Nano-remediation for the decolourisation of textile effluents: A review

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ABSTRACT
The economic development of any nation leads to the depletion of its natural resources, and water is one of them. Water pollution caused by various industries like food, leather, and textile etc. causes severe impacts on the environment and humans. To ensure water availability to the whole world, contaminated water released from industries, mainly fabric, must be treated and reused. The conventional techniques alone are not enough to treat textile effluent completely. This is why nanotechnology should be combined with these traditional techniques. Nanotechnology includes engineered nanoparticles for the alteration and detoxification of contaminants. Compared to nanoparticles produced from conventional techniques, biogenic nanoparticles are environmentally friendly and cost-efficient. Microbes such as Rhodotorula mucilaginosa, Hypocrealixii, Bacillus species, Pseudomonas aeuginosa etc., are used to fabricate nanoparticles. Among various microbes, bacteria are considered a biofactory for the fabrication of nanoparticles. Different researchers reported an average dye removal efficiency of biogenic nanoparticles between 87% and 92%. When nanoparticles are applied to actual textile waste water rather than synthetic dye, waste water gives good results through the adsorption process. In this review, various methods for dye degradation are explained, but the focus is on the biological treatment of textile waste water in combination with nanotechnology.

ARTICLE HISTORY
Received: 11-07-2022
Revised: 15-09-2022
Accepted: 20-09-2022

KEYWORDS
Wastewater;
Textile industry;
Dyes;
Nanoparticles;
Biogenic nanoparticles

1. Introduction
Water is a priceless natural resource that covers about 70% of the world. Water fulfils the fundamental needs of living beings necessary for their survival on the planet earth (Olabisi et al., 2008). Both natural and anthropogenic activities govern the quality of water in a region. Waste water alters the receiving water bodies’ physical, chemical and biological properties, which can cause significant problems to humans and aquatic organisms (Fenta, 2014). An increasing number
of growing pollutants emerging from industrial/human-made activities represents a substantial risk to the ecological and environmental balance (Bilal et al., 2018; Momin et al., 2019). A large amount of coloured effluent is produced from many industries like leather, tanning and textile, plastic, cosmetics, paints and pigments, paper and pulp (Linhares et al., 2013).

Textile industries are one of the world’s most chemical-intensive industries and potentially the leading industrial user and polluter of water in the world (Dasgupta et al., 2015; Holkar et al., 2016). Textile industries in India use maximum amount of raw material and have strength to manufacture around the value chain, making it one of the world’s biggest industries. India is 2nd in the production and exportation of textile goods after China. The contribution of the textile industry in terms of worth is 7 per cent of industrial output, 2 percent of India’s GDP, and 15 percent of export earnings for the country (Ministry of Textiles, India, 2019–20; Gupta, 2020). Thus, the fabric industry is a crucial contributor to the nation’s monetary development. Water contamination is caused due to it by the release of untreated waste water (Savin, and Butnaru, 2008; Kumar et al., 2017).

Pollution from the textile industrial effluent is caused by both quality and quantity in the environment (Mondal et al., 2017). Dyeing and finishing activities in textile industries use an enormous amount of water and thus produce a large quantity of wastewater (Wang et al., 2010; Vijayaraghavan, and Yun, 2008; Aksu et al., 2005). The textile waste water has baleful, toxic and carcinogenic pollutants, including a high concentration of dyes, residual chlorine, dissolved solids, toxic heavy metals and other non-degradable organic substances, phenol, aromatic amines etc., which is the result of improper treatment facilities coupled with extensive industrialisation and unrestricted expansion of modern textile manufacturing facilities (Vikrant et al., 2018). The release of textile waste water changes the characteristics of receiving water bodies in terms of the suspended solids, salinity, colour, total organic carbon (TOC), chemical oxygen demand (COD), biological oxygen demand (BOD) and pH range (5-12) and uprising of the organic substances (Savin, and Butnaru, 2008; Kumar et al., 2017). This review focuses mainly on problems associated with dyes. Extensive colour can be imparted to water even at a very low concentration of dye, making it aesthetically unpleasant and unfit for human consumption. Dye dissolution also poses toxicity in water bodies (Franca et al., 2020; Wang et al., 2017; Rahimi et al., 2016; Li et al., 2015). Pollution from dyes in water bodies is of great concern for environmental and chemical engineers (Kebede, and Gashaw, 2017; Geetha KS, and Belagali, 2013).

Environmental contamination is one of the critical universal issues (Younis et al., 2014), and environmental safeguard is one of the essential challenges for humanity (Bilal et al., 2018). Efforts have been made as vital tasks for the abatement and regulation of dyes which comes under hazardous and toxic pollutants by the foremost organisations and environmental agencies like United States Environmental Protection Agency (US EPA). Extensive research has also been conducted to establish both long and short term impacts on the natural ecosystem and the health of humans (Long et al., 2017; -Shabbir et al., 2017). Before the discharge of waste water having dyes into water bodies, there is a crucial requirement to treat the waste water (Rahman et al., 2016). Primary, secondary and tertiary treatment processes are used to treat wastewater. Many of the lethal materials cannot be removed by these processes. Most fabric industries have key difficulties in the dye removal (Batool et al., 2014). That is why affordable and effective advanced technologies are used for waste water treatment (Kumar et al., 2014; Gupta et al., 2015).

According to the Central Pollution Control Board (CPCB) of India, the acceptable limit for the colour in water bodies is 5 hazen and the permissible limit is 15 hazen units (BIS, 2012). To attain this limit given by CPCB various physicochemical methods like adsorption, coagulation, flocculation, reverse osmosis and ion pair extractions have been used. These methods are extremely complex and expensive; therefore cannot be affordable (Rahman et al., 2016) and produce an enormous quantity of sludge, leading to secondary pollution. Biological methods are the best alternative for such problems and are extremely economical than other chemical and physical processes (Da-Guang et al., 2007; Modi et al., 2015). Biocatalysts and microorganisms like Pseudomonas sp., Aspergillus sp. etc., can be used to treat textile dyes via bioremediation.
These have their drawbacks and advantages in decolorising performance, working capacity and suitability (Xiang et al., 2016). The load of contaminants in the environment is vast, that is why only the bioremediation process is not enough. Some processes such as nano-bioremediation, including nanoparticles or nanotechnology, have been developed to supplement the process of bioremediation (Modi et al., 2015).

Nanoremediation strives to give an innovative and effective way for environmental decontamination by playing a major role in contamination prevention, observation, monitoring, and remediation (Rajan, 2011). Nanoremediation employs nanoscale materials or nano-materials (few micrometres to less than 100 micrometres) intended for remediation (Patil et al., 2016). Nano-materials can infiltrate deeper due to a greater surface area to volume ratio. As a result treatment of water/waste water takes place, which is usually not achievable by traditional technologies (Kumar et al., 2017). Advanced waste water treatment technologies like bio-nanoremediation have high efficiency (Anjum et al., 2016). Nanoparticles synthesised using microorganisms are advantageous over chemically prepared NPs as these are eco-friendly, energy saving, cost-effective, have greater efficiency (Hakim et al., 2005; Tripp et al., 2002; Mukherjee et al., 2001) and have antibacterial, antifungal and larvicidal activities (Arasu et al., 2019).

2. Methodology

A systematic search strategy was carried out using the three procedures of identification, screening, and eligibility. Searching for published work was done as part of the identification process using Scopus, Science Direct, and Google Scholar. Additionally, a Google search was done to find online thesis and grey literature (reports). Keywords used were textile dye waste water, dye wastewater, nano-remediation, adsorption, nanoparticles, biogenic nanoparticles and bio-nano-remediation. To include more papers in this review, the references of the chosen studies were also looked at. The exclusion criteria were duplicate studies and research papers lacking quantitative data.

3. Classification of dyes and their effects

Textile industries use different types of dye to dye fabric. The textile industry ranks first among different industries in the use of dyes. In the colour index, already more than 9000 types of dye have been included (Garg et al., 2003). Since 3500BC, the art of adding colour to cloth has been recognised by humanity. In 2600 BC, for the 1st time use of dyes has been recorded in China and India. 1st man-made dye, mauveine, was discovered by the W. H. Perkins in 1856 (Saini, 2017). The application of synthetic dyes provides a broad range of colours that are fast and bright. However, synthetic dyes have a detrimental effect on all life forms (Tkaczyk et al., 2020).

According to a report by the Indian Ministry of Chemical and Fertilizers (2022), the total production of dyes and pigments in 2021-2022 was 228938 MTs. Out of which, 80% is used by the textile sector in India (Down to Earth, 2005). Wastewater produced per ton of dye intermediate production is 15-20 m³/ton. Globally about 11% of the total dye manufactured entered as effluents (Down to Earth, 2005), causing a very negative impact on the environment.

3.1. Classification of dyes

Dyes are generally divided into two groups: the first is formed by inorganic pigments, and the second includes organic pigments and organic dyes (natural and synthetic dyes). Synthetic organic dyes form a large group of aromatic compounds with aromatic rings containing delocalised electrons that are differentiated due to their chemical and physical properties such as chromogen structure, solubility or stability in fabrics (Tkaczyk et al., 2020; Saini, 2017). The colour of the dye is due to the chromogene-chromophore, i.e. acceptor of electrons, in the molecule of dye, and the dyeing capacity of the dye is due to the presence of auxochrome groups, i.e. donor of electrons (Suteu et al., 2011; Welham, 2000).

The textile dyes are mainly classified in two ways:

1. In terms of its application characteristics such as acid, basic, mordant, reactive, direct, disperse, sulphur dye, pigment, vat, azo-insoluble.

2. In terms of its chemical composition, such as carotenoid, nitro, acridine, azo, diphenyl methane, quinolone, indamine, indigoid inorganic pigments etc. (Robinson et al., 2001).
On the basis of general structure, textile dyes can be categorised as cationic, anionic and nonionic. Reactive, direct and acid dyes are the primary anionic dyes. Azo, essential, and anthraquinone disperse dyes are the main cationic dyes. In contrast, primary nonionic dyes disperse dyes (Saini, 2017) and azo dyes are currently the most prevalent substances in industrial waste water (with a contribution of > 50% to the total production of dyes annually) (Brüschweiler, and Merlot, 2017).

3.2. Effects of dyes

Presence of manmade organic dyes into the water ecosystem is one of the serious environmental problems. Severe damage to the well-being of humans and the ecosystem is caused by the different dyes (Chong, and Tam, 2020). Jian River in Luoyang, Henan Province, north China, became red in December 2011 due to red dye, which was discarded into the city’s storm water pipe network. The rivers and canals running through Dhaka, the capital of Bangladesh, have turned a pitch black due to the sludge and sewage generated by textile dyeing and processing industries (Regan, 2020).

Among other problems, along with the issue of odour, the problem of colour is more readily observed by the people (Ghalebizade, and Ayati, 2016; Gulnaz et al., 2012). Presence of dyes in water bodies causes a reduction in light penetration, which alters the process of photosynthesis and oxygen solubility (because of high chemical oxygen demand). Thus, the natural balance of flora and fauna is altered (Mashkoor et al., 2018). Dyes are non-biodegradable, bio-accumulates and magnifies in fishes and other life forms (food chain) in the water bodies, due to which polluting effects of dyes can be observed in humans too. Allergies, tissue damage and skin irritation are caused by the pollutants produced by the decomposition of dyes. These can also be carcinogenic and mutagenic.
(Salter-Blanc et al., 2016; Chequer et al., 2011; Wang et al., 2011). Fabric dyes are xenobiotic pollutants that cause a potential threat to the environment upon their dumping into the water bodies (Kurade et al., 2019).

Adsorption of azo dyes (aromatic in nature) is mutagenic; skin and lung problems and haemoglobin adducts formation is also caused by the breakdown products as amines of azo dyes via the gastrointestinal tract. Damage to the DNA is also caused by the several types of azo dyes, which results in malignant tumours. Malachite dye is carcinogenic and genotoxic, adversely affecting immune and reproductive systems. There are cyto- and genotoxic effects of blue dye on the cells of human-beings, and the DNA fragmentation is also triggered by this dye (Saini, 2017; Topac et al., 2009; Sponza, 2002).

4. Treatment options for dyes contaminated wastewater

Textile industries consume almost two-third of the world’s annual production of dyes. It has been estimated that up to 50% of that enter the environment (Holkar et al., 2016; Rawat et al., 2016; Rangabhashiyam et al., 2013). Worldwide, it has been reported that 280,000 tonnes of textile dyes get discharged annually through industrial textile waste because of the inefficient processes of dye fixation on the fibre (Franca et al., 2020). Waste water treatment is a crucial need in today’s world due to the increasing population and depleting and degrading water resources. Due to the increased population and accessibility to water, it becomes necessary to treat and reuse waste water for human consumption. Wastewater from the textile industry can’t be dumped into the water sources directly because it contains heavy metals, organic waste and dyes. Fig. 2 describes the process for textile dye effluent treatment.

Various techniques are required to treat the effluent discharged from the textile industries to decrease the pollution caused by these industries. These processes are physical, chemical and biological techniques as described in Fig. 3.

4.1. Physical method for dye removal

These dye removal methods are typically simple techniques generally performed through the process of mass transfer. The physical dye treatment methods are the most widely used of the three approaches (chemical, physical and biological). Compared with biological and chemical dye treatment approaches, the physical approach involves the least amount of chemical compounds (Katheresan et al., 2018). Various physical methods of dye removal are tabulated in Table 1.

The physical methods generally treat waste water. However, these methods are expensive and can’t be used efficiently to treat a broad range of dyes present in wastewaters. Activated carbon adsorption (ACR) has been proven to be an efficient dye removal approach, but this process is too costly (Garg et al., 2003). Several low cost substitutes have therefore been suggested, which includes vermiculite (Choi, and Cho, 1996); peat (Poots et al., 1978); sawdust (Mazet et al., 1990); wood (Asfour et al., 1985); flyash (Mall, and Upadhyay, 1998); soil (Ganjidoust et al., 1995); china clay (Gupta et al., 1992); banana pith (Namasivayam et al., 1998); bagasse pith (Mckay, 1998) and waste coir pith (Namasivayam, and Kadirvelu, 1994). However, new economical, easily accessible and highly efficient adsorbents are still required (Ververi, and Goula, 2.019).

4.2. Chemical methods for dye removal

Chemical dye removal methods utilise chemistry or its theories to accomplish dye removal (Katheresan et al., 2018). Various chemical methods are tabulated in Table 2.

Mostly chemical dye removal approaches, except electrochemical, are expensive compared to compared to physical and biological dye removal approaches (Katheresan et al., 2018). Another unwanted aspect of this technique is the production of toxic secondary waste that results in an additional disposal problem at the end of a chemical dye removal method (Wang et al., 2018).

4.3. Biological method for dye removal

It involves microorganisms like fungi, algae and bacteria etc. Biological treatment may involve aerobic and anaerobic degradation by microorganisms combination (Saini, 2017). In aerobic biological treatment, wastewater is degraded in the presence of oxygen. In anaerobic biological treatment, wastewater is degraded
Figure 2. Flow chart for dye effluent treatment
in the absence of oxygen with the help of microorganisms. Various biological methods are mentioned in Table 3.

Stable and recalcitrant natures of synthetic dyes with high durability make them resistant to biodegradation. That’s why traditional biological methods fail to remove textile dyes from textile industry waste water effectively, and this could contribute to the long-term persistence of dyes in water bodies (Dasgupta et al., 2015; Dos Santos et al., 2007). Therefore, a traditional biological treatment process is not very effective for treating dyes due to their low biodegradability.

That’s why the development of some other approaches or treatment options besides these traditional methods is necessary. In recent times, due to their small size, high surface area to volume ratio etc., nanoparticles are gaining importance in the treatment of waste, especially for wastewater treatment (Usman et al., 2012). Nano-materials...
have attracted widespread attention because of their high porosity, tunable functionalities and more surface area (Vikrant, and Kim, 2019). Recent developments in nanotechnology have accelerated our interest in fabricating the desired shape and size of nano-sized particles (Siddiqi, and Husen, 2020).

5. Nano-remediation

Nano-remediation is the process in which nanoparticles are used for the remediation of wastewater using nanotechnology. In general, nanotechnology refers to the science and engineering field mainly dedicated to materials ranging from 1 to 100 nm in size (Mody et al., 2010; Salata, 2004). The word “nano” is taken from the Greek word “dwarf” which means “extremely small”. This means $10^{-9}$ or 0.000000001 when used as prefix. One billionth of a meter is a nanometer (Thakkar et al., 2010).

Nanoparticles- In general, NPs can be defined as particles with a diameter size of less than or equal to 0.1 μm (100nm) and specific characteristics primarily based on their size (Usman et al., 2012). Nanoparticles (NPs) show exclusive and

<table>
<thead>
<tr>
<th>Physical methods</th>
<th>Description</th>
<th>Benefits</th>
<th>Drawbacks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption</td>
<td>Adsorbents are generated to adsorb dye molecules from high adsorption capacity materials.</td>
<td>Excellent method for the removal of a large range of dyes. Adsorbents can be regenerated.</td>
<td>Adsorbents can be costly.</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Irradiation</td>
<td>This includes the use of radiations, normally obtained from UV monochromatic lamps, operating below 253.7 nm.</td>
<td>A wide number of organic pollutants can be removed and dangerous microorganisms are disinfected.</td>
<td>It requires constant and sufficient oxygen supply because the efficient breakdown of an organic dye requires a significant amount of dissolved oxygen for irradiation. Use of UV light may cause health effects in the handling person.</td>
<td>Saini, (2017)</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Exchange of ions of the same charge. Use of a series-packed combination of anion exchange column and a non-polar resin.</td>
<td>Strong bonding present between dye and resin, so there will be effective removal of dye.</td>
<td>Organic solvents required for regeneration are not that inexpensive, and this increases cost of operation.</td>
<td>Siddique et al., (2017)</td>
</tr>
<tr>
<td>Ultra-filtration and nano-filtration (membrane separation)</td>
<td>A thin pored membrane is used for the separation of dye molecules from the dye wastewater to produce clean water.</td>
<td>Any type of dye can be removed.</td>
<td>High consumption of energy. High operational cost. The pores of membrane are continuously blocked by dye particles. High pressure is required. Life span is short.</td>
<td>Katheresan et al., (2018)</td>
</tr>
</tbody>
</table>

Table 1. Physical methods for dye removal with description, benefits and drawbacks
considerably different chemical, physical, and biological properties when compared with the huge aggregate substance of the same chemical composition due to their surface area to volume ratio (Bhattacharya, and Gupta, 2005; Salata, 2004; Paull et al., 2003).

Based on composition, nanoparticles may be categorised into two forms, that is, inorganic and organic nano-materials. Organic nanoparticles contain carbon while inorganic nanoparticles consist of magnetic materials like iron oxides, semiconductors like titanium dioxide and zinc oxides and noble metals like gold, silver and platinum (Fawcett et al., 2017). Physical, chemical and biological approaches are used to fabricate nanoparticles (Ingale, and Chaudhari, 2013).

<table>
<thead>
<tr>
<th>Chemical methods</th>
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<th>Benefits</th>
<th>Drawbacks</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Advanced oxidation e.g. Oxidation with hydrogen peroxide, oxidation with sodium hypochlorite etc.</td>
<td>More than one oxidation process can take place all together for dye removal.</td>
<td>Toxic materials get eliminated. Dyes can be removed in unusual conditions. Effective method.</td>
<td>Expensive. Rigid. Unwanted byproducts can be formed. Depends on pH.</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Fenton reaction (oxidation)</td>
<td>Mix of catalyst and hydrogen peroxide known as Fenton regent is used to treat dye effluent.</td>
<td>All toxins can be removed. Soluble and insoluble dye molecules or dyes with solid content can also be removed.</td>
<td>Vat and disperse dyes can’t be removed. Generation of iron sludge. Reaction time is long. Low pH is required.</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Photochemical oxidation (oxidation)</td>
<td>Wastewater containing dyes in UV treatment can degrade into smaller organic molecules, carbon dioxide and water in presence hydrogen peroxide.</td>
<td>Ultimate products are CO$_2$ and H$_2$O.</td>
<td>Effectiveness of this method depends on the UV radiation, dyes and pH.</td>
<td>Saini, (2017)</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Ozone is used in this method to remove dye from waste water.</td>
<td>Oxidising potential of ozone is 2.07 which makes it better oxidising agent.</td>
<td>Amines releases as byproducts and cause cancer. Ozone readily decomposed in water having a life span of just 20 min.</td>
<td>Siddique et al., (2017)</td>
</tr>
<tr>
<td>Coagulation and Precipitation</td>
<td>Dispersed solid molecules in water gets destabilised by reducing their surface charge and accumulating them to form large particles.</td>
<td>Completely eliminates the dye from waste water.</td>
<td>Addition of excess coagulants.</td>
<td>Ahmad et al., (2015); Collivignarelli et al., (2019)</td>
</tr>
<tr>
<td>Electrocoagulation (coagulation)</td>
<td>Metal electrode in a chamber are used to treat dye effluent.</td>
<td>Uses direct current.</td>
<td>Requires specific pH.</td>
<td>Siddique et al., (2017)</td>
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</table>

Table 2. Chemical methods for dye removal with description, benefits and drawbacks
### Biological methods for dye removal with description, benefits and drawbacks

<table>
<thead>
<tr>
<th>Biological methods</th>
<th>Description</th>
<th>Benefits</th>
<th>Drawbacks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enzymatic degradation</td>
<td>Extracted enzymes are used to degrade dye as catalysts.</td>
<td>Reusable, cheap and non-toxic.</td>
<td>Maximum decolorisation degree of about 30%.</td>
<td>Periyasamy et al., (2018)</td>
</tr>
<tr>
<td>Fungal treatment</td>
<td>Fungus are able to degrade dyes using enzymes</td>
<td>Non-toxic and environmental friendly.</td>
<td>Same types of dyes can be removed from all type of cultures.</td>
<td>Collivignarelli et al., (2019)</td>
</tr>
<tr>
<td>Biomass</td>
<td></td>
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<tr>
<td>Membrane bioreactor (MBR)</td>
<td>Combination of a membrane process like micro-filtration with a biological treatment system.</td>
<td>Simple, reliable, and cost-effective process.</td>
<td>Drawback in the operation of MBR, which leads to the decline in permeate flux and hence requires membrane cleaning.</td>
<td>Periyasamy et al., (2018)</td>
</tr>
</tbody>
</table>

Table 3. Biological methods for dye removal with description, benefits and drawbacks

### 5.1. Synthesis of nanoparticles

Several physicals, chemical, and biological methods for the fabrication of nanoparticles have been described based on the extreme advancement in nanoscience and nanotechnology in the last few years (García-Barrasa et al., 2010). Mainly there are two approaches for synthesising nanoparticles: “Top-down” and “Bottom-up”. Suitable bulk material is broken into fine particles by the size reduction using various techniques like pulse laser ablation in the top-down approach. NPs can be synthesised using chemical and biological methods in the bottom-up approach via the self-assembly phenomenon of atoms into new nuclei that develops into nanoscale particle (Rafique et al., 2017). Fig. 4 explains various approaches to nanoparticle formation.

#### 5.1.1. Chemical synthesis of nanoparticles

In the chemical method, nanoparticles are fabricated in a colloidal solution that involves the methods that enables the size and shape of nanoparticles to be precisely regulated to yield a set of monodisperse nanoparticles displaying a particular property. Generally, 1) metal precursor, 2) reducing agents and 3) stabilising agents are the components which are used for the synthesis of metal nanoparticles in the solution. There are two stages in the formation of colloidal solution from the reduction of metal ions: nucleation and growth. High activation energy is required in the nucleation step, and low activation energy is needed for the growing step. Relative rates of these processes decide the size and shape of nanoparticles, which can be regulated by adjusting the parameters of the reaction, like temperature, concentration, reducing ability, pH, etc. (García-Barrasa et al., 2010).

A large amount of nanoparticles can be synthesised via this method in little time. Nonetheless, for size stabilisation of the nanoparticles, capping agents are required in this process. Three chemical techniques have been often used for the synthesis of nanoparticles: 1) polymerisation of monomers, 2) dispersion of preformed polymers, and 3) ionic gelation or coacervation of hydrophilic polymers ( Förster et al., 2012).

#### 5.1.2. Physical synthesis of nanoparticles

In this method, evaporation-condensation is used to synthesise the metal nanoparticles, which is carried out in a tube furnace at atmospheric pressure. Vaporisation of the starting material takes place into vapours inside the boat which
is centred at the furnace. Different materials like silver, gold etc. can be used for nanoparticle synthesis using this method ( Förster et al., 2012).

5.1.3. Biological synthesis of nanoparticles

In this method, microbes, plant species and templates are used to fabricate biogenic nanoparticles (BNPs) (Ramos-Ruiz et al., 2017). Using various biological organisms such as fungi, algae, viruses, yeast and plants, a wide range of NPs can be synthesised. For the formation of NPs, each entity has its biochemical processing methods such as the oxidation/reduction of metal ions by microbes and plant species through enzymes, proteins, sugars, carboxyl, polyphenols and aldehyde groups (Lu et al., 2017). Different biological entities can be used to fabricate various types of BNPs using various metallic ions like silica, alloy, titanium, selenium, silver, gold, antimony sulphide etc. (Qu et al., 2017). Well-known biological processes for the synthesis of BNPs are biologically controlled mineralisation (BCM) and biologically induced mineralisation (BIM) (Martins et al., 2017).

Under well-defined conditions, BNPs are fabricated in the cells of organisms in BCM processes and these organisms fully control the nucleation and growth of NPs. However,
bacterial cell wall/membrane filtrate is treated with metal ion solution in BIM and reduction and/or precipitation processes are used for forming BNPs. Additionally, BNPs produced either by extra- or intracellular biomineralisation/bioaccumulation, biosorption and complexation processes by microbes (Ali et al., 2019).

The systematic fabrication of biogenic nanoparticles is described in Fig. 5, along with the reduction, capping and stabilisation of nanoparticles.

The biogenic nano-material fabrication primarily involves the bio-reduction and bio-precipitation of peptides, amino acids, polyphenols and other bioactive compounds extracted from living organisms. To prevent the agglomeration of the fabricated NPs, these compounds also act as capping and stabilising agents. Most suitable candidates are plants for synthesising NPs due to their diversity, availability and abundance in the environment. For the production of Zn, Fe, Ag, Au, Mn, Cu and Pd NPs of different sizes and shapes, the ability of plant extracts to reduce metallic salts has been successfully explored Gautam et al., (2019).

Biosynthesised NPs have some specific characteristics when compared with the NPs fabricated via traditional processes and when employed in the degradation of organic (dyes) pollutants and catalysis. These have no side effects (Naim et al., 2016). Because of their unique properties like the high specific surface area to volume ratio, catalytic activity, desired morphology etc. for the biodegradation and biosorption of dyes and other contaminants, recent biogenic nanoparticles (BNPs) fabricated using microbes/microorganisms are therefore getting tremendous research interest. In addition, polluted water can be used to manufacture BNPs, which shows a hidden potential for resource recovery and utilisation (Ali et al., 2019).
Due to the involvement of dangerous and harmful chemicals, these traditional methods used for NP fabrication are considered costly, time-consuming, and environmentally hazardous. As biological routes for NP synthesis are simple, eco-friendly, sustainable and cost-effective, researchers are more inclined toward these methods (Bachheti et al., 2020). While plant and microbial biofabrication of metal NPs do not leave toxic residues in the environment, even though their safe disposal is important (Siddiqi, and Husen, 2020).

Adsorption of dye via NPs fabricated using microorganisms like yeast, bacteria, fungi, and algae is inexpensive and eco-friendly (Forgacs et al., 2004). That is why more attention is given to the microbes that fabricate NPs through biological processes or biomineralisation in the environment (Ali et al., 2019).

### 5.2. Biogenic nano-remediation using microbes

Any microbe in nature is capable of synthesising NPs without any external chemical agents and under ambient physical conditions (Reverberi et al., 2016). Microorganisms have been investigated as potential bio-factory of metallomics nanoparticles production like cadmium, gold and silver (Priyadarshini et al., 2013; Husseiney et al., 2007). Various microorganisms, such as fungi, algae and bacteria, had been utilised to fabricate different metallomics nanoparticles (Panpatte et al., 2016).

#### 5.2.1. Bacteria as biogenic tool for nano-remediation

Among the biological methods, bacteria are an essential for fabricating NPs because of their variety and high adaptability to extreme conditions. For example, toxic ions are usually harmful to microbes’ survival, but microbes’ survival. Still, some specific bacteria have evolved and can reduce or precipitate toxic inorganic ions to insoluble and nontoxic metal NPs. The reductive ability of bacteria and the new technique for the recovery of NPs provide an opportunity to fabricate NPs through a low-cost and easily manipulated process.

The mainstream view is that bacteria can fabricate metal and metalloid NPs intracellularly and extracellularly. In an extracellular process, ions are reduced by proteins, enzymes and organic molecules in the medium or by cell wall components. Extracellular reduction appears to be more favourable than intracellular reduction due to its lower cost, simpler extraction and higher efficiency. However, in the intracellular process, carboxyl groups on the cell wall attract metal and metalloid ions through electrostatic interactions. Then, the ions enter the cells and interact with intracellular proteins and cofactors to produce NPs (Fang et al., 2019).

In addition, many studies have shown that not only the living bacteria but also the dead entities like dead biomass of the yeast *Rhodotorula mucilaginosa* (Salvadori et al., 2014), and dead biomass of the fungus *Hypocrea lxi* (Salvadori et al., 2015) can also be used for biosynthesis of NPs. However, the mechanisms of these processes are different. Generally, the metabolic process may be responsible for the bioreduction of NPs in living bacteria. However, for dead entities, metal and metalloid ions are bound to the bacterial cells that provide nucleation sites for NPs. Many researchers have reported that some functional groups, such as –NH₂, –OH, –SH and –COOH, of the proteins secreted by bacteria play essential roles in the reduction and stabilisation of NPs. These functional groups provide binding sites for fixing of metal ions, followed by reducing the metal ions outside the cells on the cell wall or in the periplasmic space (Fang et al., 2019).

Biosynthesized metal NPs have better stability and oxidation resistance than NPs provided by traditional approaches and have been applied in different fields. The fabrication of bioinspired NPs is eco-friendly, inexpensive and consumption low energy required. In environmental remediation, some biofabricated NPs are commonly used as heterogeneous catalysts, and due to their increased biocompatibility, stability and large specific surface areas, they show higher catalytic efficiency (Fang et al., 2019). In addition, because of heterogeneity, these can separate from the substrate to enable the reuse of NPs to achieve the desired sustainability and low cost (Pantidos, and Horsfall, 2014).

Different mechanisms for the biofabrication of NPs through various microbes are described in Table 4.
### Table 4. Synthesis of nanoparticles with the help of microbes and their application

<table>
<thead>
<tr>
<th>Nanoparticles (Metal/metalloid)</th>
<th>Microbes involved in biogenic synthesis of nanoparticles</th>
<th>Process for synthesis of nanoparticles / cellular</th>
<th>Shape and shape and Size of nanoparticles</th>
<th>Application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se-NPs</td>
<td>Enterobacter cloacae Z0206</td>
<td>Intra- and Extracellular</td>
<td>Rods, 100nm</td>
<td>Biosensors, Bioremediation, Biomedical therapy</td>
<td>Saini, (2017) / Park et al., (2016)</td>
</tr>
<tr>
<td>Pd-NPs</td>
<td>D. desulfuricans NCIMB8307, E.coli MC4100, Serratia sp. NCIMB 40259, Shewanella oneidensis MR1 NCIMB 146063 and Cupriavidus metallidurans NCIMB 10504 and Micrococcus luteus NCIMB 9278, Enterococcus Faecalis</td>
<td>Extracellular</td>
<td>Spherical, 100/50nm</td>
<td>Cr (VI) removal</td>
<td>Deplanche et al., (2014)</td>
</tr>
<tr>
<td>Au-NPs</td>
<td>Trichosporon montevideense WIN</td>
<td>Extracellular</td>
<td>Spherical, 53–12 nm</td>
<td>2-nitrophenol (2-NP), 3-nitrophenol (3-NP), 4-nitrophenol (4-NP) (contaminant from dye), onitrophenyl amine (o-NPA), m-nitrophenyl amine (mNPA) removal</td>
<td>Shen et al., (2016)</td>
</tr>
<tr>
<td>Fe-NPs</td>
<td>C. sinensis, S. aromaticum, M. spicata and P. granatum</td>
<td>—</td>
<td>Spherical, 50–60 nm</td>
<td>Removes Cr (VI)</td>
<td>Mystrioti et al., (2016)</td>
</tr>
<tr>
<td>Mn-NPs</td>
<td>Pseudomonas putida MnB1</td>
<td>—</td>
<td>Stick like, 8–9 nm</td>
<td>Cd(II), Zn(II) and Pb(II) removal</td>
<td>Zhou et al., (2015)</td>
</tr>
<tr>
<td>Ti-NPs</td>
<td>F. oxysporum</td>
<td>Intracellular</td>
<td>Spherical, 6–13 nm</td>
<td>in desalting plants, in cancer chemotherapy</td>
<td>Narayanan et al., (2010)</td>
</tr>
<tr>
<td>Fe3O4-NPs</td>
<td>Candida albicans</td>
<td>Extracellular</td>
<td>Spherical, 80 nm</td>
<td>Antimicrobial activity</td>
<td>Salunke et al., (2016)</td>
</tr>
<tr>
<td>PbS-NPs</td>
<td>Torulopsis sp.</td>
<td>Intracellular</td>
<td>Spherical, 2–5 nm</td>
<td>Waste water treatment</td>
<td>Samuel et al., (2020)</td>
</tr>
</tbody>
</table>
6. Degradation of dyes through biogenic nano-remediation

NPs have specific physical and chemical characteristics which are not present in bulk materials, and due to this NPs have been used to mitigate harmful and toxic dyes. Nanoparticles act as effective catalysts in reductive reactions. By facilitating smooth electron transfer from the donor to the acceptor, metal nanoparticles catalyze dye degradation. The acceptor and donor materials are adsorbed on the surface of nano-material and accelerate the process of degradation by electron transfer reaction before the degradation starts (Paul et al., 2020). The general process of dye degradation by nanoparticles is explained in Fig. 6.

Photocatalytic degradation mechanism of dyes with the help of biofabricated nanoparticles is depicted in Fig. 7. Electrons (e-) are excited from filled valence band (VB) to the empty conduction band (CB), this leaves a hole behind in the valence band in the presence of visible light that is equal or greater than the band gap. A powerful oxidising agent, hydroxyl free radical (OH\(^{•}\)) is produced when hole in the valence band and water molecules adsorbed on the surface of NPs react with each other, and a potent reducing agent, superoxide, is produced when an electron in conduction band reacts with oxygen. For the decomposition of dye adsorbed on the surface of nanoparticles into simple organic molecules, both reducing and oxidising agents are active reagents [4]. By monitoring intermediates and end products, the dye degradation process can be tracked (Raman, and Kanmani, 2016).

Different characteristics, applications and removal efficiencies of biogenically fabricated NPs for the removal of dyes are described in Table 5. Various synthetic dyes like methylene blue, malachite green, disperse blue 183, Congo red, methyl orange and rhodamine-B are removed by these biogenic nanoparticles efficiently. Table 5 summarises that the synthesis of nanoparticles with the help of microorganisms is efficiently possible, which makes the whole process more environmentally friendly and has 100% efficiency for the dye degradation while using biogenic nanoparticles.

The efficiency of different methods depends upon various conditions like temperature, pH, contact time etc. For maximum efficiency, one should provide optimum conditions for the dye removal methods. Different dye removal methods have further efficiencies; their comparison is given in Table 6. Adsorption method using nanoparticles provides reliable and spontaneous results for dye removal; however, other methods like ultraviolet irradiation and photocatalytic oxidation also showed promising results. But when one compares

Figure 6. Dye degradation by nanoparticles. Modified from (Nandhini et al., 2019).
It is important to rely on results provided by the researchers by applying nanoparticles to effluents from textile industries rather than on simulation studies. Table 7 summarises the results based on the application of nanoparticles on textile effluents from different countries. Copper nanoparticles synthesised using biological entities (Escherichia sp. strain SINT7) provides fairly good results, which is 71.8% for malachite green dye when used for the treatment of textile industry effluent through the process of adsorption. There is not enough research regarding the biological synthesis of NP used in actual wastewater treatment, which may be a limitation to concluding general suggestions regarding their efficiencies. But nanoparticles synthesised using other methods also provide reliable results when used on industrial effluents. Further, iron nanoparticles synthesised via biological methods also give fairly good results (more than 80% removal of dye) in removing dyes from textile wastewater. There is a research gap when one studies the application of biogenic nanoparticles or application of nanoparticles on actual wastewater. That is why researchers should focus in this direction. More research should be conducted on the treatment of solid waste produced by the textile industries and the application of nanoparticles in the real world to treat textile wastewater. This will provide more reliable results for the researchers to focus on the increment of efficiency.

7. Limitations of nano-remediation

Despite being too advantageous, nano-remediation too has some limitations, as mentioned below.

1. Handling of nanoparticles is difficult.
2. It has been demonstrated that nanoparticles are harmful to environmental elements.

3. Additionally, nanoparticles react with unintended substances.

4. High cost

8. Conclusion

Dyes from textile industries are the key contributor to water pollution. To solve this problem, nanoparticles are getting researchers’ attention because of their unusual properties like the high surface area to volume ratio, high stability, small size and more binding sites etc. Physically and chemically produced NPs have some impact on the environment. That is why biologically produced NPs are getting preference. Biologically produced nanoparticles are environmentally friendly and stable compared to conventional nanoparticle formation approaches. Microbially produced nanoparticles, in combination with bioremediation can significantly remove dyes from textile effluent. Biogenic nanoparticles increase bioremediation efficiency due to their surface area and volume ratio. This new technology can potentially decrease health hazards and environmental impacts when used with conventional industrial

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Microbes for biofabrication of NPs</th>
<th>Cellular process for NP synthesis</th>
<th>NP’s shape and size</th>
<th>Application</th>
<th>Removal efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS- NP</td>
<td>Clostridiaceae sp.</td>
<td>Extracellular</td>
<td>Cubic NPs, 50<em>50</em>100 nm</td>
<td>Degradation of methylene blue in the presence of H₂O₂</td>
<td>61.6%</td>
<td>Yue et al., (2016)</td>
</tr>
<tr>
<td>Pd- NPs</td>
<td>Marine bacterium Bacillus sp. GP</td>
<td>Extracellular</td>
<td>15–40 nm</td>
<td>4-nitrophenol (contaminant from dye)</td>
<td>—</td>
<td>Zhang et al., (2018)</td>
</tr>
<tr>
<td>Au-NPs</td>
<td>Trichosporon montevideense WIN</td>
<td>Extracellular</td>
<td>Spherical, 53–12 nm 5–3 0nm</td>
<td>4-nitrophenol (4-NP) (contaminant from dye)</td>
<td>—</td>
<td>Shen et al., (2016)</td>
</tr>
<tr>
<td></td>
<td>Marine bacterium Bacillus sp. GP</td>
<td>Extracellular</td>
<td></td>
<td></td>
<td>—</td>
<td>Zhang et al., (2018)</td>
</tr>
<tr>
<td>AgNPs</td>
<td>Bacillus pumilus, Bacillus paralicheniformis and Sphingomonas paucimobilis Marinospirillum alkaliphilum Bacillus pumilus Bacillus amyloliquefaciens MSR5</td>
<td>Extracellular</td>
<td>spherical to oval 4 to 20 nm</td>
<td>Malachite green dye removal</td>
<td>90%</td>
<td>Allam et al., (2019)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Extracellular</td>
<td>Cubic, 30–70 nm</td>
<td>Disperse Blue 183 dye removal</td>
<td>100%</td>
<td>Nazari et al., (2021)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Extracellular</td>
<td>rod and oval, 5-93 nm</td>
<td>Congo red dye removal</td>
<td>13%</td>
<td>Modi et al., (2015)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Extracellular</td>
<td>spherical, 20–40 nm</td>
<td>4-nitrophenol (4-NP) (contaminant from dye)</td>
<td>98%</td>
<td>Samuel et al., (2020)</td>
</tr>
<tr>
<td>ZnO NPs</td>
<td>Bacillus Subtilis</td>
<td>--</td>
<td>Hairy, 10–15 nm</td>
<td>Methylene blue (MB), Methyl orange(MO), Rhodamine-B (Rho-B) dye degradation</td>
<td>100%</td>
<td>Dhandapani et al., (2020)</td>
</tr>
</tbody>
</table>

Table 5. Biogenic nanoparticles in dye removal
procedures. Nanoremediation technology is less
time-consuming, eco-friendly, cheaper, and highly
efficient. E.g. CuNPs produced using *Escherichia*
sp. strain SINT7 when applied on textile effluent
yield good results for the removal of malachite
green dye through the process of adsorption in
combination with photocatalysis. *Clostridiaceae*
sp., marine bacterium *Bacillus* sp. GP, *Clostridium*
*pasteurianum* BCI, *Trichosporon montevideense*
WIN, *E. coli* K12, etc. are some microbes that can
be used to synthesise NPs to degrade dye. With
all these benefits, like any other technology, nano-
remediation also has limitations. Nanoparticles
have a minimal size. This makes the handling of
NPs a bit difficult. Some other limitations of NPs
are their regeneration after using them in treatment
processes and specific types of NPs in a particular
type of waste to be treated. The limit which should
be given attention is that if used in excess or not
recovered for reuse NPs can cause a different kind

<table>
<thead>
<tr>
<th>Method</th>
<th>Dyes</th>
<th>Maximum efficiency %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption using nano-materials</td>
<td>Methylene blue (MB) and Brilliant green (BG)</td>
<td>MB-99.7%</td>
<td>Kataria et al., (2019)</td>
</tr>
<tr>
<td>Magnetic sawdust carbon nanocomposites</td>
<td>Brilliant green (BG)</td>
<td>BG- 96.7%</td>
<td></td>
</tr>
<tr>
<td>Carbonaceous nano-materials</td>
<td>Methylene blue (MB) and Methyl orange (MO)</td>
<td>MB-99.8%</td>
<td>Ahlawat et al., (2020)</td>
</tr>
<tr>
<td>Green fabricated zinc oxide nanoparticles</td>
<td>Congo Red (CR) and Malachite Green (MG)</td>
<td>CR-87.3%</td>
<td>Chauhan et al., (2020)</td>
</tr>
<tr>
<td>Average removal rate</td>
<td></td>
<td>95.5%</td>
<td></td>
</tr>
<tr>
<td>Physical methods</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption and filtration</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biomimetic dynamic membrane (BDM)</td>
<td>Crystal violet (CV)</td>
<td>90%</td>
<td>Chen et al., (2019)</td>
</tr>
<tr>
<td>Reverse osmosis (RO)</td>
<td>Anthrasol brown IBR</td>
<td>94%</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Irradiation by ultrasound exfoliated graphite</td>
<td>Acid brown 348</td>
<td>90%</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Ion-exchange</td>
<td>Rhodamine B (Rh-B)</td>
<td>96%</td>
<td>Saruchi et al., (2019)</td>
</tr>
<tr>
<td>Chemical method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Photocatalytic/photochemical oxidation (UV)</td>
<td>Reactive blue 19 (RB 19)</td>
<td>99%</td>
<td>Hadjitaief et al., (2019)</td>
</tr>
<tr>
<td>Ozonation</td>
<td>Methyl orange (MO)</td>
<td>72%</td>
<td>El Hassani et al., (2019)</td>
</tr>
<tr>
<td>Sono-Fenton (H₂O₂)</td>
<td>Red 195 Azo dye</td>
<td>85%</td>
<td>Baştürk et al., (2019)</td>
</tr>
<tr>
<td>Ultraviolet irradiation (ZnO NPs)</td>
<td>Acid red 4092</td>
<td>~100%</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Biological method</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bio-inspired underwater superoleophobic PVDF membranes</td>
<td>Methylene blue (MB)</td>
<td>96.8%</td>
<td>Zhang et al., (2019)</td>
</tr>
<tr>
<td>Industrual microbial waste</td>
<td>Orange G (OG)</td>
<td>92.7%</td>
<td></td>
</tr>
<tr>
<td>Algal degradation</td>
<td>Methylene blue (MB) and crystal violet (CV)</td>
<td>&gt;97%</td>
<td>Liu et al., (2019)</td>
</tr>
<tr>
<td>Immobilised <em>Desmodesmus sp.</em></td>
<td>Methylene blue</td>
<td>98.6%</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Fungal culture</td>
<td>Malachite green</td>
<td>82.6%</td>
<td>Katheresan et al., (2018)</td>
</tr>
<tr>
<td>Immobilised <em>Aspergillus niger</em> fungal biosorbent</td>
<td>Malachite green</td>
<td>82.6%</td>
<td></td>
</tr>
</tbody>
</table>

Table 6. Dye removal efficiency of various methods
of pollution. Despite these limitations, NPs have more benefits when used in various industries. In wastewater treatment specifically for dye removal, it is better to use NPs via the adsorption process as this technique is quite efficient. It is crucial to study the microbes for synthesising NPs in combination with resource recovery.

**Declaration of Competing Interest**

The authors reported no potential conflict of interest.

**Acknowledgements**

The first author (SY) thanks Dr. Saloni Gupta for her help.

**Funding**

This work was supported by the University Grants Commission, Delhi, India (UGC-JRF) [NTA Ref. No. - 190510167473].

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