ABSTRACT

Mushroom growth of dye and textile industries in urban as well as rural riverside areas result in the accumulation of highly contaminated water bodies. Similarly leaching of agrochemicals such as insecticides and pesticides intermediate equally contribute to water pollution. These harmful pollutants are the real trouble makers for the water bodies present in our environment. If these pollutants remain in the waterbodies as such, they will create severe ecological problems to the environment especially to human beings and other flora and fauna. Hence, prior treatment is needed before their disposal into the environment. Several treatment methods such as membrane filtration, coagulation, flocculation, filtration, adsorption, ion exchange, electrolysis, etc., to mitigate the problem but they have their own merits and demerits. Most of these methods are not greener methods as they do not lead to complete destruction of the pollutants but only transfer the contaminant from one phase to another phase. Hence, a highly effective and environmentally benign process is sought all over the world. Advanced oxidation process using heterogeneous, semiconductor based photocatalysts is the promising alternative technology for the purification of wide variety of pollutants. Large number of semiconductors such as TiO$_2$, Fe$_2$O$_3$, ZnO, ZrO$_2$, Nb$_2$O$_5$, WO$_3$, SrTiO$_3$, Bi$_2$O$_3$, SnO$_2$, etc., have been employed as photocatalysts for the destruction of the pollutants. To date, TiO$_2$ (Eg > 3.2 eV) has been proved to be one of the best catalysts for widespread environmental applications due to its high photosensitivity, stability and non-toxicity. SrTiO$_3$ is another widely used semiconductor photocatalyst with similar bandgap and similar properties. However these two semiconductors present some drawbacks as (i) only small amount of photons are absorbed in the visible region with consequent need to irradiate with UV light, (ii) high
recombination rate for the photo produced electron hole pairs and (iii) deactivation in the absence of water vapour in gas-solid systems. Therefore, the research in heterogeneous photocatalysis has been addressed to enhance its photo efficiency by modifying some morphological and electronic properties of TiO$_2$ and SrTiO$_3$. Doping, loading and sensitization of photocatalysts were mainly aimed to shift the light absorption towards visible light and/or to increase the lifetime of the photoproduced electron-hole pairs.

The present study focuses on the preparation, characterization and photocatalytic performance of nano TiO$_2$, Ni/Ru impregnated TiO$_2$, SrTiO$_3$ and Ni/Ru doped SrTiO$_3$ photocatalysts. Titanium dioxide was synthesized using sol-gel method and Ni/Ru impregnated TiO$_2$ were synthesized using simple wet impregnation method. Strontium titanate catalysts were synthesized using sol-gel technique. All the synthesised photocatalysts were characterized by using various instrumental techniques namely X-ray diffraction (XRD), UV- Diffuse reflectance spectroscopy (UV-DRS), Raman spectroscopy, Fourier Transform Infrared spectroscopy (FT-IR), Scanning Electron Microscopy with Energy Dispersive Spectrum (SEM-EDS), Transmission Electron Microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

Anatase phase of titania and cubic phase of strontium titanate were established by their XRD patterns. Bare titania was found to have higher BET surface area than the metal impregnated catalysts whereas in the case of strontium titanate catalysts, not much difference in the surface area values was seen between bare and metal doped strontium titanates. Impregnation of nickel or ruthenium over titania slightly decreased the bandgap, but a significant reduction in the bandgap values was observed when the same metals were doped into strontium titanate lattice. Such impregnated/doped catalysts with reduced bandgaps are normally active even under visible
irradiation. Raman studies of these two titania and titanate catalysts further confirmed the presence of anatase and cubic phases of the catalysts. The morphology of the catalysts was known from SEM images and the presence of elements in catalysts was confirmed by EDS spectra. From the TEM images the morphology and the particle size of titania and strontium titanate particles were found. SAED pattern confirmed that the titania and strontium catalysts were highly crystalline. XPS technique showed the presence of elements in titania and strontium titanate catalysts and their oxidation states.

The photocatalytic activities of titania and titanate catalysts were evaluated towards the degradation of three dyes, Amidoback -10B (AB-10B), Congored (CR) and Rhodamine-B (Rh-B) and three insecticides namely Acetamiprid (ATP), Imidacloprid (IMI) and Thiamethoxam (TMX) under UV irradiation. The parameters such as effect of initial concentration, effect of catalyst weight and effect of pH were optimized to get maximum degradation efficiency. Complete (100%) degradation of all the dyes and insecticides was observed but at different reaction times for both titania and strontium titanate catalysts. Among the nickel impregnated titania catalysts (1%) Ni/TiO₂ and among the ruthenium impregnated titania catalysts (1%) Ru/TiO₂ showed maximum decolourization/degradation of dyes / insecticides at the shortest reaction times. The impregnated Ni/Ru metal trap electrons from the conduction band of titania under irradiation, suppresses the recombination of electron-hole pairs and causes better charge separation which in turn increase the degradation efficiency. Between Ni and Ru impregnated titania catalysts, Ru impregnated catalysts showed higher photocatalytic activity than the nickel impregnated catalysts. This may be due to the lowest bandgap of the Ru impregnated titania catalysts. The best catalyst (1%) Ru /TiO₂ degraded the dyes AB-10B, CR and Rh-B at 3½, 3 & 5 h whereas the insecticides
ATP, IMI & TMX degraded at 5½, 4 & 5 h. Visible irradiation studies of titania catalysts show that the catalysts were also active in visible region.

Similarly bare strontium titanate catalyst showed less activity than metal doped strontium titanate catalysts. Among strontium titanate catalysts, (1%)Ni-SrTiO\(_3\) (NiST) showed better photocatalytic activity than other catalysts. Visible irradiation studies of strontium titanate catalysts confirmed their visible activity. The best catalysts (1%) Ru /TiO\(_2\) and (1%) Ni-SrTiO\(_3\) has been tested in solar irradiation and the results were very similar to UV irradiation results. Recyclability tests were carried out for four cycles and confirmed the photo stability of the catalysts. Highly contaminated textile effluent irradiated about 8 h using (1%) Ru /TiO\(_2\) and (1%) Ni-SrTiO\(_3\) catalysts showed 25% and 17% mineralization of effluent respectively. Among the dyes CR degraded quickly whereas among insecticides IMI degraded quickly. In order to understand the complete mineralization and formation of intermediate products, in depth analysis of the degraded samples was made using UV –Vis spectrophotometer, HPLC and TOC analyzer using the best catalyst (1%) Ru/TiO\(_2\). UV- spectral studies showed 100% degradation of all the dyes and insecticides at different times of irradiation, HPLC results showed the dyes were degraded completely (100%) whereas only 67-80% insecticides were degraded. Lower % degradation of insecticides obtained by HPLC indicate that dearomatization of the insecticide occurred. The fragmentation is so fast that it undergoes rapid dearomatization through multiple hydroxylation at different positions of the ring followed by oxidation leading to the products such as formate, acetate, chloride, nitrate, sulphate ions, CO\(_2\) and water.