Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process

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ABSTRACT

The problem of textile dye pollution has been addressed by various methods, mainly physical, chemical, biological, and acoustical. These methods mainly separate and/or remove the dye present in water. Recently, advanced oxidation processes (AOP) have been focused for removal of dye from waste water due to their advantages such as ecofriendly, economic and capable to degrade many dyes or organic pollutant present in water. Photocatalysis is one of the advance oxidation processes, mainly carried out under irradiation of light and suitable photocatalytic materials. The photocatalytic activity of the photocatalytic materials mainly depends on the band gap, surface area, and generation of electron–hole pair for degradation dyes present in water. It has been observed that the surface area plays a major role in photocatalytic degradation of dyes, by providing higher surface area, which leads to the higher adsorption of dye molecule on the surface of photocatalyst and enhances the photocatalytic activity. This present review discusses the synergetic effect of adsorption of dyes on the photocatalytic efficiency of various nanostructured high surface area photocatalysts. In addition, it also provides the properties of the water polluting dyes, their mechanism and various photocatalytic materials; and their morphology used for the dye degradation under irradiation of light along with the future prospects of highly adsorptive photocatalytic material and their application in photocatalytic removal of dye from waste water.

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Introduction

Environmental pollution is one of the greatest problems the world is facing today, increasing with every passing year and causing serious and irreparable damage to the earth. Environmental pollution consists of three basic types of pollution, namely: air, water, and soil (Legrini et al., 1993; McLaren and Williams, 2015). Among these, the causes of water pollution are industrial discharge, excess use of pesticides, fertilizers in agriculture sector, pharmaceutical residue, and landfilling of domestic waste (Lianos, 2011). Various organic compounds such as solvents, dioxins, dibenzofurans, pesticides, polychlorinated biphenyls (PCBs), chlorophenols, and dyes are found in the contaminated water (Reddy and Kim, 2015; Nguyen and Jiang, 2015; Shinde et al., 2014; Jo and Tayade, 2014a). These dyes are serious contributors to pollution as the most of the industries use dye and their industrial waste water discharge contains large amount of dye (Jo and Tayade, 2014b). Some of the dyes are often difficult to decompose in water as they have composite molecular structures that turn them to be more stable toward light and resistant to biodegradation (Mckay, 1979).

The use of natural dye for textile dyeing has been practised since the last 5000 years. The discovery of synthetic dyes was stated in 19th century, which has suppressed the use of natural dye. The synthetic dyes can be produced largely and can be utilized in various industries such as fabrics, leather, paper, food, cosmetics, agricultural research, pharmaceuticals, electroplating, and distillation. They can be grouped into different classes: acid, basic, direct, disperse, metallic, mordant, pigment, reactive, solvent, sulphur and vat dyes, which reflect their macroscopic behaviour and also their prevailing functionalities. More than one lakh commercial dyes are currently available in the market and throughout the world more than 7 × 10^5 tons of dyestuff are produced annually (Ajmal et al., 2014). It is estimated that 10–15% of dyes are lost in wastewater during manufacturing and application processes (Natarajan et al., 2013a).

A variety of synthetic dyestuffs released by various industries pose a threat to environment and public health. The contamination in wastewater due to the dyes can be recognized quite easily as a very small amount of synthetic dye in water (<1 ppm) are highly visible, affecting the aesthetic merit, transparency of water bodies. They adsorb and reflect the sunlight entering water, thereby interfering with the aquatic species growth and hindering photosynthesis. Additionally, they can have acute and/or chronic effects on organisms depending on their concentration and length of exposure. So the degradation of dyes from the wastewater is the major concern toward environmental pollution abatement.

A wide range of technologies has been developed for the removal of dyes from waters and wastewaters to decrease their environmental impact. These methods can be classified into four categories: (1) Physical (2) Chemical (3) Biological and (4) Acoustical, Radiation and Electric processes (Gupta and Suhas, 2009). Various methodologies such as sedimentation (Cheremisinoff, 2002), filtration (microfiltration, ultrafiltration, nanofiltration and reverse osmosis) using various types of membranes (Avlonitis et al., 2008; Linebarger et al., 1995; Marmagne and Coste, 1996; Al-Bastaki, 2004), chemical treatments (coagulation and filtration) (Shi et al., 2007; Zhou et al., 2008), oxidation (chemical oxidation and ultraviolet (UV) assisted oxidation using chlorine, hydrogen peroxide, fenton’s reagent, ozone, or potassium permanganate) (Namboodiri et al., 1994; Hage and Lienke, 2006; Wang, 2008), electrochemical (electro-oxidation, electro-coagulation, and electro-degradation) (Dogan and Turkdemir, 2005), advanced oxidation process (photo-fenton’s reagent oxidation, ultraviolet oxidation, photocatalysis, photolysis and sonolysis) (Bandala et al., 2008; Aguadach et al., 2005; Hong et al., 1999; Maezawa et al., 2007), and biological (aerobic, anaerobic, combined aerobic and anaerobic treatments) (Barragan et al., 2007; Rai et al., 2005; Delee et al., 1998) fall under the above mentioned categories. In addition to this, adsorption process has been also widely used for the removal of dyes from the waste water (Bansal and Goyal, 2005; Danis et al., 1998).

Physical methods such as membrane-filtration processes (nanofiltration, reverse osmosis, electrodialysis) and sorption techniques; chemical methods such as coagulation or flocculation combined with flotation and filtration, precipitation flocculation, electro-flotation, and electro-kinetic coagulation found to be suitable for the removal of various dyes. These methods do not degrade the dye but only decrease the dye concentration in water bodies by converting it from one form to another, thereby creating secondary pollution. Also, biological methods such as aerobic and anaerobic microbial degradation, and the use of pure enzymes were also reported in literature for dye removal from waste water. The disadvantages of the biological methods are that they are time consuming, even some dyes are resistant to aerobic treatment. It has also been reported that the production of carcinogenic compounds such as aromatic amines can occur during the anaerobic treatment of dyes (Freeman, 1989).

In the recent past, advanced oxidation processes have gained much attention for the removal of pollutant from waste water. These processes are ecofriendly, economic, and capable to degrade many dyes or organic pollutants present in waste water. These advanced oxidation processes were carried out in the presence of solar and ultraviolet irradiation.
Additionally to increase the rate of degradation or adsorption of pollutant on the surface of photocatalyst, advanced oxidation processes were assisted by hydrogen peroxide (H₂O₂) and ultrasonication (Srivastava et al., 2013; Rao et al., 2009; Sobana and Swaminathan, 2007; Aleboyeh et al., 2012). However, among the various advanced oxidation processes, photocatalytic degradation of dyes has been mainly carried out using various semiconductor based photocatalyst such as iron oxide (Fe₂O₃, 2.2 eV), cadmium sulphide (CdS, 2.5 eV), ilmenite (FeTiO₃, 2.8 eV), vanadium oxide (V₂O₅, 2.8 eV), bismuth oxide (Bi₂O₃, 2.8 eV), zinc oxide (ZnO, 3.2 eV), titanium dioxide (TiO₂, 3.2 eV), strontium titanate (SrTiO₃, 3.4 eV), zinc sulphide (ZnS, 3.6 eV), and tin oxide (SnO₂, 3.5 eV) (Huang et al., 2013; Tayade et al., 2007b; Mills and Lee, 2002; Lee and Mills, 2004; Natarajan et al., 2013b). Additionally, these catalysts were modified in order to enhance their photocatalytic degradation efficiency (Natarajan et al., 2015).

Another approach to enhance the photocatalytic efficiency and the easy separation of the photocatalyst from treated water is by anchoring of the photocatalytic materials on the surface of high surface area materials such as silica, zeolite, and clay (Mogal et al., 2012; Tayade et al., 2011; Tayade et al., 2008; Tayade et al., 2007a). The advantages of these materials are that they are inert, provide higher surface area for the photocatalytic reaction and the channel or pores of these materials act as a micro reactor for photocatalytic reactions. In addition to this, these materials have good adsorption properties due to their higher surface area and charge density present on them. Some of the materials were also demonstrated for the easy separation capability.

In the present review we have tried to summarize properties of the dyes used in various industries and their properties as well as their impact on environment. It also discusses the photocatalytic nanostructured materials synthesized and applied for the degradation of dyes, their dye adsorption and degradation capabilities. In the end the degradation mechanism of dyes and the synergic effect of adsorption on the photocatalytic degradation of dyes are also discussed.

1. Dye classification

A dye is a coloured substance that has an affinity for the substrate to which it is being applied. It is coloured because it absorbs light in the visible range of the spectrum at a certain wavelength. Dye is an ionizing and aromatic organic compound. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fibre. Dyes are applied everywhere, from plastic toys to those fabrics we wear, from food to wood; hardly there is any industry where dyes are not used commercially. Dyes are basically ionizing and aromatic compounds having different chromophore molecules responsible for their colour. Their structures have aryl rings that have delocalised electron systems. These structures are said to be responsible for the absorption of electromagnetic radiation that has varying wavelengths based on the energy of the electron clouds. Chromophores make the dyes proficient in their ability to absorb radiation. Chromophores act by making energy changes in the delocalised electron cloud of the dye. This alteration invariably results in the compound absorbing radiation within the visible range of colours and not outside it. Table 1 shows the type, property, and nature of the dyes reported in literature.

In ancient days, dyes were obtained from natural sources. Natural colouring agents are mainly of inorganic origin (clays, earths, minerals, metal salts, and even semi-precious stones, such as malachite) or organic dyestuffs traditionally divided into two groups, one of animal and the other of plant origin (Patil et al., 2011). In addition to this, botanical sources like lichens, insects and shellfish were also used to obtain dyes. Dyes can be classified in several ways; each class has a very unique chemistry, structure and particular way of bonding. Some dyes can react chemically with the substrates forming strong bonds in the process, and others can be held by physical forces. Fig. 1 shows the classification of dyes. Classification of dyes can be done based on their synthesis, use of source materials, and nature of their respective chromophores and the nature of electronic excitation. A large variety of natural or synthetic dyestuffs are available for various applications. The applications of various dyes are tabulated in Table 2.

Textile industries are the major industries which mainly use different classes of dyes based on the fibres. For example reactive dyes are mostly used for dyeing of natural fibres like wool, cotton, and silk. In the case of synthetic fibre such as polyester, acrylic and rayon, the acidic and basic dyes are used. These acid and basic dyes have become more popular due to their high wet-fastness, brilliance and range of hues; also can be used for natural fibres like wool, cotton, and silk. Direct dyes can be used for colouring rayon, paper, leather, and to small extent nylon. The application of mordant dyes is limited to the colouring of wool, leather, furs and anodized aluminium. Solvent dyes are used for colouring inks, plastics, wax, fat and mineral oil products. The natural dyes are mainly used for food industry.

1.1. Influence of properties of dyes on adsorption and degradation efficiency

A good dye has some qualities such as colour, fixes itself to fabrics, fastness to light, resistant to the action of water, diluted acids, alkalis (all detergents and washing soaps are alkaline in nature) and various organic solvents used in the dry cleaning. The properties of the dyes are based on the following factors (Patil et al., 2011):

- Shade (brightness or dullness)
- Fastness requirements
- Level dyeing properties
- Ease of application and dusting
- Environmental concerns
- Economy

There are many parameters which affect the adsorption as well as photocatalytic degradation efficiency of dyes, particularly adsorption and photocatalytic degradation depend upon the type and chemical structure of the dyes; adsorptive and photocatalytic properties of the materials used for the
<table>
<thead>
<tr>
<th>Dye name</th>
<th>Type</th>
<th>Colour</th>
<th>Molecular formula</th>
<th>Molecular weight (g/mol)</th>
<th>Absorption maxima (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Red 114</td>
<td>Azo</td>
<td>Dark red powder</td>
<td>Cₗ₂H₆₂N₄Na₂O₁₅S₃</td>
<td>830.81</td>
<td>514</td>
</tr>
<tr>
<td>Acid Red 27</td>
<td>Azo</td>
<td>Dark red to purple</td>
<td>C₁₂H₁₁N₂Na₂O₇S₂</td>
<td>604.47</td>
<td>520</td>
</tr>
<tr>
<td>Acid Orange 7,</td>
<td>Azo</td>
<td>Orange</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>350.32</td>
<td>483</td>
</tr>
<tr>
<td>Acid Orange 8</td>
<td>Azo</td>
<td>Red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>364.35</td>
<td>490</td>
</tr>
<tr>
<td>Acid Yellow 17</td>
<td>Azo</td>
<td>Yellow</td>
<td>C₂₀H₁₁Cl₂N₄Na₂O₂S₂</td>
<td>551.29</td>
<td>400</td>
</tr>
<tr>
<td>Allura Red AC</td>
<td>Azo</td>
<td>Red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>496.42</td>
<td>504</td>
</tr>
<tr>
<td>Acid Red 14</td>
<td>Azo</td>
<td>Dark red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>502.43</td>
<td>515</td>
</tr>
<tr>
<td>Acid Yellow 23</td>
<td>Azo</td>
<td>Yellow</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>534.37</td>
<td>455</td>
</tr>
<tr>
<td>Acid Black 1</td>
<td>Azo</td>
<td>Dark brown</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>616.49</td>
<td>620</td>
</tr>
<tr>
<td>Acid Red 73</td>
<td>Azo</td>
<td>Yellow light red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>556.48</td>
<td>507</td>
</tr>
<tr>
<td>Acid Brown 14</td>
<td>Azo</td>
<td>Red light brown</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>622.54</td>
<td>465</td>
</tr>
<tr>
<td>Acid Orange 10</td>
<td>Azo</td>
<td>Bright orange</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>452.37</td>
<td>478</td>
</tr>
<tr>
<td>Acid Red 186</td>
<td>Azo</td>
<td>Purplish red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>548.46</td>
<td>455</td>
</tr>
<tr>
<td>Acid Orange 6</td>
<td>Azo</td>
<td>Yellow</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>316.27</td>
<td>387</td>
</tr>
<tr>
<td>Alizarin Red S</td>
<td>Anthraquinone</td>
<td>Orange-yellow</td>
<td>C₁₂H₁₆NaO₇S</td>
<td>342.26</td>
<td>517</td>
</tr>
<tr>
<td>Acid Blue 80</td>
<td>Anthraquinone</td>
<td>Red light blue</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>678.68</td>
<td>626</td>
</tr>
<tr>
<td>Acid Blue 25</td>
<td>Anthraquinone</td>
<td>Dark blue</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>416.38</td>
<td>600</td>
</tr>
<tr>
<td>Acid Blue 7</td>
<td>Triaryl-methane</td>
<td>Blue</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>630.81</td>
<td>625</td>
</tr>
<tr>
<td>Acid Blue 1</td>
<td>Triaryl-methane</td>
<td>Dark blue</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>566.67</td>
<td>630</td>
</tr>
<tr>
<td>Acid Blue 9</td>
<td>Triaryl-methane</td>
<td>Violet</td>
<td>C₁₂H₁₂N₂O₇S₂</td>
<td>787.90</td>
<td>625</td>
</tr>
<tr>
<td>Acid Yellow 73</td>
<td>Xanthene</td>
<td>Brilliant yellow</td>
<td>C₁₂H₁₂NaO₅S</td>
<td>376.27</td>
<td>490</td>
</tr>
<tr>
<td>Basic Red 46</td>
<td>Azo</td>
<td>Dark red</td>
<td>C₁₂H₁₂BrNaS</td>
<td>401.3</td>
<td>530</td>
</tr>
<tr>
<td>Basic Violet 3</td>
<td>Triaryl-methane</td>
<td>Bright blue purple</td>
<td>C₁₂H₁₂ClN₂S</td>
<td>407.98</td>
<td>590</td>
</tr>
<tr>
<td>Brilliant Green</td>
<td>Triaryl-methane</td>
<td>Blue-green</td>
<td>C₁₂H₁₂H₂O₅S₂</td>
<td>482.63</td>
<td>624</td>
</tr>
<tr>
<td>Basic Blue 41</td>
<td>Azo</td>
<td>Dark violet</td>
<td>C₁₂H₁₂N₂O₇S₂/C₃H₂ClN₄O₂S</td>
<td>482.57/450.98</td>
<td>600</td>
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<tr>
<td>Congo Red</td>
<td>Azo</td>
<td>Red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>696.66</td>
<td>510</td>
</tr>
<tr>
<td>Crocein Orange G</td>
<td>Azo</td>
<td>Bright orange</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>350.32</td>
<td>488</td>
</tr>
<tr>
<td>Direct Blue 160</td>
<td>Azo</td>
<td>Dark grey</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>1373.0</td>
<td>570</td>
</tr>
<tr>
<td>Direct Red 80</td>
<td>Azo</td>
<td>Purple</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>1373.08</td>
<td>529</td>
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<tr>
<td>Direct Red 81</td>
<td>Azo</td>
<td>Red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>675.6</td>
<td>510</td>
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<tr>
<td>Direct Red 23</td>
<td>Azo</td>
<td>Purple</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>813.73</td>
<td>508</td>
</tr>
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<td>Direct Yellow 27</td>
<td>Azo</td>
<td>Yellow</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>662.63</td>
<td>398</td>
</tr>
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<td>Direct Yellow 50</td>
<td>Azo</td>
<td>Red light yellow</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>956.82</td>
<td>395</td>
</tr>
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<td>Direct Violet 17</td>
<td>Azo</td>
<td>Dark blue purple</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>891.79</td>
<td>546</td>
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<tr>
<td>Direct Yellow 12</td>
<td>Azo</td>
<td>Deep yellow</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>680.66</td>
<td>395</td>
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<td>Gentian Violet</td>
<td>Triaryl-methane</td>
<td>Violet</td>
<td>C₁₂H₁₂NaCl</td>
<td>407.98</td>
<td>536</td>
</tr>
<tr>
<td>Indigo Carmine</td>
<td>Indigotin</td>
<td>Indigo to dark blue</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>466.35</td>
<td>610</td>
</tr>
<tr>
<td>Janus Green B</td>
<td>Azo</td>
<td>Violet</td>
<td>C₁₂H₁₂ClN₂S</td>
<td>511.07</td>
<td>544–550</td>
</tr>
<tr>
<td>Methylene Blue</td>
<td>Aniline</td>
<td>Dark green</td>
<td>C₁₂H₁₂N₂ClS</td>
<td>319.85</td>
<td>664</td>
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<td>Methyl Orange</td>
<td>Azo</td>
<td>Orange-yellow</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>327.33</td>
<td>460</td>
</tr>
<tr>
<td>Methyl Red</td>
<td>Azo</td>
<td>Dark red</td>
<td>C₁₂H₁₂NaO₇S₂</td>
<td>269.30</td>
<td>540</td>
</tr>
<tr>
<td>Orange G</td>
<td>Azo</td>
<td>Orange</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>452.38</td>
<td>495</td>
</tr>
<tr>
<td>Ponceau S</td>
<td>Azo</td>
<td>Light red</td>
<td>C₁₂H₁₂NaO₇S₂</td>
<td>672.63</td>
<td>514</td>
</tr>
<tr>
<td>Reactive Black 5</td>
<td>Azo</td>
<td>Black</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>991.82</td>
<td>597</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td>Azo</td>
<td>Reddish-violet</td>
<td>C₁₂H₁₂ClN₂S</td>
<td>479.02</td>
<td>554</td>
</tr>
<tr>
<td>Reactive Yellow 2</td>
<td>Azo</td>
<td>Bright yellow</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
<td>872.97</td>
<td>400</td>
</tr>
<tr>
<td>Reactive Yellow 14</td>
<td>Azo</td>
<td>Yellow</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
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<td>410</td>
</tr>
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<td>Reactive Yellow 17</td>
<td>Azo</td>
<td>Yellow</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
<td>682.79</td>
<td>426</td>
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<tr>
<td>Reactive Yellow 145</td>
<td>Azo</td>
<td>Orange</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
<td>1026.20</td>
<td>419</td>
</tr>
<tr>
<td>Reactive Red 22</td>
<td>Azo</td>
<td>Red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>590.51</td>
<td>511</td>
</tr>
<tr>
<td>Reactive Red 15</td>
<td>Azo</td>
<td>Big red</td>
<td>C₁₂H₁₂ClN₄O₇S₂</td>
<td>876.09</td>
<td>500</td>
</tr>
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<td>Reactive Blue 4</td>
<td>Anthraquinone</td>
<td>Dark blue</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
<td>681.39</td>
<td>596</td>
</tr>
<tr>
<td>Remazol Brilliant Blue R</td>
<td>Anthraquinone</td>
<td>Blue-black</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>626.54</td>
<td>592</td>
</tr>
<tr>
<td>Reactive Orange 16</td>
<td>Azo</td>
<td>Red</td>
<td>C₁₂H₁₂N₂NaO₇S₂</td>
<td>617.54</td>
<td>494</td>
</tr>
<tr>
<td>Reactive Red 2</td>
<td>Azo</td>
<td>Purplish red</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
<td>615.34</td>
<td>538</td>
</tr>
<tr>
<td>Reactive Yellow 84</td>
<td>Azo</td>
<td>Yellow</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
<td>918.4</td>
<td>420</td>
</tr>
<tr>
<td>Reactive Orange 4</td>
<td>Azo</td>
<td>Orange</td>
<td>C₁₂H₁₂Cl₂NaO₇S₂</td>
<td>781.47</td>
<td>490</td>
</tr>
<tr>
<td>Sudan 1 V</td>
<td>Azo</td>
<td>Reddish brown</td>
<td>C₁₂H₁₂NaO₅S</td>
<td>380.44</td>
<td>520</td>
</tr>
<tr>
<td>Sulforhodamine-B</td>
<td>Azo</td>
<td>Red</td>
<td>C₁₂H₁₂NaO₅S</td>
<td>558.67</td>
<td>565</td>
</tr>
</tbody>
</table>
Fig. 1 – Classification, applications and method of applications of dyes.
adoption and photocatalytic degradation, nature of substitut-
ents attached on the dye molecules (ex. methyl group
(Neppolian et al., 2002), nitrite group (Qamar et al., 2005),
chloro group (Tanaka et al., 2000), hydroxyl group (Qamar
et al., 2005; Tanaka et al., 2000), carboxylic group (Guillard
et al., 2003), alkyl side chains (Bouzaïda et al., 2004), and
sulfonic substituent (Tanaka et al., 2000)). These factors have
been discussed by different researchers in the reported
literature. Epling and Lin (2002) have studied the visible light
assisted degradation of a range of organic dyes with varied
chemical structures such as thiazine, xanthene, anthraqui-
one, phenanthrene, quinoline, indigo, triphenylmethane
and azo dyes as follows: Methylene Blue (thiazine, cationic),
Methylene Green (thiazine, cationic), Dinitro Methylene Blue
(thiazine, cationic), Eosin B (xanthene, anionic), Rose Bengal
(xanthene, anionic), FD&C Red 2 (monoazo, anionic), D&C
Green 5 (anthraquinone, anionic) D&C Green 6 (anthraqui-
one, neutral), FD&C Green 3 (triphenylmethane, anionic),
FD&C Blue 2 (indigo, anionic), D&C Violet 2 (anthraquinone,
neutral), FD&C Red 40 (monoazo, anionic), D&C Red 33
(monoazo, anionic), D&C Yellow 10 (quinoline, anionic) and
D&C Green 8 (phenanthrene, anionic) using Degussa P-25 TiO2
as a photocatalyst. It was observed that the anionic food dye
degradation efficiency is high compared to the cationic and
neutral dyes. In cationic dyes, the presence of electron
withdrawing groups makes it resistant to photo-degradation,
approving with the photosensitizing oxidation mechanism.
Conversely, Rose Bengal showed a higher rate of photocata-
lytic degradation even if it has an additional electron with
drawing groups compared to the Eosin B which may be due to
the involvement of photo-reduction mechanism. Hence,
they concluded that the decolorization rate of dyes was in
ordered as indigo > phenanthrene > triphenylmethane > azo = quinoline > xanthene = thiazine > anthraquinone. In contrast,
Rauf and Salman (2009) reported that the cationic dyes degrade
at a faster rate compared to anionic dyes and that diarylmethane
dyes and anthraquinonic dyes exhibit the fastest and slowest
degree degradation rates, respectively. The rate of degradation
of dyes in this study follows: Auramine O > Safranin O > Malachite
Green > Amido Black > Rhodamine B > Carmine. Moreover,
they suggested that during photocatalytic degradation molecu-
lar structure of dye molecules plays precise role and based on
this they have correlated the percentage degradation of dye with
type of dyes. Similarly, Khataee et al. (2009) have studied the
degradation of three azo dyes (i.e., C.I. Acid Orange 8 (AO8), C.I.
Acid Orange 10 (AO10), C.I. Acid Orange 12 (AO12) under UV light
irradiation using supported TiO2 in a circulation photochemical
reactor equipped with 15 W UV lamp (λ = 365 nm). It was found
that the photocatalytic decolorization kinetics were in the order
of AO10 > AO12 > AO8. The additional of two sulfonic groups
and high molecular weight of acid orange AO10 dye made higher
adsorption yield than other two dyes. Furthermore, the presence
of electron donating group in the AO8 molecular structure
marginally decreased the adsorption than AO12. Another reason
may be the absorption of light photon by dye molecule itself
leading to a less availability of photon for hydroxyl radical
generation. It was observed that AO8 strongly absorb near UV
irradiation compared to AO10 and AO12 leading to lesser photo

<table>
<thead>
<tr>
<th>No.</th>
<th>Types of dyes</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Leather dyes</td>
<td>In leather, fat soluble components from these dyes by applying high temperature have an affinity to migrate upwards into the layers to give the smooth finish to leather surface. These dyes are used as colourant material for hair.</td>
</tr>
<tr>
<td>2.</td>
<td>Oxidation dyes</td>
<td>These dyes are used in making distempers, soaps, spirit inks, lacquers, plastic, rubber, ink for High Density Polyethylene (HDPE) woven bags, wood gloss finish, metallised polyester film, paddle dyeing of wool skins and furs, etc.</td>
</tr>
<tr>
<td>3.</td>
<td>Solvent dyes</td>
<td>They are also used in making distempers, soaps, spirit inks, lacquers, plastic, rubber, ink for High Density Polyethylene (HDPE) woven bags, wood gloss finish, metallised polyester film, paddle dyeing of wool skins and furs, etc.</td>
</tr>
<tr>
<td>4.</td>
<td>Fluorescent dyes</td>
<td>It is used as penetrant liquids for crack detection, plastics, synthetic resins, printing inks, non-destructive testing, and sports ball dyeing. Merantine Brilliant Yellow 8G fluorescent dye is used in the textile applications.</td>
</tr>
<tr>
<td>5.</td>
<td>Fuel dyes</td>
<td>Used in fuels</td>
</tr>
<tr>
<td>6.</td>
<td>Smoke dyes</td>
<td>Coloured smoke used for smoke signals in a military context. It can be produced by smoke grenades, or by various other pyrotechnical devices.</td>
</tr>
<tr>
<td>7.</td>
<td>Sublimation dyes</td>
<td>These dyes have printing applications. These are readily available in the market as inkjet ink, toner for laser printers, or as ribbons for the thermal-transfer printing.</td>
</tr>
<tr>
<td>8.</td>
<td>Inkjet dyes</td>
<td>Writing industry including the inkjet printers</td>
</tr>
<tr>
<td>9.</td>
<td>Leuco dyes</td>
<td>It is used in the security printing, novelty bath toys, swimming pool toys, battery testees.</td>
</tr>
<tr>
<td>10.</td>
<td>Direct dyes</td>
<td>Direct dyes are widely used on cotton, paper, leather, wool, silk and nylon. They are also used as pH indicators and as biological stains.</td>
</tr>
<tr>
<td>11.</td>
<td>Vat dyes</td>
<td>Sulphur dyes are water insoluble dyes and have no affinity for the cellulosics as such, but solubilized when treated with reducing agent to form a leuco compound. These leuco compounds are water soluble and have affinity for the cellulosic materials such as cotton, viscose, jute and flex etc.</td>
</tr>
<tr>
<td>12.</td>
<td>Sulphur dyes</td>
<td>Coloured smoke used for smoke signals in a military context. It can be produced by smoke grenades, or by various other pyrotechnical devices.</td>
</tr>
<tr>
<td>13.</td>
<td>Organic pigments</td>
<td>Used in cotton, cellulosic, blended fabrics and paper</td>
</tr>
<tr>
<td>14.</td>
<td>Reactive dyes</td>
<td>Reactive dyes is the important method for the coloration of cellulosic fibres. It can also be applied on wool and nylon</td>
</tr>
<tr>
<td>15.</td>
<td>Dispersed dyes</td>
<td>It is commonly used to dye polyester fibres and nylon</td>
</tr>
<tr>
<td>16.</td>
<td>Acid dyes</td>
<td>Acid dyes are used for dyeing protein fibres such as wool, angora, cashmere and silk. Apart these, milk protein fibres like Silk Latte, Soya Protein etc., can also be used.</td>
</tr>
<tr>
<td>17.</td>
<td>Azoic dyes</td>
<td>These dyes are used in printing inks and pigments</td>
</tr>
<tr>
<td>18.</td>
<td>Basic dyes</td>
<td>For dyeing acrylic fibres, basic dyes are used and also for dyeing of jute, cut flowers, dried flower, coir, etc.</td>
</tr>
<tr>
<td>19.</td>
<td>Developed dyes</td>
<td>Developed dyes are applied in the cellulosic fibres and fabric</td>
</tr>
<tr>
<td>20.</td>
<td>Mordant dyes</td>
<td>These water soluble dyes are affinity for silk, wool and polyamides</td>
</tr>
</tbody>
</table>
degradation. The extinction coefficient \( \lambda_{230-240} \) of these three dyes in UV range follows the order: AO8 > AO12 > AO10. The strong absorption of light by dye molecules prevents the photo-generation of holes or hydroxyl radicals, because of the insufficiency contact between the photons and immobilized TiO\(_2\). Thus the photo-degradation efficiency decreased, via the dye molecules to adsorb the light and thus obstructing the photons to reach the photocatalyst surface.

Vinu et al. (2010) have compared the degradation efficiency of five anionic dyes (i.e., Orange G (mono-azoic), Amido Black 10B (di-azoic), Alizarin Cynane Green (anthraquinonic), Eosin Y (xanthene fluorone), Indigo Carmine (indigo)), using combustion-synthesized nano-TiO\(_2\) (CS TiO\(_2\)) and Degussa P-25 TiO\(_2\) (DP-25) and studied the effect of functional group of dye molecules in the photocatalytic degradation. The photocatalytic decolorization process was performed using a high pressure mercury lamp (\( \lambda = 365 \) nm) with an incident intensity of \( 4.24 \times 10^{-7} \) Einstein/L/sec. The order of decolorization of anionic dyes was found to be: Indigo Carmine > Eosin Y > Amido Black 10B > Alizarin Cynane Green > Orange G using CS-TiO\(_2\) as photocatalysts gave higher rates of decolorization compared to DP-25. The presumed reason of decolorization order of cationic and anionic dyes is because of the dye molecular structure and surface properties of photocatalyst used. The important structure of the above all anionic dyes is the presence of sulfonic group, which is not present in eosin Y molecule. The formation of sulphate ions (SO\(_4^{2-}\)) is the main step of the degradation for these sulfonated anionic dyes which help to further breakdown of the dye structure. It was observed that the order of the reactivity for the formation of sulphate ions in terms of point of the attachment of the sulfo-group in the dye molecule is as follows: –SO\(_3^-\) attached to the benzene ring > –SO\(_3^-\) attached to the naphthalene ring > hetero = S= – in the aromatic link. Another reason for the fast degradation of indigo carmine may be due to the presence of intermolecular hydrogen bonding. The presence of intermolecular hydrogen bonds in the dye molecules disturb the molecular planarity with the solvent molecules, leading to higher degradation due the breaking of central –C=C– bond. Therefore, the photocatalytic degradation of these dyes strongly influenced by the structure and functional groups, thus decide the degradation efficiency of the same type of dyes.

2. Impact of dyes on environment

The role of dye is important in our day to day life as it is used in various textile industries, the leather tanning industry, paper production, food, colour photography, pharmaceuticals and medicine, cosmetic, hair colouring, wood stanning, agricultural, biological and chemical research, light-harvesting arrays, and photo electrochemical cells (Surolia et al., 2010; Ackacha et al., 2003). Other than this, synthetic dyes have been employed for the efficacious control of sewage and wastewater treatment, for the determination of specific surface area of activated sludge for ground water tracing, etc. (Kuhad et al., 2004). It is reported by Zollinger, that approximately 40,000 different synthetic dyes and pigments are used in various industries and about 450,000 tons of dyestuff are produced worldwide. The largest consumer of these dyes is the textile industry, accounting for approximately 65% of its market (Couto, 2009; Forgacs et al., 2004; Zollinger, 1987; Kuo and Ho, 2001). The annual production of synthetic dyes is more than 7 × 10\(^6\) tons (Forgacs et al., 2004). During the dyeing process, approximately 15% of these non-biodegradable textile dyes are discharged into natural stream and water bodies in the form of textile waste effluent. As per estimation made by World Bank, nearly 17%–20% water pollution has the major contributors related to textile finishing and dyeing industries. According to a study by Chakrabarti, out of major identified wastewater toxic chemicals, 72 chemicals were solely released by the textile dyeing and nearly 30 of such chemicals were not treatable (Chakrabarti and Dutta, 2004). As per the survey of Ecological and Toxicological Association of Dyestuffs and Manufacturing Industry (ETAD), it is reported that out of 4000 screened dyes, 90% dyes were found having their lethal dose (LD\(_{50}\)) values greater than 2 × 10\(^3\) mg/kg and among the tested dyes di-azo, direct and basic dyes showed the highest rates of toxicity. From the literature, it is clear that the bright coloured water soluble dyes such as reactive and acid dyes are difficult to remove from the water (Beyene, 2014).

The contamination due to the dye in the water at very low concentration can be identified easily through naked eyes due to their very high visibility. The presence of dye even at low concentration affects transparency and gas solubility in water. Dyes absorb and reflect the sunlight entering water, and interfering with the aquatic species growth which interferes in the photosynthesis as well as they can also provide acute or chronic effect on the organisms depending on the concentration and length of exposure. Generally dye wastewater is considered to have higher chemical oxygen demand (COD) values because of the presence of organic compounds, a high inorganic and organic dissolved substance content, inconsistent pH, and low degradability by biological reagents. During the reduction of dyes and their intermediates, the formation of highly carcinogenic or mutagenic compounds can occur, which has a detrimental impact on microorganisms and aquatic life (Carliell et al., 1996). Human consumption of water contaminated with these compounds can cause a variety of adverse health effects such as wide-ranging immune suppression, breathing problems, central nervous system (CNS) disorders, behavioural problems, allergic reactions, tissue necrosis, and infections of the skin and eyes (Pan et al., 2012). So it is essential to remove the dye from the wastewater by not just only the removal of dye colour from water but also elimination or decrease of its toxicity.

Recently, in developed and developing countries the government legislation regarding removal of dyes from the industrial effluents is becoming increasingly strict and enforcement of law will continue to ensure that the effluent from the dye utilizing industries is as per the required standard (Anjaneyulu et al., 2005).

3. Adsorption

Adsorption is defined as a process that involves interphase accumulation or concentration of substances on the surface of a solid or a liquid (adsorbent). The unbalanced inward forces of attraction or free valences at the surface of the
adsorbent have the property to attract and retain the molecules (adsorbate) onto their surface as they come in contact. This process can occur between any two phases, such as liquid–liquid, gas–liquid, or liquid–solid interfaces. Adsorption is operative in several systems such as physical, biological, and chemical systems, and it is widely used in water purification. Adsorption is surface phenomenon mainly practised from the ancient times by using solids such as carbon for the removal of substances from either gaseous or liquid solutions (Lasa, 2009). When the adsorbate adheres onto the surface of adsorbent through weak intermolecular forces such as Van der Waals forces it is called physisorption or physical adsorption. Physisorption is characterized by low heat of adsorption (~20 to 40 kJ/mol), and the reaction is generally reversible in nature. However, if the adsorbate adheres onto the surface of adsorbent through chemical bonds, it is called chemisorption or chemical adsorption. This type of adsorption evolves high heat of adsorption and is generally irreversible (Jaycock and Parfitt, 1981; Sigh, 2000; Weng et al., 2009). The removal of adsorbate from the surface of the adsorbent is called desorption. The extent of adsorption depends on the nature of adsorbate such as molecular weight, molecular structure, molecular size, polarity and solution concentration. It also depends on the surface properties of adsorbent such as particle size, surface area, and surface charge. Adsorption process is a very effective separation technique and it is considered to be superior compared to other available techniques for wastewater treatment in terms of initial cost, simplicity of design, ease of operation and insensitive to toxic substances. Moreover, parameters associated with dye adsorption such as pH of the effluent, salts present in the waste water, type of the adsorbent, adsorbent dosage, nature of the adsorbent, surface chemistry of the adsorbent, temperature, contact time, and agitation rate determine the effective of the process (Natarajan and Bajaj, 2016). Adsorption equilibrium isotherm is one of the most important parameters required to understand the behaviour of adsorption process. The shape of an isotherm gives the idea about the affinity of dye molecules and possible mechanism of adsorption. The most commonly used adsorption isothersms for evaluation of adsorption data are Langmuir and Freundlich models (Langmuir, 1918; Freundlich, 1906). Kinetic study of the adsorption processes is often used to describe the efficiency of adsorption and feasibility of scale-up operation. Kinetics of adsorption equilibrium is also needed to evaluate the effectiveness of the adsorbate, with pseudo first-order and pseudo second-order kinetics being the most commonly used adsorption kinetics for evaluation of data (Gunay et al., 2007; Ho, 2006). From the early days of using bone char for decolourization of sugar solutions and other foods, to the later implementation of activated carbon for removing nerve gases from the battlefield, to today’s thousands of applications, the adsorption phenomenon has become a useful tool for purification and separation. However, compounds with colour and those that has taste or odour tend to bind strongly. Compounds that contain certain chromogenic groups, which provide colour to the pigment very often, are strongly adsorbed on adsorbent like activated carbon. A schematic representation of removal of dye using adsorbent from the waste water is shown in Fig. 2.

Fig. 2 – Dye adsorption process using adsorbent.
naturally and can be prepared synthetically also. Zeolites have ion exchange property and based on the exchange of ions they act like selective adsorbents (Adebajo et al., 2003). In addition to this materials like alumina and silica gel having surface area of 200–300 m²/g and 250–900 m²/g are also used for removal of dyes. Recently, many researchers have reported new low-cost alternative natural materials. The adsorption capacity of various adsorbents mainly depends on the surface area, porosity, and charge on the adsorbent. Gupta and Suhas (2009) have provided a very good summary on the various dyes such as acid, basic, other than acid and basic dye adsorption capability of various commercial activated carbon and other alternative adsorbents.

Besides these operational parameters, other factors responsible for excellent adsorption ability are different types of interactions between the adsorbate and adsorbent involved in the adsorption process. Natarajan and Bajaj (2016) reported the speedy adsorption of organic dye, Methylene Blue (MB), on the Graphene oxide (GO), in the presence of spent lithium-ion batteries (LIBs), wherein, 100% of the dye got adsorbed within 10 min. This quick adsorption of MB was attributed to two different types of interaction between GO and dye molecules (Fig. 3) including: (i) electrostatic attraction between positively charged methylene blue and negatively charged graphene oxide (ii) π-π interactions between the aromatic dye and the delocalized π-electron system of graphene oxide.

In the same work, GO showed maximum adsorption capacity of 134.1 mg/g for Congo Red (CR) dye due to the following mechanisms: (i) The negatively charged oxygen atom of carboxylate ion (COO⁻) in the GO can interact with amino (-NH₂) group of CR via hydrogen bonding (ii) hydrogen bonding interaction between the hydroxyl group (-OH) of GO and negatively charged oxygen atom of sulfonyl (-SO₃) group (Fig. 4). (iii) Another possible way for the interaction of CR onto GO is π-π interaction between the GO basal planes and the aromatic ring of dye molecules. Moreover, MB adsorption on GO is higher than CR not due to the surface physical properties such as surface area and pores but due to the surface chemistry.

Activated carbon prepared from Enteromorpha prolifera by zinc chloride activation removed 59.88 mg/g of Reactive Red 23, 71.94 mg/g of Reactive Blue 171, and 131.93 mg/g of Reactive Blue 4 from aqueous solution. The adsorption process in this activated carbon is mainly controlled by intraparticle diffusion mechanism (Sun et al., 2013). Zhu et al. (2016) investigated the adsorption behaviour of CR from aqueous solution onto synthesized novel multi-functional NiFe₂O₄/ZnO. The hydrothermally synthesized hybrid adsorbed 221.73 mg/g of CR which was higher than those adsorbed on NiFe₂O₄, ZnO and mechanically mixed NiFe₂O₄/ZnO hybrids. Hierarchical porous zinc oxide microspheres were used as adsorbent for the removal of CR from aqueous solution. The maximum adsorption capacity of CR on GO was found to be in the following order: K⁺ > Na⁺ > Mg²⁺ for cations and Cl⁻ > NO₃⁻ > ClO₄⁻; and sorbent content on the sorption of Co(II) ions on M-RGO have been studied. The sorption of Co(II) on M-RGO was found to be in the following order: K⁺ > Na⁺ > Mg²⁺ for cations and ClO₄⁻ > NO₃⁻ > Cl⁻ for anions. A steady increase in adsorption was observed with increasing adsorbent content attributed to the more available sites of solid content. Generally, variations in the ionic strength will affect the sorption ability of adsorbent due to the outer-sphere complex formation, but in the case of Co(II) sorption on M-RGO exhibited negligible effect due to the

![Fig. 3 – Schematic illustration of the mechanism of Methylene Blue (MB) adsorption by Graphene Oxide (GO).](image)
inner-sphere surface complexation rather than outer-sphere surface complexation.

Natarajan et al. (2014) investigated the preferential adsorption of MB dye on the surface hydroxyl enriched TiO$_2$ nanotube. They have used mixture of MB and Rhodamine B (RhB) dye and found the preferential adsorption of MB dye on the surface of titanium nanotube due to the surface hydroxyl group present on the surface of titanium nanotube. Their result showed that the 87.7% of MB dye and 6.8% RhB dye were adsorbed on the surface of titanium nanotube due to the electrostatic interaction between the cationic MB dye and surface hydroxyl group enriched negatively charged titanium nanotube surface.

4. Photocatalysis

Photocatalysis can be described as a change in the rate of chemical reactions or their initiation under the action of light in the presence of substance called photocatalyst that absorbs light quanta and takes part in the chemical transformation of the reaction participants. A photocatalyst is a substance that produces electron–hole pairs by absorption of light quanta and makes chemical transformations of the reaction participants that come into contact with it and regenerates its chemical composition after each cycle of such interactions (Fox and Dulay, 1993).

A photocatalytic process occurs via the following steps (Schiavello, 1988)

1. Generation of electron–hole pairs by exciting a semiconductor with radiation of a suitable energy;
2. Separation of electron–hole pairs by traps that have trapping rate higher than the recombination rate;
3. Redox reaction by separated electrons and holes with adsorbed substrates, according to thermodynamic and kinetic constraints;
4. Evolution of products and regeneration of the surface.

The working mechanism for the photocatalytic process can be defined as a chemistry of “redox mechanism” and the role of light is mainly to excite the solid, which must essentially be a semiconductor. In photocatalytic degradation of any organic or dye compound present in air or water, the bandgap of the photocatalytic material plays a major role. The photocatalytic degradation capability of the photocatalyst mainly depends on the band position of the photocatalyst rather than the bandgap because the band position determines the oxidation or reduction power of the photocatalyst. It is well known that, the band gap of various semiconductors lies in the range of 0.7 to 5 eV. Band gap of the semiconductor can be defined as the difference in energy between the valance band and the conduction band of solid materials. It is also called as energy gap, an energy range of the solid where no electron state can exist. The use of various semiconductors has been carried out on band gap of the semiconductor. Particularly, in photocatalytic applications such as degradation of pollutant present in water, mainly photocatalyst having band gap in the range of 2.0 to 3.3 eV was reported in the literature.

4.1. Indirect photocatalytic mechanism

As shown in Fig. 5, when the semiconductor photocatalyst absorb photon energy from irradiation sources (such as solar...
light, artificial ultraviolet light and/or light emitting diodes (LEDs) greater than its band gap, it generates electron and hole at conduction and valance band respectively due to the excitation of electron from valance band to conduction band upon absorption of energy. The hole generated at the valance band absorbs water molecule and create hydroxyl radical (OH), whereas electron reacts with the oxygen to form anionic superoxide radicals (O$_2^-$). These radicals are capable to oxidize the adsorbed organic molecules and the organic intermediates are further oxidized by molecular oxygen and/or OH radicals producing the carbon dioxide and water. The electron in the conduction band forms the anionic superoxide radical (O$_2^-$) by taking the oxygen itself. Further protonation of superoxide radical (O$_2^-$) lead to formation of hydroxyl radical. These radicals then form molecular oxygen and hydrogen peroxides. Thus, the photo excited semiconductor photocatalyst allows both oxidation and reduction to take place on the surface (Litter, 1999). The general detailed mechanism of dye degradation upon irradiation by TiO$_2$ is given by the following equations.

i. Dye + h$_v$ → Dye$^*$
ii. Dye$^*$ + TiO$_2$ → Dye$^+$ + TiO$_2$
iii. TiO$_2$(g) + O$_2$ → TiO$_2$ + O$_2^-$
iv. O$_2^-$ → TiO$_2$(g) + 2H$^+$ → H$_2$O$_2$
v. H$_2$O$_2$ + TiO$_2$(g) → OH + OH$^-$
vi. Dye$^*$ + O$_2$ (O$_2^-$ or OH$^-$) → Peroxylated or hydroxylated intermediates → degraded or mineralized products

4.2. Direct photocatalytic mechanism

Another process called direct photocatalytic mechanism has two different approaches as discussed below:

(i) Heterogeneous photocatalysis—the Langmuir–Hinshelwood process

Generally, the Langmuir–Hinshelwood kinetic technique is used to explain the heterogeneous photocatalysis mechanism. It is based on the generation of electrons and holes by the irradiation of the photocatalyst. Then the hole is trapped by the catalyst surface adsorbed dye molecule to produce reactive radical states which can decompose as a result of recombination with a photogenerated electron. Subsequently, the catalyst is regenerated for further use. Langmuir–Hinshelwood (L–H) process is expressed as given below (Rauf and Salman, 2009; Machado et al., 2003):

$$ \frac{1}{r} = \frac{1}{k_r} + \frac{1}{k_a k_r C} $$

where $r$ is the reaction rate for the oxidation of reactant (mg/L min), $k_r$ is the specific reaction rate constant for the oxidation of the reactant (mg/L min), $k_a$ is the equilibrium constant of the reactant (L/mg) and $C$ is the dye concentration. When the chemical concentration $C_o$ is a milli molar solution ($C_o$ is small) the equation can be simplified to an apparent first order equation:

$$ \ln \frac{C_o}{C} = k_k t = k_{app} t $$

or

$$ C = C_o \exp(-k_{app} t) $$

A plot of $\ln \frac{C_o}{C}$ versus time ($t$) represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant ($k_{app}$). Generally first-order kinetics is
suitable for the concentration of substrate range up to few ppm, numerous studies were available where this kinetic model well fitted.

(ii) The Eley–Rideal process

In this process, the electron hole pairs (charge carriers) are generated in the presence of light irradiation followed by the holes are trapped by surface defects or active sites (D). Then the surface defect or active sites (D) can interact with the dye molecules through the chemisorption mechanism to produce an adduct species like (D–dye)* which can further degrade into form a products or can recombine with photogenerated electrons. This reaction process is described as follows (Rauf and Salman, 2009; Serpone and Emelie, 2002):

\[ \text{Photocatalyst} + h\nu \rightarrow e^- + h^+ \] (photogeneration of free carriers).

\[ D^+ + h^- \rightarrow D^- \] (hole trapping by surface defects).

\[ D^+ + e^- \rightarrow D \] (physical decay of active centres).

\[ D^+ + \text{dye}^- \rightarrow (D-\text{dye})^+ \] (chemisorption).

\[ (D-\text{dye})^+ \rightarrow D + \text{products}. \]

In case of photosensitized oxidation in presence of visible light, the dye absorbs light of wavelength greater than 400 nm and introduce e– on to the conduction band of photocatalyst. Excited dye converts to cationic dye radicals (Dye*) and e– in photocatalyst leads to the formation of oxidation species (O2, HO2 or HO–).

4.3. Degradation of dye using synergic effect of adsorption and photocatalysis

In ancient days, the removal of dyes was practised by application of adsorbents. Few decades ago, Carry et al. demonstrated the potential application of semiconductor based photocatalyst for the degradation of organic pollutant and later in 1970s Fujishima and Honda discovered the phenomenon of photo induced water cleavage on TiO2 electrode (Carey et al., 1976; Fujishima and Honda, 1972). This has led to the utilization of semiconductor in the photocatalytic application for the environmental clean-up (Hoffmann et al., 1995; Fujishima et al., 2000; Mills and Hunte, 1997; Blake, 1997). Till today many researchers have demonstrated numerous photocatalytic activities of various photocatalytic materials for degradation of different organic compounds present in water including dyes (Etacheri et al., 2015; Abou-Gamra and Ahmed, 2016; Wu et al., 2015; Hamad et al., 2016). From all these studies based on the photocatalytic application for degradation pollutant, it is evident that, the band gap, crystallinity, phase composition, electron hole recombination rate, penetration of light through photocatalytic materials, surface area and adsorption capability of the pollutant on the surface of photocatalysts are the important parameters which help in the enhancement of the photocatalytic activity (Anandan and Yoon, 2003; Corma and Garcia, 2004). Based on this, researchers were fascinated toward the synthesis of higher surface area photocatalysts which can provide higher catalytic surface and higher adsorption of pollutant on the surface of photocatalytic materials. In order to enhance the surface area of the photocatalytic materials, the reduction in size of i.e., synthesis of nanocrystalline tubular, rod-like, needle-like, and flower-like structure of different photocatalytic materials such as TiO2, ZnO, CdS are prepared and utilized for the degradation of various pollutants present in the water. It is observed that the titanium nanotube has 3-4 fold times higher surface area than the bulk TiO2 (Tayade and Key, 2010). The synergistic effect has been reported by using AC powders and TiO2 powders (Arerachakul et al., 2007; Matos et al., 2007; Velasco et al., 2010). Sun et al. (2016) reported on the synergistic effect of adsorption and photocatalysis by TiO2 onto sulfanyl/activated carbon composite using molecular self-assembly method and their synergistic effect was studied through MB degradation by pure TiO2 and TiO2/sulfanyl/activated carbon composite. The synergistic relationship between adsorption and photocatalysis was quantified by comparing the degradation of MB. This work proposed important information on understanding this synergistic effect which was important for the effective preparation of TiO2/HS/AC materials and their applications in waste water treatment.

The incorporation of photocatalyst with adsorbents offers a new design of a photocatalytic system. Some nanocomposites which have a high adsorbing capacity as well as a high efficiency for the photocatalytic degradation have been prepared such as TiO2/zeolite (Al-Harbi et al., 2014), TiO2/Al2O3 (Zhang et al., 2012), TiO2/SiO2 (Huang et al., 2011; Lazar et al., 2015), TiO2-graphene nanocomposites (Shanmugam et al., 2016), and multi-walled carbon nanotubes (MWCNT)/Gd,N,S-TiO2 nanocomposites (Mamba et al., 2015). In that way, numerous novel materials and composites have been developed as the photocatalysts with visible light response, such as TaON (Higashi et al., 2012), CaBi4O6 (Wang et al., 2012b), Ag–AgBr/SBA15 (Hu et al., 2015), Ag3PO4 (Ge et al., 2012), BiOBr-PVP hybrids (Li et al., 2015), BiO1 (Wang et al., 2011), CdS (Luo et al., 2012), ZnO (Liu et al., 2013), (BiO)2CO3-based photocatalysts (Ni et al., 2016), ZnBiYO4 (Cui and Luan, 2015), BiOBr/montmorillonite composites (Xu et al., 2014) and so on. These photocatalytic materials exhibit higher photocatalytic activity under visible light irradiation, but there still exist two main obstacles for their practical applications. On one hand, the presence of noble metal or transition metal in these photocatalyst makes the operational cost higher; on the other hand, some metal elements used are toxic and unsafe, which might be the latent hazards for the ecological environments. Recently, a novel metal-free photocatalyst, graphite-like carbon nitride (g-C3N4) shows high photocatalytic performance for degradation of organic dyes under visible light irradiation due to the unique physico-chemical property and electronic band structure. Due to its polymeric properties, this metal-free material has high chemical stability compared to the inorganic metal based semiconductors, making it a promising photocatalyst in aqueous solution. Li et al. (2014) reported synergistic effect of efficient adsorption g-C3N4/ZnO composite for photocatalytic property. In this study, a possible photocatalytic mechanism was suggested about the synergistic effect of the g-C3N4 adsorption and photocatalytic capacity in the RhB degradation process. Fig. 6 showed the electron–hole separation process and synergistic
effect of adsorption capacities under visible-light driven by g-C_{3}N_{4}/ZnO composite.

4.4. Morphology

It is well known that, size, shape and morphology of any catalytic material play an important role in its performance.

In environment clean-up applications, particularly using photocatalytic processes, various types of nanomaterials having different morphologies play a major role. This is mainly due to the change in morphology that provides a large specific surface area, numerous size defects, ion-exchangeable capability and promising application in photocatalysis. Furthermore, the change in size and morphology of the photocatalytic materials has a positive effect of their properties like surface area, photons carrying ability, followed by movement of electrons and holes along the morphology (Li et al., 2016; Natarajan et al., 2013b). The increase in surface area of the photocatalytic materials also enables the increase in higher adsorption of pollutant, which leads to higher photocatalytic degradation efficiency. Many reports demonstrated that the conversion of titanium dioxide, zinc oxide and many other photocatalytic materials into nanomaterials possesses higher surface area as compared to their bare materials upon their conversion to different morphologies such as nanotube, nanosphere, nanobelt, nanoflower, and nanoribbon. Fig. 7 shows the images of different morphological materials used in photocatalytic applications. Some of the work carried out on the adsorption and photocatalytic performance of different morphological photocatalytic materials are discussed below.

Titanium dioxide, a widely used photocatalytic material had been synthesized with different morphologies and used for the environmental abatement. After the discovery of carbon nanotube by Iijima in 1991, first titanium nanotube synthesis was reported by Kasuga et al. (1998) by treating

Fig. 6 – Scheme of reversible adsorption of recyclable adsorption and electron–hole separation transportation at the g-C_{3}N_{4}/ZnO photocatalyst interface. C: Rhodamine B (RhB) concentration in solution. Reprinted with permission (Li et al., 2014).

Fig. 7 – (a) Nano flakes, (b) spheres, (c) nanotubes, (d) nanowires, (e) flower-like, (f) hollow spheres, (g) microspheres and (h) nano rod photocatalytic materials.
crystalline TiO₂ with highly concentrated NaOH solution. In literature numerous reports are available on the synthesis and characterization of titanium nanotube for the efficient adsorption and the photocatalytic degradation of dyes. It clearly indicated that the enhancement of surface area due to titanium nanotube (8–10 times higher than that of bare TiO₂) leads to the higher adsorption and photocatalytic degradation of various dye pollutant present in waste water (Costa and Prado, 2009; Nah et al., 2010; Kitano et al., 2007; Sun et al., 2010; Xu et al., 2011). Although titanium nanotubes were considered as the promising photocatalyst for the organic dye degradation because of its many intrinsic properties, it has its own limitations such as faster recombination of photo generated electron–hole pairs, fast backward reaction, and incompetency in utilization of visible light of solar spectrum. To overcome these problems, considerable efforts that have been carried out to modifying titanium nanotube by dye sensitization (Lei et al., 2010), metal ion doping (Shon et al., 2008), anion doping (Junpeng et al., 2011), and also addition of electron donors (hole scavengers) have been investigated. Among all these modifications, doping using various metal ions (Ag, Cu, Co, Fe, Cr, V, Nb, Si, Al, K, Mn, and Pd) and non-metal ions (C, N, S, and P), showed a promising result under solar light irradiation.

It is reported that the non-metal ion doped catalysts are better for extending the photocatalytic activity of the titanium dioxide into visible region of solar spectrum as compared to the metal ion doping (Zhang et al., 2009b; Devi and Kavitha, 2016). Recently, titanium nanotube grown on the surface of titanium metal plate was also used for the degradation of dyes present in water. These highly ordered and vertically aligned TiO₂ nanotubes can be obtained by potentiostatic anodization of Ti metal under suitable electrolyte and processing conditions. TiO₂ nanotubes are obtained after the process. The process involves initially the formation of barrier layer followed by rather well-defined nanoporous structure (Grimes, 2007; Lai and Sreekantan, 2011; Natarajan et al., 2011). The Ti metal was used as substrate for growing TiO₂ nanotubes. The amorphous TiO₂ nanotubes can be obtained at the end of the anodization process and can be crystallized by high temperature calcination treatment (Lai and Sreekantan, 2012). Other than the tubular morphology, Lin et al. (2009) synthesized photoactive Ag-ZnO composite nanofiber by electro-spinning method and used as photocatalyst for the degradation of RhB dye. They found that the degradation of RhB dye (2.5 × 10⁻⁵ mol/L, 10 mL, pH = 5.4) took place in 50 min using 10 mg Ag-ZnO nanofiber. Nanosheets and nanorods of Bi₂MoO₆ were synthesized via solvothermal and microwave solvothermal techniques by Bi et al. (2007). The surface area of the prepared nanosheets and nanorods of Bi₂MoO₆ was 32.3 and 10.7 m²/g and crystallite sizes of 17 and 35 nm. The highest photocatalytic activity was obtained by Bi₂MoO₆ nanosheets on RhB dye. All the experiments were carried out using 80 mg of Bi₂MoO₆ with 80 mL of RhB (10⁻⁵ mol/L).

Sponge-like, rose-like and plate-like Bi₂O₂CO₃ microspheres were synthesized by hydrothermal method without any templates and their photocatalytic activity was estimated for the degradation of different dyes (Rhodamine B (RhB), Methyl Orange (MO), and Methylene Blue (MB)). The surface area of prepared sponge-like, rose-like and plate-like Bi₂O₂CO₃ samples was 43.99, 39.50 and 5.13 m²/g. Forty milligrams of sponge-like Bi₂O₂CO₃ microspheres degraded 50 mL of RhB dye (10⁻⁵ mol/L) in 10 min, but the rose-like Bi₂O₂CO₃ taken 15 min and plate-like Bi₂O₂CO₃ degraded RhB dye to the extent ~ 87% only, after 15 min while the sponge-like Bi₂O₂CO₃ microspheres degraded the 80% MO in 55 min and 90% MB in 30 min under same conditions under UV illumination. Under solar light, over 95% of the RhB degraded after 60 min between the light intensity 38 and 45 mW/cm². The results revealed that Bi₂O₂CO₃ microsphere is a higher promising photocatalyst for photocatalysis (Zhao et al., 2011).

A flower-like Bi₂MoO₆ hollow spheres were prepared by solvothermal process by ethylene glycol and its photocatalytic efficiency for the degradation of RhB dye was evaluated. The surface area of calcine and synthesized Bi₂MoO₆ hollow spheres were 20 and 40 m²/g. The Bi₂MoO₆ also synthesized by solid-state reaction method which has surface area of 0.9 m²/g. The 0.05 g of calcined hollow spheres displayed excellent 95% photocatalytic efficiency with 50 mL of 10 mg/L RhB dye solution while the calcine sample showed 78% degradation of RhB dye and the SSR-Bi₂MoO₆ exhibited only 55% in 120 min. All samples showed higher photocatalytic activity than that of P-25 sample (Tian et al., 2011).

BiOCl micro flowers and nanosheets were synthesized via hydrothermal treatment. The as-synthesized BiOCl flowers have the surface area of 53.5 m²/g with a diameter of 1–2 μm. The adsorption and photocatalytic activity of both synthesized samples were studied for the degradation of RhB dye. The adsorption capability of BiOCl flowers for RhB dye was ~ 30% with 20 mg/L of RhB (100 mL) dye solution. But the BiOCl nanoplates showed the low adsorption efficiency (0.9%) and also TiO₂ nanoparticles which have a similar BET surface area exhibited 17.2% adsorption efficiency under same conditions. 20 mg/L of BiOCl flowers degraded the 99% of 20 mg/L of RhB (100 mL) dye solution after 15 min due to its (001) facets with the rate constant of 0.272/min. The BiOCl nanoparticles exhibit shower rate of degradation (only 0.0324/min) indicating its lower degradation efficiency compared to the BiOCl flowers. For comparison, TiO₂ has the surface area of 50 m²/g almost equal to the BiOCl flowers and showed only 1.87 × 10⁻⁵/min rate of degradation 144 times lesser than that of BiOCl micro flowers (Wang et al., 2012a).

Under different reaction conditions, CuO nanorods, nanoleaves and nanosheets were obtained by hydrothermal treatment. The structures were characterized by SEM, TEM and XRD techniques. The crystallite size of CuO nanorods, nanoleaves and nanosheets were 16, 14 and 18 nm (determined from the Scherer equation). These different morphologies of CuO were applied for adsorption and photocatalytic degradation of CR dye. The higher adsorption efficiency was obtained by CuO nanorods (46%) compared to nanoleaves (~14%) and nanosheets (~2%) over 100 mL of CR dye solution (20 mg/L) with 0.05 g of each photocatalyst. Likely, in photocatalytic degradation CuO nanorods exhibited 67% degradation efficiency over CR dye while nanoleaves and nanosheets acquired 48%, 12% after 210 min under UV illumination with same reaction conditions (Sadollahkhani et al., 2014).

ZnO dumb-bell shaped microcrystal was synthesized by hydrothermal method without the addition of surfactant. The diameter and length of as-synthesized ZnO dumb-bell shaped
were 5 μm and 10 μm respectively, clearly observed by SEM analysis. To check the photocatalytic activity of this ZnO, three different dyes such as Crystal Violet, Methyl Violet and Methylene Blue were used. 1 g of prepared ZnO degraded 68.0% Crystal Violet, 99.0% Methyl Violet and 98.5% Methylene Blue of each 1000 mL dye solutions respectively after 75 min. TOC removal efficiencies achieved were 43.2%, 59.4% and 70.6% respectively (Sun et al., 2009). ZnO sphere-like, flower-like, sheet-like structures were obtained by two-step hydrothermal method. The size of the sphere-like, flower-like observed by SEM was 30 nm and 2 μm respectively. Both the flower-like and sheet-like ZnO thickness were 80 nm. The photocatalytic activity of these different structures was applied into MO dye solution. These different structures failed to adsorb the MO dye solution. ZnO sheet-like photocatalyst degraded 89% MO (300 mL, 20 mg/L) after 60 min while in the case of flower-like exhibited 75% and sphere-like caught only 56% (Xie et al., 2011).

The marigold-like ZnIn2S4 microspheres were synthesized by a hydrothermal treatment. ZnIn2S4 has a surface area of 85.53 m2/g and the diameter about 3.7 μm. ZnIn2S4 microsphere photocatalytic activity has been investigated using three dyes for namely MO, CR, and RhB. 40 mg of ZnIn2S4 microspheres degraded the 80 mL of 10 ppm of MO after 180 min; 80 mL of 20 ppm of CR after 300 min; and 80 mL of 30 ppm of RhB after 180 min (Chen et al., 2009).

ZnSe cubic and spherical flower-like morphologies were obtained by solvothermal treatment by using ethylene glycol. The ZnSe cubic-like and spherical flower-like microspheres have the surface area of 83.13 and 58.67 m2/g. 30 mg of each photocatalyst completely degraded the 30 mL of 5 × 10−5 mol/L MO solution (Zhang et al., 2009a).

4.5. Composite materials

To enhance the adsorption capability of dye on the photocatalyst surfaces and effective degradation, various composites have been reported in the literature with the aims of developing photocatalytic materials with high adsorption, efficient electron–hole recombination, and easy separation of catalysts and effective degradation of dyes. This type of materials were used in suspended batch type reactors and also applied by developing photocatalytic surface on suitable support materials. These composite materials mainly include few high surface area materials such as zeolite, various forms of carbons such as activated carbon, carbon nanotube, graphene and photocatalytic materials such as TiO2 and ZnO. In addition to this various composites were synthesized in order to use solar light, efficient electron hole recombination, effective charge trapping which include, Ag based photocatalyst, co-doped photocatalysts, and using two semiconductors. The details of some important composites which are mainly synthesized for enhancement in the adsorption capacity and photocatalytic activity are discussed below.

It is well-known that the carbonaceous materials have extraordinary absorption properties, low cost, and environmental friendly properties which made it a potential support material to be used in various environmental applications. Many researchers synthesized carbon based composite photocatalytic materials by immobilizing photocatalytic materials on the surface of various carbon materials such as activated carbon, carbon nanotube, graphite, and graphene. Wang et al. (2009b) synthesized composite photocatalysts with TiO2 immobilized on granular activated carbons with different porosities (TiO2/AC) by dip-hydrothermal method using peroxotitanate as precursor. They showed that the porosity of activated carbon had a significant influence on the adsorption, the amount of TiO2 deposited on the external surface of activated carbon and the activity of composite photocatalysts for the degradation of MO dye. Due to the immobilization of TiO2 on the activated carbon, 10% reduction in the surface area of activated carbon due to the blocking of mesopores was noted. They found that the pores with width or diameter that is 1.7–3 times of the dimension of adsorbates are most favourable for the adsorption. The highest adsorption on composite having 2.1 nm diameter reached 91% of the saturated adsorption in 20 min but the highest degradation was obtained using composite having the highest TiO2 content on the surface of composites with pore diameter of 2.05 nm due to the synergetic effect of adsorption. They have also proposed the mechanism based on the synergetic effect of adsorption of activated carbon and TiO2 photocatalysis.

Saleh and Gupta (2012) synthesized a composite photocatalyst (surface area: 190 m2/g) consisting of multi-walled carbon nanotube and titanium dioxide for effective adsorption of MO dye and effective degradation through photocatalytic TiO2 material by avoiding the high rate of electron hole recombination. They also reported that the multi-walled carbon nanotube acts as dispersing agent preventing TiO2 from agglomerating activity during the photocatalytic process, providing a high surface active photocatalytic surface area and demonstrated how carbon nanotube can enhance the efficiency of photocatalysts based on the synergic effect. They observed that the degradation of MO (dye concentration: 0.05 mol/L, irradiation source: 40 W ultraviolet lamp) using TiO2 was only 65%, and by using composite materials it enhanced to 93% due to the synergic effect.

Another form of carbon, graphene, is also used to develop composite photocatalytic materials (Du et al., 2011). Ferera et al. (2012) synthesized high surface area small diameter composite materials, consisting graphene and TiO2 nanotube by hydrothermal method and examined the effect of loading of graphene oxide. Titanium nanotube was decorated on the surface of reduced graphene oxide. They used commercially available TiO2 nanoparticles of small diameter (ca. 9 nm) to decorate graphene oxide in alkaline medium and followed by hydrothermal method, graphene-TiO2 nanotube composites were synthesized. They found that the ratio of deoxygenated graphene oxide (hGO) and titanium nanotube (TNT) in the composite significantly affect the photocatalytic activity. Higher amount of hGO in hGO-TNT composite had lower photocatalytic activity as compared to the pure TNT photocatalytic activity. The optimum amount of hGO was 10%, which demonstrated 3-fold photocatalytic efficiency enhancement for the degradation of Malachite Green (MG) dye due to the synergic effect of hGO and titanium nanotube. Other than carbon materials, mesoporous materials like zeolite were also used to make composite materials.

The attractive properties of the zeolite materials are that they have large surface areas, internal pore volume, unique
uniform pores, and channel size of 12–18 nm. They can also act as interesting hosts to disperse semiconductor photocatalyst on their surfaces. Their surface area which is in the range of 400–650 m²/g with pore volumes of above 0.1 cm³/g is common for conventional zeolites (Green and Rudham, 1993; Liu et al., 1993; Chen et al., 2002; Schiavello, 1993).

Zeolites exhibit several other specific features that make them suitable for their use as hosts for photocatalysts, such as the following: (i) full photochemical stability and large thermal and chemical inertness; (ii) transparency to UV-visible radiation above 240 nm, thus allowing a certain penetration of the exciting light into the solid opaque powder to reach the substrate molecules located in intraparticle positions; (iii) zeolite’s high adsorption for organic compounds from solution concentrating the substrate molecule in the proximity of active sites of the photocatalyst; (iv) the polarizing strength inside the zeolite pores by varying the nature of internal charge balancing cations and the size of the channels; (v) the ability of the zeolite framework to participate actively in electron-transfer processes, either as electron acceptor or electron donor. For example, upon photoexcitation, an encapsulated molecule can eject an electron that will become delocalized through the framework or in clusters of the charge balancing cations. Also, there are reverse processes in which electron-rich sites of the zeolite can donate an electron to a photoexcited molecule (Matsuoka and Anpo, 2003; Hashimoto, 2003).

In our previous reported study, TiO₂-coated NaY and HY zeolite composite photocatalysts demonstrated enhanced photocatalytic activity as compared to pristine TiO₂ material. These composite catalysts were synthesized by coating TiO₂ particles on the surface of zeolite materials by hydrothermal method. This study showed that the 1% TiO₂ coating on the surface of zeolite had better photocatalytic efficiency than the higher amount of TiO₂ coated on the surface of NaY and HY zeolites. It is found that with increase in amount of TiO₂ the surface area of bare zeolite materials decreases. The adsorption capacity of composite materials was in the range of 23%–25% and 32%–39% in the case of TiO₂ coated NaY and HY zeolite composite respectively, whereas it was found 4% on the surface of pristine TiO₂ material. The complete degradation of MB dye was obtained within 2–3 hr using zeolite based composite materials, whereas it was found 82% using pristine TiO₂ in 4 hr irradiation of ultraviolet light which was also supported by chemical oxygen demand analysis (Tayade et al., 2007a). Further enhancement in the TiO₂ coated HY zeolite was also reported by our group showing the effect of silver metal ion exchange on the composite materials for degradation of organic contaminant like acetophenone and nitrobenzene as well as dyes like MB and MG (Tayade et al., 2008).

Similar to zeolite materials, clay’s materials also have some unique properties which make them an ultimate choice as adsorbents or catalytic support such as low cost, high

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Table 3 – Various composite materials used for degradation of dyes.

<table>
<thead>
<tr>
<th>Dye name</th>
<th>Photocatalyst</th>
<th>Percentage of degradation</th>
<th>Reaction condition</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Red 27</td>
<td>2 mol% W-doped TiO₂₃</td>
<td>42.9%</td>
<td>i — 2 mg/L, ii — 2 mg/L,</td>
<td>Shahmoradi et al. (2011)</td>
</tr>
<tr>
<td></td>
<td>5 mol% W-doped TiO₂₃</td>
<td>74.39%</td>
<td>iii — 1.4 g/L.</td>
<td></td>
</tr>
<tr>
<td>Acid Red 8</td>
<td>Er³⁺-doped YAI₂O₇/ZnO</td>
<td>13.85%</td>
<td>i — 10 mg/L, ii — 1000 mL, iii — 1 g/L, v — 5.91.</td>
<td>Wang et al. (2009a)</td>
</tr>
<tr>
<td>Acid Red 73</td>
<td>TiO₂ coated sackcloth fibre</td>
<td>92.24%</td>
<td>i — 25 mg/L, v — 3.0, vi — 0.5 mg/L, vii — 0.69 mg/L.</td>
<td>Vaez et al. (2012)</td>
</tr>
<tr>
<td>Black Dispersatyl</td>
<td>Nb₂O₅, Ag/Nb₂O₅</td>
<td>38.14%</td>
<td>i — 10 mg/L, ii — 200 mL, iii — 1 g/iv — 24 hr.</td>
<td>Silva et al. (2002)</td>
</tr>
<tr>
<td>Black Neutracyl</td>
<td>Nb₂O₅, Ag/Nb₂O₅</td>
<td>9.89%</td>
<td>i — 10 mg/L, ii — 200 mL, iii — 1 g/iv — 24 hr.</td>
<td>Silva et al. (2002)</td>
</tr>
<tr>
<td>Blue Dispersatyl</td>
<td>Nb₂O₅, Ag/Nb₂O₅</td>
<td>22.39%</td>
<td>i — 10 mg/L, ii — 200 mL, iii — 1 g/iv — 24 hr.</td>
<td>Silva et al. (2002)</td>
</tr>
<tr>
<td>Brilliant Blue For</td>
<td>2 mol% W-doped TiO₂₃</td>
<td>70.14%</td>
<td>i — 2 mg/L, ii — 2 mg/L,</td>
<td>Shahmoradi et al. (2011)</td>
</tr>
<tr>
<td>Colouring of Food</td>
<td>5 mol% W-doped TiO₂₃</td>
<td>93.25%</td>
<td>iii — 1.4 g/L,</td>
<td></td>
</tr>
<tr>
<td>Direct Blue 53</td>
<td>ZnO/AC</td>
<td>0.0519/min</td>
<td>i — 288 mg/L, ii — 50 mL,</td>
<td>Xu et al. (2010)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>iii — 5.0 g/L, iv — 60 min, v — 9</td>
<td></td>
</tr>
<tr>
<td>Direct Green 99</td>
<td>N-doped metatitanic acid</td>
<td>86</td>
<td>i — 10 mg/dm³, ii — 100 mg, iv — 240 min, v — 6.</td>
<td>Wawrzyniak and Morawski (2006)</td>
</tr>
<tr>
<td>Dark Blue Neutracyl</td>
<td>Nb₂O₅, Ag/Nb₂O₅</td>
<td>33.77%</td>
<td>i — 10 mg/L, ii — 200 mL, iii — 1 g/iv — 24 hr.</td>
<td>Silva et al. (2002)</td>
</tr>
<tr>
<td>Orange Dispersatyl</td>
<td>Nb₂O₅, Ag/Nb₂O₅</td>
<td>99.45%</td>
<td>i — 10 mg/L, ii — 200 mL, iii — 1 g/iv — 24 hr.</td>
<td>Silva et al. (2002)</td>
</tr>
<tr>
<td>Reactive Blue 4</td>
<td>ZnO/sepiolite</td>
<td>100</td>
<td>i — 200 mg/L, ii — 100 mL, iii — 0.5 g/L, iv — 120 min, v — 11.</td>
<td>Xu et al. (2010)</td>
</tr>
<tr>
<td>Reactive Red 198</td>
<td>N-doped metatitanic acid</td>
<td>45</td>
<td>i — 198.5 mg/dm³, iii — 100 mg, iv — 240 min, v — 6.</td>
<td>Wawrzyniak and Morawski (2006)</td>
</tr>
<tr>
<td>Yellow Neutracyl</td>
<td>Nb₂O₅, Ag/Nb₂O₅</td>
<td>14.96%</td>
<td>i — 10 mg/L, ii — 200 mL, iii — 1 g/iv — 24 hr.</td>
<td>Silva et al. (2002)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95.79%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

i: dye concentration; ii: Volume; iii: catalyst amount; iv: time; v: pH; vi: H₂O₂ concentration; vii: anion concentration.

Light Source: a — UV, b — UV (6 W low pressure mercury lamp, Philips, Netherlands), c — four UV-A lamps (9 W, Philips, 31,250–25,000/cm), d — UV lamp (15 W, λ_max = 200–380 nm), e — UV (Philips, 100 W lamp), f — solar.
mechanical and chemical stability, availability, affordability, ion exchange capability, and environmentally friendly material (Garrido-Ramirez et al., 2010; Herney-Ramirez et al., 2010). Considering the advantages of the clay materials, various clays such as tunisian, montmorillonite, laponite, and palygorskite were used for synthesis of photocatalyst-clay composites for photocatalytic pollutant removal (Herney-Ramirez et al., 2010; Hadjiltaiief et al., 2016; Zhang et al., 2008; Paul et al., 2012; Dvininov et al., 2009; D jellabi et al., 2014).

Hadjiltaiief et al. (2014) synthesized TiO2-coated clay by impregnation method and used for the photocatalytic degradation of Reactive Blue dye under ultraviolet A (UVA) and solar irradiation. They found 100% decolourization within 20 min using Tunisian clay based composites, but according to UV (UV-Solar), UV-vis, High Performance Liquid Chromatography (HPLC), and chemical oxygen demand measurement it was found that the complete mineralization of dye took place in 45 min. They also synthesized ZnO-TiO2/Clay composite material supporting on natural clay for degradation of Methyl Green dye and also studied the influence of operation parameter such as pH, catalyst dosage, initial dye concentration, UV irradiation intensity, as well as the influence of the presence of different oxidant (Tian et al., 2009). A TiO2 supported palygorskite clay composite was synthesized and tested for the degradation of Orange G (OG) dye by Bouna et al. (2013). They found that the photodegradation of OG was highest for an optimum photocatalyst loading of ca. 0.8g/L.

Additionally, composites using various other metal such as Ag3PO4/TiO2, Au-TiO2, Cu2O/TiO2, Er3+: YAlO3/ZnO-TiO2, PbS quantum dots/TiO2 nanotube, and Al (II) modified TiO2 were also synthesized and used for the degradation of dyes to study the effective charge separation, adsorption and photocatalytic properties (Yao et al., 2012; Zhao et al., 2008; Ratanatawanate et al., 2009; Wang et al., 2010; Yang et al., 2010; Shahmoradi et al., 2011).

Various composite materials used for degradation of dyes are tabulated in Table 3.

5. Future prospects

The use of adsorptive materials for various purposes had been proven and well-practised since ancient days for various separation purposes. For the treatment of water mainly, charcoal, which is a low cost, easily available, and eco-friendly materials was utilized till today. However, after a few run, the adsorption capacity toward the purification of water decreases and needs to be regenerated for further use. Similarly many adsorptive catalysts have been utilized for the purification of water for the removal of dyes and other organic compound from the waste water, and also need regeneration by washing or by heat treatment for few cycles. Some of the adsorptive materials cannot be regenerated and need to be dispose after use, which creates secondary pollution. However, these problems with the adsorptive materials can be overcome by the designing of composite photocatalytic porous materials with different porosities, with higher surface area and some electrostatic charges in order to have interaction with charged dye molecule for effective adsorption property. Due to the high surface area, higher adsorption of dye molecule can be obtained and under the irradiation of particular wavelength of light for photoexcitation of photocatalytic materials the degradation can be achieved on the surface of the composite photocatalytic materials. Recently, few efforts have been made for the synthesis of high surface area photocatalytic materials by incorporation of photocatalytic materials like TiO2 and ZnO in or on the surface of high surface area materials like zeolites, clay, silica and metal organic framework. The advantages of these materials are that they can be easily separated from the treated water and the dangerous effect of contamination due to nanomaterials in water can be avoided. Due to the synergic effect of adsorption, photocatalytic degradation efficiency of dyes may get enhanced. The separated photocatalytic materials can easily be regenerated by solar light irradiation which reduces the cost of regeneration due to electrical energy.

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REFERENCES


Ag₃PO₄/TiO₂ visible light photocatalyst for the degradation of methylene blue and rhodamine B solutions. J. Mater. Chem. 22, 4050–4055.