

Hydrogenation Reduction of Organic Dyes by Noble Metal /Fe₃O₄ Nanoparticles Anchored on Nanocellulose

Mariagrazia Iuliano^{a*}, Eleonora Ponticorvo^b, Claudia Cirillo^a, Maria Sarno^a

^a Department of Industrial Engineering and Centre NANO_MATES (Research Centre for Nanomaterials and Nanotechnology at the University of Salerno) University of Salerno, Via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy.

^b Department of Physics "E.R. Caianiello" and Centre NANO_MATES (Research Centre for Nanomaterials and Nanotechnology at the University of Salerno) University of Salerno, Via Giovanni Paolo II, 132 - 84084 Fisciano (SA), Italy. mauliano@unisa.it

The object of this study was to evaluate the discolorization efficiency of sunset yellow (SY) anionic dye from aqueous solutions by using new noble metal /Fe₃O₄ nanoparticles anchored on nanocellulose. Ag/Fe₃O₄@PEI nanoparticles (NPs) were synthesized through a solvothermal method. The prepared magnetic nanoparticles were added to nanocellulose dispersion to obtain Ag/Fe₃O₄@PEI/CNCs nanocomposite by the self-assembled method. The discolorization process, of SY dye, by Ag/Fe₃O₄@PEI/CNCs nanocomposite, was investigated in the time. The small amount of this nanocomposite (5 mg) is applicable for the removal of high concentrations of SY dye in 8 min. The nanocomposite showed high stability for the 5th cycle of the discolorization reaction.

1. Introduction

Water resource pollution is a contemporary global problem that demands regular monitoring and improved remediation strategies implementation.

Organic dyes are one of the major leading causes of water pollution. The main sources of these effluents are the textile, paint, printing, food, and cosmetic industries. In particular, sunset yellow dye (SY dye, Yellow 6 or E110) is a petroleum-derived orange azo dye (Dotto et al., 2011). It is a mono-azodisulfonated hydroxyl dye and it is commonly used in food products, e.g. juices, soft drinks, candies, jellies, and snacks, to give them a yellow-orange coloring (Goncalves et al., 2015). Side effects reported for SY dye include gastric upset, hives, runny nose, allergies, hyperactivity and occurrence of tumors in animals, mood swings, and headache.

Several methods such as biological (enzyme degradation), physical (adsorption), and chemical (catalysis) were applied for dye removal. Among these approaches, catalysis is very favorable. In particular, the catalytic hydrogenation reaction using NaBH₄ as a reducing agent is considered a very promising technique for various advantages such as low cost, simple operation, and so on. However, dye chemical reduction in presence of NaBH₄ alone is a very slow process (Omidvar et al., 2017).

In this contest, metal nanoparticles (NPs) can improve the Discoloration processes of organic dyes. In particular, noble metal NPs like gold (Au), silver (Ag), palladium (Pd), and platinum (Pt) have been able to gain tremendous importance in catalytic dye degradation because of their good electron relaying capability arising from their appropriate redox potentials (Saikira et al., 2017). However, the drawback of these nanoparticles is the difficulty in recovery of the reaction media and reusability, in this scenario, the combination of magnetic nanoparticles with noble metal nanoparticles provides a recyclable magnetically active nanocatalyst for the discoloration of organic dyes. On the other hand, metal nanoparticles possess a strong tendency to agglomeration (Zhang et al., 2019), which can lead, during catalytic dye degradation, to the partial blocking of the active sites, decreasing the degradation efficiency.

Immobilization of the nanoparticles on nanocellulose (CNCs) is a good alternative to overcome the nanoparticles aggregation problem. Moreover, the high nanocellulose surface area may also enhance the nanoparticle catalytic properties, helping the molecule's absorption step during the discoloration reaction.

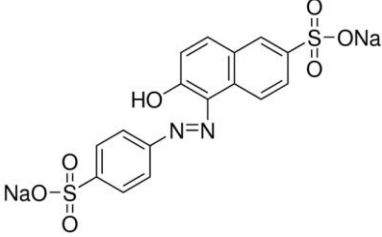
Here, we report the synthesis of Ag/Fe₃O₄@PEI/CNCs magnetically separable nanocatalysts and the evaluation of the catalytic activity for sunset yellow dye reduction reactions. The stability and reusability of the magnetic nanocatalyst were also evaluated.

2. Experimental

2.1 Materials

The sunset yellow dye (Table 1) was procured from Aldrich Chemical and was used without any further purification. Commercial microcrystalline cellulose (α -cellulose, 50 μ m), iron(III) chloride (FeCl₃·6H₂O), silver nitrate (AgNO₃, 97%), sodium acetate (>99%), polyethyleneimine (PEI, Mw ~ 10,000 g/mol), sodium acetate anhydrous, ethylene glycol, and all other chemicals were acquired from Aldrich Chemical Co. All chemicals were of analytical grade.

Table 1: Characterization of the studied dye.

Dye	Sunset yellow (SY)
Structure	
Molecular formula	C ₁₆ H ₁₀ N ₂ Na ₂ O ₇ S ₂
Molar mass	452.37 g/mol
CAS number	2783-94-0

2.1 Preparation of Ag/Fe₃O₄@PEI nanoparticles

A solvothermal method was adopted for Ag/Fe₃O₄@PEI NPs synthesis (Sarno et al., 2019; Iuliano et al., 2022). Firstly, FeCl₃·6H₂O (~3 g) and AgNO₃ (~ 0.040 g) were dissolved in ethylene glycol (30 ml), and after NaAc (2 g) and PEI (0.3 g) were added. The mixture was energetically stirred at 60°C for 30 min and put into an autoclave at 220°C for 2 h. After 2h of synthesis, the nanoparticles were washed with ethanol and water several times and recovered by an external magnetic field and dried at 60 °C for 24 h.

2.2. Preparation of Ag/Fe₃O₄@PEI/CNCs nanocomposite

A self-assembled method was adopted for the synthesis of Ag/Fe₃O₄@PEI/CNCs nanocomposite. In particular, CNCs are prepared from microcrystalline cellulose by acid hydrolysis as reported in Iuliano et al., (Iuliano et al., 2022).

The Ag/Fe₃O₄@PEI/CNCs nanocomposite was prepared by self-assembly of Ag/Fe₃O₄ NPs with CNCs. Briefly, the CNCs (0.2 g) were dispersed in deionized water (10 ml) and sonicated at an output power of 100 W to be homogeneous. Then an aqueous dispersion containing Ag/Fe₃O₄@PEI NPs (0.050 g, 10 mL) was dispensed into the CNCs dispersion. The mixture was sonicated for 20 min at an output power of 100 W while cooling in an ice bath to avoid overheating. Finally, the resulting Ag/Fe₃O₄@PEI/CNCs nanocomposite was separated by a magnet and washed with deionized water and freeze-dried.

2.3 Degradation of SY by Ag/Fe₃O₄@PEI/CNCs nanocomposite

The catalytic activity study of Ag/Fe₃O₄@PEI/CNCs nanocomposite was investigated by monitoring the reduction reaction of SY with the help of the UV-Visible spectrophotometer (Evolution™ 60S, Thermo Scientific™).

In detail, 20 ml of a solution containing Ag/Fe₃O₄@PEI/CNCs nanocomposite (0.005 g) and SY aqueous solution (1 × 10⁻⁴ M) were mixed by mechanical stirring at room temperature. The solutions were mixed for about 30 min to obtain the adsorption equilibrium. After this time a solution of NaBH₄ (20 ml, 5 × 10⁻⁴ M) was added. The progress of the reaction was examined at fixed time intervals by UV-Vis spectroscopy, and the concentration of the organic dye was determined at $\lambda_{\text{max}} = 470$ nm. After reaction time the Ag/Fe₃O₄@PEI/CNCs nanocomposite was isolated from the reaction mixture using an external magnetic field and washed with distilled water and ethanol, dried at room temperature for further use. Moreover, the effect of

Ag/Fe₃O₄@PEI and NaBH₄ alone was analyzed under the same operating conditions to establish efficiency comparison results. All assays were performed in triplicate.

The discoloration efficiency (DE%) was calculated using Eq. (1)

$$DE\% = \frac{C_o - C_t}{C_o} * 100\% = \frac{A_o - A_t}{A_o} * 100\% \quad (1)$$

where C_o is the initial dye concentration, and C_t is the concentration of the dye in the solution at a given time (t). A_o and A_t are the initial absorbance and the absorbance of the dye sample at time t, respectively. The reusability study was also performed for Ag/Fe₃O₄@PEI/CNCs nanocomposite for five catalytic cycles.

3. Results and discussion

3.1 Ag/Fe₃O₄@PEI nanoparticles characterization

The XRD pattern of the Ag/Fe₃O₄@PEI was acquired by a Bruker D2 Phaser X-ray diffractometer, using CuKα radiation. The sample shows the diffraction peaks of Fe₃O₄ and Ag (Figure 1a). The XRD profile evidences the typical peaks of the magnetite at 35.7°, 43.3°, 53.4°, 56.9°, and 62.7° are assigned to (311), (400), (422), (511), and (440) of Fe₃O₄ (JCPDS card no. 65-3107), respectively. The Ag NPs peaks can be observed at 38.2°, 45.1° and 64.8° and 78.1° which correspond to (111), (200), (220), and (311) crystal planes of Ag (JCPDS card no. 87-0720).

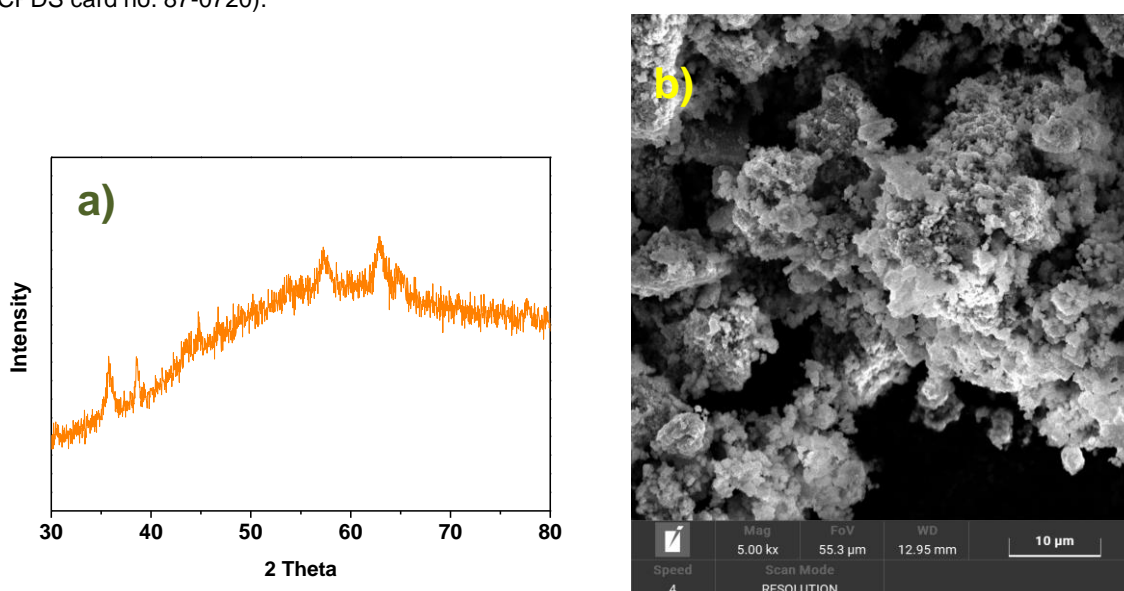


Figure 1: XRD profile of Ag/Fe₃O₄@PEI nanoparticles (a); SEM images of Ag/Fe₃O₄@PEI nanoparticles (b).

The morphology of the surface of Ag/Fe₃O₄@PEI nanoparticles was analyzed by scanning electron microscopy (SEM) (TESCAN-VEGA LMH; 230 V). Figure 1b shows the SEM image of the Ag/Fe₃O₄@PEI nanoparticles, the sample reveals an irregular shape with a size distribution ranging from 200 to 500 nm.

3.2 FT-IR studies of Ag/Fe₃O₄/CNCs nanocomposite

FT-IR spectroscopy a Nicolet iS50 was used to analyze the progress preparation of the nanocomposite. Figure 2 shows the FTIR spectra from 2000-500 cm⁻¹ of, commercial cellulose, Ag/Fe₃O₄@PEI, PEI, CNCs, and Ag/Fe₃O₄@PEI/CNCs nanocomposite.

The FT-IR profile of the CNCs evidence vibrational band at 1158 cm⁻¹, 1032 cm⁻¹, and 680 cm⁻¹ corresponding to C-O-C of the nanocellulose structure. At 555 cm⁻¹ the typical band of the β-glucosidic bond of sugar units is evident. In the profile, FT-IR of the Ag/Fe₃O₄@PEI is evidence of the intense peak at 541 cm⁻¹ due to the Fe-O vibration (Sarno and Iuliano, 2020). Moreover, around 1370 cm⁻¹ and 1575 cm⁻¹ are visible vibration bands due to the -NH₂ scissoring vibration of the PEI molecules (Xu et al., 2009). When the Ag/Fe₃O₄@PEI nanoparticles were added to the CNCs, in the spectra Ag/Fe₃O₄@PEI/CNCs nanocomposite, the typical band of the β-glucosidic bond of sugar units of the CNCs was hidden by the band of Fe-O vibration,

which shifts at 561 cm^{-1} . Moreover, the hydrogen bond between CNCs and $\text{Ag}/\text{Fe}_3\text{O}_4@PEI$ nanoparticles probability occurred due to the band shift from 1575 cm^{-1} to 1649 cm^{-1} (Liu et al., 2012). the FT-IR analysis confirms the successful anchoring of Fe_3O_4 nanoparticles on the NC surfaces. Figure 2b was depicted the schematic interaction between $\text{Ag}/\text{Fe}_3\text{O}_4@PEI$ NPs and CNCs

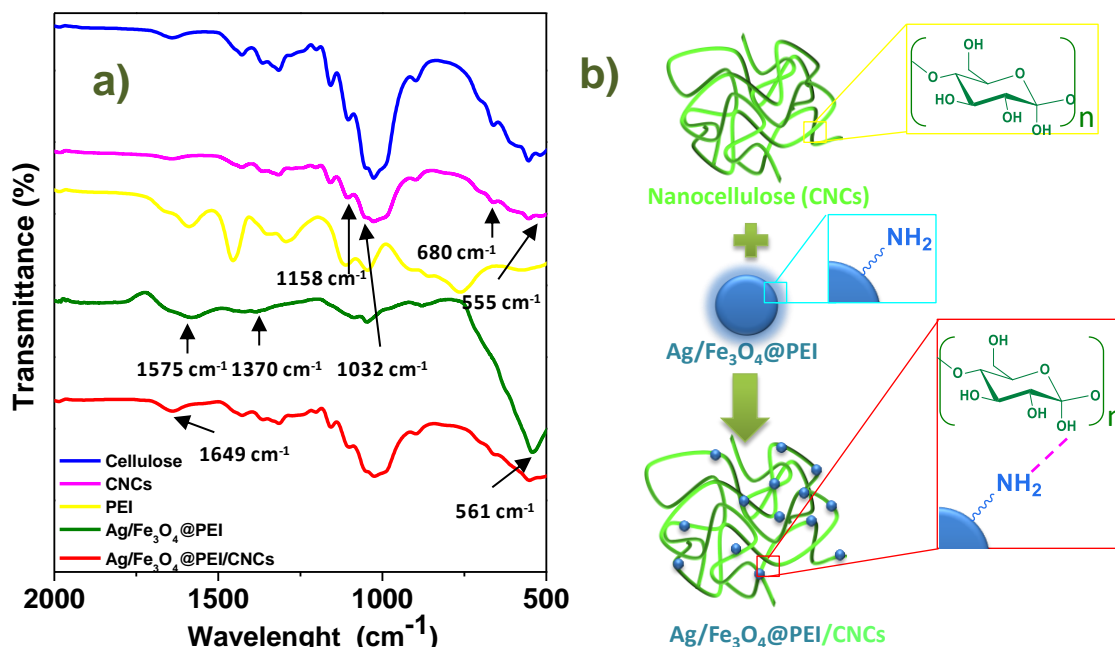


Figure 2. FT-IR spectra in the range of wavenumber $2000\text{--}500\text{ cm}^{-1}$ of cellulose, PEI (Sigma Aldrich), $\text{Ag}/\text{Fe}_3\text{O}_4@PEI$, CNCs, and $\text{Ag}/\text{Fe}_3\text{O}_4@PEI/CNCs$ nanocomposite (a) schematic preparation of the $\text{Ag}/\text{Fe}_3\text{O}_4@PEI/CNCs$ (b).

3.3 Catalytic performance of $\text{Ag}/\text{Fe}_3\text{O}_4@PEI/CNCs$ nanocomposite

Sunset Yellow is an azo dye, having conjugated aromatic rings with azo-bond ($-\text{N}=\text{N}-$). The reduction of Sunset yellow by NaBH_4 using catalyst $\text{Ag}/\text{Fe}_3\text{O}_4@PEI/CNCs$ nanocomposite was monitored by UV-visible spectroscopy at 470 nm . Figure 3 shows the reduction progress of SY dye with NaBH_4 , and $\text{Ag}/\text{Fe}_3\text{O}_4@PEI/CNCs$ nanocomposite in the time, the organic dye reduced almost completely within 8 min with a DE (%) $>98\%$.

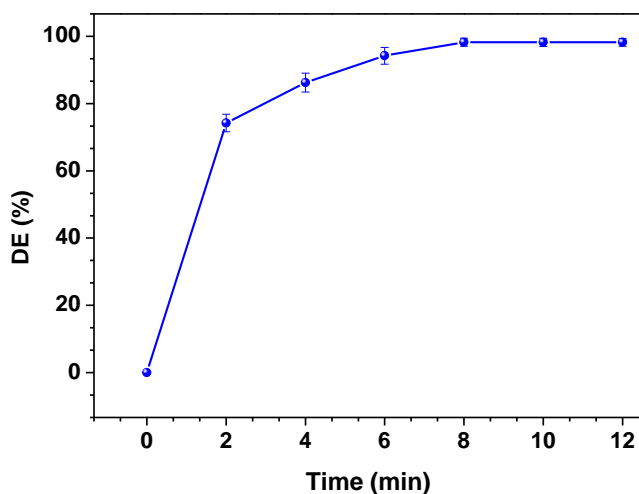


Figure 3. Discoloration efficiency versus catalytic hydrogenation reaction time for SY dye reduced, in the presence of NaBH_4 , using $\text{Ag}/\text{Fe}_3\text{O}_4@PEI@CNCs$ nanocomposite.

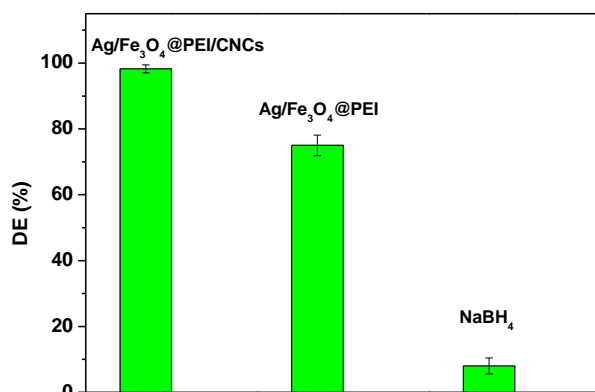


Figure 4. Discoloration efficiency of SY dye by NaBH₄ alone and in the presence of Ag/Fe₃O₄@PEI NPs and Ag/Fe₃O₄@PEI/CNCs nanocomposite.

Figure 4 shows the DE (%) of the SY dye in presence of NaBH₄ without catalyst, with Ag/Fe₃O₄@PEI+NaBH₄, and Ag/Fe₃O₄@PEI/CNCs+NaBH₄, after 8 min of the organic dye degradation reaction, to comparison. The NaBH₄ alone does not cause any appreciable effects in the reduction of the dyes, with the DE (%) of about 8%, after 8 min. While the Ag/Fe₃O₄@PEI with silver nanoparticles, which is the well-known catalyst for the reduction/decomposition of SY dye, brought the discoloration efficiency >70 % after 8 min. However, when the nanocellulose was added, SY dye removal was >98% at the same reaction times. In summary, in the absence of the catalyst, negligible reduction reaction was detected. This result clearly demonstrates that the catalyst is necessary for this process and the catalytic reduction occurs at the surface of catalyst.

Indeed, Ag NPs can function as the electron mediator between BH₄⁻ and dye (SY), and the electron transfer occurs via the Ag NPs. The reduction of dye typically proceeded in 2 steps: (i) diffusion of BH₄⁻ and adsorption of dye to the surface and (ii) electron transfer mediated by the catalyst surface from BH₄⁻ to dyes. However, in presence of nanocellulose the DE (%) was very high >98% after 8 min. This indicates that the nanocellulose favours the hydrolysis of NaBH₄ (Abdelhamid et al., 2020) by improving the hydrogenation rate. Moreover, the dye adsorption step on the nanocellulose occurs probability, which improve the interaction of the dye with the metal noble increasing the electron transfer on the silver surface and then accelerate the hydrogenation of organic dyes. Therefore, the SY dye will be adsorbed, and reduced at the surface of the Ag/Fe₃O₄@PEI/CNCs nanocomposite and finally desorbs from the surface to generate a available space for the reaction to continue.

3.4 Reusability of Ag/Fe₃O₄@PEI@CNCs nanocomposite

The reusability of the Ag/Fe₃O₄@PEI/CNCs nanocomposite in the reduction of SY dye was investigated and the results showed in Figure 5. The nanocomposite showed excellent catalytic activity in the reduction of SY dyes. Indeed, the time required for a >98% reduction of SY dye was found to be almost the same up to the 5th cycle. These results indicate that our nanocomposite retains strong stability in each cycle.

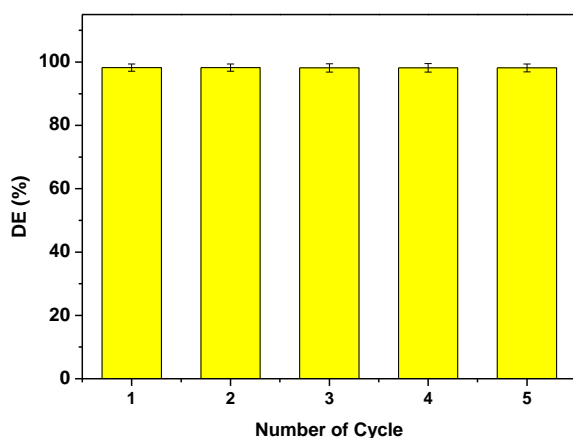


Figure 5. The reusability of Ag/Fe₃O₄@PEI/CNCs nanocomposite for the reduction of SY dye.

4. Conclusion

In this present work Ag/Fe₃O₄@PEI/CNCs nanocomposite was synthesized by the self-assembled method. The highly stable Ag/Fe₃O₄@PEI/CNCs nanocomposite was used for catalytic reduction of the azo dye SY by NaBH₄. The catalyst promoted the reduction of SY dye in the presence of NaBH₄ in times considered fast with an efficiency of >98%, converting the colored and toxic form of the dyes into its colorless and low toxicity form called leuco or hydrogenated form. The nanocellulose shows a crucial role in the removal SY dye in the water, improving the hydrogenation rate. The reuse data from the catalysts showed that it maintains its efficiency in the >98% range after five cycles. The structural integrity of the nanocatalyst was maintained after five successive catalytic cycles. The catalyst proved to be significantly stable, recyclable, and with a high potential to be applied in discolorization reactions of the organic dyes in wastewater treatment.

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