International Journal of Science and Research (IJSR)
ISSN: 2319-7064
Impact Factor 2024: 7.101

Comparative Studies on the Catalytic Behaviour of Green Iron Oxide Nanoparticles Containing Biostabilizers for the Oxidative Degradation of Aqueous Organic Compounds

Dr. V. Dhanalakshmi

Corresponding Author Email: *drdanachem[at]gmail.com*

Abstract: ***Worldwide technological and agricultural development, are often contaminating surface water by a variety of toxic organic pollutants such as Nitrophenols, Bisphenol A, Di amino naphthalene etc at the trace level. In this study green iron oxide nanoparticles was synthesized using biostabilizers via sol gel method and were characterized using FTIR. The ability of the green catalyst to degrade the organic pollutants was investigated. Kinetic parameters are obtained from the time variance UV - Visible spectra, under pseudo first order conditions. Among Iron oxide stabilized with chitosan and starch, catalytic efficiency of Iron oxide stabilized with chitosan was found to be higher.***

Keywords: biostabilizers, IOnps, NP, BP, DAN, chitosan, starch

1. Introduction

Anthropogenic compounds number in thousands and are used in everyday life in every industry and cause pollution in the environment [1]. The U. S. Environmental Protection Agency (USEPA) has considered nitrophenols, DAN as hazardous waste and one of the 129 priority toxic pollutants [2]. Bisphenol A was one of the endocrine disruptor substances which are released due to industrial activities [3]. In this work iron oxide nanoparticles [4] were prepared by sol gel method using biostastabilizers and its catalytic efficiency is investigated for the oxidative degradation organic pollutants such as NP, BP, DAN.

Materials and Preparation of Fe_2O_3 nanoparticles with chitosan and starch bio stabilizers

Ferric Chloride, Chitosan, Sodium hydroxide, Hydrogen peroxide were purchased from Loba Chemie Pvt Ltd. Triple distilled water was used throughout the analysis.

Into a three necked 100ml capacity round bottom flask, 10ml of 1mM ferric chloride solution was added through one neck and into the other 5ml of 1.5% by weight aqueous solution of chitosan was added and freshly prepared 0.02M sodium hydroxide was added drop wise until the dark red gel was formed with continuous stirring for one hour at 45^0C [281]. The gel was washed, dried in air oven at 80^0C, and then a dark brown powder iron oxide so formed was washed with water, filtered and dried in air oven at 80^0C.

Characterization of Fe_2O_3 nanoparticles

FTIR spectra are recorded in KBr pellets for the pure capping agents, chitosan, gelatin, agar - agar, starch, chitosan - Fe_2O_3, starch - Fe_2O_3, at 25^0C using Bruker Tensor 27 instrument. Figure 1. showed FTIR spectra of the pure samples of chitosan, starch respectively. In Figure 1a, the characteristic peaks of the chitosan were displayed at 1658 cm^{-1}, 1589 cm^{-1} which are attributable to amide bands I, II and at 3409 cm^{-1} attributable to hydroxyl band. In Figure 1c. the characteristic vibrational peaks of starch namely the hydrogen - bonded stretching at 3359 cm^{-1}, the OH bending of the adsorbed water at 1645 cm^{-1}, the CH stretching at 2, 921 cm^{-1}, the HCH and OCH in - plane bending vibrations at 1453 cm^{-1}, the CH deformation vibration at 1373 cm^{-1}, the COC, CCO, and CCH deformation modes. As shown in Figure 1c, in the fingerprint region of the soluble starch there were three peaks characteristic of –C–O– stretching. The peak at 1150 cm^{-1} was ascribed to C - O bond stretching of the C–O–H group, and the two peaks at 1080 cm^{-1} and 1020 cm^{-1} were attributed to C - O bond stretching of the C–O–C group in the anhydroglucose ring.

In FTIR spectra of starch iron oxide np, there was a high intensity broad band at around, due to the Fe_2O_3 peak. The –C–O– stretching peaks of soluble starch shifted in the presence of Fe_2O_3 indicating that an interaction existed between the starch and Fe_2O_3 in starch iron oxide, but no obvious covalent bonds were formed.

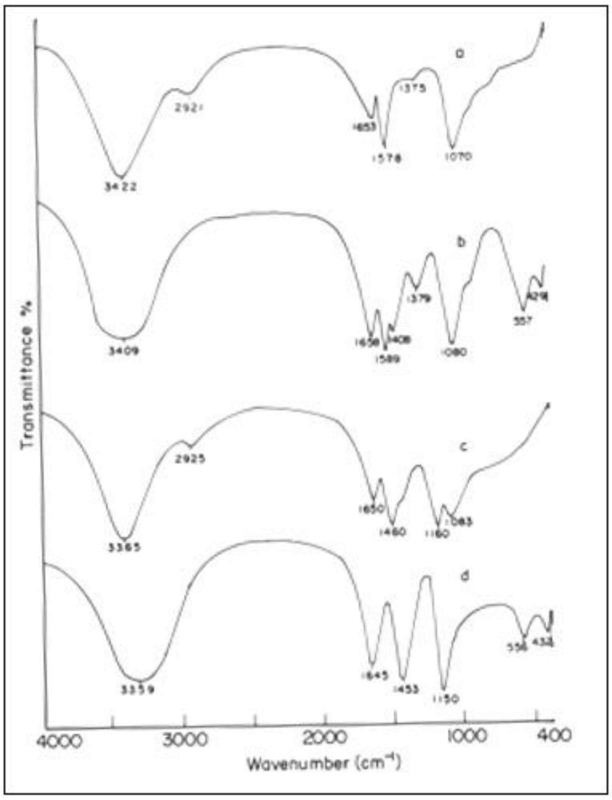

Figure 1: FTIR of (a) chitosan and (c) starch and (b) and (d) are the iron oxide nanoparticles stabilized with the chitosan and starch

Reaction catalysis

In a typical experiment double walled three necked 100ml glass round bottom flask was used into which 0.5ml of fresh aqueous 0.01M H_2O_2 solution was added drop wise. Through separate necks 10ml of 0.01M diamino naphthalene in 50% acetone aqueous solution and 1mg of chitosan iron oxide nanoparticle are added and the reaction mixture was stirred continuously. The temperature was maintained at 25^0C by thermostated water. The inception of the reaction was considered from the time of addition of 0.5ml of 0.01MH_2O_2. Additions were completed within 30 sec and small aliquots of the sample are drawn out at regular intervals of time (5min) and subjected to UV - Visible spectra scan. The completion of the reaction was noted with the gradual decrease in the absorbance falling to the base line. The procedure was repeated with other catalyst and organic compounds such as bisphenol in 50% of THF solution, and p - nitro phenol in water.

Kinetic studies

Figure.2 depicts the time dependent UV - Visible spectra of the organic compounds. During the oxidation processes the time of completion of the oxidation reaction varies with the chemical nature of the organic compounds.

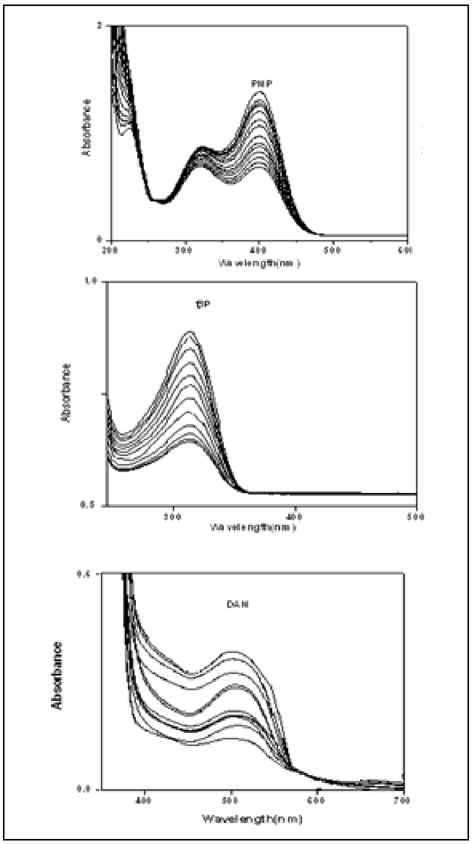

Figure 2 Time dependent UV - Visible spectra of the organic compounds, PNP - p - nitrophenol, BP– Bisphenol A and DAN – 1, 8 diamino naphthalene in presence of H_2O_2 and chitosan - iron oxide nanoparticles at 25°C. The first order rate coefficient (k) values are determined from the slope values of the kinetic plots which are multiplied with 2.303 The best fit linear plots are found in the kinetic analysis only for adopting pseudo first order conditions. In Table 1 the rate coefficient values (k) and **t** ½ of the various organic compounds studied are presented. Adopting similar procedure the rate coefficient values and catalyst mass, ranging from 0.5mg, 1mg and 1.5mg are determined and given in Table 2.

Keeping all other conditions constant, overall trend observed in the oxidative degradation rate constant of the organic compounds, catalyst are **DN>NP>BP** and iron oxide nps stabilized with 1 mg - **chitosan>starch**

In the Iron oxide nps aided degradation of reactant organic compounds in aqueous medium, iron oxide surfaces are surrounded with O atom of the OH group of the chitosan capping agent as well as to some extent N atom from the amino group of the same chitosan.

Table 1: Pseudofirst order rate coefficient (k), half life period t $_{1/2}$, optimum pH of the three organic compound determined in presence of H_2O_2 and iron oxide nanoparticles stabilized with chitosan, starch at 25^0C

Organic compound	**k (10^{-4}/s)**		**t $_{1/2}$ (10^3s)**	
	chitosan – IOnps	starch – IOnps	chitosan – IOnps	starch – IOnps
DAN	4.337	3.915	1.598	1.770
PNP	1.536	1.382	4.515	5.015
BP	0.769	0.610	9.016	10.030

Table 2: Pseudofirst order rate coefficient (k) values of BP, PNP and DAN for different catalyst feeds using chitosan stabilized iron oxide

[chitosan – IOnps] mg	k (10^{-4}sec^{-1})		
	DAN	PNP	BP
0.5	4.013	1.342	0.522
1.0	4.337	1.536	0.769
1.5	4.428	1.599	0.772

2. Conclusions

In this study a green iron oxide nanoparticles with chitosan and starch biostabilisers were synthesized in a greener method and utilized for the oxidative degradation of organic pollutants namely BP, DAN, NP in a eco - friendlier way. The reaction kinetics was followed from the time variation in the UV - Visible spectral measurements. The pseudo first order rate coefficient values are determined from the kinetic plots. The trend in the catalytic activity among the two iron oxide nps for the organic pollutants studied in the present work was as follows.

Fe_2O_3 nps - chitosan> starch

Acknowledgement
The author was forever grateful for her evergreen catalyst Dr. J. Santhanalakshmi Madam (Ex HOD Physical Chemistry Department –UOM), BWC.

References

[1] NurHanis. H, Chin. F. S, Marlia. M, Nurfornia. Z, afarizal. N, Che. Z., Nor. H. (2021), “A review of nanotechnological applications to detect and control surface water pollution. ” Environmental technology and Innovation, 24, 102032.
[2] Cheng. H, Chen, ShiaoS. K, Chen. Y. C (2012), “Degradation of phenolic compounds in water by nonthermal plasma treatement.” Journal of water Chemistry and Technology, 34, 179 - 189.
[3] Hunge Y. M, Yadav A. A, Fuji Shima. A (2021), “Photocatalytic degradation of bisphenol using TiO2[at]nanaodiamond composites under UVlight illumination.” Journal of Colloid Interface Science, 582, 1058 - 1066.
[4] Andrade M., SantosTRT, Fernandes. S, Vieir. M, Bergamasco. R, Hamoudis (2019), “Grapheneoxide impregnated with iron oxidenanoparticles for the removal of atrazine from aqueous medium.” Separation Science Technology, 54, 2653 - 2670