

Composite Membranes for Environmental Applications

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ABSTRACT

The paper reports the synthesis and design of a membrane and its process for treatment of chromium, a major concern in tannery effluents. This study was focused on the preparation and characterization of PSf/titanium dioxide composite membranes for treatment of chromium solution. Different concentrated composite membranes were used for photocatalytic reduction of toxic chromium (VI) to non-toxic chromium (III). X-ray diffraction study, transmission electron microscopy and Infrared spectral analysis were used to study the morphology and microstructure of the membranes. 100% reduction of 10 ppm chromium was observed.

Keywords: membrane, pollutant, chromium, Semiconductor, catalysis.

1 INTRODUCTION

In leather industries it was estimated that 30 - 35 L of water was used per kilogram of leather processed, generating about 680 x 106 L/d of effluent. The effluents were enriched with nitrogen, sulphides, and also some neutral salts like sulphates and chlorides, oils & grease, chromium compounds, and other metals like aluminum, cadmium, zirconium, etc. These are inevitable by-products of leather manufacturing process and cause significant pollution unless treated in some way prior to discharge. Tannery effluents are especially large contributors of chromium pollution. According to Indian survey, about 2000 - 3000 tone/year of chromium escapes into the environment with concentration ranging between 2000 to 5000 mg/l and this is more than the recommended permissible discharge limits of 2 mg/L.

Chromium (VI) is motile and highly toxic, carcinogenic, mutagenic, soluble in water and it is a strong oxidizing agent that causes severe damage to cell membranes. Thus it is necessary to remove or recover the chromium before disposal of tannery waste. Different methods have been developed for the removal of chromium from waste water, some of which are reverse osmosis, solvent extraction, reduction, ion exchange, electroplating. Recently, the photocatalytic reduction of chromium (VI) using the semiconductor photocatalysis technology has received

considerable attention. Compared with conventional water treatment approaches such as ozonization, UV irradiation and advanced filtration processes, photocatalysis has a number of advantages including high oxidation efficiency and minimal disinfection byproducts. Titania nanoparticles showed much more attention in reduction of chromium (VI) to chromium (III). This process has a disadvantage, where the removal of titania is also an extra process. Hence, it is very necessary to require a material carrying titania for reduction process.

Meanwhile polymeric membranes are gaining more importance in versatile applications. Specially, polymer and inorganic composite membranes which were formed by inorganic particles uniformly dispersed in a polymer matrix have received much attention in the field of gas separation, pervaporation and ultra filtration membranes [1]. They possess properties of both organic and inorganic membranes such as good mechanical strength, thermal and chemical stability and adaptability to the harsh environments. Thus organic-inorganic hybrid materials as new membrane materials have attracted more and more interest [2]. Polysulfone-titania composite membranes were prepared and used as a reducing agent in photocatalytic reduction of Cr (VI). These composite membranes are the best materials for the Cr (VI) reduction.

The present work focusses on photocatalytic reduction of Cr (VI) using the prepared membrane. The effect of organic and inorganic acids in photocatalytic degradation was also studied.

2 EXPERIMENTAL

All the chemicals were procured from Sigma-Aldrich and Merck chemicals and were used without any further purification. Titanium tetrachloride (Loba Chemie) was used as titanium source for the preparation of TiO₂. Polysulfone (PSf) was obtained from Sigma-Aldrich. The source for chromium (VI) is potassium dichromate and some other addition chemicals like Formic acid, Perchloric acid, Acetic acid, Sulfuric acid, Ammonia were purchased from Merck chemicals.

2.1 Synthesis of TiO₂

Fine grain powders of anatase form of nano-TiO₂ were prepared by gel to crystalline conversion method using TiCl₄. 100 mL of high purity titanium tetrachloride (Loba

Chemicals, purity 99.9%) was carefully diluted by drop wise addition to 100 mL ice cold, well-stirred, double-distilled water. About 50 mL of the diluted titanium tetrachloride solution was further diluted to 5 L with distilled water. It was then mixed with 1 mL of concentrated sulfuric acid in a beaker. Liquor ammonia was added till a pH of 7–8 was attained. The gel obtained was allowed to settle and filtered through Whatman No. 41 filter paper. The recovered precipitate was washed free of chloride and ammonium ions. The precipitate was first oven dried between 105°C and 120°C for 48 h to remove water content. The dried crystals were pulverized using high energy ball mill (SPEX 8000M Mixer/Mill) equipped with tungsten carbide vial for an optimum time of 90 min. The milled powder was subjected to annealing at 600°C for 6 h to get anatase phase of nano-TiO₂.

2.2 Preparation of composite membranes

The membranes were prepared by phase inversion process as described in [3] and TiO₂ dispersed uniformly during the phase inversion process.

2.3 Photocatalysis

Photodegradation studies were performed using a reactor vessel of area 176.62 cm² into which sunlight was directly focused and the photon flux was found to be $\gg 77 \text{ Wm}^{-2}$ and the experiments were conducted on bright sunny days between 11.00 am and 2.00 pm during the month of November at Bangalore city (13° 00.57' N and 77° 34.15' E). However, no steps were taken to maintain the intensity of sunlight during subsequent reactions. The photocatalysis was done on the pollutant, of 10 ppm concentration with the immovable membrane- photocatalyst suspended in it. The extent of degradation of the pollutant was studied by withdrawing samples for analysis at specified intervals of minutes. The residual concentration of the pollutant was estimated from standard calibration curves of absorbance versus concentration of the pollutant at a particular value of λ_{max} .

2.4 Characterization

X-ray diffraction (XRD) patterns of the powders were recorded with Shimadzu X-ray diffractometer-model XRD 7000 with CuK α radiation at a scan rate of 1° min⁻¹. Crystallite size was determined using Scherrer's equation ($0.9\lambda/180/\pi\text{FWHM}_{\text{hkl}} \cos \theta$, where FWHM_{hkl} is the full width at half maximum θ value, λ = X-ray wavelength). The absorption spectra were recorded on a Shimadzu 1650 PC UV-Visible spectrophotometer for micromolar suspensions of the catalysts prepared by ball milling to avoid reflection of light to a maximum extent. The powder samples were examined under a transmission electron microscope using a Technai 10 Philips TEM microscope to study the particle size and diffraction patterns. Energy

dispersive X-ray analysis was used in conjunction with scanning electron microscopy (Cambridge instruments) to show the elementary level analysis of samples. The specific surface area was found from the multipoint Brunauer Emmett Teller (BET) adsorption method using a Nova-1000 Version 3.70 instrument with Nova enhanced data reduction software version 2.13.

3 RESULTS

The XRD powder patterns for the membrane photocatalyst depicted anatase phase of titania. The d-spacing and intensities were identical to theoretical values of 100% TiO₂ (anatase phase). Although rutile phase was thermodynamically more stable there were no trace of the phase after preparation. An N₂ adsorption study measured the specific surface area of the TiO₂ to be 70 m² g⁻¹. The crystallite sizes calculated by Scherrer's equation were in the range of 17 nm.

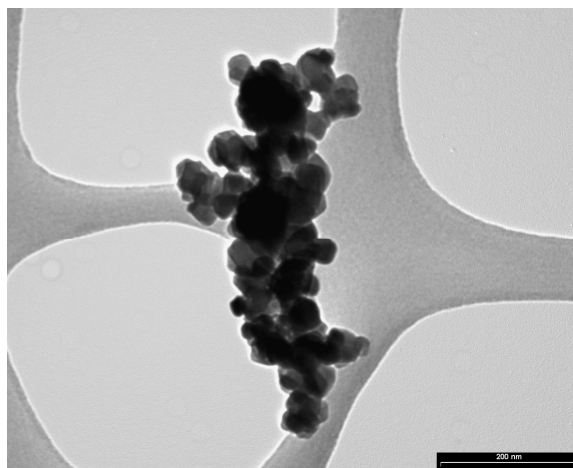


Fig 1. Transmission electron micrograph of the photocatalyst

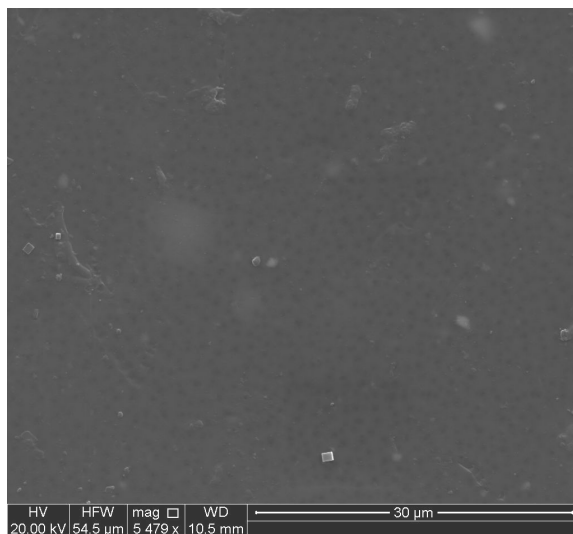


Fig 2. Scanning electron micrograph of the composite membrane

Figure 1 represents the micrographs of the CA- TiO_2 and the doped catalyst examined under transmission electron microscope (TEM). The particle size of samples appears to be more uniform and spherical indicating retention of anatase phase. Figure 2 represents the scanning electron micrograph of the composite membrane. The scanning electron micrograph clearly depicts titania agglomerates linked to the membrane surface. EDAX analysis also confirms the titania in the membrane. The photocatalyst on absorption of photons lead to the excitation of electrons from the valence band to the conduction band, thus generating electron-hole pairs. The electron in the conduction band is captured by oxygen molecules dissolved in the suspension and the hole in the valence band can be captured by H_2O_2 or OH^- species adsorbed on the surface of the catalyst to produce the hydroxyl radicals. Hence, photocatalyst mediated reactions cause the generation of a number of reactive oxygen species (ROS) and hydroxyl (OH^\cdot) radicals. These OH^\cdot radicals are very potent and need to be scavenged to cause reduction. Acids have been used for that purpose.

Figure 3 depicts the extent of photocatalytic reduction occurring in different acids and with different concentrations of PSf/ TiO_2 composite membrane. 100 % reduction of 10 ppm chromium was observed within 2.5 h in presence of perchloric acid.

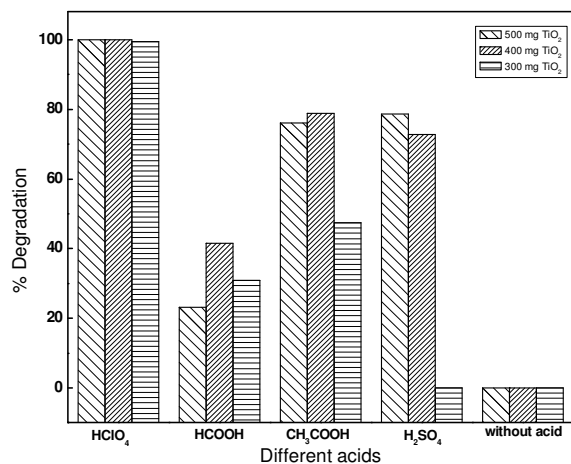
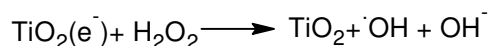
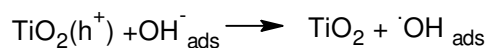
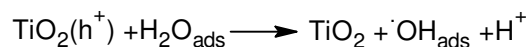


Fig 3.. Extent of photocatalytic reduction of Cr (VI) with different concentrations of PSf/ TiO_2 composite membrane and in presence of different acids

4. DISCUSSION

Initially formic acid in the form of formate ion was thought to scavenge these hydroxyl radicals. Addition of formic acid would facilitate the formation of CO_2^\cdot by scavenging OH^\cdot . The carboxyl ion formed in the process acts as the main reducing species for Cr (VI). The catalytic efficiency of TiO_2 thus is observed to enhance by 60% in presence of formic acid. An efficient charge transfer process of such formate and TiO_2 catalysed photoreactions can also be attributed to the appropriation of relevant potential level of Cr (VI) species which is thermodynamically below (more positive than) the conduction band potential of the semiconductor and the potential level of reducing specie being above the valence band position of the semiconductor facilitating the transfer. But inorganic acids seem to prominently increase the rate much more. The extent of dissociation in perchloric acid being the strongest (with a very large value of K_a comparatively) effectively enhances the rate and extent of reduction.



An optimal concentration required to enhance the reduction capacity of the composite membrane to a maximum extent was investigated and is as depicted in the Fig 3. Higher number of radicals produced from higher quantity of catalyst allowed faster rate of reduction. Hence 500mg of catalyst was better in performance compared to 400 mg of catalyst which gave better activity than 300 mg of catalyst in the membrane. The membrane acts as a support but also opens up the scope for using it for both the filtration and for the treatment applications.

4 CONCLUSIONS

The synthesized anatase phase of TiO_2 with a comparatively lower band gap energy responds well to solar light to produce electron hole pair. These electron hole pairs produce a number of free radicals which when properly channelled by use of acids, allows proton exchange leading to $\cdot\text{OH}$ scavenge, electron trapping and formation of H^0_{ads} facilitating reduction of Cr (VI).

5. ACKNOWLEDGEMENT

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6. REFERENCES

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