Chapter 7

TITANIA NANO HYBRIDS- SELECTIVE APPLICATIONS

Jaseela P K[1] and Shamsheera K O*

[1]*Department of Chemistry, Govt.Polytechnic College, Kunnamkulam*

**PG and Research Department of Chemistry*

Korambayil Ahamed Haji Memorial Unity Women's College,Manjeri,

Email:shamsimanu@gmail.com

Many challenges that have directly or indirectly impacted mankind in recent decades, such as environmental degradation, the energy crisis, metal depletion, etc., are now major research topics. Due to rapid industrialization, the demand for metals and alloys is growing in construction, aerospace, containers, packaging, transport, etc. [1]. At a time when environmental damage is a growing problem, corrosion is the primary cause of the depletion of our natural resources. It causes significant inconvenience to people and frequently results in fatalities [2]. Corrosion is the most important metal consumer known to man. It is one of the oldest problems that have ever challenged the industrial world and remains as a challenging problem in the 21st century. The durability and efficiency of metallic alloys can be improved by applying anti-corrosion coatings has been an active area of materials science for many years [3, 4]. Environmental pollution, especially water resources has increased in the last few decades including the agricultural, industrial, pharmaceutical and plastic industries[5]. The unmanageable discharge of several hazardous contaminants and pollutants into aquatic streams troubles human health. It comprises of 300–400 MT of filthy waste deposited annually by businesses, as well as sewage that is directly dumped into water bodies (World Water Assessment Programme United Nations).Water pollution raises environmental risks that can result in eutrophication, water scarcity, and even grave health risks for humans [6]. Adopting novel waste management techniques is a necessity in order to preserve the health of the global community and ecosystem. Research into the production of hybrid systems based on TiO_2 constitute a new group of compounds exhibiting strictly designed physicochemical properties have the potential applications in different fields[7]. This chapter presents a brief outline regarding its anticorrosion and waste water remediation applications.

Titanium dioxide is one of the most heavily investigated oxide materials in addressing energy and environmental crises. Among the different applications of TiO_2 hybrids, anticorrosion, adsorption, photocatalysis and wettability control over various fields as represented in figure 1.

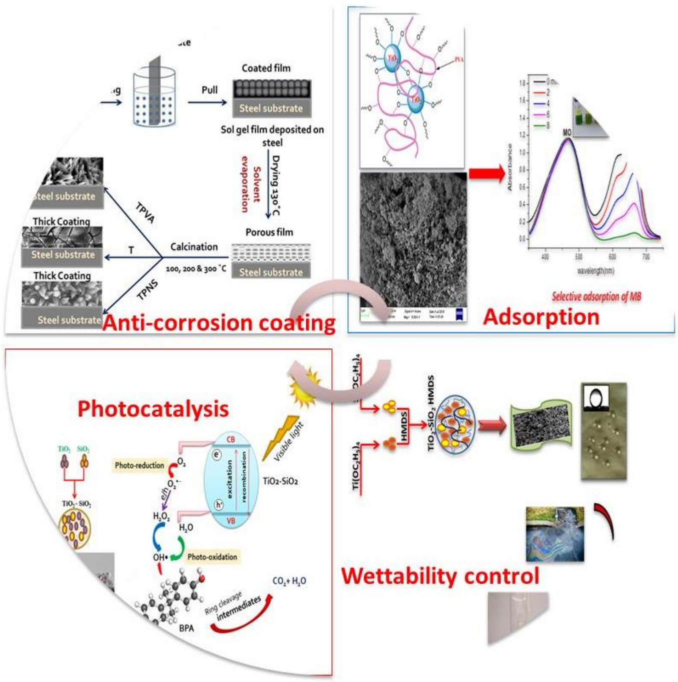
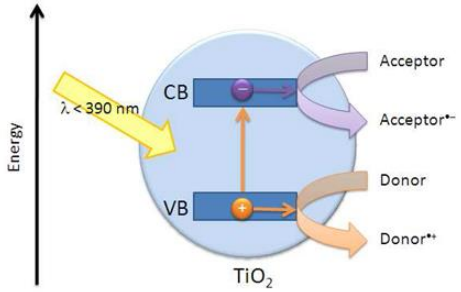


Figure 1.Image on the applications of TiO_2 hybrids.

Titania and titania based composite coatings on mild steel surface have always been a research focus for their versatile applications. They can be used as protective materials such as protective layers on metals surface to improve the wear and corrosion resistance. Guin et al. developed titania containing organic-inorganic hybrid sol-gel film using titanium isopropoxide as precursor and methyl hydrogen silicone as coupling agent. Nowadays hybrid metal oxide sol-gel coatings are widely accepted materials to improve corrosion resistance on various metals like Al, Mg, Fe and alloys. This is because they have good adhesion to metallic substrates and good barrier effect to corrosion substances. Hybrid sol-gel coatings have attracted attention of many researchers in recent years due to their ability to enhance the corrosion resistance of metal. The application of sol–gel coatings, infact has been projected as a better replacement for the environmentally unacceptable chromate conversion coatings. The titania hybrid sol-gel coatings over metallic substrates act as adhesion promoters and are used to protect the metals against corrosion. There are many advantages using sol–gel coatings. The most important features are listed as follows (i) sol-gel protective coatings have shown excellent chemical stability, oxidation control and enhanced corrosion resistance for metal substrates. (ii) sol-gel method is an environmentally friendly and cost-effective technique of surface protection. (iii) sol-gel coating showed the potential and are able to effectively replace environmentally unacceptable chromate conversion coatings (iv) sol-gel process has potential to be used for preparation of inorganic or organically modified protective coatings. (v) sol-gel procedure allows deposition of a thin oxide film even at room temperature. Sol–gel process is very attractive and versatile to prepare inorganic or hybrid films with tunable thickness. Moreover, mild synthetic conditions provided by sol–gel chemistry are advantageous for the incorporation of organic components into the inorganic network, allowing the preparation of a variety of hybrid architectures. Jaseela et al developed a stable, low cost thiourea doped titania- Poly vinyl alcohol (PVA) hybrid nano composite anticorrosion coating on mild steel via sol-gel dip-coating method. The coating on metal provides good protective efficiency, allowing the exposure period in 1M HCl to be extended to 70 days. This is significantly better than the traditional sol-gel coating, which gradually loses its effectiveness [8, 9].

A plethora of research has been done for the remediation of waste water. Water pollutant species present in water are micro-organism, pesticides, pathogens, and other organic materials. Dyes considered as type of organic pollutants and represent one of the problematic groups. They are emitted into water from various industrial branches exhibit toxic effects on microbial as well as mammalians. Most of the dyes used in textile industries are light-stable and not biologically degradable. A number of methods such as ozonation, coagulation, precipitation, ion exchange, have been used for the removal of dyes from water. Each of these methods has inherent limitation. These have been limited since they require high capital and operational costs. However, adsorption among them is considered as an effective and economical method. Adsorption is considered to be one of the best methods because of its effectiveness and low cost. Many traditional adsorbents, such as active carbon, zeolites, and polymeric materials, have been used for removing pollutants. TiO_2 is reported to possess a high adsorption capacity. But due to its poor mechanical stability might limit their practical application in some fields. The literature reports that modification into TiO_2 enhances the surface area by controlling the growth of crystallites and gives higher porosity leading to high adsorption efficiency. Apart from this the introduction of selective adsorbent is an important goal in the frontiers of research. The adsorbent can selectively adsorb one of the contaminant without any concentration change in the other molecules from a mixture. Factors that influence the adsorption efficiency include adsorbate-adsorbent interaction, adsorbent surface area, adsorbent to adsorbate ratio, adsorbent particle size, temperature, pH etc.[10] Numerous efforts have been taking on the construction of environmentally benign hybrids to enhance and extend the application to separate selectively dyes from contaminated water. Lim et al. synthesized sodium titanate nanobelts and nanotubes via hydrothermal synthesis using TiO_2 and TiS_2 as precursors respectively, and discovered that both nanostructures follow the Langmuir model in the adsorption of methylene blue (MB) [11]. The dual phase anatase/titanate nanoparticles reported by Cheng et al. also follow the Langmuir model in the adsorption of MB with a capacity of 162.19 mg g^{-1}. It was also reported that the removal of MB by anatase-covered titanate nanotubes follow the Langmuir model [12]. Jaseela et al proposed very simple, quick and practical method for the synthesis of inorganic –organic hybrid nanocomposite containing TiO_2 and PVA and investigated the remarkable adsorption selectivity for methylene blue (MB), from the mixture of methylene blue and methyl orange (MO) in aqueous environment. The nanocomposite exhibited 97.1% of MB removal within 8 minutes [13].

Photocatalysis is a promising, environmentally friendly technology for the conversion of solar energy into chemical energy. It is the acceleration of a chemical transformation by the presence of a catalyst with light. Common photocatalyst are semiconductors such as ZnO, TiO_2 Fe_2O_3 etc. When a semiconductor metal oxide is illuminated by light with energy equal to or greater than band-gap energy, the valence band electrons can be excited to the conduction band, leaving a positive hole in the valence band and an extra electron in the conduction band. Subsequent electron-hole recombination occurs when positive holes combine with promoted electrons to reverse the promotion process and releasing the input energy as heat, with no chemical effect. Nevertheless, if the electrons (and holes) migrate without recombination to the semiconductor surface, they may be involved in various oxidation and reduction reactions with adsorbed species such as water, oxygen and other organic or inorganic species other than the semiconductor itself. Photo-generated positive holes can react with electron donors to oxidise these molecules. Photo-generated electrons on the other hand tend to reduce electron donors exposed to the surface of the semiconductor. Three factors mainly pertaining to the band structure of semiconductor have the greatest effect on photocatalytic reactions. Generally, the photocatalytic power of a semiconductor widely depends: 1. Light absorption characteristics - Band gap energy determines which wavelength is more effective 2. Position of lowest point in the CB-determines the reducing power of catalyst and it should be negative with respect to the SHE potentials 3. Position of highest point in the VB determines the oxidizing power of catalyst and it should be positive with respect to the SHE potential**.** 4. Rate of redox reaction by electron-hole pair on the surface of semiconductor 5. Rate of e--h+ recombination has greatest effect on photocatalytic reactions. The wide band gap, high exciton binding energy, tunable crystal structure (rutile, anatase, and brookite), environmentally friendly nature of TiO_2 at nano scale have been employed to develop high capacity and selective sorbents for contaminants removal and in fuel synthesis namely in the field of Photocatalysis. Among the wide range of photocatalysts TiO_2 (Eg = 3.2 eV), WO_3 (Eg = 2.8 eV), $SrTiO_3$ (Eg= 3.2 eV), a-Fe_2O_3 (Eg = 3.1 eV), ZnO (Eg = 3.2 eV), and ZnS (Eg = 3.6 eV) in use, the most promising material is TiO_2, in view of its high photochemical activity. TiO_2 remains the most popular material and can be considered as a benchmark in the field of Photocatalysis. The report entitled "Autooxidation by TiO_2 as a photocatalyst" might be the first study regarding photocatalysis with respect to TiO_2 developed by Kato and Masho in the year 1956. In 1972, the main breakthrough towards TiO_2-based photocatalysis is reported by Honda and Fujishima by the discovery of water photolysis on a TiO_2 electrode. This was considered as the land mark study which aroused much attention and contribution towards photocatalysis. TiO_2 is really considered as a hot subject in the area of photocatalysis on account of the fact the number of publications exponentially growing till now. And it is interesting that studies have become more intensive in the last 20 years. In general, photocatalytic reaction on TiO_2 consists of three steps 1) photo-excitation generates electrons (e^-) and holes (h^+). 2) The electrons and holes migrate to the TiO_2 surface. Finally, the electrons and holes react with adsorbed electron acceptors and donors, respectively, to complete the photocatalytic reaction. The redox potential of photo-generated holes is + 2.53V compared with the standard hydrogen electrode (SHE). After reaction with water, these holes can produce hydroxyl radicals (OH.), whose redox potential is only slightly decreased. Both are more positive than that for ozone. The redox potential of conductive band electron is −0.52 V, capable of reducing dioxygen to superoxide $O_2^{\bullet -}$, or hydrogen peroxide H_2O_2.Depending upon the exact conditions, the holes, OH radicals, $O_2^{\bullet -}$, H_2O_2 and O_2, all can play important role in the photocatalytic reaction mechanisms. The mechanism of titania Photocatalysis is shown in the figure 2. Although the detailed mechanism of photocatalysis reactions of TiO_2 differs from one pollutant to another, it has been widely recognized that superoxide and, in particular, OH hydroxyl radicals act as active reagents for the degradation of organic compounds.



Process	Name
$TiO_2 + h\upsilon \rightarrow h_{VB}^{+} + e_{CB}^{-}$	Charge Separation
$h_{VB}^{+} + H_2O \rightarrow OH^{\bullet}$	$OH^{\bullet}$Generation (VB)
$e_{CB}^{-} + O_2 \rightarrow O_2^{\bullet -} + H_2O \rightarrow OH^{\bullet}$	$OH^{\bullet}$Generation (CB)

Figure 2. Mechanism of Titania photocatalysis

The extensive availability of visible light makes interest for the development of visible light active photo-catalysts. A small band gap is strongly desirable for an effective visible light photocatalyst. Much effort is currently focused on to meet these criterias and to harvest visible light (43% of the solar spectrum) for better solar energy conversion. A limitation of TiO_2 is its wide band gap of 3.2 eV which allows only UV light to be absorbed that covers limited area of solar spectrum (< 387 nm, accounting for 5% of the solar spectrum). So in order to achieve outstanding photocatalytic performance advances must be made to improve the light absorption, charge separation, and surface reactivity of TiO_2. Different strategies have been adopted to achieve the modification of the above-mentioned factors by either introducing morphological changes, such as increasing surface area and porosity, or by integrating additional components into the TiO_2 structure as chemical modifications. Figure 3 a) gives titania Photocatalysis under visible light and b) gives additional components influence. Important photocatalytic modifications can be obtained by surface modification of TiO_2. Modifications include: • the addition of transition metal ions (such as Cr, V, Zr, Mn, Fe, Mo); • preparation of the reduced form TiO_{2-x}; • sensitisation using dyes • doping with non-metals (such as N, S, C) • use of hybrid semiconductors such as TiO_2 /SiO_2 , TiO_2 /Al_2O_3 , etc. Fabrication of mesoporous titania hybrids as one of the most promising ways to achieve excellent photo-catalytic performance TiO_2. Recently, mesoporous and microporous oxides as well as their mixtures have become a rather popular research area. Zhou et.al.

determined the photocatalytic properties of a TiO_2 /ZrO_2 system obtained by the sol-gel method. Physicochemical analysis showed the material to have an anatase crystalline structure. The specific surface areas of the materials (for all variant methods of synthesis) lay in the range 187.0–219.2 m^2 /g.[14] Cheng et al. determined the photocatalytic properties of a hybrid material (UTZ) consisting of 3D nanospherical TiO_2 with a “hedgehog” shape and one-dimensional ZnO in the form of “nanospindles”. The resulting system was highly homogeneous and contained the crystalline structure of anatase (TiO_2) and the hexagonal wurtzite structure (ZnO) [15]. Yan et al. obtained a novel three-dimensional (3D) reduced graphene oxide/TiO_2 (rGO/TiO_2) hybrid composite by wrapping TiO_2 hollow microspheres with rGO sheets via a facile solvothermal route using poly(L-lysine) (PLL) and ethylene glycol (EG) as coupling agents.[16] Modifying the electron structure of titanium dioxide is the formation of hybrid oxide systems has been shown to have (i) modify the surface properties such as surface area of TiO_2 (ii) enhance thermal stability of the anatase phase (iii) enhance the electron–hole separation, (iv) extend the light absorption into the visible range Jaseela et al. used sol-gel hydrothermal process to create mesoporous titania (TiO_2) and titania-silica (TiO_2 - SiO_2) nanocomposites. The prepared Titania and its silica composites rapidly degrade an endocrine disrupting compound Bisphenol A (BPA) when exposed to visible light [17].

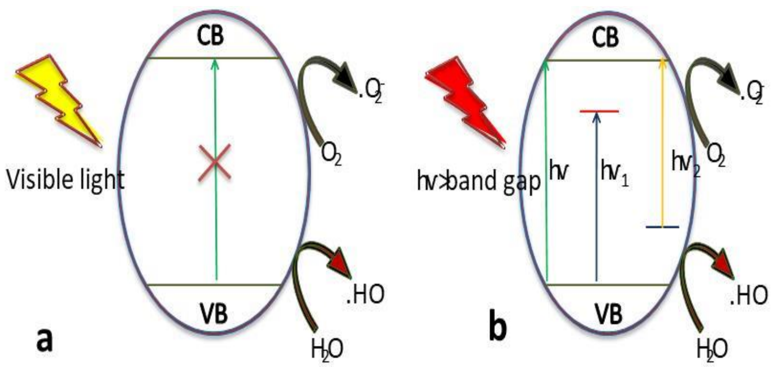


Figure 3 a) Titania Photocatalysis under visible light and b) effect of additional components on titania.

A solid surface that strongly repels water drops is called a superhydrophobic surface. Based on the contact angle and the wetting behavior, the solid surfaces are classified into four categories: (1) superhydrophilic, if the contact angle is less than 10, (2) hydrophilic, if the contact angle is between 10 and 90, (3) hydrophobic, if the contact angle is between 90 and 150, and (4) superhydrophilic, if the contact angle is above 150 . Contact angle is usually used as a measure of hydrophobicity or wettability. It is the angle made by the water drop with the contacting solid surface at the contact line. Understanding the wetting behavior of a water drop on a solid surface is the basis for designing a superhydrophobic surface. Numerous super-hydrophobic artificial surfaces have been created inspired by living creatures with unique wettability that possess super-hydrophobic properties. Nearly all methods for achieving superhydrophobicity consist of two steps: first, making a hierarchical surface roughness, and then surface modification of some materials such as fatty acids, fluoroalkyl silans, etc. by means of a low surface energy solution. Superhydrophobic surfaces and coatings have a unique behaviour against water droplets. This unique behaviour result into a new set of applications including self-cleaning, antibacterial, oil-water separation, corrosion resistance. To date, various strategies have been proposed for imparting superhydrophobic surface to substrates, such as template methods, colloidal self-assembly, sol–gel processing electro-spinning, layer-by-layer deposition, lithography and others.There have been many reports of oil contaminants in sea waters and rivers due to the leakage and sudden accidents. It has always been challenging and expensive to remove oil contaminants from water. Special wetting membranes with simultaneous superhydrophobicity and superoleophilicity making it a promising candidate for water purification. . Different methods have been introduced by scientists. Super hydrophobic cotton as filter material has been used recently.The development of bio-inspired special wettability in textile industries concerned with cloths/paper for oil (or organic solvents)-water separation. Many findings have also been reported for preparation of super-hydrophobic surfaces and the oil–water separation efficiency by using super-hydrophobic cotton fabric. Indranee et.al reported. Fluorinated silyl functionalized zirconia has been synthesized using the Sol-Gel process to create an extremely durable superhydrophobic coating on cotton fabrics. The integration of chemical stability, and photocatalytic activity of TiO_2 material enables the convenient removal of the contaminants by ultraviolet irradiation, and allows facile recovery of the separation ability, making it promising for sustainable and highly efficient oil-water separation applications [18].Li et al. reported a facile electrochemical anodizing method for fabricating porous TiO_2 membrane with special wettability. Fluorinated compounds are expensive, toxic, non- biodegradable can easily react with other materials and harmful to human health. Therefore, super-hydrophobic and super-oleophilic coated fabrics must be manufactured using fluorine and chlorine-free precursors. The wetting ability control on TiO_2 nanostructure, the rate of wetting property change, stability under UV, and mechanical strength should be carefully studied. The durability of the coating under severe environmental conditions is also an essential requirement for suitable application in oil–water separation. jaseela et al proposed a simple but feasible method to fabricate super-hydrophobic coating on cotton fabric via sol-gel process. , WCA reached up to 161.5˚. In the work they focussed in the treatment of wastewater contaminated by oil which results from some industrial activities such as oil production, oil delivery, oil refining and petrochemical operation. Figure 4 showing water droplets on super hydrophobic titania hybrid coated a) fabric b) paper. The coated fabric can effectively separate a series of oil–water mixtures through an ordinary filtering process with high separation efficiency .The as synthesized fluorine and chlorine free coated fabric can be effectively utilized in various fields [19].

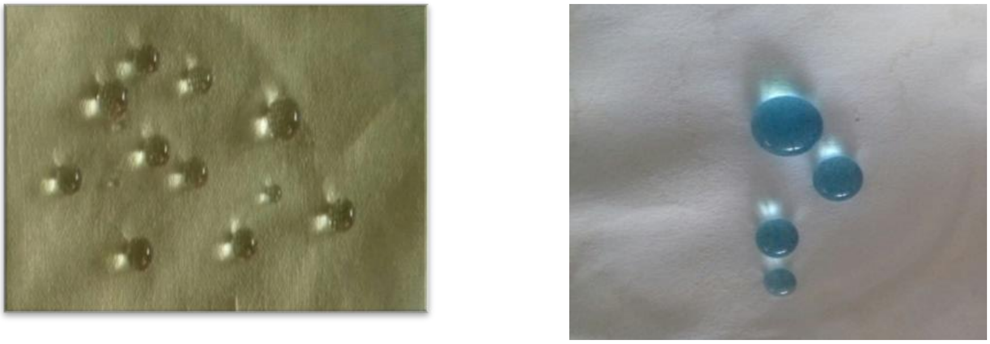


Figure 4. Water droplets on super hydrophobic titania hybrid coated a) fabric b) paper.

The degradation of the environment goes on increasing day by day by many ways. Among these metal degradation and water pollution are two major issues that have a direct impact on humanity and lead to huge problems. titania hybrids were found to have great potential in a variety of fields. This chapter presented a brief outline regarding its anticorrosion and waste water remediation applications. Apart from these, titania hybrids have broad potential for use in a variety of industries and fields, with extensive applications.

References

[1] P.A. Schweitzer, Fundamentals of metallic corrosion: atmospheric and media corrosion of metals, CRC press2006.

[2] L. Umoru, O. Ige, Effects of Tin on Aluminum–Zinc–Magnesium Alloy as Sacrificial Anode in Seawater, Journal of Minerals & Materials Characterization & Engineering, 7 (2007) 105-113.

[3] A. Popoola, O. Olorunniwo, O. Ige, Corrosion resistance through the application of anti-corrosion coatings, Developments in corrosion protection, 2 (2014) 241-270.

[4] R.B. Figueira, I.R. Fontinha, C.J. Silva, E.V. Pereira, Hybrid sol-gel coatings: smart and green materials for corrosion mitigation, Coatings, 6 (2016) 12.

[5] M. Tauqeer, M. Ahmad, M. Siraj, A. Mohammad, O. Ansari, M. Baig, Nanocomposite Materials for Wastewater Decontamination, Modern Age Waste Water Problems, Springer2020, pp. 23-46.

[6] Ariyanti, Dessy, Aprilina Purbasari, Dina Lesdantina, Filicia Wicaksana, and Wei Gao. Modified TiO2 Nanomaterials as Photocatalysts for Environmental Applications, Food Sustainability, Environmental Awareness, and Adaptation and Mitigation Strategies for Developing Countries, IGI Global, 2023, pp. 103-117..

[6] Y. Zhang, Z. Jiang, J. Huang, L.Y. Lim, W. Li, J. Deng, D. Gong, Y. Tang, Y. Lai, Z. Chen, Titanate and titania nanostructured materials for environmental and energy applications: a review, RSC Advances, 5 (2015) 79479-79510.

[7] K. Siwińska-Stefańska, T. Jesionowski, Advanced Hybrid Materials Based on Titanium Dioxide for Environmental and Electrochemical Applications, Titanium Dioxide, DOI (2017) 143

[8] P.K. Jaseela, A. Joseph, Development of Flower Like Hierarchical Thiourea Loaded Titania–PolyVinyl Alcohol Nano Composite Coatings for the Corrosion Protection of Mild Steel in Hydrochloric Acid, J. Inorg.
Organomet. Polym. Mater.28 (4) (2018) 1-15

[9] K.O. Shamsheera, A.R.Prasad, P.K. Jaseela, A. Joseph, Development of self-assembled monolayer of stearic acid grafted chitosan on mild steel and inhibition of corrosion in hydrochloric acid, Chemical Data Collections, (2020) 100402
[10] J. Garvasis, A.R. Prasad, K.O. Shamsheera, P.K. Jaseela, A. Joseph, Efficient removal of Congo red from aqueous solutions using phytogenic aluminum sulfate nano coagulant. J.Mate. Chem.Phy., (2020) 123040
[10] Y. W. L Lim, Y. Tang, Y. H. Cheng , Z. Chen, Morphology, crystal structure and adsorption performance of hydrothermally synthesized titania and titanate nanostructures. Nanoscale, 2(12), (2010), 2751-2757.
[11] K. Cheng, Z.Ca, J. Fu, X. Sun, W. Sun, L. Chen, W. Liu, Synergistic adsorption of Cu (II) and photocatalytic degradation of phenanthrene by a jaboticaba-like TiO_2/titanate nanotube composite: An experimental and theoretical study. Chemical Engineering Journal, 358, (2019), 1155-1165
[12] P K. Jaseela, J. Garvasis, A. Joseph, Selective adsorption of methylene blue (MB) dye from aqueous mixture of MB and methyl orange (MO) using mesoporous titania (TiO2)–poly vinyl alcohol (PVA) nanocomposite, J. Mol. Liq., 286 (2019) 110908
[14]Zhou, W., Liu, K., Fu, H., Pan, K., Zhang, L., Wang, L., & Sun, C. C. Multi-modal mesoporous TiO2–ZrO2 composites with high photocatalytic activity and hydrophilicity. Nanotechnology, 19(3), (2007), 035610.
[15]Cheng, P., Wang, Y., Xu, L., Sun, P., Su, Z., Jin, F., ... & Lu, G. 3D TiO 2/ZnO composite nanospheres as an excellent electron transport anode for efficient dye-sensitized solar cells. RSC advances, 6(56), (2016), 51320-51326.
[16] W. Yan, F. He, S. Gai, P. Gao, Y. Chen, P. Yang, A novel 3D structured reduced graphene oxide/TiO 2 composite: synthesis and photocatalytic performance. Journal of Materials Chemistry A, 2(10), (2014), 3605-3612.
[17] P.K. Jaseela, K.O. Shamsheera, Mesoporous Titania-Silica nanocomposite as an effective material for the degradation of Bisphenol A under visible light, J. Saudi Chem. Soc. (2020)
[18]I. Das, G. De, Zirconia based superhydrophobic coatings on cotton fabrics exhibiting excellent durability for versatile use. Scientific reports, 5(1), (2015), 18503.
[19] P.K. Jaseela, A. Joseph, HMDS-GPTMS modified Titania Silica nanocomposite-A new material for Oil-Water separation, J. Inorg. Organomet. Polym. Mater. (2019) 1-8.