Scientific Research Publishing

Open Journal of Applied Sciences, 2022, 12, 892-900
https://www.scirp.org/journal/ojapps
ISSN Online: 2165-3925
ISSN Print: 2165-3917

Catalytic Reduction of Textile Dyes by N-Doped Ti-Melamine Capped Ag_2S Nano Composites

Mohammad Farhadur Rahman[1*], Nargish Jahan Ara[1], Sakib Hasan[2], Zubair Hasan[3]

[1]Department of Chemistry, Bangladesh University of Textiles, Dhaka, Bangladesh
[2]Department of Fabric Engineering, Bangladesh University of Textiles, Dhaka, Bangladesh
[3]Department of Mathematics and Physical Science, East West University, Dhaka, Bangladesh
Email: *chemistry.butex2010@gmail.com

How to cite this paper: Rahman, M.F., Ara, N.J., Hasan, S. and Hasan, Z. (2022) Catalytic Reduction of Textile Dyes by N-Doped Ti-Melamine Capped Ag_2S Nano Composites. *Open Journal of Applied Sciences*, **12**, 892-900.
https://doi.org/10.4236/ojapps.2022.126061

Received: January 10, 2022
Accepted: June 17, 2022
Published: June 20, 2022

Abstract

Waste water expulsion containing toxic and hazardous ingredients from textile industry is one of the biggest concerns in this modern age. N-doped nano composites as an efficient catalyst are playing a significant role in reducing the toxicity of that textile effluent. N-doped Ti-Mel capped Ag_2S NCs (N-Ti-C/Ag_2S NCs) and N-doped TiO_2 capped Ag_2S NCs (TiO_2/Ag_2S NCs) were synthesized via calcinations at 700˚C, whereas Ag_2S NCs was prepared by simple hydrothermal treatment process at 120˚C and confirmed by FTIR and SEM (EDX). N-Ti-C/Ag_2S NCs were applied in presence of reducing agent $NaBH_4$ with a green method to decolorize the textile dyes Levafix Amber RR (LA) and Remazol Blue RR (RB). Moreover, Ag_2S NCs, TiO_2/Ag_2S NCs, $NaBH_4$ and TiO_2 were also investigated. Using UV-visible spectroscopy the progress time was measured to decolorize textile dye RB and completed within 3.15 mins, 12.15 mins, 12.15 mins for N-Ti-C/Ag_2S NCs, Ag_2S NCs and TiO_2/Ag_2S NCs respectively, while for LA the catalytic reduction taken for the same NCs was 8.15 mins, 12.15 mins and 30.15 mins respectively. N-Ti-C/Ag_2S NCs based catalyst afforded excellent catalytic reduction activity in both cases. Interestingly the effect of $NaBH_4$ itself and TiO_2 in presence of $NaBH_4$ was less than 5% after 30 mins. Finally, the reusability for Ti-Mel capped Ag_2S NCs evaluated up to four cycles.

Keywords

Catalytic Reduction, N-Doped Nano-Composites, Levafix Amber RR, Remazol Blue RR

1. Introduction

In nanochemistry community, nanocomposites NCs have diverted the field in a

significant way, playing most vital role in green chemistry, while NCs consist of more than one phase with different physicochemical properties [1] [2] [3] [4] [5]. The majority of binary and tertiary nanocomposites are being attracted to the researchers due to their simple nanostructures shapes, small size and large surface area through easiest synthetic process [6] [7].

N-doped metal/non-noble metal carbon composite is another new addition in nanocomposites field. Besides other NCs catalysts like photo-catalytic degradation [8], electro-oxidation [9], biological treatment [10]; reductive catalyst is also easily appealing in decolorized toxic organic compounds or dyes [11]. The surface reactivity or the electrical properties eventually improves for enhancing electron density in carbon architecture by the incorporation of N atoms [12] [13] [14]. Moreover, narrow band-gaped (1.1 ev) semiconductor and low toxic nanomaterial Ag_2S [3] and TiO_2 capped Ag_2S [4] are important metal chalcogenides, which are mostly used in photosynthesis or photocatalytic degradation [3] [4]. Ag_2S is also reported in biomedical and sensor application [15], fuel cell [16], solar cell [17] and so on.

Notably, no report is published yet where N-doped Metal-carbon reductive catalyst is capped with Ag_2S NCs to decolorize toxic organic dyes or textile dyes effluent in reductive process. Textile effluent is considered as the most pollutant and hazardous element in the textile growing country like Bangladesh. The condition becomes more eyes curious when it not only pollutes surface and surface water, but also soil and air [18] [19] [20]. The Bangladesh Textile Mills Association reported that the country has around 450 spinning mills, 1200 weaving mills and around 5000 export-oriented dyeing factories [21], which predicted that from 100,000 commercially accessible dyes are manufactured 700,000 tones of various textile effluents each year [22] [23]. Among all effluents the textile industry releases (54%) the highest amount of dye effluent, contributing to more than half of the existing dye effluents seen in the environment around the world [24] [25]. If the current situation is not improved the Textile industries would be dumping 203,000 million liters of untreated wastewater into the country's water bodies every year from 2021 [21].

Levafix Amber RR (LA) and Remazol Blue RR (RB) are the two most useful azo textile dyes in textile factories. So, treatment before release of textile dyes effluent is highly up-and-coming demand. For this purpose we have selected that textile azo dye for decolorization/degradation to nontoxic colorless compound with N-doped Ti-Mel capped Ag_2S NCs reductive catalyst.

2. Materials and Experimental Method

The widely used textile dyes Levafix Amber RR and Remazol Blue RR were supplied by Dye Star Ltd, Dhaka, Bangladesh and all other chemicals were supplied by Sigma & Aldrich chemicals supplier Kuri & Chemicals, Dhaka, Bangladesh.

2.1. Synthesis of Ag_2S NPs

Ag_2SNPs was synthesized first according to D Ayodhya method [3] [4]. A 300

mL round bottom flask (RBF) was charged with 40 ml of 0.015 M silver nitrate solution and 40 ml of 0.015 M sodium sulfide solution was added drop wise under continuous magnetic stirring at room temperature. The obtained black dispersion was stirred vigorously for further 60 min at the same temperature. After that, the reaction mixture was transferred into a stainless steel autoclave and placed in an oven. Then the mixture was heated at 120˚C for 2 h. The reaction mixture was filtered and the black precipitates were washed with distilled water (10 mL × 2) and ethanol (5 mL × 1), followed by drying at 230˚C in an oven for 5 h, to obtain Ag_2S NPs.

2.2. Synthesis of Ti-Melamine Composite

0.160 g (2 mmol) anatase phase TiO_2 and 5.0 g (0.04 mol) melamine were charged with 200 mL RBF and dissolved into 25 mL distilled water. Then the reaction mixture was continuously stirred for 3 h at 80˚C. Later, the mixture was cooled to room temperature and filtered, followed by being dried at 120˚C using an oven to obtain white powder Ti-Melamine composite.

2.3. Synthesis of N-Doped Ti-Mel Capped Ag_2S NPs (N-Ti-C/Ag_2S NCs)

To a 200 mL, 1.0 g Ti-Mel composite was taken and 25 ml of 0.015 M silver nitrate solution was added drop wise at room temperature with continuous vigorous stirring. After 30 minutes, 25 ml of 0.015 M sodium sulfide solution was added drop by drop for 15 minutes to the obtained white turbid dispersion at room temperature. The white turbid dispersion mixture was continuously stirred for further 3 h at room temperature. Later the reaction mixture was transferred into a stainless steel autoclave and placed inside an oven. The reaction mixture was heated for 60 min at the constant temperature of 120˚C. After that, the reaction mixture was cooled to room temperature and filtered using sintered glass. Then obtained white precipitates of Ti-Mel capped Ag_2S NPs were washed with distilled water (10 mL × 2) and dried over an oven. Finally the composites were heated at 700˚C in a tube furnace under an inert atmosphere using continuous flow of nitrogen gas for 2 h [11].

2.4. Synthesis of TiO_2 Capped Ag_2S NCs

TiO_2 capped Ag_2S NCs were synthesized in the same way as N-doped Ti-Mel capped Ag_2S NPs. To a 200 mL, 1.0 g anatase phase TiO_2 was taken and 25 ml of 0.015 M silver nitrate solution was added drop wise at room temperature with continuous vigorous stirring. After 30 minutes, 25 ml of 0.015 M sodium sulfide solution was added drop by drop for 15 minutes to the obtained white turbid dispersion at room temperature. The white turbid dispersion mixture was continuously stirred for further 3 h at room temperature. Later the reaction mixture was transferred into a stainless steel autoclave and placed inside an oven. The reaction mixture was heated for 60 min at the constant temperature of 120˚C. After that, the reaction mixture was cooled to room temperature and filtered

using sintered glass. Then obtained white precipitates of TiO_2 capped Ag_2SNPs were washed with distilled water (10 mL × 2) and dried over an oven. Finally the composites were heated at 700˚C in a tube furnace under an inert atmosphere using continuous flow of nitrogen gas for 2 h.

2.5. Characterization Techniques

The morphology of all types of nanocomposite was characterized by Scanning Electron Microscopy (SEM, JEOL JSM-7600F) with Energy-dispersive X-ray spectroscopy (EDX). X-ray diffraction (XRD, GNR, RGC-100, Agilent Technologies, Bruker X-ray diffractometer equipped with graphite-monochromated CuKα radiation at λ = 1.541 Å) with a 2θ range of 10˚ - 85˚. The FTIR spectra were recorded in transmittance mode on a Shimadzu spectrophotometer in the wave number range of 650 - 4000 cm^{-1}. Spectrophotometer (Shimadzu UV-1800) was used to measure the catalytic reduction of textile dyes in the wavelength range of 200 - 700 nm.

3. Result and Discussion

The FTIR spectroscopic measurements were carried out to identify the interactions between the Ag_2S and TiO_2, Ti-Mel capping materials on the surface of the Ag_2S NCs. Figure 1 showed a comparison of the FTIR spectra of pure Ag_2S NPs, TiO_2 capped Ag_2S NCs, N-doped Ti-Mel capped Ag_2S NCs in the measured spectral range (650 - 3000 cm^{-1}). The different peak position between (750-1200 cm^{-1}) confirmed the formation of nanocomposites.

The morphology and microstructure of the samples were investigated by SEM (EDX) (Figure 2), nanoparticles were self-assembled to form uniform spherical nanostructures. SEM provides information on the morphology, crystalline and chemical composition of the prepared samples. The samples of prepared NCs have a mixture of spherical and cubic nanoparticles.

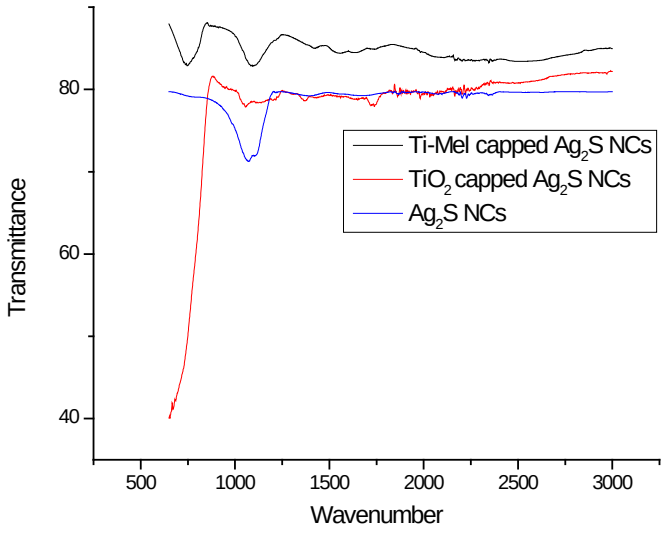
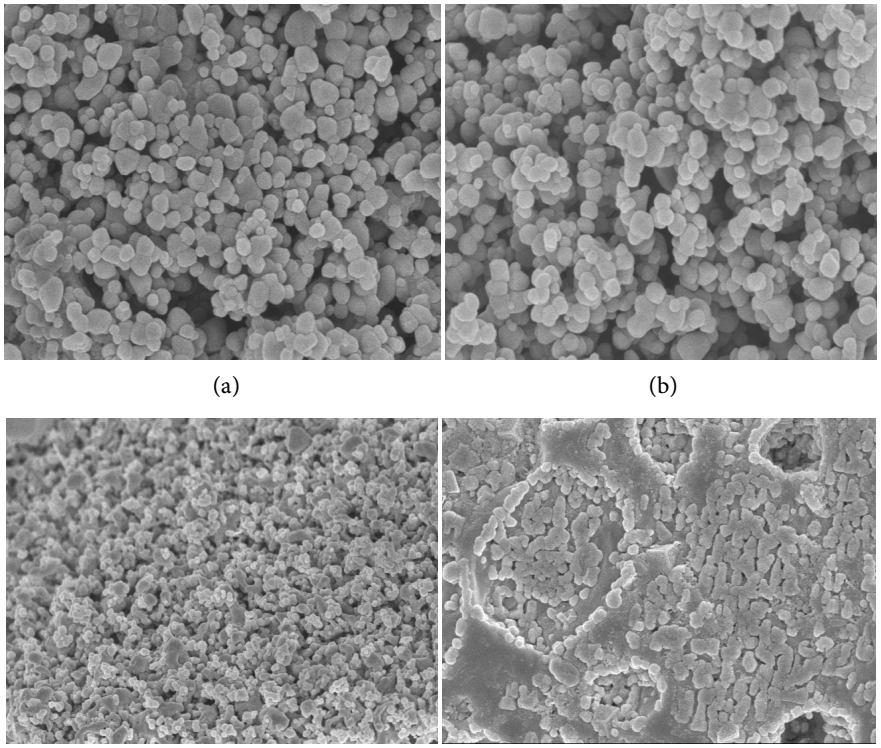


Figure 1. FTIR for Ag_2S NCs, TiO_2 capped Ag_2S NCs, N-doped Ti-Mel capped Ag_2S NCs.



(a) (b)

(c) (d)

Figure 2. SEM for Ag_2S NCs, TiO_2, TiO_2 capped Ag_2S NCs, N-doped Ti-Mel capped Ag_2S NCs. (a) Ag_2S NCs; (b) TiO_2; (c) TiO_2 capped Ag_2S NCs (TiO_2/Ag_2S NCs); (d) N-doped Ti-Mel capped Ag_2S NCs (N-Ti-C/Ag_2S NCs).

Application of N-doped Ti-Mel capped Ag_2S NCs, TiO_2 capped Ag_2S NCs and Ag_2S NCs

The linearity of Levafix Amber RR (LA) and Remazol Blue RR (RB) was evaluated by using calibration curve to calculate co efficient of correlation and intercept values. The concentration range was 6.25 ppm to 125 ppm and the calculated value was 0.99986 and 0.9997 respectively for Levafix Amber RR and Remazol Blue RR and χ_{max} of Levafix Amber RR and Remazol Blue RR is 410 nm and 603 nm respectively (S1).

In case of optimization of concentration of $NaBH_4$, almost similar results on found on both 0.6 M and 0.7 M $NaBH_4$ concentration than 0.5 M $NaBH_4$. So, 0.6 M $NaBH_4$ was selected as the optimum dose for the reducing agent. During optimization and catalytic reduction 0.2 mL $NaBH_4$, 0.2 mL catalyst and 3.0 mL dyes solution was used.

Reduction reaction of the reducing agent 0.6 M $NaBH_4$ and TiO_2 (0.2 mL) itself (in presence of 0.2 mL 0.6 M $NaBH_4$) reacted very slowly in absence of nanocomposites catalyst. After 30 minutes and 35 minutes less than 5% reaction was completed for $NaBH_4$ and TiO_2 respectively (S3). But in presence of nanocomposites the reaction progress is very fast (**Figure 3**). N-doped Ti-Mel capped Ag_2S NCs took less time to complete the catalytic reduction on both dyes Levafix Amber RR (8.15 mins) and Remazol Blue RR (3.15 mins) than other NCs.

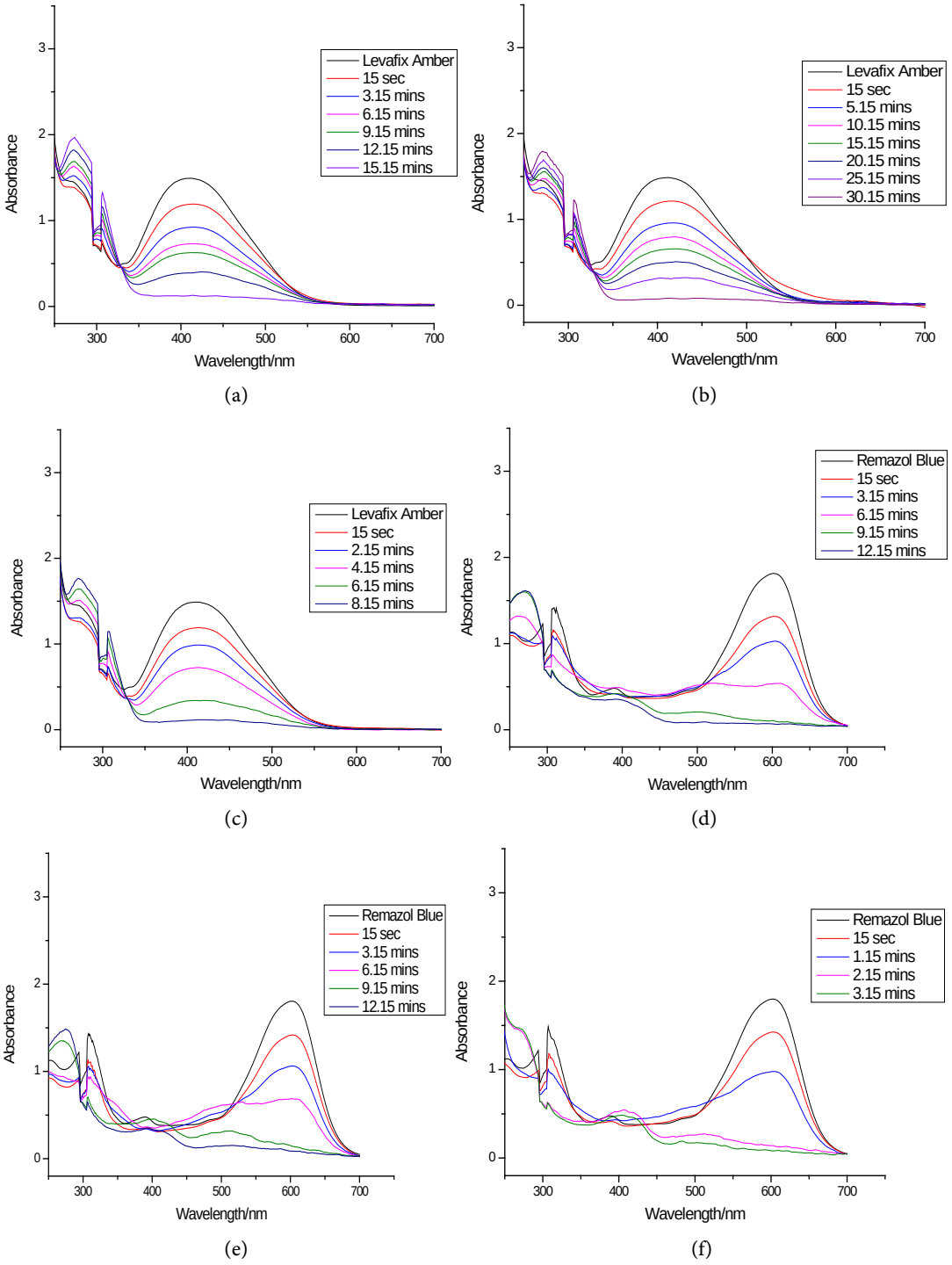


Figure 3. Catalytic reduction of Ag_2S NCs, TiO_2 capped Ag_2S NCs, N-doped Ti-Mel capped Ag_2S NCs on Levafix Amber RR (a-c) and Remazol Blue RR (d-f) in presence of 0.6 M $NaBH_4$ presence. (a) Ag_2S NCs; (b) TiO_2 capped Ag_2S NCs; (c) N-doped Ti-Mel capped Ag_2S NCs; (d) Ag_2S NCs; (e) TiO_2 capped Ag_2S NCs; (f) N-doped Ti-Mel capped Ag_2S NCs.

Ag_2S NCs and TiO_2 capped Ag_2S NCs finished the reduction of dyes Levafix Amber RR (15.15 mins, 30.15 mins) and Remazol Blue RR (12.15 mins, 12.15 mins) respectively. So, we concluded that N-doped Ti-Mel capped Ag_2S NCs

showed better catalytic activity for those reduction reactions.

Kinetics study revealed that the catalytic reduction reaction of Levafix Amber RR (r^2 value 0.9392) and Remazol Blue RR (r^2 value 0.76018) followed 1st order reaction (S4).

Reusability of N-doped Ti-Mel capped Ag_2S NCs

N-doped Ti-Mel capped Ag_2S NCs were easily recovered and reused due to their heterogeneous phase on solvent. The reusability on Remazol Blue RR was evaluated up to fourth cycles (Figure 4, S5) and time required 10.15 mins for the complete catalytic reduction of Remazol Blue RR with excellent recovery. The time required was more than freshly used N-doped Ti-Mel capped Ag_2S NCs catalyst, but less than to other freshly used NCs catalysts. It suggested the high efficiency and stability of N-doped Ti-Mel capped Ag_2S NCs.

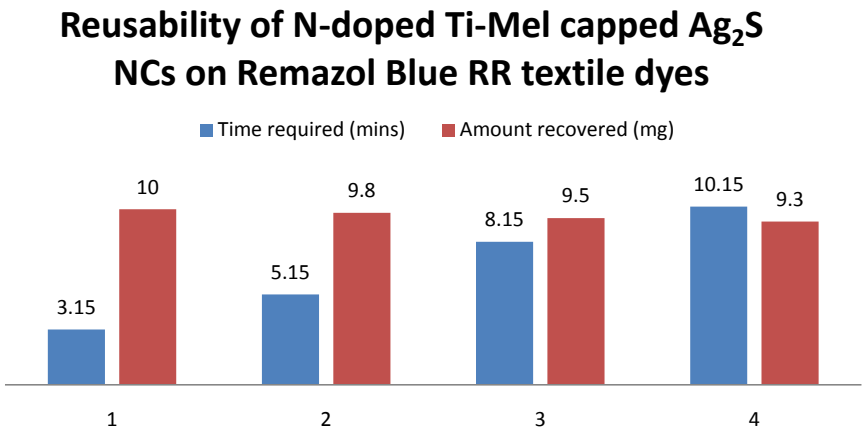


Figure 4. Reusability of N-doped Ti-Mel capped Ag_2S NCs.

4. Conclusion

In summary, we have successfully synthesized some high efficient NCs for the catalytic reduction of Levafix Amber RR and Remazol Blue RR. The N-doped Ti-Mel capped Ag_2S NCs required less time to decolorize than Ag_2S NCs and TiO_2 capped Ag_2S NCs. The reusability of N-doped Ti-Mel capped Ag_2S NCs measured up to fourth cycle and found good recovery of catalyst with less reaction completion time. Since textile effluents are now the burning problem over the world, the highly efficient, stable and reusable NCs may show the path of decreasing the toxicity of textile effluents. We will synthesize more efficient N-doped nonnoble metal composite for the decolorization of a wide range of textile dyes/effluents.

Acknowledgements

Authors are thankful to Bangladesh University of Textiles (Butex) and East West University for instrumental support.

Conflicts of Interest

The authors declare no conflicts of interest.

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