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Ultrasonicated Organic Acid Doped Polyaniline Nanotubes for Anionic Dyes Detection in Waste Water

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Abstract: ***Self-doping polyaniline (PANI) nanotubes prepared via the self-assembly process using oxalic acid. In this polymerization process, oxalic acid plays the role of surfactant as well as dopant for the self-doping PANI. The morphology and ultra-violet absorption studies of self-doped PANI are investigated. A method for the removal of anionic (sulfonated) dyes from aqueous dye solutions using the chemical interaction of dye molecule with the ultrasonicated conducting polyaniline nanotubes is reported. Ultrasonication of as-prepared organic acid doped polyaniline nanotubes provided the energy for chemical reaction between sulfonated dyes and charged backbone of PANI, leading to significant adsorption of the dyes. This phenomenon of selective adsorption of the dyes by PANI promises a green method for removal of sulfonated organics from waste water. The experimental observations from ultraviolet-visible spectroscopy rule out the possibility of secondary doping of polyaniline salt by sulfonated dye molecules. A possible mechanism for the chemical interaction between the polymer and the sulfonated dye molecules is proposed.***

Keywords: Conducting polymer, Polyaniline nanotubes, Ultrasonication, Self-assembly, Sulfonated dyes, Adsorption.

1. Introduction

Conducting polymers represent an important class of functional organic materials for next-generation electronic and optical devices [1-4]. Conducting polymers have recently received much attention due to their long conjugation length, metallic conductivity, and their promise for applications in molecular wires, nano-electronics, optoelectronic devices, and biomedical devices [5–7]. Because of their low cost synthesis and easy processability, these polymers are becoming the most promising new materials for next generation electronic devices [8]. Polyaniline (PANI) is one of the most extensively used and studied conducting polymers [9-11]. The major practical advantages of polyaniline are its high environmental stability, high electrical conductivity and easy synthesis. Polyaniline has versatile applications in plastic batteries, optical storage lithography, harmonic generators, display devices, magnetic recording, solid state sensors, and corrosion inhibitors [12-14]. Conducting polymers synthesized in the form of nanomaterials are of particular interest since their properties significantly differ from the properties of corresponding macroscopic materials. Recently, nanostructurization of conducting polymers and their composites emerged as a new field of research and development, directed to creation of new smart materials for use in modern and future technologies. The nanostructured form of the conducting polymers particularly provides advent to this field with high electrical conductivity and high surface area. Researchers have extensively studied nanostructure conducting polymer polyaniline (PANI) [15-18]. Low-dimensional nanostructured PANI, such as nanoparticles, nanofibers and nanotubes, nanosheets and nanobelts, have received considerable attention owing to their huge potential applications, especially in polymeric conducting molecular wires, light-emitting and electronic devices, chemical sensors, and biosensors [19]. In the past few years, several novel methodologies have been developed for the preparation of nanostructured PANI in the form of dispersions, nanowires, nanofibers, and nanotubules [20-22]. In comparison with the external acid doped PANI method, a self-doping monomer does not need to be removed after PANI polymerization because the dopant also plays the roles of surfactant and co-monomer of PANI. Ultrasonication of PANI will improve its reactivity and provide a proper binding site.

The dyes from textile sources are major sources of environmental pollution because they are nondegradable. Many methods such as flocculation, reverse osmosis and activated carbon adsorption have been used in waste water treatment. However, photocatalysis is often used as a technique to degrade dyes because it is simple and cost-effective. Conventionally inorganic semiconductors are used as photocatalysts and TiO_2, doped TiO_2, and ZnO are extensively used for the degradation of dyes in waste water. Conducting polymers have band gaps in the same range as inorganic semiconductors. Further, the band gaps of these polymers can be tuned by chemical manipulation of the backbone. Therefore conducting polymers with suitable band gaps, could, in principle, act as photocatalysts for dye. In this study, we report that polyaniline in the form of nanotubes can remove anionic (sulfonated) dyes with the application of UV and visible light through a chemical interaction with the sulfonated dyes. Thus, the objective of the article is to examine the use of polyaniline nanotubes for the removal of various sulfonated dyes from aqueous solutions and propose a mechanism of chemical interaction between the sulfonated dyes and conducting polyaniline.

2. Experimental

2.1. Materials and Methods

Aniline (99.5%), oxalic acid (99.5%) and ammonium persulphate (99.5%) were procured from E. Merck. Aniline monomer was distilled under reduced pressure. Ammonium persulfate (APS) and oxalic acid were used as received. All other supplementary chemicals were of analytical grade and solutions were prepared with de-ionized water. UV-Vis spectra were recorded by using UV-1800 Shimadzu automatic recording double beam spectrophotometer in the range of 200 - 1100 nm. SEM images were taken on JEOL JSM-6360 analytical scanning electron microscope.

2.2. Preparation of Polyaniline Nanotubes

0.2M oxalic acid was taken in 100 ml water then 0.2M aniline was added and the mixture was stirred continuously for half an hour. Then 0.2M ammonium persulfate was added drop wise. The color was changed from colorless to pale yellow finally dark green color was obtained, and the stirring was stopped immediately. The mixture was kept overnight and next day it was filtered and washed several times with ethanol and distilled water. The precipitate was dried in vacuum oven at 80 ^{o}C. The removal of anionic (sulfonated) dyes from aqueous dye solutions using the chemical interaction of dye molecule with the ultrasonicated conducting polyaniline nanotubes provided the energy for chemical reaction between sulfonated dyes and charged backbone of PANI, leading to significant adsorption of the dyes.

3. Results and discussion

3.1 Scanning Electron Microscopy

SEM image of PANI nanotubes is shown in Fig. 1. The nanotubes formation of PANI is clearly seen in SEM image. Oxalic acid plays the role of surfactant and dopant for the self-doping PANIs. First, oxalic acid and aniline cations form micelles in aqueous solution. The aniline cations can appear in the interface of micelles and water. The polymerization initially occurs at the surface of the micelles as the oxidant APS is added. In addition, the micelles tend to aggregate and react along the direction of the polymer chain in the polymerization process. The micelles act as the template in the self-assembly of PANI to form nanotube structures.

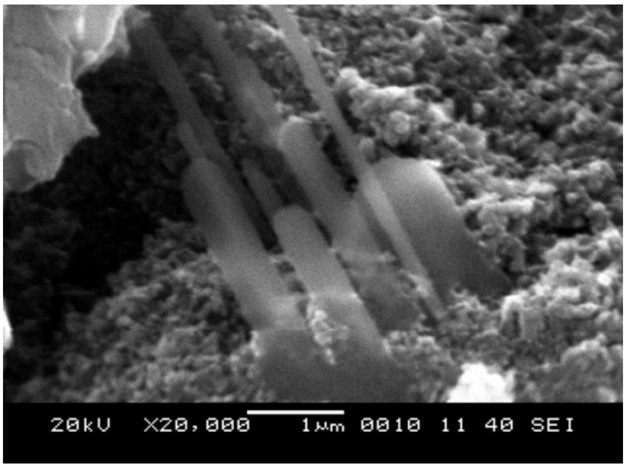

Figure 1: SEM image of PANI nanotubes

3.2 Ultraviolet-Visible Spectroscopy

For adsorption experiments, the synthesized ultrasonicated polyaniline was added to methyl orange dye solution with concentration of 100 ppm. The chemical interaction of dye molecule with the ultrasonicated conducting polyaniline nanotubes provided the energy for chemical reaction between sulfonated dyes and charged backbone of PANI, leading to significant adsorption of the dyes. The solution was stirred for 2 hr. During this process, samples were collected from the reaction beaker at different time intervals, and the concentration of the dye was determined by UV-Vis absorption spectroscopy. The dye concentration was calibrated with the beer-Lambert law at λ_{max} value of 480 nm. After adsorption of the dye, the PANI samples were washed with distilled water, dried and used for absorption spectroscopy. Figure 2(a) and 2(b) shows the variation of the dye concentration with time in the presence of doped PANI. All experiments were carried out for 2 hr, but after 75 min there was no significant adsorption after this time. The experiments were conducted with different initial concentrations of methyl orange in the presence of PANI for 2 hr. When the initial concentration of the dye was 50 ppm, the dye was completely adsorbed in 1 hr. At higher concentrations of the dye, it was not completely adsorbed, indicating that there is a saturation limit for the polymer above which it does not remove the dye.

Ecosystem of river is extremely polluted by waste of industries and city. To detect methyl orange in NAG river of Nagpur, the synthesized PANI nanotubes have been used and tested. But in city areas, methyl orange was not detected indicating that the waste water in NAG river of Nagpur is free from methyl orange.

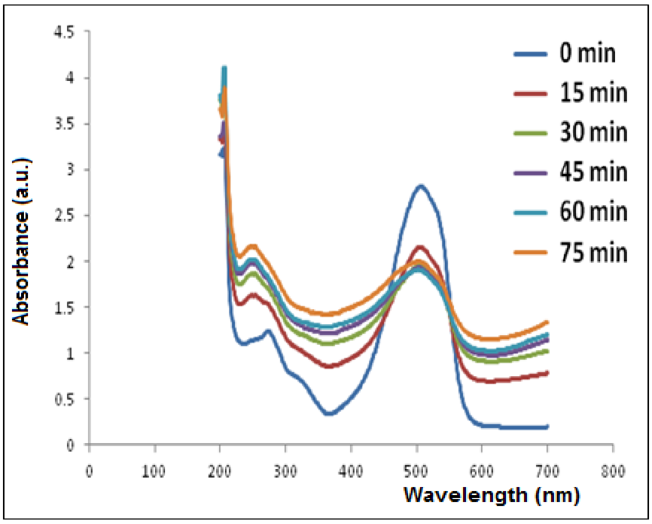

Figure 2(a): Variation of concentration of methyl orange dye of 100ppm with time in the presence of PANI doped with oxalic acid

It was found that the polymer adsorbs the respective dye from the solution. The presence of the dye in the polyaniline was confirmed from the UV-Vis spectra of the polyaniline samples after the reactions.

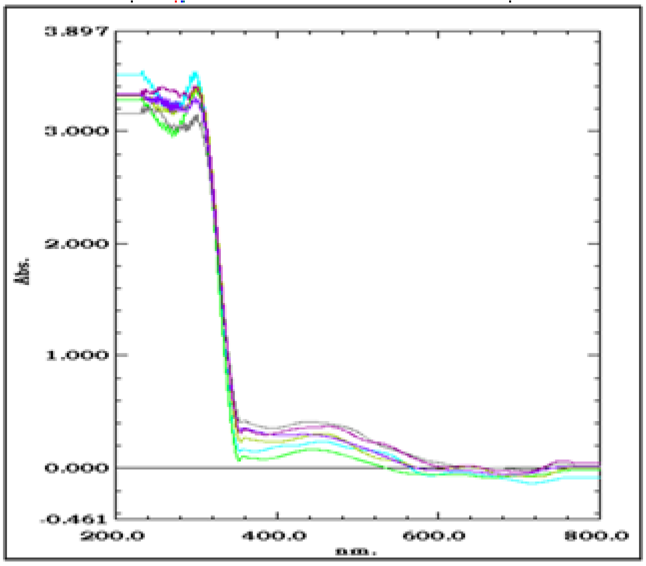

Figure 2(b): To examine the presence of methyl orange in NAG river using PANI doped with oxalic acid.

When the reaction of polyaniline emeraldine base was attempted for the removal of the dyes, it was found that the activity of emeraldine base toward the removal of the dyes from solution was considerably less than that of the salt form. It is well known that the degree of ionization of a dye molecule depends on the pH of the aqueous medium. Methyl orange contains one sulfonated group ($-SO_3Na$). In acidic aqueous solutions, the functional group of methyl orange ($-SO_3Na$) gets ionized, and the dye exists in anionic form as shown in Fig. 3. When PANI emeraldine salt is added to water, the pH of the water becomes acidic (pH= 3.9) and does not change during the course of adsorption. The addition of dyes with sulfonated functional groups to this aqueous solution results in the dissociation of the functional group into its anionic form.

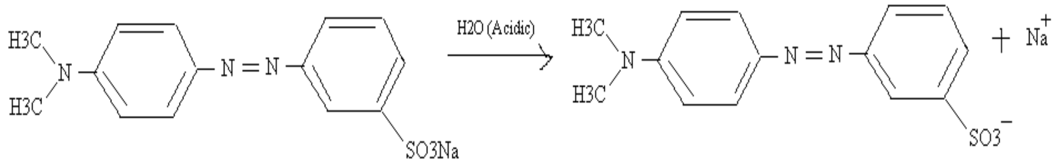

Figure 3: Dissociation of methyl orange

The $-SO_3^-$ group on the dye could lead to chemical interactions with the positively charged backbone of PANI emeraldine salt, and Na^+ ions interact with the oxalate ions that are invariably present in doped PANI. This will lead to the adsorption of various sulfonated dyes on the emeraldine salt of PANI. In basic aqueous solutions (dispersion of emeraldine base in water), the dissociation of the functional group of the dye would be inhibited, and no chemical interaction with the PANI backbone would be expected. When the emeraldine base of polyaniline is used instead of the emeraldine salt for the above experiments, we found that the base form cannot remove the dye from solution. This indicates that the positively charged backbone and oxalate ions that are invariably present in the ES (emeraldine salt) form are the possible sites for chemical interactions with the sulfonated dye molecules. After the dye was adsorbed on PANI, a base (ammonium hydroxide) was added to the solution. This base dedoped PANI and resulted in desorption of the dye. The above studies seem to indicate that the adsorption of the dye was due to chemical interactions.

4. Conclusion

In this study, polyaniline emeraldine salt was synthesized by chemical oxidation method and it was then further treated with methyl orange dye for adsorption of sulfonated dye from water. A mechanism was proposed based on the chemical interaction of PANI with the sulfonated group of the dye. Polyaniline doped with various organic acids was used for the adsorption of methyl orange as a dye representative from the application point of view for the adsorption of sulfonated dyes from water through chemical interaction. It has been studied that ultrasoniction improves the rate of adsorption.

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