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Syntheses, characterization and luminescence properties of pyridine-N-oxide based polymeric complexes of manganese

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Abstract:

Manganese oxides nanomaterials with notably increased surface area and greatly reduced size have been widely used in many applications. MnO_2 nanoparticles was prepared pyrolytically employing coordination polymers $[Mn(pyo)_2(dca)_2]_n$ as a sole precursors. Particle sizes and morphologies of the synthesized MnO_2 nanoparticles had been studied by physicochemical techniques. Such nanomaterial served as a unique catalyst having enormous beneficial aspects during the photocatalytic degradation of organic dyes. The nanoparticles also showed a brilliant catalytic activity as compared to the bare manganese oxide too.

Introduction

Textile industry effluents contain a variety of complex and hard to degrade pollutants such as dyes that may cause significant water pollution when they are released to our environment.[1] The environmental-health concern of these potentially carcinogenic pollutants in these contaminated waters has drawn the attention of many workers.[2] Numerous studies have reported various methods for treating textile dye wastewaters including various chemical, physical and biological processes, for examples chemical coagulation,[3] anaerobic and aerobic,[4] microbial degradation, adsorption on activated carbon,[5] biosorption, chemical oxidation (using agents such as ozone, hydrogen peroxide, and chlorine),[6] deep-well injection, incineration, solvent extraction and irradiation.[7–10] However, biological processes do not always give satisfactory results, especially applied to the treatment of industrial wastewaters, because many organic substances are resistant to biological treatment.[11] The Advanced Oxidation Process (AOP)

is one of the emerging technologies that are capable of converting organic pollutants into harmless products.[12,13] Catalytic oxidation reactions could provide complete mineralization of organic substances while being environmentalfriendly.[14]

Manganese oxides nanomaterials with notably increased surface area and greatly reduced size have been widely used in many applications.[15,16] In particular, due to their ion-changing, molecular adsorption, electrochemical and magnetic properties,[17] Manganese oxides catalysts exhibit considerable activity in oxidation–reduction reactions; they are among the most efficient transition-metal oxides catalysts for gas- phase reactions, such as carbon monoxide hydrogenations,[18] high-temperature methane combustion[19,20] and the selective catalytic reduction of nitric oxide by hydrocarbons[21,22] and by ammonia,[23–25] as well as for epoxidation reactions. However, to the best of our knowledge, there are a few reports for degradation methylene blue from waste water[26–29] using manganese dioxide nanocrystals as photocatalyst.

A variety of wet chemical routes have been developed to fabricate MnO_2 nanoparticles with various morphology.[30-35]

4B.2 Experimental Section

Physical Methods and Materials. High purity Pyridine-*N*-oxide purchased from Alfa Aesar, sodium dicyanamide from Fluka; and Cadmium (II) nitrate and Manganese (II) Chloride from Aldrich Chemical Company Inc. Methylene blue was purchased from Merck (India). All the chemicals were of analytical grade and used without further purification. X-ray powder diffraction patterns of the products were recorded on a Philips (PANalytical), (model: PW1830) X-ray diffractometer equipped with graphite monochromatized Cu-K radiation. The morphology and size of nano- sized MnO_2 have been characterized by Hitachi S-3400N scanning electron microscopy (SEM). Infrared spectra (4000-400 cm^{-1}) were recorded at 25°C using a Perkin-Elmer Spectrum RXIFT-IR System where KBr was used as medium. UV-vis spectra were obtained at 25 °C using a U-3501 HITACHI, Japan. Thermal analyses (TG–DTA) were carried out on a TGA/SDTA851^e Metler-Toledo thermal analyzer in flowing dinitrogen (flow rate: 40 cm^3 min^{-1}).

Photocatalytic studies. The catalytic capacity of the MnO_2 nanoparticles was tested for the decolorization of methylene blue dye. All the photocatalytic experiments were carried out in a 100 mL capacity borosil glass reactor under similar conditions with exposure of light. 50 mL aqueous solution of methylene blue (2×10^{-6} M), 200 µL 30% solution of H_2O_2 and 4 mg of MnO_2 nanoparticles were dispersed and mixed thoroughly by sonication. At different time intervals, definite aliquots were taken

out with the help of a syringe and filtered through a Millipore syringe filter. The absorption spectra were recorded on UV-vis spectrophotometer and rate of decolorization was

observed in terms of change in intensity at λ_{max}, i.e., 665 nm for dye. Same experiment was again repeated under same condition except using the catalyst. The experiment was performed for 160 minutes and within this time the dye was 83 % degraded only 6 % degradation of MB was observed in absence of catalyst.

4B.3 Results and Discussion

In order to estimate the appropriate calcination temperature, the thermal behavior of the complex, $[Mn(pyo)_2(dca)_2]_n$ was investigated by TGA. The calcination temperature should be more than 700 C, as there is no change in sample weight indicating the formation of pure inorganic oxide. The FTIR spectra of synthesized MnO_2 exhibited bands in the region between 400-800 cm^{-1} could be assigned to Mn–O lattice vibration.[36] X-Ray powder diffraction patterns of synthesized MnO_2 are shown in **Figure 4B.1**. All the visible peaks can be well indexed to the semi-tubular structure.[37] We have then calculated the crystallite size by using the Scherrer formula,

$$d = \frac{k\lambda}{\beta_s \cos\theta} \qquad 4B.1$$

where d is the average size of the crystallite grains, k is 0.9, λ is the wavelength of Cu-K radiation, β_s is the full width at half maximum (FWHM) of the diffracted peak of sample and is given by $\sqrt{\beta^2 - \beta^2}$, θ is the Bragg angle of diffraction. The estimated particle size of the MnO_2 was found to be ~ 62 nm. The morphologies of the synthesized MnO_2 are characterized by FESEM. The SEM image of synthesized MnO_2 shown in **Figure 4B.2** illustrates the particle size of synthesized MnO_2 to be in nanometer range.

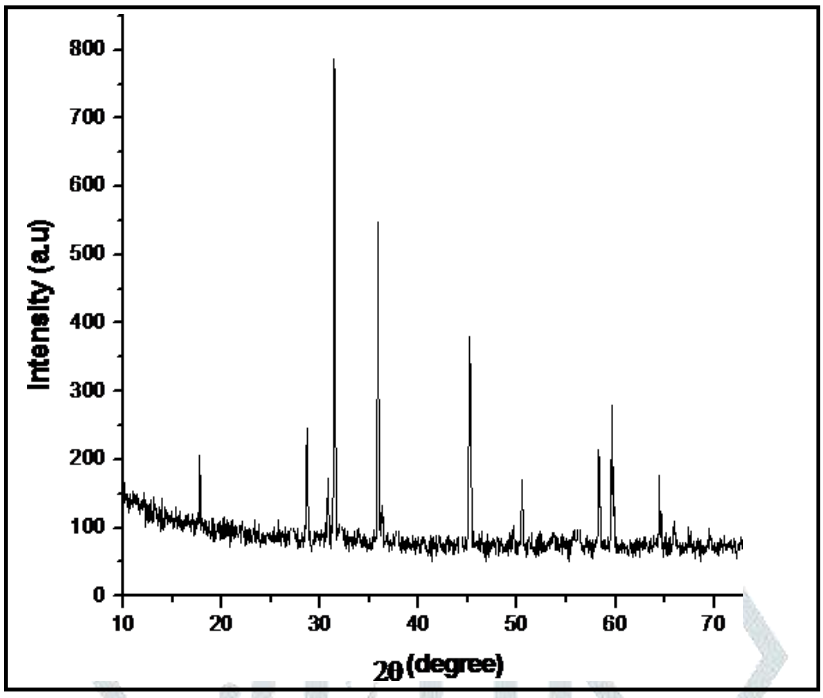

Figure 4B.1. Powder XRD pattern for MnO_2 nanoparticles.

4B.4 Conclusion

In summary, MnO_2 nanoparticles was prepared pyrolytically employing coordination polymers $[Mn(pyo)_2(dca)_2]_n$ as a sole precursors. Particle sizes and morphologies of the synthesized MnO_2 nanoparticles had been studied by physicochemical techniques. Such nanomaterial served as a unique catalyst having enormous beneficial aspects during the photocatalytic degradation of organic dyes. The above nanoparticles also showed a brilliant catalytic activity as compared to the bare manganese oxide too. It exhibited ~ 84%, degradation of MB under UV irradiation for 2 h 40 min. Without presence of the catalyst only 6 % disappearance of each dye has been observed at the identical set of conditions, after completion the catalyst was removed.

4B.5 References

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