ABSTRACT

Water is the prime source for human survival and industrial development. Effective management of water resources and control of water pollution are becoming increasingly important for sustainable development and human welfare. Due to rapid industrialisation, many new industries have been set-up and the already existing industries expanded and thus water consumption has grown rapidly. 95% of water used for industrial processes are contaminated and are discharged as wastewater. The common pollutants encountered in industrial wastewater are soluble organics/inorganics, suspended solids, volatile matter and refractory substances. The organic pollution is mainly due to the presence of polynuclear aromatic hydrocarbons, phenolic compounds, halogenated hydrocarbons, polychlorobiphenyls (PCBs) and synthetic compounds like dyes and pigments. The widespread presence of persistent organic compounds as pollutants in the effluents from industries is a serious environmental problem, especially since such compounds can be found in ground water and surface water. Wastewater from tanneries, textile industries and dye manufacturing industries contain dyes which are toxic to microorganisms, aquatic life and human beings and they have to be removed effectively to achieve the discharge standard.

The removal of toxic wastes produced in tanneries has been a complex problem and this cannot be resolved by simple disposal like primary and secondary treatment. Before disposal of these toxic wastes it is imperative to convert them to be non-toxic by proper chemical reactions. Heterogeneous photocatalysis is a promising new method which has been successfully used to eliminate toxic and bioresistant organic and inorganic compounds from aqueous solution through transformation into harmless species. Many researchers have been attempting the photocatalytic degradation of water borne environmental contaminants mediated with TiO₂ and ZnO.
This technique appears to offer a great deal of hope in converting hazardous and toxic chemical wastes into harmless end products at ambient temperature. In view of the advantages of heterogeneous photocatalysis in the treatment of wastewater it has been aimed in the present study to decolourise and degrade aqueous solution of the commonly used leather dyes viz., Acid green 16 and Acid brown 14 using solar/UV light and TiO\textsubscript{2}/ZnO catalyst. Laboratory scale batch studies were conducted to optimise the various parameters for effective degradation of leather dyes.

The various parameters viz., concentration of dye, catalyst loading, irradiation time, light intensity and pH were optimised for the maximum degradation of dyes. The influence of these parameters on decolourisation and degradation rate is significant. Experiments were also performed with different commercial photocatalysts like TiO\textsubscript{2}, ZnO, SnO\textsubscript{2}, ZrO\textsubscript{2}, α-Fe\textsubscript{2}O\textsubscript{3}, WO\textsubscript{3} and CdS in order to evaluate the most suitable catalyst for the degradation of leather dyes. TiO\textsubscript{2} and ZnO are found to be the most effective catalysts for the degradation of Acid green 16 and Acid brown 14 leather dyes. The performance of supported catalysts on the rate of photocatalytic degradation were carried out in order to find out the suitable support for higher degradation rate. The results indicate that the alumina supported catalyst out performed compared to glass supported catalyst under identical operational conditions suggesting that the dye molecules are adsorbed on the alumina supports to make high concentration environment around the loaded catalyst. In order to verify the photocatalytic activity of the prepared metal doped photocatalysts, the degradation of leather dyes were investigated. The catalytic activity is improved by loading the catalysts with noble metals such as Pt, Au, Ru and Pd. The results indicated that the photocatalytic activity of the metal doped TiO\textsubscript{2} is in the order Pt > Au > Ru > Pd and Au > Pd > Pt > Ru for AG 16 and AB 14 dyes respectively. The photocatalytic activity of the metal doped ZnO catalysts is in the order Au > Pt > Ru > Pd and Au > Pd > Pt ~ Ru for AG 16 and AB 14 dyes respectively. The performance of loading of lower bandgap photocatalysts such as α-Fe\textsubscript{2}O\textsubscript{3}, WO\textsubscript{3} and CdS over TiO\textsubscript{2} and ZnO (coupled semiconductor system) on the rate of photocatalytic degradation of leather dyes was
studied. The results revealed that the photocatalytic activity of TiO₂ and ZnO can be greatly improved by loading α-Fe₂O₃, WO₃ and CdS on the surface of TiO₂ and ZnO catalysts. The physico-chemical characterisation of the supported photocatalysts were carried out using sophisticated techniques such as SEM, XRD, DRS, BET surface area analyser and particle size analyser in order to assess the surface morphology, crystallinity, light absorption capacity, bandgap, surface area and particle size of the catalysts. The influence of inorganic oxidants such as H₂O₂, FeCl₃, Fenton’s reagent on the rate of photocatalytic degradation of dyes and also the influence of bubbling oxygen gas on the rate of photocatalytic degradation of dyes was also investigated. Oxygen provides a natural sink for the photogenerated electrons on the catalyst surface. Hydroxyl radicals are then formed via the oxidation of catalyst surface-sorbed water or hydroxyl ions by the surviving holes. The bubbling of more oxygen (electron acceptor) than dissolved oxygen which is already present in the aqueous system might be beneficial for enhancement of photocatalytic activity. The effluents from the tanneries contain large amount of chloride and sulphate ions. Hence the influence of sodium chloride and sodium sulphate on the photocatalytic degradation of dyes was studied and it was observed that degradation rates are markedly affected by the presence of chloride and sulphate ions. The performance of photocatalytic degradation of dyes upon irradiation with UV and sunlight source was investigated. The results indicate that the high energy UV light source is found to be an effective source for the degradation of leather dyes compared to sunlight in the presence of TiO₂ catalyst which absorbs large fraction of the UV light. But in the case of ZnO, sunlight is found to be an effective source for the degradation of leather dyes because ZnO absorbs wide range of sunlight.

Thus the present study demonstrates the activity of photocatalyst in the degradation of leather dyes. In addition to the removal of colour, simultaneous reduction of COD, TOC and formation of NO₃⁻, NH₄⁺ and SO₄²⁻ suggest the mineralisation of dissolved dyes. Hence this technique may be a viable method for the safe disposal of tannery dye effluents.