (both municipal and industrial) and affect mostly the area near it.

Every type of source related to pollution causes its own consequences and health issues. The substances which are considered as major water pollutants are thus classified into several groups which are organic compounds (pesticides, hydrocarbons, dyes, and oil), inorganic substances (salts, acids, phosphate, sulfates, fluorides, and toxic heavy metals) or microbial (bacteria, protozoa, and viruses). If any substance exceeds their sill, then it will cause a series of issues which will be harmful to human as well as aquatic life. Apart from these, the waste from textiles and paint industries have colored components (persistent color, organics, toxicants, surfactants, chlorinated, and inhibitory compounds), that are resultants from dyeing also one of the major issues.

Water pollutants may be (i) Organic and (ii) Inorganic water.

(1) Organic water pollutants:

Contaminants include organic wastes such as detergents, disinfection by-products found in food processing waste, insecticides, chemically disinfected drinking water, herbicides, chlorinated solvents, petroleum hydrocarbons, volatile organic compounds, etc.

(2) Inorganic water pollutants:

Inorganic pollutants include acidity causing substances from industrial discharges, ammonia from food processing waste, chemical waste as industry by-products, fertilizers containing nutrients such as nitrates and phosphates, heavy metals form motor vehicles, secretion of creosote preservative into the aquatic ecosystem, slit sediment (adapted from [14]).

Non-point sources

The non-identifiable sources which are appeared from numerous sources of origin and number of ways by which contaminants that may enter into groundwater or surface water and occur in the environment. Water drained from agricultural lands and waste from cities are some examples. Causing severe pollution in one place is known as transboundary pollution. The best example of this pollution is radioactive waste. This waste will flow to the ocean and different water bodies, thereby resulting in disaster. The main non-point sources of pollution are the following:

- Industrial Wastes: Waste coming out from factories and mines will come under this category. Industrial wastes are of different types, some may be chemical, scrap metal, solvents, food waste from hotels. These wastes may be in liquid, solid or semi-solid form.
- Agro-chemical Wastes: This waste includes a wide area of pesticides which includes herbicides, fungicides, nematicides, and insecticides. Agro waste also includes some hormones synthetic fertilizers.
- Nutrient enrichment: Heavy production of nutrient will damage the algal growth and affect finally with a high toxicity. It manages rich productivity in water which will either be natural or artificial.
- Thermal pollution: Unexpected rise in the temperature of a water body is thermal pollution. When a plant put back in water with change in temperature will cause this pollution.
- Sediment pollution: Land erosion is the main reason for sediment pollution.
- Acid Rain Pollution: Chemicals that were excreted into the surroundings will cause acid rain. It may be because of oxides of nitrogen and sulfur dioxide. Exhausts from trucks, buses, and cars are also one of the reasons.
- Radioactive waste: This is one of the most dangerous waste which is the after effect of nuclear research, nuclear medicine, etc.

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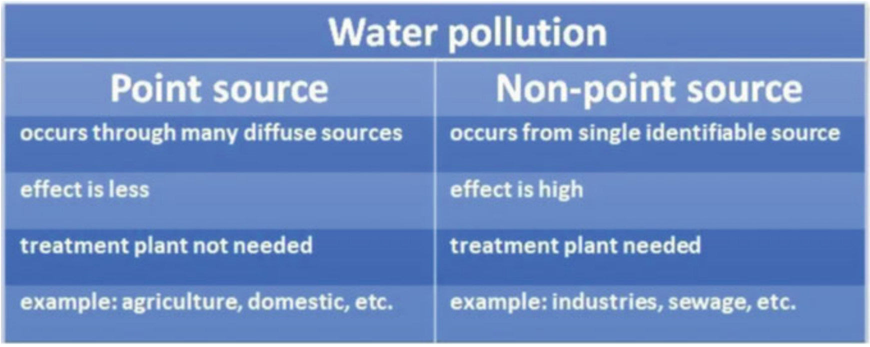
3 Different Sets of Pollution

Water can be polluted by different factors. Some are described briefly as follows (Fig. 1).



Water pollution	
Point source	**Non-point source**
occurs through many diffuse sources	occurs from single identifiable source
effect is less	effect is high
treatment plant not needed	treatment plant needed
example: agriculture, domestic, etc.	example: industries, sewage, etc.

Fig. 1 Sources of water pollution

3.1 *Chemical Pollution*

The cause for chemical pollution may be either through organic or inorganic species. Dyes and pesticides include in organic chemicals and also their derivatives such as nitrophenols, trihalomethanes, etc. [15, 16]. Another category such as hydrocarbon, namely phenols, benzene, toluene, xylene, in which an amount of 10–59% gasoline is the regular contaminant of natural waters. Most newborns have been observed to be at potential risk of drinking elevated levels of sodium ions [17]. These chemicals are highly toxic for kidney, liver, and nervous system. Toxic heavy metals having inorganic ions cause cancer, hypertension, poisoning, and infantile cyanosis [18].

3.2 *Heavy Metal Pollution*

Zinc, arsenic, cobalt, nickel-like heavy metals released into the environment of textile industries is great consternation all over the world as these pose a high risk to aquatic life, human life, and nature. Also these are damaging non-biodegradable nature, biological half-lives, and potential to accumulate in the body. Due to solubility also, some metals are highly toxic. Metals like Cu, Mn, Mo, Zn having lower concentration, plays a vital role in physiological functions in marine as well as human life. These metals are even more dangerous in their free state and also in combined form. Heavy metals are one of the old toxicants for humans [18].

3.3 *Water Pollution Due to Organic Dyes*

Diverse dyes are used in various applications and they are dispersed to nature in the form of sewage or effluents. Out of several types of dyes, azo dyes are commonly used because of their stability and versatility, it is used in textiles, printing cosmetics, and tattooing. However, their non-biodegradability and durability cause pollution once these dyes are released into the water bodies. Some of the azo dyes are very toxic, carcinogenic, and mutagenic [19]. One of the malignant pollutants is wastewater discharge. This discharge consists of almost all types of contaminants that causes a severe threat to humanity [18].

3.4 Dyes-The Major Pollutant and Its Types

One of the most beautiful words which might give the human a visual pleasure is none other than color!!! At the same time, it kills us as a sweet poison!!! Color enhances its self-appearance. Nowadays, pigments and dyes are commonly used in mills, and various coloring compounds are being utilized for the dyeing process. The most dangerous and toxic nature of coloring compounds became a threat to aquatic life. Thus, various methods have been undergoing for the removal of these dyes from water such as filtration, oxidation, etc. [20].

The major class of dyes is reactive dyes. They are highly distinguished because of their excellent binding capability due to the covalent bond formation with the reactive groups of dyes and surface groups seen on textile fibers. Dyes when discharged into the environment, cause a disturbance to the ecosystem, thereby increasing the level of toxicity and threat to humanity. Most common dyes can be seen in fabric materials (Fig. 2).

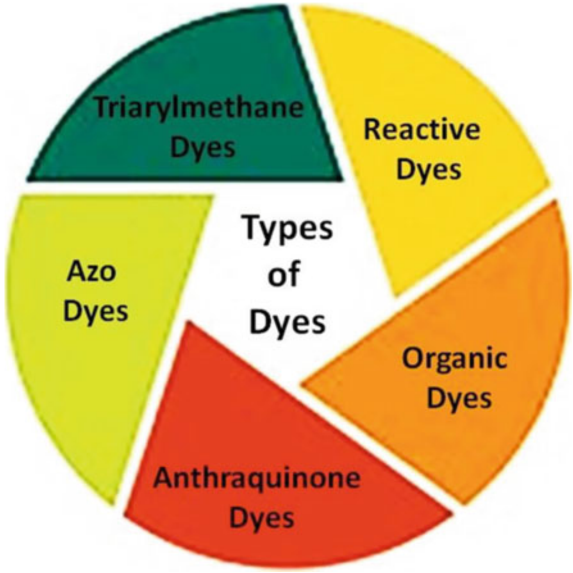


Fig. 2 Types of dyes

3.4.1 Azo Dyes

Azo dyes (mono, dia, tria, poly) account for the majority of synthetic aromatic dye, which are composed of one, two, three or more (N=N) groups and connected to benzene and naphthalene rings that are substituted frequently with some functional groups, e.g., triazine amine, chloro, hydroxyl, methyl, nitro, and sulphonate. They are basically used in cosmetics, paper printing, pharmaceutical, textile dyeing, and food. However, 80% of azo dyes are used in textiles because of high stability, low cost, and color variation. Studies estimated that 10–15% of dyes from textiles are released into water bodies. For example, the dyestuff of 30–60 g and water of 70–150 L were needed for dyeing 1 kg of cotton, and about half percent of the dyes which are used ones were thrown by either direct or indirect sources [21].

3.4.2 Reactive Dyes

Dyes are formed by the formation of covalent bonds between diflurochloropyrimidine, chlorotriazine, vinyl sulfone, trichloropyrimidine. In contrast to other classes of dyes, reactive dyes have many advantages in textiles because of their simple application techniques with low energy consumption bright colors, which are water-fast. Thus, reactive dyes are usually used at present. During the dyeing process, covalent bond bonds faster with reactive dyes. These are widely used in wool an cotton dyeing processes. Coloring cellulose fibers is done through reactive dyes. Second case these dyes also be put in nylon, wool but under weaker conditions. In reactive dyes, the functional groups create hydrolysis by bonding with water resulting in low utilization.

Reactive dyes are the most problematic dyes among others, as they tend to pass unaffected through conventional treatment systems [Vol. 4, No. 1, 22–26 (2012) Natural Science http://dx.doi.org/10.4236/ns.2012.41004].

However, reactive dyes were found to be mutagenic and carcinogenic and even the intermediate products, i.e., mineralization, aromatic amine, and arylamine, also have severe adverse effects on human beings, including damages caused to the brain, liver, kidney, central nervous system, and reproductive system [22].

3.4.3 Anthraquinone Dyes

After azo dyes, another set of dyes that are commonly used in textiles were Anthraquinone dyes and have been widely used in the garments owing to their different colors, fastness properties and ease of application, and low energy consumption. Another major advantage of anthraquinone dyes applied in dyeing processes is their high affinity to silk and wool. However, due to their fused aromatic structure, anthraquinone dyes exhibit a lower rate of decolorization. Most of these dyes are mutagenic, carcinogenic, and toxic, therefore, the removal of anthraquinone dyes has attracted an enormous recognition.

3.4.4 Triarylmethane Dyes

Triphenylmethane dyes are aromatic xenobiotic compounds that were formed by a carbon atom placed in center connected with two benzene rings and one p-quinoid group-chromophore. The common auxochromes are –NH2, NR2, and –OH. These dyes have brilliant colors with typical shades of green, violet, red, and blue, such as Malachite green (MG), Crystal violet (CV), Bromophenol blue (BB), etc. These dyes are widely applied in the garments for coloring the substrates like modified nylon, polyacrylonitrile, cotton, silk, and wool.

Another important application of triphenylmethane dyes is their use in paper and leather industry. Their relatively inexpensive dyeing, high tinctorial strength, and low light fastness, especially in the slow washing and light are considered apt for dyeing a wide range of garment substrates. In addition, triphenylmethane dyes have been extensively employed in medicine as medical disinfectants, because these dyes exhibit antibacterial, antifungal, and antiprotozoal properties, they can be used for the disinfection of post-operative wounds, and also employed in controlling diabetes. Some of these dyes (phenolphthalein, fuchsine, and fluorescein) are used as indicator dyes because of their pH sensitivity.

3.4.5 Other Dyes

One of the most popular azo dyes is Congo red (CR). Congo Red is an anionic dye (diazo benzidine) that contains –N=N– linkage (double azo). This is highly dangerous, carcinogenic too. Janus Green B (JGB) is incorporated by conjugating dimethyl aniline to diethyl safranine through double azo linkage. It has been used for reduction–oxidation capability. The color of JGB is blue. The dyes which are highly used in the manufactural and industrial processes such as textile dyeing, cosmetics, and food includes triphenylmethane dyes. These dyes are carcinogenic for microbes and mammals. This will result in abnormalities in the reproduction of aquatic animals. An aromatic amine and an important element of polymers, drugs are o-Phenylenediamine (OPD). It has been found that this dye is highly dangerous in case of eye contact and inhalation. A synthetic dye that consists of a large amount of organic compounds is Brilliant Cresyl Blue (BCB). Some of the cationic dyes are BCB, JGB, etc., are some organic dyes that have different industrial as well as scientific applications. Rhodamine 6G (R6G) is widely used in biotechnological applications. This dye is one among the rhodamine family of dyes. This dye shows unfortunate effects on humans and microorganisms. R6G is water-soluble and shows photostability with better absorption coefficient.

Another water-soluble dye which is commonly used as a coloring agent in garments and food industries is Rhodamine B (RhB). It is basically N-[9-(ortho-carboxyphenyl)-6- (diethylamino)-3Hxanthen-3-ylidene. RhB is an irritant to eyes, skin, and highly toxic.

A water-soluble anthraquinone dye, Alizarin Red S (ARS). It is basically salt known as 1,2-dihydroxy-9,10-anthraquinonesulfonic acid, sodium. ARS is meant to be a biologically active dye, which is highly toxic toward human life.

Methylene blue (MB) is a cationic dye that is yet another dye used widely for colouring in paper, leather, and wool industries.

Crystal Violet (CV) is commonly used in textiles and also used as detection of structures or tissues in veterinary and human medicine. This causes tumors in fishes and is also a poisoning agent.

A benzidine-based dye, namely Malachite Green (MG) has been used preferably in fish farms to stop infections caused by fungi. The combination of MG and leucamalachite green causes severe health hazards toward humans as well as the environment. Direct contact of MG will affect our eyes and irritate the skin, which results in redness [18, 23].

4 Detection of Dyes in Water Samples

In water samples, the detection of dyes is a big issue. As we know the dyes are colored and spectrophotometry is not possible as the interference of spectral lines in a mixture may contain a number of dyes including both anionic as well as cationic dyes, namely BCB, R6G, MB, CV < MO, AO, etc. The quickest analysis of dyes in water effluents is strenuous, excessive, and requires particular techniques and procedures. Several dyes may undergo biological, chemical, and photochemical degradation in water. The final products formed from degradation were tenacious to the environment and more injurious to water bodies. Studies reported that under direct sunlight the photodegradation green dye is transformed into more toxic chemicals. Due to this degradation, some dyes form intermediates like benzidine, benzene, etc., which makes the detection even more difficult [18, 24].

5 Removal of Dyes

One of the huge water consumption industries is the textile industry. The resultant coming from these industries include different chemicals and coloring compounds that should be properly treated before disposal. But this treatment is difficult as the sewage contains various compounds for which the differentiation is tougher. Currently, the usage of a combination of different methods of treatment so as to remove the contaminants seen in wastewater treatment (Holkar 2016). Thus, adsorption became the most effective method for the removal of dye in textile water.

In adsorption, the affordable source of adsorbents is sludge (plant biosolids), magnetically modified brewer's yeast, cassava peel activated carbon, tapioca peel activated carbon, soil, fly ash, jack fruit peel activated carbon, groundnut shell activated carbon activated with Zinc chloride solution, neem leaf powder, kaolinite, montmorillonite, hazelnut activated carbon, bagasse pith, natural clay, maize cob, rice bran based activated carbon, guava seeds activated with Zinc chloride solution followed by pyrolysis, etc. These sources are commonly used for the removal of colors from dye-house by various research studies.

5.1 Dye Removal Techniques

The major removal techniques involve physical, chemical, and biological method. The limitations that are faced under these techniques are huge capital costs, lower efficiency, and formation of excess sludge. Out of these methods, some are adaptable and better, and appropriate for the removal of dyes [25].

5.1.1 Physical Methods

The physical method involves, first, membrane filtration, which includes reverse osmosis, nanofiltration, and electrodialysis, Second, it involves ion exchange, and third is the adsorption. In membrane filtration, the demand for periodic replacement have a severe problem in membrane fouling, which is the major limitation. Because of low cost, easy operative, simple design, high efficiency, the adsorption technique became attractive, and also it serves as a better alternative compared to other treatments. A detailed description of every method is given below.

5.1.2 Membrane Filtration

A membrane is a thin layer material that separates the substance when a force is applied. This method involves microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), an advanced treatment technology to remove color, biochemical oxygen demand (BOD) and chemical oxygen demand (COD). Usually, the pore size is determined to check whether the particle is passing or retaining within the membrane, which is the core principle for membrane filtration accompanied by different membrane techniques. When particles are larger than the pore size of the membrane, particles will be hindered to pass through.

Membranes with a pore size of 0.03–10 microns having molecular mass greater than 1,000,000 daltons and low feed water pressure of 100–400 kPa are separated using microfiltration process.

For treatment of organic colloids or inorganic particles having a separation of 0.05–0.15 μm, is generally used in ultrafiltration method (UF). The studies were carried out with Reactive Black 5 [26]. The rejection remained as 70% for dye concentration of 500 mg/L. Thus, UF is considered less suitable for dye removal.

Nanofiltration involves the size of the pore ranging from 1 to 10 angstronm. Nanofiltration is a combination of ultrafiltration and reverse osmosis. Compared to

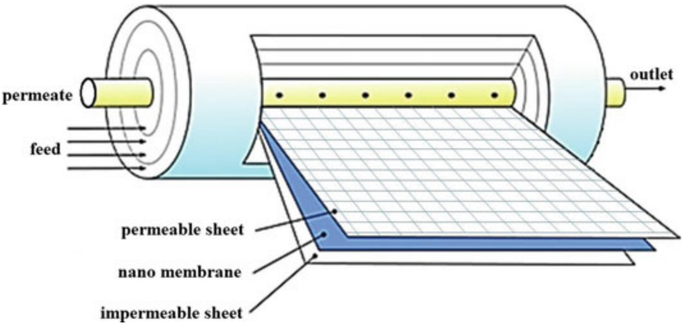


Fig. 3 Nanofiltration process

UF and RO, the maintenance costs, low operation, low investment, higher diffusion of flux, detention of salts were lower. So nanofiltration is considered superior to UF and RO (Fig. 3).

Usage of cellulose nanocrystals proved as an effective filtration process for removal of dye (Methylene blue (MB), Victoria blue (VB), and Methyl violet (MV)). Later Reactive black 5 was studied by Amin et al. using nanofiltration technique from sewage under different conditions such as flow rate, pressure, temperature, etc. The results show as the rejection of dye exceeding 99% is possible with a pressure of 15 bar, temperature of 35 °C, and flow rate of 480 L/h. From this study, nanofiltration is a highly efficient technique in the removal of reactive dyes. Inorganic contaminants present in water are removed by reverse osmosis (RO). RO removes natural organic substances, radium. The advantages of reverse osmosis are low waste concentration is possible, removes nearly all ions contaminated in water, bacteria, and particles are removed.

5.1.3 Ion Exchange

An attractive feature with high efficiency, low cost for the purification of water is the Ion exchange method. The strong interaction of functional groups and charged dyes on the exchange of resins is possible in the removal of dyes in aqueous solution. Resins are classified into four parts, namely cation exchange membrane, anion exchange membrane, cross-linkage membrane, and other ion exchange membrane. Out of these four categories, anion and cation are mostly used for the removal process. Anion exchange removal represents positively charged groups such as $–NH^{3+}$, $–NRH^{2+}$, $–NR2H^{+}$, which pass anions and restrict cations. Whereas cation exchange membrane contains negatively charged groups, namely-SO^{3-}, $–COO^{-}$, etc. which allows only cations and prevents anions.

Some removal examples are depicted below.

Congo Red (CR) an anionic dye is removed from water bodies using an anion exchange membrane studied by Ismail et al. [18]. The study showed that the membrane dosage and contact time is a significant influence on CR removal efficiency. The effect of temperature and ionic strength was compared to be very less.

Removal of Acid dye Orange (AO7) through anion exchange was carried out by Akazdam and Chafi. The studies include various parameters like pH, contact time, temperature, adsorbent dosage, agitation speed, etc. The results indicated that solution pH is an important factor for the removal. The resin almost removed 75% of AO7 within 100 min. Results indicate that the experimental data was fitted well to the Langmuir isotherm model with the maximum adsorption capacity of 200 mg/g. Adsorption kinetics showed that the adsorption process followed the pseudo-second-order model and thermodynamic studies further confirmed that the adsorption of AO7 on the macroporous basic anion exchange resin under the investigated conditions was a spontaneous and exothermic process.

5.1.4 Adsorption

Sticking of ions or atoms or molecules of dissolved solid or liquid or gas to a surface is known as adsorption. On the surface of the adsorbent, a thin film of the adsorbate will be created during the process. Adsorption is different from absorption as the absorption phenomenon involves the volume of the material and adsorption involves only surface.

The adsorption process is categorized into two, namely: physical adsorption and chemical adsorption depending upon how the adsorbate is adsorbed on the adsorbent surface.

Physical adsorption involves the sticking of adsorbate to adsorbent through Van der Waals force (weak force), hydrogen bonding, hydrophobicity, static interactions, polarity, dipole interactions, and π-π interactions. Whereas in chemical adsorption, adsorbates are chemically bound to the surface of an adsorbent by the force of the electrons exchange.

For environmental remediation purposes, this adsorption method is widely used as it has been considered superior to other dye removal methods. Moreover, adsorption does not cause hazardous substances and avoids secondary pollution. Adsorption by eco-friendly and cost-effective adsorbent was selected for the adsorption process depending on the adsorption capacity, surface area, and potential for reuse cost of the materials (Fig. 4).

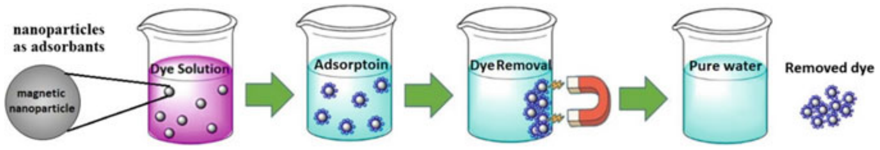


Fig. 4 Nanoparticles as adsorbents

5.1.5 Chemical Methods

Chemical methods include ozonation, coagulation-flocculation, precipitation-flocculation with $Fe^{2+}/Ca(OH)_2$, photocatalytic degradation, electrochemical treatment. These chemical techniques are efficient for the removal of dyes from wastewater, but the excessive use of chemicals causes the difficulty of sludge disposal and the possibility of a secondary pollution problem. In addition, high electrical energy and high cost are needed for these techniques resulting in limited use.

5.1.6 Ozonation

The introduction of ozone into water is known as ozonation or ozonization. It is basically chemical water treatment. One of the strong oxidants is Ozone (contains 3 oxygen atoms).

They can easily decompose into oxygen and free radicals. These free radicals then combine with dyes causing color destruction. Ozone can strike on pollutants by the indirect or direct reactive path.

The direct path involves the ozone molecular activity and the indirect path results in highly oxidative free radicals. The rate of decomposition of ozone is truly affected by pH and dye concentration. For a low pH, the ozone will be present as molecules to react with dye as an electrophile.

At high pH, ozone can decay suddenly into hydroxyl radicals in solution, which are a powerful, effective, and nonselective oxidizing agent. The decolorization efficiencies of Reactive orange 7 (RO 7), Reactive blue 19 (RB 19), and Reactive black 5 (RB 5) were almost 100% are reported in Shaikh et al. For pH 4, 7, 9, and 11 the percentage of color removal was studied in RO7 as 19, 50, 60, and 75%. The homogenous trend can be noted in the decolorization of RB 5 when the pH reached 11. O^3 decomposition and OH radicals production occurred at higher pH values which hold the performance of decolorization. The research investigated by Manali and coauthors demonstrated that the degradation of Methylene blue (MB) was up to 94.6% after 26 min [27].

5.1.7 Coagulation–Flocculation

The treatment of drinking water, textile wastewater, and reducing cop partly were carried out using coagulation–flocculation technique. It is considered an essential and most efficient method. The usefulness is being reported in Sanchez-Martin et al. [28].

By adding coagulant to neutralize the negative charges is accompanied with the destabilization of colloids is happening in the coagulation process.

In the flocculation process, the huge particles are collected to form microflocs that will be taken out in subsequent sedimentation stages or flotation stages. An agent that causes a liquid or sol to coagulate is called a coagulant.

Coagulants are divided into two main types coagulants and coagulant aid. Coagulants are either metallic salts, polymers or naturally occurring materials. The removal of dyes by aluminum sulpfate and polyaluminium chloride has been reported. Khayet et al. stated that the effectiveness of aluminum sulpfate for the removal of Acid black 210 (AB 210) is more than 90% under the condition of 40 mg/L of dosage, 4–8 range of pH, and 35 mg/L of dye concentration [29].

To modify or to assist a process, coagulant aid is always used. It is basically not a coagulant. It can be a material or can be a chemical. The use of a coagulant aid will increase the density of slow-settling flocs and increase the toughness of the flocs so that they do not break up during the mixing and settling processes.

5.1.8 Electrochemical Methods

In recent years, the most attractive method due to complete decolorization, low final temperature, operating under moderate pH range, reduced BOD and COD with no sludge formation is the electrochemical method. Electrochemical method is used in the preparation of compounds or retrieval of metals, huge growth of decolorization of dye applications. In this process, highly toxic pollutants are destroyed either directly or indirectly by oxidation process.

In anode surface, the pollutants are adsorbed first and then destroyed by an anodic transfer reaction, which is a direct anodic oxidation process.

Strong oxidants are released during electrolysis and then destroyed in the oxidant solution during its oxidation process, which is known as the indirect anodic oxidation process [30].

5.1.9 Biological Methods

The most regular and universal technique used in wastewater dye treatment is biological treatment [31]. Microbial technique implementation is shown to be highly economical, less intensive to treat industrial waste or sewage. These can be treated better through microbial biosorption and biodegradation. Transformation of dye molecules to be harmless is done through microorganisms. Functional groups like amino, hydroxyl, phosphate, carboxyl present in cell wall components are accredited with the above property of microorganisms. This will result in a strong attractive force between the cell wall and azo dye.

Different species were used for the mineralization and decolorization of various dyes. This method is advantageous with inexpensive, low run cost, nontoxic resultants. Biological methods are of two types: aerobic and anaerobic, but sometimes a combination of aerobic and anaerobic is also predicted which is depicted below in detail [32–36].

5.1.10 Aerobic Treatment

The potentiality to treat dye wastewaters was carried out by bacteria and fungi worldwide. Bacteria present in wastewater secretes enzymes which will give out organic compounds. Aerobic bacteria isolation has been still persisting [37]. Straining *Kurthia* sp. Triphenylmethane dyes such as crystal violet, pararosaniline brilliant green, malachite green have decolorized upto 92–100%. In this study, after biotransformation, the COD reduction of cell extracts triphenylmethane more than 88% except ethyl violet (70%). Synthetic dyes does not allow to decompose by activated sewage in aerobic process [38]. Anerobic strain of bacteria through decolorization showed outstanding ability on the structure of dye [39].

Research is still going on which is based on the study of decolorization of azo dyes and triphenylmethane dyes with the help of fungal strains [40]. Different studies were performed with different fungi, namely Phanerochaete chrysosporium for the decolorization of dyes. For the same purpose, several microorganisms were also included. For example, Cyathus bulleri, Funalia trogii, etc. They concluded during various tests that concentration, temperature, pH like factors are affecting the decolorization process.

5.1.11 Anaerobic Treatment

Degradation of synthetic dye was demonstrated [41]. Under aerobic condition, dye decolorization was succeeded but in conventional aerobic systems perception of non biodegradability still persists [37]. Mordant Orange 1 and azodisalicylate were decolorized through methanogenic granular sludge [42]. Zee Van der demonstrates the possibility of the application of anaerobic granular sludge for the decolorization of 20 azo dyes [43].

The problem of bulk sludge can be avoided through anaerobic pretreatment. It was also possible for exclusion of expensive aeration. With the removal of BOD, decolorization of dyes can be done easily. And also foaming problems can be rectified with the surfactants, through sulfate reduction heavy metals can be maintained, effluents' high pH can be acidified, refractory organics degradation can be initiated. The main disadvantage was insufficient on BOD removal, dyes were loving, nutrients were not removed [41].

5.1.12 Combined Aerobic–Anaerobic Treatment

A combined form of aerobic and anaerobic treatment is advised to get better results of decolorization of dyes from industries. A major advantage of this treatment is the full mineralization through the collaboration of microorganisms. Enhancing the controlled anaerobic bioreactors resulting in the reduction of azo bond, colorless aromatic amines. Hence, it will make azo dye treatment fetching. Thus, the combination is now advised for dye treatment in wastewaters [44–46].

The factors influencing this treatment are the concentration and pH of the dye and the temperature of sewage. The main disadvantage of the biological method is low biodegradability of dyes, less flexibility in design and operation, larger land area requirement, and longer times required for decolorisation–fermentation processes, thereby making it incapable of removing dyes from effluent on a continuous basis in liquid state fermentations [47].

5.1.13 Bioremediation of Dyes

Biodegradation or biological degradation means degradation of the dyes to a less toxic compound, which is economically feasible, eco-friendly, and eventually aids color removal [48]. The removal mechanism of azo dyes involves two steps. In the first step, azo bonds were broken down to form amines and in the second step, the amines were metabolized into nontoxic molecules under aerobic condition [49]. Under aerobic and anaerobic environments, the bacteria have to survive so that the degradation will be completely fulfilled for the formation of azo bonds within the dyes themselves.

The wastewater treatment with using different fungi in dying industries has been reported [50]. With the combination of aerobic and anaerobic treatment by different microbes, biological degradation of textile dyes has been noticed a better improvement [51]. Replacement of physical and chemical with the fungal based dye decolorization have conducted [52]. An important tool for the effluent treatment from textiles, paper and pulp industries that comprises PAH-polycyclic aromatic hydrocarbon is Phanerocheate chrysosporium [53]. This develops lignin and manganese peroxidases like enzymes. Another study involves Trichoderma harzianum, introduced for cleaning the sludge from different industries [54]. Combo of bromophenol blue dyes and Congo red were completely degrades using semi-solid PDA as a medium with fungal mycelium process. The growth of Trichoderma harzianum was inhibited by the medium which contains Basic blue, Congo red, Acid red, Direct green, and Bromophenol blue.

Bromophenol blue was considered as a good inhibitor compared to other dyes. Fungi is distinct as it is fast-growing with larger biomass and the hyphal spectra are comparatively higher than bacteria. Fungi have a high surface to cell ratio, thus it is considered as a string degrader [55]. Filamented fungi can be developed as a strong degrader as it has high surface to cell ratio. The degradation of textile dyes like Orange 3R was studied based on the combination of Aspergillus Strain (MMF3) with NaCl having different concentrations [54].

The high decolouration even in a naïve condition, the fungal strain is considered in the biological treatment of the wastes from the dyeing mills. The anthraquinone dye-Reactive Blue4 dye can be removed by marine derived fungus as bioremediation process [56] involves two steps for degradation. First is the partial treatment of purified laccase and the second is with compounds (with low molecular weight) as the final enzymatic degradation process. It is found that 29% reduction is confirmed in total carbon and in toxicity, a twofold reduction is found. The azo dyes found in wastewater by the biosorption of paramorphogenic form of Aspergillus oryzae are reported [57]. The laccase enzyme isolated from Trametes polyzona strain WR710-1is examined for the decoloration and deprivation of bisphenol-A and other synthetic dye. About 61% decoloration was observed by Anthraquinone dye (Reactive Blue 4) and was found that the COD was reduced by twofold in 12 h by laccase treatment. The whole process of metabolites synthesis was monitored by mass spectrometry, UPLC, and UV–vis spectroscopy to analyze the Characterization. Recently, for eliminating tannins along with dyes, Biodegradation combined with ozonation has been investigated to minimize pollutant load in the effluent. The biodegradation of wattle extract and various synthetic dyes was extensively studied using various fungal cultures, like Penicillium sp. and Aspergillus niger. The removal process of tannins and dyes was successful with the usage of a hybrid model of ozonation and biodegradation. As the degradation rate is higher in ozonation, this method is highly beneficial compared with biodegradation. The pollution level of different physical parameters like BOD, COD, TOC, TSS, and TDS was found to be at a minimum by this combined model [58].

5.1.14 Bacterial Degradation of Dyes

In bioremediation, microorganisms capable of catabolizing the organic pollutants to either recognize the toxic pollutants or to degrade the dyes in wastewater is to be thoroughly studied [59, 60]. The study of the dye degradation ability of bacteria must be done vigorously because it is easy to culture and grow them. Further, it is found that chlorinated and aromatic hydrocarbon-based organic pollutants are catabolized by bacteria. Carbon source will decompose the bacteria and the same bacteria have the ability to oxidize the sulfur-based textile dyes to sulphuric acid. Many bacteria were identified to degrade different azo-based dyes at a faster rate. By the reduction of azo dyes, different bacterial group under traditional aerobic, anaerobic and under extreme oxygen deficient conditions are employed for decolorization. The azo dyes start with the breaking of –N=N– linkage is the first chemical reaction during the reduction under anaerobic environment by the azoreductase enzyme which results in a colorless solution of aromatic amines. It is also reported that after dye reduction, the metabolites formed [61] can further be catabolized using aerobic or anaerobic processes. Also during dye decolorization, the intermediate products can also be reduced by hydroxylase and oxygenase and other enzymes produced by the bacteria [62, 63]. The aerobic bacteria that propagates in azo compounds are responsible for the formation of intermediate sulfonated amines which are aerobically degraded. Bacillus subtilis, Clostridium perfringens, Proteus sp., Pseudomonas aeruginosa, Pseudomonas putida are some Gram-positive bacterial strains that were found to decolorize various structurally different textile azo dyes effectively. Similarly, Klebsiella pneumonia, Enterococcus sp., and Escherichia coli, being Gram-negative bacterial strains, exhibit decolorizing efficacy on various dyes. Thus, some naturally occurring bacteria in the natural water and soil systems are used to biodegrade textile wastewater.

6 Advanced Oxidation Processes

Advanced Oxidation processes (AOPs) are the processes that involves the powerful generation of hydroxyl radical (•OH). The hydroxyl radical, •OH, is the neutral form of the hydroxide ion. Hydroxyl radicals are short-lived and highly reactive. Hydroxyl radicals are produced from different kinds of energy (electrical, sound, etc.), hydrogen peroxide, ozone, catalyst. AOPs play a vital role in removing organic waste from the water. Numerous studies were out regarding the AOPs in water treatment. Generally, in AOPs •OH radical will be released for the degradation of pollutants. They attack the molecules quickly and unselectively. AOPs depend on the production of highly reactive hydroxyl radicals (•OH). Hydroxyl radicals are strong oxidants, can oxidize anything present in water. It also reacts indiscriminately and can easily fragmented results in the conversion of small inorganic molecules. These radicals are formed with the help of hydrogen peroxide, ozone or UV light. Two types of systems are possible in AOPs. Homogenous system and Heterogeneous system.

Nonbiodegradable materials such as pesticides, aromatics, some volatile compounds present in water can be cleansed up using AOP process. The secondary treated water with sewage can be treated using AOPs known as tertiary treatment. The contaminants will undergo mineralization. The ultimate goal of AOPs is the purification of water from chemical contaminants there by reducing the toxicity of water (Fig. 5).

For the generation of hydroxyl radicals, the AOPs are classified into different types.

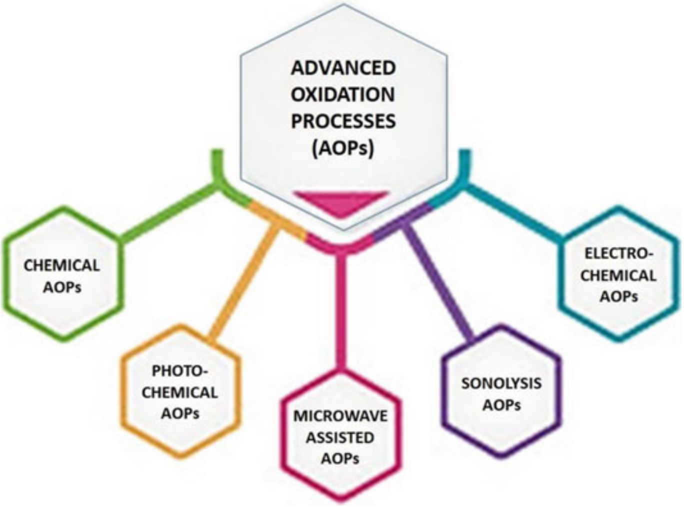


Fig. 5 Advanced oxidation process-brief

6.1 Chemical AOPs

Various combinations of chemical agents produce some temporary products. Usually, hydrogen peroxide is used as an oxidant, sometimes ozone and air are also used.

Fentons' Reagent (Fe^{2+}/H_2O_2)

A combination of soluble ion (II) salt and H_2O_2 known as Fenton's reagent is used for the degradation process. As it was developed by Fenton, the reagent was later known as Fenton's reagent. Fenton tried a mixture of Fe^{2+} and H_2O_2 for the tartaric acid destruction and oxidation.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^- \text{ (initiation of Fenton's reagent)}$$

By reduction of oxygen on different electrodes such as gas diffusion electrodes, graphite hydrogen peroxide can be formed.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

With the addition of Fe^{2+} ions as a catalyst, very strong, active oxidant hydroxyl radical can be generated which initiate the oxidation of pollutant (RH) molecules

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + \bullet OOH + H^+ \quad \text{(regeneration of } Fe^{2+} \text{ catalyst)} \quad (3)$$

$$\bullet OH + RH \rightarrow R\bullet + H_2O \quad (4)$$

$$H_2O_2 \rightarrow HO\bullet + HOO\bullet + H_2O \quad \text{(Self scavenging and decomposition of } H_2O_2\text{)}$$

Controlled production of radicals is the advantage of the Fenton process. Fenton process has been studied in vast contaminants such as pesticides, organic molecules, also degradation of benzene ring compounds, azo dyes. As this process is easy to handle, simple inexpensive chemicals and energy output truancy paved the advantages toward the water treatment.

Heterogeneous Fenton Process (Fenton Like Reactions)

Homogeneous Fenton process has shortcomings for Fenton reactions, heterogeneous Fenton process taken into account. In this system, the Fe (III) species immobilized within the structure of pores of catalyst generates hydroxyl radicals from H_2O_2. In this method, the strain of iron ions into water results in the precipitation of iron hydroxide is prevented.

This method is easily separable, recovery of the catalysts and extendable during continuous operations. In this process, nano zerovalent iron (NZVI) is highly acceptable. Oxidation of NZVI delivers an alternative solution for the production of Fenton's reagent.

$$O_2 + Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2O_2$$

Nano zerovalent iron commonly influences Carbon-based materials, palygorskite composites, chitosan, etc.

Catalytic Wet Peroxide Oxidation (H_2O_2/Catalyst)

The heterogeneous Fenton process using water-soluble catalyst is known as the Catalytic wet peroxide oxidation process. It involves Fe^{2+}/Fe^{3+} ions for degradation process. Some variable valency materials such as cobalt, copper, gold, nickel, and carbon-based materials will decompose hydrogen peroxide to hydroxyl radical.

Perozonation (O_3/H_2O_2)

A fast reaction of O_3 and H_2O_2 which produces hydroxyl radical is known as perozonation.

$$O_3 + HO_2^- \rightarrow O_2 + \bullet OH + O_2^-$$

This process is simple and has good bacterial activity. For this reason, perozonation is highly recommended for the disinfection of potable waters. However, the drawbacks of this process are sensitivity to pH, temperature, and low water solubility.

Catalytic Ozonation (Ozone/Catalyst)

Due to the efficient oxidation capacity of ozone, it plays a vital role in water treatment. Mainly the removal of contaminants from drinking water is carried out in the catalytic ozonation process. Heterogeneous catalysts are used to improve the reactivity through milder conditions, reduces the cost. A complex will be formed in between the catalyst and organic compound which will dispose into ozone and metal particles.

$$Fe^{2+} + O^3 \rightarrow Fe^{3+} + O_3^-$$

$$O_3^- + H^+ \leftrightarrow HO_3 \rightarrow O_2 + \bullet OH$$

Materials like $NiFe_2O_4$, MgO, Co_3O_4 have been tried as a catalyst in ozonation.

Catalytic Wet Air Oxidation (O_2/Catalyst)

Molecular oxygen is used as an oxidizing agent for the treatment of water. This process needs high temperature (473–593 K) and pressure (20–200 bar) for the generation of hydroxyl radicals. This method is frequently used for the treatment of sewage having organic matter, COD, defiant to biological purification. The compounds will break down in the form of easily treatable, simple before their release.

$$RH + O_2 \rightarrow R_{\bullet} + HO_{2\bullet}$$

$$RH + HO_{2\bullet} \rightarrow R_{\bullet} \rightarrow H_2O_2$$

$$H_2O_2 + M \longrightarrow 2\bullet\ OH + \text{þzM}$$

The main disadvantage of the wet air oxidation process is that it's unfit for mineralization. Mixed oxides, ruthenium, Ru/nitrogen-doped carbon nano fibers have been used for the oxidation process.

6.2 Photochemical Advanced Oxidation Processes

Light is generally used in photochemical advanced oxidation processes as it is clean, inexpensive, more efficient than chemical AOPs, can disinfect waters. In this method, UV radiations are coupled with ozone and hydrogen peroxide with the catalyst either Fe^{3+} or TiO_2.

This method can be degraded under three processes, namely photooxidation in presence of H_2O_2, photodecomposition in presence of O_3 on UV irradiation, and oxidation by photocatalysis.

Photo Peroxidation (H_2O_2/UV)

H_2O_2 is ionized by absorption of UV radiations (200–300 nm). The decomposition of uncharged radicals of O–O bond of hydrogen peroxide molecule leads to form hydroxyl radicals through the following reactions

$$H_2O_2 + h\nu \rightarrow 2\bullet OH$$

$$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet$$

$$HO_2\bullet + H_2O_2 \rightarrow \bullet OH + H_2O + O_2$$

$$\bullet OH + HO_2^- \rightarrow HO_2\bullet + OH^-$$

$$2\ HO_2\bullet \rightarrow H_2O_2 + O_2$$

$$\bullet OH + HO_2\bullet \rightarrow H_2O + O_2$$

$$2\bullet OH \rightarrow H_2O_2$$

For higher efficiency degradation it is advisable to use a higher concentration of hydrogen peroxide as the molar absorption of hydrogen peroxide is weaker in UV radiation.

Photo Ozonation (O_3/UV)

Ozone present in water absorbs UV region releases hydroxyl radicals which are proven highly efficient for sewage removal. The series of reactions are as follows:

$$O_3 + H_2O + h\nu \rightarrow 2\bullet OH + O_2$$

$$O_3 + \bullet OH \rightarrow HO_2\bullet + O_2$$

$$O_3 + HO_2\bullet \rightarrow \bullet OH + 2\,O_2$$

$$\bullet OH + HO_2\bullet \rightarrow H_2O + O_2$$

Heterogeneous Photocatalysis

When light is exposed to a semiconductor having bandgap, valence electron is excited to conduction band leaving a hole in the valence band. In photocatalysis method, the electron hole pair will move to the surface of the semiconductor leading to redox reactions, and as a result, hydroxyl radicals with ion radicals are formed. The hole thus formed in a semiconductor serves as an oxidant which degrades the contaminants directly and hence purifies the water. Titania nanoparticles under this photocatalysis method are exclusively studied and now emerged as second widest method for purification of water.

Photo-Fenton/Fenton Like Systems

UV radiation dissociates hydrogen peroxide directly into hydroxyl radicals with a range of 250–400 nm. The intensity of UV radiation is significant in the degradation process. Various materials like ferric hydroxide, Fe/ZSM-5 zeolite Fe- supported bentonite, nanostructures like nickel ferrite have been experimented under this process.

6.3 Microwave Enhanced AOPs

Microwave enhanced AOPs are categorized into two processes namely homogenous and heterogeneous processes. In a homogeneous process, the chemical oxidants are activated primarily under the influence of microwaves and result in the production of hydroxyl and superoxide anion free radicals which will help in the degradation of pollutant species. In a heterogeneous process, primarily the formation of solid substrates (including solid catalyst) and hot spots on the edges occur. These are also under the influence of microwaves. The hotspots make the formation of hydroxyl and superoxide anionic radicals which will prompt the degradation of organic pollutants.

In this process, microwaves are generated at 2.5 GHz frequency and electrodeless discharge lamps were used as a source of ultraviolet radiation. Under continuous microwave exposure, it will give an ultraviolet–visible electromagnetic spectrum. There will be a glass tube containing electron–ion plasma material that acts as a plasma chamber. When the microwave enters the chamber, the electrons get excited and collide with the gas atoms and ionize them to produce more excited electrons.

In the microwave coupled ultraviolet process, microwaves cause the dye molecules to get stabilized at high energy excited states which promote the generation of hydroxyl radicals and result in rapid decay of dyes. In microwave-assisted ultraviolet/H_2O_2 process, H_2O_2 yields a huge quantity of additional hydroxyl radicals under ultraviolet radiation. A combined microwave/ultraviolet/H_2O_2 process is highly recommended for the removal of dyes as coupling of microwaves will rise the temperature of the aqueous pollutant matrix, thereby resulting in enormous production of hydroxyl radicals and increasing the degradation of microwave/ultraviolet/H_2O_2 process.

The microwave/Fenton process improves the efficiency of dye removal. The priorities in this process involve pH-insensitive, less floc formation, better settling, and no need for pretreatment. This method is efficient for the degradation of dyes/mineralization due to synergistic effect of ultraviolet/microwave radiation. The limitations of ultraviolet/H_2O_2 and ultraviolet Fenton processes are encountered by the investigation of microwave coupled photocatalysis. In this method, secondary pollutants are produced and offer low mineralization.

Acid Orange 7 is degraded through microwave radiation by using polyaniline as a catalyst in the absence of light source. Bromothymol blue dye in an aqueous medium is degraded through microwave/ultraviolet/TiO_2/O_3/H_2O_2 hybrid process [64].

6.4 *Sonolysis/Sonochemical AOPs*

In sonolysis, ultrasonic irradiation is used to produce hydroxyl radicals through the pyrolysis of water. For removing the toxic pollutants, this process won't produce any exterior chemicals in the water system. Accordingly, sonolysis is referred to as the "green method". Initially, acoustic bubbles were formed during the ultrasound irradiation. The bubble formation is controlled by changing the frequency and power that were given in the form of ultrasound serves as a parameter for controlling the degradation rate of pollutants. Sonochemical treatment efficiency is controlled by cavitational activity which is yet another crucial parameter in this process. Usage of intense ultrasonic waves increases the temperature and pressure of the aqueous matrix resulting in the destruction/oxidation of organic compounds or pollutants into simpler products due to the formation of highly free reactive radicals.

The major drawback of this process is that it does not require any additional chemicals for the production of hydroxyl radicals. Later it requires high energy and extra chemicals for mineralization. With this drawback, the sonolysis process is limited with lab scale or low initial COD value pollutants. The final products of this process are carbon dioxide, water, inorganic salts, hydrogen, etc. The combination of ultrasonic, photocatalytic, Fenton, ultrasonic radiation process has more influence on the degradation of dyes by the release of a huge amount of hydroxyl radicals.

6.5 Electrochemical Advanced Oxidation Processes (EAOPs)

The electrochemical AOPs involve electrochemical treatments which are used to remove toxic pollutants. This method is based on the generation of the most powerful oxidizing agent known as hydroxyl radicals, able to destroy the organic compounds present in the water. Electrochemical AOPs basically involves three methods

1. Anodic Oxidation: One of the popular EAOP is Anodic oxidation, where organic compounds are directly oxidized at the anodic surface by electron transfer or indirectly oxidized by •OH weakly physisorbed at anodic surface or agents at the bulk solution (active chlorine species, O_3, persulfates, and H_2O_2). When anodic oxidation is combined with cathodic electrogeneration of H_2O_2, then the process can be named anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2). The oxidation process in anodic oxidation is carried out by the following processes:

    - Direct electron transfer to anode surface “X”
    - During the oxidation of water to oxygen, heterogeneous reactive species are formed as intermediates including physisorbed •OH at anode surface [X(•OH)], H_2O_2 (weaker oxidants produced from [X(•OH)]) and ozone formed from water discharge at the anode surface
    - Other weaker oxidant agents produced electrochemically formed from ions existing in the bulk.

    The equations for anodic oxidation:

$$X + H_2O \rightarrow X(\bullet OH) + H^+ + e^-$$

$$2X(\bullet OH) \rightarrow 2MO + H_2O_2$$

$$3H_2O \rightarrow O_3 + 6H^+ + 6e^-$$

The efficiency of anodic oxidation is purely dependent on the mass transfer of pollutants from the bulk solution to the anode surface. Anodes are usually made up of Ti-based alloys, TiO_2, graphite, Ru or Ir oxides, boron-doped diamond (BDD). Studies arose interest in the mineralization of organic pollutants by direct electrochemical oxidation using boron-doped diamond. These studies then conclude that BDD exhibits good chemical and electrochemical stability, a wide potential for water discharge, and longer durability.

2. Electro-Fenton (EF) Process

Electro-Fenton (EF) process is the most known method in EAOP, which involves an indirect electrochemical way to produce/generate hydroxyl radical in aqueous solutions. This method was developed to overcome the drawbacks of the chemical Fenton process. It can also be called as electrochemically assisted Fenton process. •OH is generated through Fenton's reagent (please refer chemical AOPs) in which Fenton's reagent is electrochemically produced in situ preventing the use of high quantities of H_2O_2 and Iron (II) salt. The production of hydrogen peroxide is one of the crucial parameters as H_2O_2 controls the rate of Fenton's reagent. Hydrogen peroxide is continuously supplied to wastewater in an electrochemical reactor from the two-electron cathodic reduction of oxygen gas, directly injected as compressed air.

$$O_2(g) + 2H^+ + 2e^- \rightarrow H_2O_2$$

The above H_2O_2 production efficiency is not high and depends on operating conditions such as solubility, temperature, pH, O_2).

The second component of Fenton's reagent is Fe^{2+} ion, which is formerly started in a catalytic amount (0.1 nM) in the form of ferrous salts and is electrocatalytically regenerated from the reduction of Fe^{3+} formed by Fenton's reaction. Now, this Fenton's reagent is produced continuously producing hydroxyl radicals through Fenton's reaction, thereby destroying the organic pollutants. The hydroxyl radicals react in the bulk solution with organic compounds resulting in mineralization/oxidation [65].

The main advantages of the EF process over the classical Fenton process are:

- Elimination of parasitic reactions that waste hydroxyl radicals.
- Probability of controlling the degradation kinetics and performing mechanistic studies.
- In situ controlled generation of Fenton's reagent.
- Full control of processing by current/potential control.
- Total mineralization of organic compounds including the intermediates.

The selection of the electrochemical process is purely dependent on the structure and nature of the electrode material, electrolyte composition, and experimental conditions which prevent electrical fouling. Due to versatility, efficiency, easy handling, safer toward environment compatibility, electrochemical AOPs are highly recommended.

7 Nanomaterials in AOPs

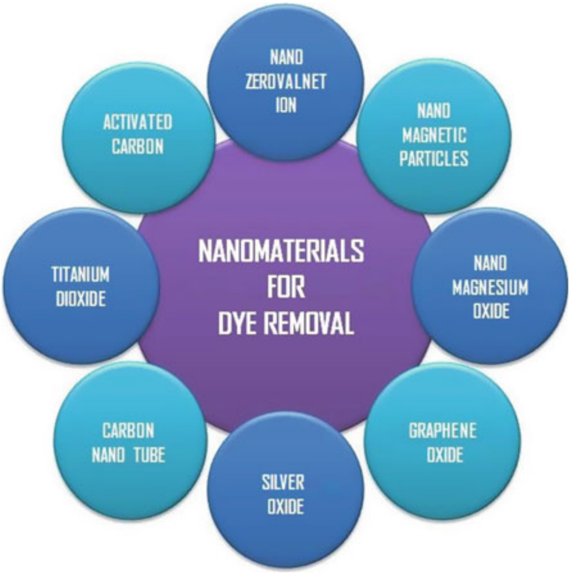
The metal, metal oxide, and inorganic nanomaterials like nano zerovalent zinc, magnetic Fe_3O_4, magnesium oxide (MgO), titanium dioxide (TiO_2), zinc oxide (ZnO) are broadly used for the removal of dyes. It is mainly due to their provide high surface area and specific affinity properties. Further, it is found that nano metal oxides have a low impact on the environment, low solubility, and no secondary pollution (Fig. 6).

7.1 Nano Zerovalent Iron

Nano zerovalent iron (nZVI) is powerful in eliminating pollutants like nitrates, organochlorine pesticides, chlorinated compounds, heavy metals, and dyes. It is assumed that the oxidation of the Fe^0 is responsible for the reactivity of core–shell nanoparticles of ZVI with their microscale counterparts. The high density and high intrinsic reactivity of their reactive surface sites also lead to their higher reactivity.

nZVI is effectively found to remove three azo dyes like Sunset yellow, Acid blue A, and Methyl orange [66]. Increasing the dosage of nZVI, increased the decolonization of the dyes. But the degradation decreased with an increase in the concentration of dyes. The acidic condition was favorable in pH effect to the adsorption which may be due to reduction of H^+ ions to atoms by the electrons released from iron particles. A cleavage of formed by the chromophore group and conjugated system in dyes by these

Fig. 6 Nanomaterials for dye removal



atoms with the decrease of pH. The results in the highly efficient decolorization of Sunset yellow, Acid blue A, and Methyl orange by nZVI. Reactive black 5, Reactive red 198 and Light green are removed. 500 mg of nZVI with concentration of 100 ppm removed Reactive black 5 and Reactive red 198 completely and effectively removed 97% of light green dye.

7.2 Nanomaterials with Magnetic Properties

Iron oxide like magnetite (Fe_3O_4), hematite (γ-Fe_2O_3), and maghemite (α-Fe_2O_3) [67] due to their high ratio of surface area to volume, high magnetic susceptibility, and excellent biocompatibility, have the tendency to oxidation by air and aggregation in aqueous systems.

Fe_3O_4 nanoparticles coated with humic acid (HA), which enhances the stability by reducing oxidation of Fe_3O_4 are used to remove Rhodamine B (Rh B). The adsorption of Rh B by Fe_3O_4/HA reached equilibrium within 15 min, with a maximum adsorption capacity of 161.8 mg/g. It removed over 98.5% of Rh B at an optimized pH [68]. Fe_3O_4 nanomaterials were fabricated from cetyltrimethylammonium bromide by chemical precipitation method. This was used as a surfactant to remove Acridine orange (AO), Coomassie brilliant blue R-250 (CBB), and Congo red (CR) at pH of 4 for CBB, 6 for AO and CR, and at the dosage amount of 0.02 g. Methylene blue (MB) was removed by impregnating magnetic nanoparticles onto maize cobs with 99.9% efficiency. Reactive red 120, Rhodamine 6G, and Direct blue 15 were removed by surface modification of IONPs like ionic liquids, polyacrylic acid, and silica-based cyclodextrin (Al-CD-MNPs) [69].

7.3 Nano Magnesium Oxide

Nano magnesium oxide (nano-MgO), a nanosized alkaline earth metal oxide with high surface reactivity and adsorption capacity, is used as a destructive adsorbent for the removal of many toxic chemicals. Besides, it has excellent optical, electrical, thermodynamic, mechanical, electronic, and special chemical properties. Hence, it is utilized as catalyst support, for toxic-waste remediation, refractory as an additive, in paints and superconducting products, and as bactericide and adsorbent [70]. It is reported that MgO nanoparticles act as an effective sorbent for Reactive black 5 (RB 5) and Reactive orange 122 (RO 122) with maximum adsorption capacity of 500 mg/g and 333.34 mg/g, for RB 5 and RO 122, respectively [71].

Removal of toxic dyes such as Congo red and malachite green has been studied with different morphologies of MgO such as nanorods, nanoflakes, etc. Hence, synthesis of MgO with enhanced surface area with varying morphologies such as rods, wires, belts, tubes were recently attempted [72]. In a comparative study of MgO as nanorods, hierarchical nanostructures and nanoflakes for removal of dyes were done. It exhibited excellent adsorption with maximum sorption capacities of 1205.23 mg/g and 1050.81 mg/g, respectively, for the removal of both the dyes which was relatively considered much higher than other absorbents, maybe due to the high surface area and hierarchical structures.

An advanced composite material fabricated by the modification of nano-MgO form was used as the adsorbent for the removal of Rhodamine B (Rh B) [73]. The adsorption process was explained by Langmuir isotherm, where the maximum adsorption capacity of 16.2 mg/g at pH of 6.75, dosage of 100 mg, and contact time of 2 h was observed. By using modified co-precipitation method, Rice straw charcoal/MgO nanocomposites were prepared to investigate the ability to remove Reactive blue 221 (RB 221) from aqueous solutions by varying the amount of shaking time of 90 min, shaking speed of 200 rpm, pH of 7.0, temperature of 26 °C and adsorbent dosage of 250 mg at an initial adsorbate concentration of 30 mg/L. The pseudo first-order kinetics and the Freundlich isotherm were attributed for the adsorption of this dye. The Langmuir isotherm was calculated to be 27.78 mg/g as the maximum adsorption capacity. Thus, adsorption of RB-221on nanocomposite of rice straw charcoal/MgO nanocomposite from aqueous solutions was shown possible.

7.4 Graphene Oxide and Graphene Oxide Based Nanomaterials

A two-dimensional nanomaterial with tightly packed six-membered rings of sp^2 carbon atoms is known as graphene. Graphene has strong mechanical, electrical, and optical properties. It is found in applications like nano-electronic devices, sensors, and nanocomposite materials. Further, it to have strong π-π stacking due to the graphitized basal plane structure, found to strongly interact with the aromatic moieties present in various dyes [73]. Graphene oxide (GO) containing oxygen-rich functional groups on its surface, (i.e., carboxyl, carbonyl, hydroxyl groups) is found to disperse in water and enhance the electrostatic interactions with cationic dye molecules. Hence, it is considered as a promising substrate for the preparation of various graphene-based nanocomposites.

Graphene oxide is found to have high efficiency in removal of lead to the increase of solution pH. Thus, the magnetite/reduced graphene oxide nanocomposites (MRGO) are used to remove Rh B (over 91%) and MG (over 94%) [74]. And the removal efficiencies were over 80% even after five cycles. Hence, MRGO may effectively be used for the removal of dye pollutants. Reduced graphene oxide-supported nanoscale zerovalent iron (nZVI/rGO) was used in the removal of Rh B using artificial intelligence tools [75]. To optimize and predict the optimum conditions for the maximum removal efficiency Response surface methodology (RSM) and artificial neural network hybridized with genetic algorithm (ANN-GA) were used. The results predicted and experimental value by the ANN-GA model were found to be

(90.0%) and (86.4%), respectively. Freundlich isotherm was used to fit the experimental data, and the maximum adsorption capacity based on the Langmuir isotherm was 87.72 mg/gm [76].

7.5 Silver Nanoparticles.

Antibacterial mechanism and microbial inactivity in water is investigated in silver. Their lower toxicity nature is reported [77]. Silver nanoparticles are derived from silver chloride and silver nitrate. The effectiveness of silver nanoparticles in dye degradation is well studied [78].

Water treatment with silver and medicine with silver nanoparticles has been studied. Anti-infective efficiency is more in silver nanoparticles. Compared to bulk material, the antimicrobial characteristics of Ag NPs are improved with mechanical, physical, and chemical properties. For diabetic patients, antimicrobial bandages with Ag NPs is the most promising application. According to the synthesis of Ag NPs, the efficiency varies. Some of such applications are the type of metal precursors, solvents, and reducing agents. Silver nanoparticles are synthesized as a reducing agent in which water is the primary solvent, thereby efficiency is determined.

Methyl Orange (MO) can be degraded using silver as a nanocatalyst under photodegradation/visible light. In general, Ag Nanoparticles have been used as a catalyst for the degradation of dyes namely CR, MO through chemical reduction by NaBH4 method [18]. Silver nanoparticles incorporated with the novel nanocomposite adsorbent, namely the graft copolymer of Poly (AA)/GG have been studied for the removal of methylene blue from the water [79].

Silver nanoparticle with activated carbon was examined for the removal of methylene blue [80]. Silver nanoparticles with nano silica powder combination show the removal of dyes such as Eosin yellow, Bromophenol blue 2, Congo Red, Brilliant blue on adsorption. Novel composite of silver nanoparticles with ploy (styrene-N-isopropyl-methacrylic acid) reduces adsorption of methylene blue (Sivasankari Marimuthu 2020).

7.6 TiO_2 Nanoparticles

The most promising nanoparticle used for water purification is TiO_2 nanoparticles. It has been used as a photocatalyst because of its nontoxic nature, highly stable, and reactive nature.

The removal of Direct black 38 (DB 38) with UV/TiO_2 shows the decolorization process which is sensitive to pH, which arrives to the conclusion that pH is a controlling factor in the removal process [81]. Ni-doped TiO_2 thin films developed through chemical bath deposition under UV light irradiation method are prominent for removal of PonceauS dye [82]. RB 5 a prominent azo dyes are removed by the synthesized TiO_2-NPs through adsorption process. The behavior of the adsorption process can be explained with pseudo second-order kinetic model. The initial concentration of RB5 increases with the adsorption of RB 5 on TiO_2. The synthesized Titanium oxide nanoparticles thus proved to remove azo dyes from aqueous solution in better proportion. Further, the adsorbate and adsorbent ratio provides an economical way to produce expensive semiconductor material support which is convenient for the detoxification of pollutants.

7.7 Carbon Nanotubes (CNT)

Carbon nanotubes are one of the remarkable materials in nanotechnology which is used for different applications. Though it possess in single walled and multi walled, both were used for water remediation. Multi walled Carbon nanotube was studied for the removal of Ismate violet 2R dye from contaminated water [83]. The effects were studied using a batch process with influencing factors such as pH, adsorbent dosage, dye concentration, etc. Multi walled CNT, magnetically modified, was used for the removal of cationic dyes such as Crystal violet (CV), Thiionine (Th), Janus green B (JG B), and Methylene blue (MB) from contaminated water. This was easily adsorbed in water and separated magnetically. The influencing factors like pH, concentration, adsorbent were studied and concluded by Madrakian et al. [84]. Fe_3O_4 nanoparticles with multi walled CNT through chemical methods were used for removing dyes such as methylene blue and neutral red [85].

7.8 Activated Carbons

Water is polluted by synthetic dyes that are released from textile wastewater. Dyes and their degradation products are highly venomous. Activated Carbon (ACs) are known as good absorbents. ACs are used in many processes to remove the contaminants as they readily adsorb color and odor from wastewater as well as drinking water. The particle size, pH, surface properties of activated carbon affect the adsorption of dye. Activated carbon has a distinct molecular structure and it is considered to have high affinity to a variety of dyes. Methods like physical and chemical methods of dye wastewater treatment can be boosted by the addition of activated carbon [86].

AC prepared from waste cassava peel employing physical and chemical methods were tested in the removal of dyes and metal ions from an aqueous solution. The material impregnated with H_3PO_4 was reported more efficient than the heat-treated materials although both efficient as adsorbents for dyes and metal ions. The removal of Rhodamine-B was removed by using tapioca peel activated carbon as an adsorbent was reported [87]. The dye wastewater mainly consists of dying ingredients, sodium sulpfate anhydride (Na_2SO_4), and PVA (polyvinyl alcohol). Granular activated carbon (GAC) and zeolite was used as the adsorbent for dye wastewater [88].

Activated carbon obtained from peel, crown, and core of pineapple with phosphoric acid can be used for the adsorption of methylene blue and malachite green by the chemical activation method. The abundance of pineapple waste problem can be solved through this process [89].

Activated carbon with ground nut shell powder and Zinc Chloride as an adsorbent was used for the dye removal process. The results concluded with the high adsorption and high removal. Activated carbon with neem leaf powder was used for the removal of dyes, namely congo red, methylene blue, and brilliant green. The influence factors were tested and their interactions were studied [90].

The removal of acid red 183 from an aqueous solution was studied by activated carbon, raw kaolinite, and montmorillonite using an agitated batch adsorber [91]. Rice bran-based activated carbon and guava seeds activated carbon, followed by pyrolysis were also used as adsorbents to remove dyes from aqueous solutions.

8 Summary

Contamination of water through disposal of dyes was a major threat for human beings and the environment. Various aspects of dyes, their origin, effects toward human health and hazards, detection and degradation were explained in detail. Advanced oxidation processes, a vital process for dye removal, offer a promising solution for the degradation or removal of dyes (both organic and inorganic) from contaminated water. In future, we can expect more studies in this area for making mankind conservative (Table 1).

Table 1 Nanomaterials and the dyes removed

Nanomaterials	Dyes removed	References
Nano zerovalent iron (nZVI)	Sunset Yellow Acid blue A Methyl Orange	Rahman [66]
nZVI	Reactive red 198 Light Green Reactive black 5	Ruan [76]
Humic Acid coated with Fe3O4	Rhodamine B (Rh B)	Chaudhary [68]
Fabricated Fe3O4	Acridine Orange (AO) Coomassie brilliant blue R-250 (CBB) Congo Red (CR)	Liang [92]
Ionic nanoparticles (ionic liquids, polyacrylic acid and silica-based cyclodextrin (Al-CD-MNPs)	Reactive Red 120, Rhodamine 6G, Direct Blue 15	Absalan [69]
Nano-MgO	Reactive Black 5 Reactive Orange 122 (RO122)	Jamil [71]
MgO nanoflakes, hierarchical nanostructures, nanoflakes	Malachite Green Congo Red	Dhal [72]
Rice straw charcoal/MgO nanocomposite	Reactive Blue 221 (RB 221)	Moazzam [73]
nZVI/rGO	Rh B	Shi [75]
Magnetite/reduced graphene oxide nanocomposites	Rh B MG	Sun [74]
Silver NP loaded Activated Carbon	Methylene Blue	Ghaedi [80]
Nano silica powder fabricated with Ag NPs	Congo Red Eosin Yellow Bromophenol blue 2 Brilliant Blue	Sivasankari Marimuthu (2020)
UV/TiO2	Direct Black 38 (DB 38)	Seyyedi [81]
Ni-doped TiO2	PonceauS Dye	Marathe [82]
TiO2	RB 5	Hussein (2014)
Multi walled CNT	Ismate violet 2R	Abualnaja [83]
Multi walled CNT with magnetically modified	Crystal violet (CV), Thiionine (Th), Janus green B (JG), and methylene blue (MB)	Madrakian [84]
Fe3O4 nanoparticles with multi walled CNT	Methylene blue and neutral red	Qu [85]

(continued)

Table 1 (continued)

Nanomaterials	Dyes removed	References
Tapioca peel with activated carbon	Rh B	Fathima [87]
Activated carbon with neem leaf powder	congo red, methylene blue, and brilliant green	Sharma [90]
Activated carbon from pineapple with phosphoric acid	Malachite Green, methylene blue	Selvanathan [89]

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