

Article

Highly Efficient and Magnetically Recyclable Non-Noble Metal Fly Ash-Based Catalysts for 4-Nitrophenol Reduction

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Abstract: 4-nitrophenol (4-NPh) is a harmful compound produced in large amounts in the chemical industry, and its reduction to aminophenol (4-APh) using noble metals as catalysts is one of the most studied processes. The development of noble metal-free catalysts represents an economic advantage in large-scale applications and contributes to the sustainability of raw materials. Coal fly ash (FA), a major waste stream from coal combustion, contains an easily recoverable magnetic fraction (FA_{mag} sample) composed of Fe-rich particles that could substitute noble metal catalysts in 4-NPh reduction, with the concomitant advantage of being easily recovered via magnetic separation. For this purpose, a new composite material containing copper ferrite nanoparticles (FA_{mag}@CS@CuFe) was prepared via a facile, environmentally friendly and cost-effective method based on three components: FA_{mag} as the core, a biobased polymer chitosan (CS) as the linker and copper ferrite CuFe₂O₄ nanoparticles (CuFe) as the active sites. The structure, morphology, composition and magnetic properties of the FA_{mag}@CS@CuFe material were studied to assess the efficiency of the preparation. It was found that the biopolymer prevented the aggregation of CuFe nanoparticles and enabled a synergistically outstanding activity towards the reduction of 4-NPh in comparison to the pristine FA_{mag} and bare CuFe nanoparticles. The FA_{mag}@CS@CuFe catalyst showed efficiency and stability in the conversion of 4-NPh of up to 95% in 3 min over four consecutive cycles. Such remarkable catalytic results demonstrate the potential of this catalyst as a substitute for expensive noble metals.

Keywords: fly ash; non-noble metal composites; pollutant valorization; nitro compounds; catalytic reduction



Citation: Kuźniarska-Biernacka, I.; Ferreira, I.; Monteiro, M.; Santos, A.C.; Valentim, B.; Guedes, A.; Belo, J.H.; Araújo, J.P.; Freire, C.; Peixoto, A.F. Highly Efficient and Magnetically Recyclable Non-Noble Metal Fly Ash-Based Catalysts for 4-Nitrophenol Reduction. *Catalysts* **2024**, *14*, 3. <https://doi.org/10.3390/catal14010003>

Academic Editor: Maria Manuel B. Marques

Received: 9 November 2023

Revised: 10 December 2023

Accepted: 12 December 2023

Published: 19 December 2023



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1. Introduction

The extensive use of aromatic nitro compounds by various industries, such as in the manufacturing of papers, pharmaceuticals, leather, dyes, pesticides and herbicides, has led to environmental contamination of soil and groundwater [1]. As nitroarenes are highly toxic and cancerogenic, various techniques have been employed to reduce their concentrations in water, including physical (e.g., adsorption/desorption processes [2]), chemical (e.g., oxidative degradation [3], photodegradation [4] and catalytic reduction [5]) and biological techniques (e.g., microbial treatment via anaerobic and aerobic biodegradation [6]). An advantage of the catalytic reduction of 4-nitrophenol (4-NPh) is the selective formation of 4-aminophenol (4-APh), which is significantly less toxic and a valuable product since it is an important intermediate in the production of agrochemicals, dyes and drugs, such as paracetamol and phenacetin [7].

Noble metals, especially Au, Pt and Pd nanoparticles, have been extensively used as catalysts for 4-NPh reduction with excellent results (total 4-NPh reduction in less than 3 min [8]). However, their tendency to aggregate during the reaction leads to a significant reduction in catalytic activity [9]. This activity suppression and the high cost of noble metals make this process unattractive to be applied at an industrial scale.

Meanwhile, the search for alternatives to noble metals has been growing in recent years, and transition metal oxides have shown to be promising. Nevertheless, active site aggregation, which results in lower catalytic activity [10,11], still needs to be overcome.

In this context, nanoparticle impregnation via a proper support is being actively used as an efficient methodology to avoid aggregation. For example, the use of carbonaceous materials, such as carbon nanotubes [12], activated carbons [13], carbon black [14] or biochar [15], is excellent for this purpose due to their high surface area and active site separation. However, their production demands harsh conditions and multi-step processes [16–18].

Meanwhile, composite materials (natural biopolymer–metallic or metal oxide nanoparticles) have been successfully employed in catalysts for advanced oxidation processes [19], but studies regarding their application in catalytic reduction are scarce [20] despite the fact that composite preparation is simple, environmentally friendly and cost-effective and leads to highly stable, well-dispersed nanoparticles in the biopolymer matrix [21,22].

Among natural biopolymers originated from poly-saccharides, chitosan (CS) is mostly used as a dispersing or supporting agent since it readily forms hydrogels via crosslinking in an acidic medium, and also due to its polymeric chain functional groups (–OH and –NH₂), which may chemically or electrostatically interact with metal ions and immobilize them in the matrix via the formation of ion pairs or ion exchange [23]. Moreover, chitosan is a very cheap and easily accessible biopolymer that can be obtained from crustacean shell wastes, thus contributing to minimizing their disposal in landfills [24].

Recently, chitosan-modified Cu₂O nanoparticles were tested as a catalyst in 4-NPh reduction and exhibited improved photocatalytic abilities ($K_0 = 2.28 \times 10^{-1} \text{ min}^{-1}$), with the reduction rate increased by 1.7 times compared to free Cu₂O nanoparticles ($K_0 = 1.32 \times 10^{-1} \text{ min}^{-1}$). This improvement was attributed mainly to chitosan-induced formation of (111) crystal surfaces of Cu₂O. However, the catalyst efficiency dropped after three catalytic cycles to 63% and 76% for Cu₂O and chitosan-modified Cu₂O catalysts, respectively, in comparison to the total 4-NPh conversion in the first cycle [25]. Similarly, the catalytic activity of ruthenium supported on magnetically recyclable biopolymer-based nanocatalysts, where MnFe₂O₄ was used as the magnetic core and chitosan [26] or chitosan–carrageenan [27] as the biopolymer, was evaluated for 4-NPh reduction. Both catalysts showed a high catalytic performance of 100% in the reduction of 4-NPh in less than 1 min and could be reused in at least 10 cycles without losing their catalytic activity, which confirmed their high stability [26,27].

Regarding catalyst support materials, it is crucial to improve studies based on alternative low-cost materials coming from recycling streams such as coal fly ash (FA), which are mainly composed of aluminosilicate glass and minor amounts of other materials, including Fe-rich particles such as ferrospheres [28,29] that are easily recovered via magnetic separation [2–4]. For example, Gadore and Ahmaruzzamn [30] reviewed the use of FA-based nanocomposites as effective photocatalysts for water remediation; Saputra and co-authors [31] prepared a Co-supported fly ash catalyst to promote phenol oxidation and observed a total degradation after 90 min at 45 °C; Yusuff et al. [32] used FA-supported ZnO as a catalyst in biodiesel production from used oil and obtained an 83.2% yield after 180 min at 140 °C; Dong et al. [33] used coal fly ash as a Ni–Re catalyst support for CO₂ methanation. The bimetallic catalyst achieved 99.55% of CO₂ conversion and 70.27% of CH₄ selectivity under the following conditions: 400 °C, 2000 h^{–1}, 1 atm and H₂:CO₂:N₂ = 4:1:0.5.

In a recent study, it was found that the synergy caused by the combination of two transition metals (Cu and Fe) in bimetallic NPs, and the presence of iron oxide in FA can increase the efficiency of the catalyst due to enhanced electron transfer [34]. Thus, a

facile synthesis was developed and tested using a magnetically recyclable three-component composite material containing copper ferrite (CuFe), FA_{mag}@CS@CuFe.

As far as is known, for the first time, CuFe nanoparticles were immobilized on ferrosphere surfaces using chitosan as linker, creating an innovative composite material to efficiently reduce 4-NPh and potentially other derivatives.

2. Results and Discussion

2.1. Materials Characterization

The XRF results are listed in Table 1. The FA_{mag} sample had the highest Si and Al concentrations, compared to the modified samples. However, after covering of FA_{mag} with CS using acetic acid (sample FA_{mag}@CS), Si decreased from 36.77 to 16.73 wt.%, and the Al concentration decreased from 19.01 to 7.82 wt.%, respectively, which was due to some leaching promoted by acetic acid [35–37]. Consequently, the relative concentration of Fe increased from 41.63 wt.% in FA_{mag} to 68.49 wt.% in FA_{mag}@CS.

Table 1. XRF results (wt.%) regarding elements of the initial and modified samples.

Sample	Al	Si	P	K	Ca	Ti	Mn	Fe	Cu	Zn	Sr
FA _{mag}	19.01	36.77	0.0	1.30	0.25	0.55	0.30	41.63	0.00	0.05	0.08
FA _{mag} -AA ^a	13.75	27.40	0.00	2.04	1.42	0.78	0.47	54.06	0.00	0.04	0.04
FA _{mag} @CS	7.82	16.73	4.45	0.57	1.01	0.65	0.21	68.40	0.00	0.03	0.05
FA _{mag} @CS@Cu	4.83	18.10	0.08	1.01	1.30	0.48	0.50	72.72	0.91	0.01	0.04
FA _{mag} @CS@CuFe	5.72	13.17	3.64	0.38	0.30	0.33	0.26	61.68	14.37	0.00	0.04
FA _{mag} @CS@CuFe ^b	5.23	13.16	0.64	1.07	0.87	0.45	0.31	61.64	0.84	0.01	0.02

^a The FA_{mag}-AA sample—FA_{mag} washed with diluted acetic acid (AA). Conditions: 500 mg of FA_{mag} sample with 150 mL of 0.5% AA was stirred for 60 min at room temperature. ^b after 5th catalytic cycle.

Further modifications of FA_{mag}@CS, by the incorporation of Cu or CuFe, resulted in the increase in Cu content (from absence to 0.91 and 14.37 wt.%, respectively, for samples FA_{mag}@CS, FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe) and Fe content (from 41.63 wt.% to 61.68 wt.%, respectively, for samples FA_{mag} and FA_{mag}@CS@CuFe). These results confirmed the successful formation of the tri-component composites FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe.

The FTIR spectrum of chitosan (Figure 1) shows characteristic bands for carbohydrate, amide and amine groups [38]. A broad, intensive band at 3430 cm^{−1} is attributed to the O–H stretching vibration of adsorbed water and carbohydrate ring (CS), and a weak shoulder at 3240 cm^{−1} is due to N–H stretching vibration. The weak bands at 2925 and 2875 cm^{−1} are usually associated with C–H stretching vibrations. The amine deformation vibrations usually produce strong to very strong bands in the 1660–1575 cm^{−1} region [39], and the band observed at 1654 cm^{−1} can be associated with the N–H bending amide vibration. In addition, C–N stretching vibrations occur in the 1190–920 cm^{−1} region and overlap the vibrations of the carbohydrate ring (observed as a band at 1075 cm^{−1}) [40,41]. These most intensive bands due to O–H, C–H, N–H and C–N vibrations were observed in the modified FA_{mag}@CS, FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe materials, confirming the successful coating of FA_{mag} by CS (Figure 1).

The band at 580 cm^{−1} in FTIR spectra, usually assigned to metal–oxygen stretching vibrations [42–44], was only presented in FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe samples. This agrees with XRF results (Table 1) and corroborates the success of the preparation of the multicomponent FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe samples.

To further support the formation of composites containing Cu and CuFe, Raman spectroscopic analysis was performed for the as-prepared respective samples, which allowed us to identify magnetite and hematite in the FA_{mag} sample (Figure 2A), as previously observed [45].

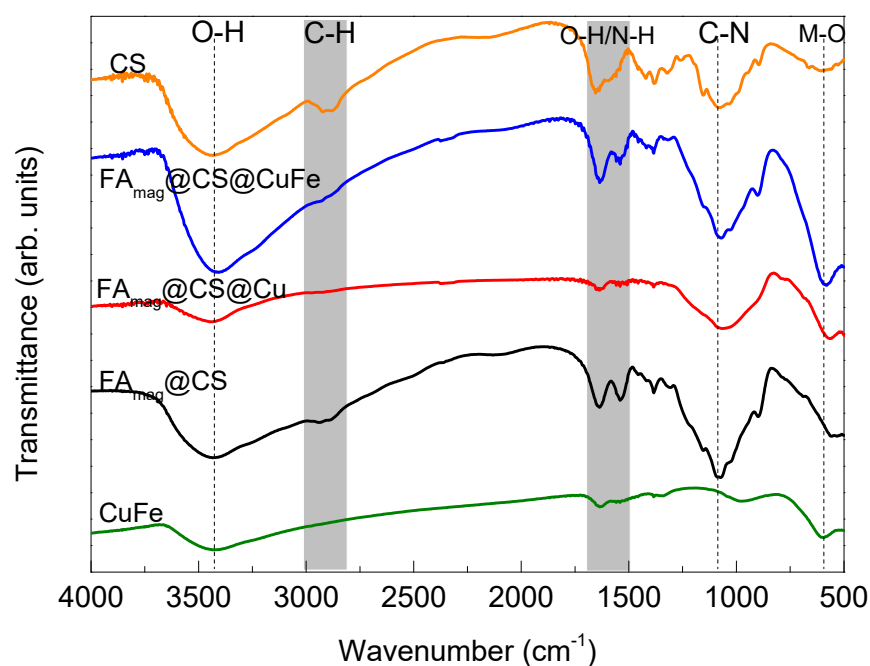


Figure 1. FTIR spectra of pristine CS, FA_{mag}, CuFe nanoparticles and FA_{mag} based composite materials in 4000–500 cm^{−1} region.

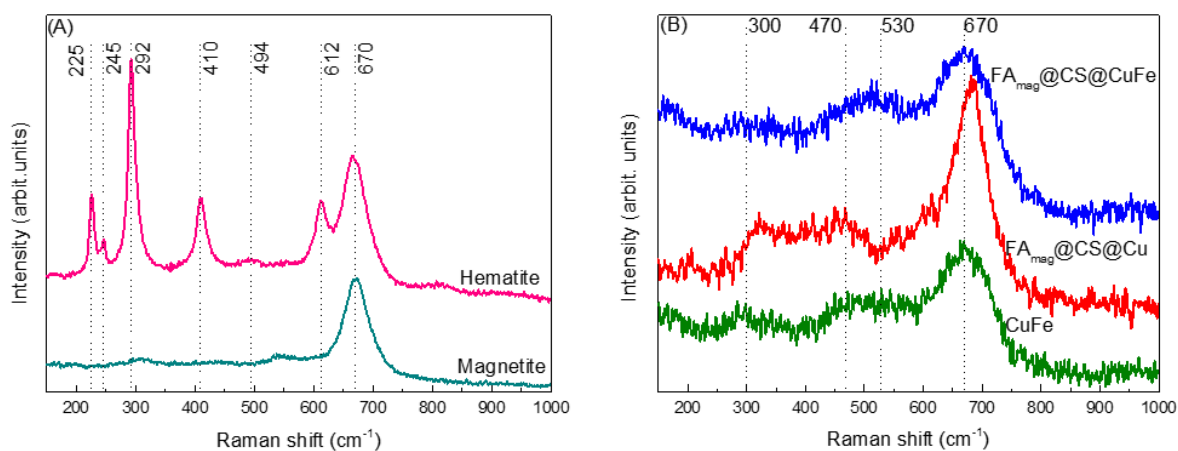


Figure 2. Raman spectra of the Fe-bearing morphotypes (A) and FA_{mag} based composite materials (B) in 150–1000 cm^{−1}.

The Raman spectra of the CuFe nanoparticles (Figure 2B) show four Raman active modes at 670 (A_{1g}), 530 (F_{2g}), 470 (T_{2g}) and 300 (E_{1g}) cm^{−1} and the position of the bands in agreement with the literature data [46–48]. The band at 670 cm^{−1} is usually attributed to the local lattice effect in the tetrahedral sub-lattice, and the band at 470 cm^{−1} is typically related to local lattice in the octahedral sublattice [47,48]. However, in the Raman spectrum of the tri-component sample (FA_{mag}@CS@CuFe), these bands are overlapped with characteristic bands of iron oxides (from FA_{mag}), which confirm the presence of CuFe nanoparticles in the composite material. The Cu–O modes at ~600 cm^{−1} and ~300 cm^{−1} in the Raman spectrum of FA_{mag}@CS@Cu are expected, but they are overlapped by higher intensity bands of iron oxides present in FA_{mag}.

Scanning electron microscopy (SEM-EDS) experiments were performed to characterize the samples of FA_{mag} and FA_{mag}-composite materials (samples FA_{mag}@CS, FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe). The detailed imaging of the FA_{mag} sample (Figure 3) confirms that it is mainly composed by Fe-rich morphotypes. The morphotypes are spheres with variable amounts of aluminosilicate glass embedding Fe-minerals (e.g., wüstite-magnetite

dendritic crystals, maghemite, hematite, and magnesioferrite) with variable amounts of Fe (ferrospheres), Fe and Mg (magnesiaspheres and magnesiaferrospheres), and Fe, Ca and Mg (calcimagnesiaferrospheres) (Figure 3A–D) [31].

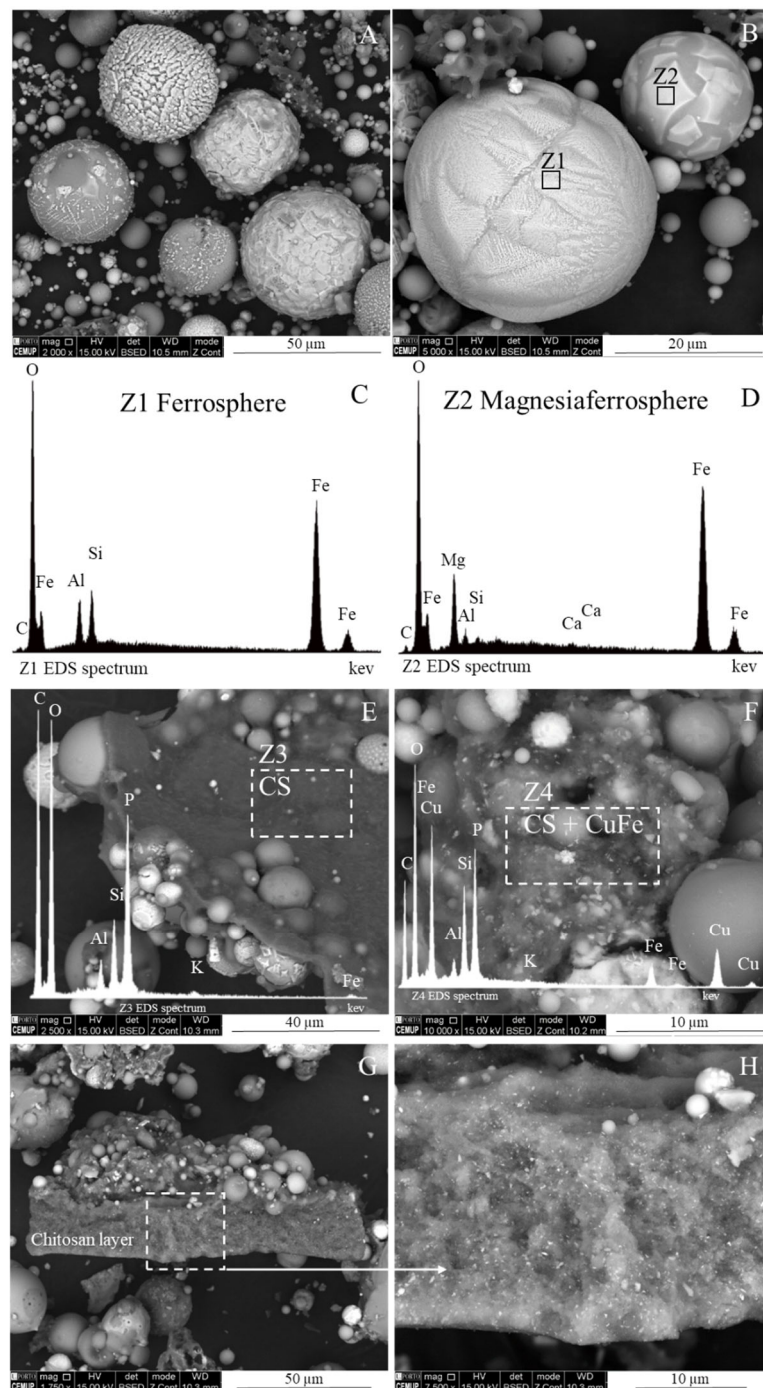


Figure 3. Detailed imaging and X-ray microanalysis of samples FA_{mag}, FA_{mag}@CS and FA_{mag}@CS@CuFe (SEM-EDS, BSE mode): (A) overview of Fe-rich spherical morphotypes in sample FA_{mag} (×2000); (B) FA_{mag}, example of ferrosphere (Z10) and magnesiaferrosphere (Z11) (×5000); (C,D) EDS spectra Z10 and Z11 of black square areas in “B”; (E) FA_{mag}@CS sample, chitosan (dark grey) binding magnetic spheres, and Z3 EDS spectrum of chitosan layer (×2500); (F–H) micrographs of FA_{mag}@CS@CuFe sample showing homogeneous distribution of CuFe nanoparticles (EDS spectrum Z4 in (F); ×10,000) on chitosan ((G,H); ×1750 and ×7500, respectively).

Chitosan coating of FA_{mag} particles is clearly observed in Figure 3E, as well as the successful incorporation of Cu (Figure S1, Supporting Materials) and CuFe nanoparticles on the chitosan surface, Figure 3F–H. It is clear that CuFe nanoparticles are uniformly dispersed (Figure 3G,H) in the chitosan film (FA_{mag}@CS@CuFe material), as observed by the EDS mapping images of FA_{mag}@CS@CuFe, presented in Figure S2 (Supporting Material). These observations are in accordance with ones observed in the literature for composites using different metals (Ag–Au, Ag–Pd, and Au–Pd) and gum kondagogu as natural biopolymer [20].

The XRD diffractograms of FA_{mag}, FA_{mag}@CS, FA_{mag}@CS@CuFe and CuFe NP samples are presented in Figure 4. The CuFe nanoparticles show diffraction lines at 18.4°, 30.1°, 35.6°, 38.8°, 43.2°, 53.8°, 57.1°, and 62.6°, corresponding to the tetragonal structure of the copper ferrite [49,50]. The XRD pattern of FA_{mag} confirms the presence of SiO₂ (quartz) with a diffraction line localized at 26.6° and iron oxides with diffraction peaks at 2θ = 18.2°, 30.2°, 35.6°, 43.2°, 53.8°, 57.1° and 62.8°, corresponding to the spinel structure of Fe₂O₃ or Fe₃O₄. In the FA_{mag}@CS@CuFe composite, the diffraction peaks of CuFe were detected along with a characteristic diffraction peak of FA_{mag} at around 26.6° (2θ), corresponding to quartz, indicating the successful preparation of the material.

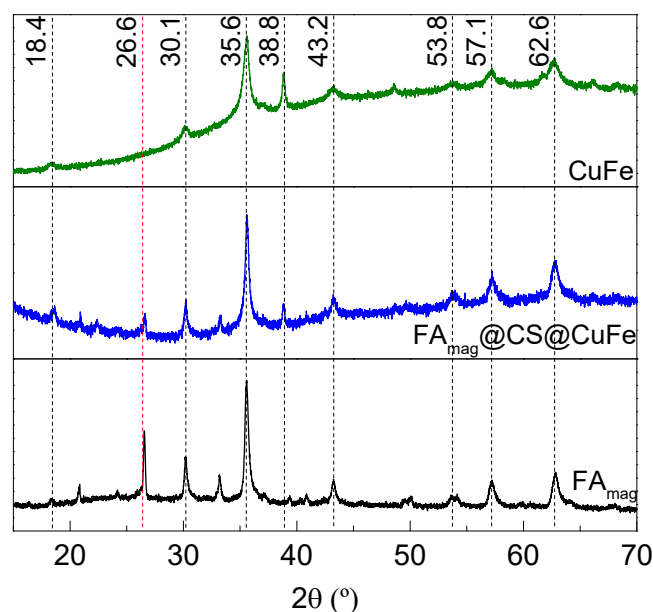


Figure 4. XRD patterns of CuFe nanoparticles, parent FA_{mag} and composite FA_{mag}@CS@CuFe.

2.2. Catalytic Performance

Prior to catalytic tests, the 4-NPh adsorption studies were performed using the as-prepared samples (FA_{mag}, CuFe and composites: FA_{mag}@CS, FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe). It was found that the materials had a negligible adsorption of 4-NPh after 180 min of contact. The maximum of 4-NPh adsorption capacity (3.6%) was observed for the pristine FA_{mag} sample. Thus, no kinetic studies of the 4-NPh adsorption process were further performed.

The reduction of 4-NPh, performed in the presence of NaBH₄ at room temperature and using the catalysts listed above, is expected to take place in two steps [51]. Firstly, the 4-NPh is spontaneously converted to p-nitrophenolate ion (4-NPh[−]) by the addition of NaBH₄ (pH_{reaction medium} ~ 11, pK_a(4-NPh) = 7.1) [52], which changes the color of the solution from pale to deep yellow. In the second step, in the presence of catalysts, the hydrogenation of 4-NPh[−] takes place to form a colorless solution of 4-APh.

The catalytic reduction of 4-NPh in the presence of CuFe nanoparticles, FA_{mag} and multicomponent composites is shown in Figure 5, and the evolution in the UV-Vis spectrum of the 4-NPh solution during the catalytic reduction is presented in Figure S3,

Supporting Material and the catalytic reduction profiles presented in Figure 5. The catalyst FA_{mag}@CS@CuFe showed the best catalytic performance, with total 4-NPh conversion in 3 min (Table 2, Figure 5).

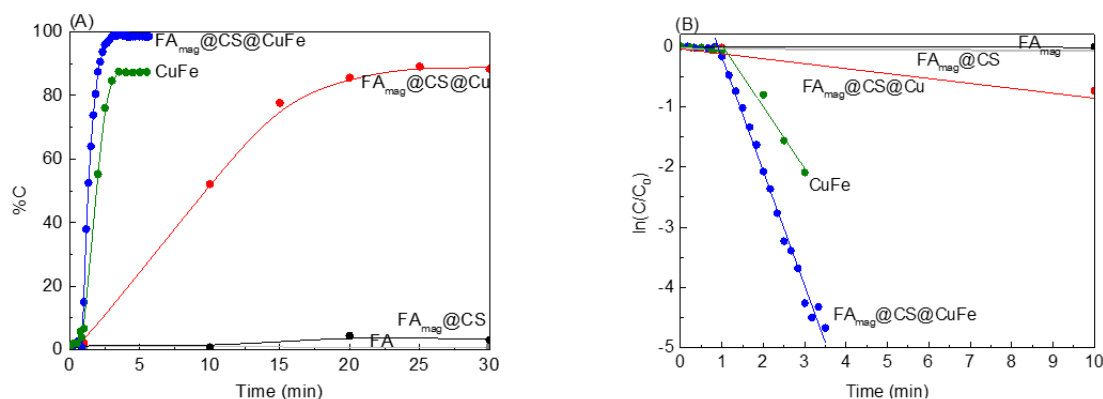


Figure 5. Catalytic reduction process for 4-NPh with CuFe nanoparticles, FA_{mag}, and two- and three-component composites: (A) kinetic plot; (B) linear fit between ln(C/C₀) of 4-NPh and time.

Table 2. Results of catalytic reduction of 4-NPh with pristine FA_{mag} and FA_{mag} composite-based catalysts ^a.

Entry	Run	Catalyst	Time ^b (min)	%C ^c	K1 ^d (min ⁻¹)	R ² ^e	K'1 ^f (min ⁻¹ g ⁻¹)
1	1	CuFe	3(1)	88	1.02×10^0	0.98	10.2
2	1	FA _{mag}	180	53	4.00×10^{-3}	0.99	0.04
3	2	FA _{mag}	20(5)	98	1.86×10^{-1}	1.00	
4	1	FA _{mag} @CS	180	8	5.00×10^{-4}	0.97	0.005
5	2	FA _{mag} @CS	180(20)	52	4.70×10^{-3}	1.00	
6	1	FA _{mag} @CS@Cu	30	88	8.18×10^{-2}	0.95	0.818
7	2	FA _{mag} @CS@Cu	30(5)	94	1.22×10^{-1}	0.98	
8	1	FA _{mag} @CS@CuFe ^g	3(1)	99	1.98×10^0	0.99	19.8
9	2	FA _{mag} @CS@CuFe ^g	6(2.5)	81	4.96×10^{-1}	1.00	
10	3	FA _{mag} @CS@CuFe ^g	10(3)	97	4.79×10^{-1}	0.99	
11	4	FA _{mag} @CS@CuFe ^g	10(3)	96	4.02×10^{-1}	0.99	
12	5	FA _{mag} @CS@CuFe ^g	10(3)	85	1.82×10^{-1}	0.99	
13	1	FA _{mag} -AA ^h	180	48	3.8×10^{-3}	0.98	0.04

^a Experimental conditions: initial 4-NPh concentration (5×10^{-5} mol · dm⁻³), NaBH₄ (5×10^{-2} mol · dm⁻³) and catalyst loading (100 mg), volume total V = 30 mL under stirring. ^b Reaction time, in parenthesis induction time. ^c Conversion of 4-NPh calculated from %C = 100 − [(A_f/A₀) × 100%], where A₀ and A_f are absorbance values of 4-NPh (λ = 400 nm) at t = 0 and at the end of the reaction (min). ^d K1 is apparent first-order kinetic rate constant (min⁻¹), calculated from ln(A_f/A₀) = −K1 × t. ^e Correlation coefficient. ^f K'1 is activity parameter calculated from K'1 = K1/m, where m is the total catalyst mass (g) used in the reaction. ^g Reaction was performed in sealed spectroscopic cell (V = 3 mL) experimental conditions: initial 4-NPh concentration (5×10^{-5} mol · dm⁻³), NaBH₄ (5×10^{-2} mol · dm⁻³) and catalyst loading (10 mg). ^h The FA_{mag}-AA sample—the parent FA_{mag} washed with diluted acetic acid (AA); conditions: a mixture containing 500 mg of FA_{mag} sample with 150 mL of 0.5% AA was stirred for 60 min at room temperature.

The bare CuFe, under the same experimental conditions, showed 88% conversion of 4-NPh in 3 min. The FA_{mag}@CS@Cu also presented catalytic activity in 4-NPh reduction (substrate conversion 88% in 30 min), but the efficiency was far less than that of pristine CuFe or the FA_{mag}@CS@CuFe composite, due to the need for an induction period. The FA_{mag} and FA_{mag}@CS showed almost no activity after 30 min (less than 10% of substrate conversion) and led to conversion of only 53% and 8% of 4-NPh, respectively, after 180 min.

The reproducibility of FA_{mag} utilization as catalyst in the 4-NPh reduction was tested in three independent experiments under the same experimental conditions. The kinetic profiles and the substrate conversion (Figure 6; Figure S4 Supporting Material) suggest that the active sites in FA_{mag} are uniformly distributed, resulting in Δ %C_{4-NPh} < 1, as previously observed by the authors using magnetic size-fractions of FA [45].

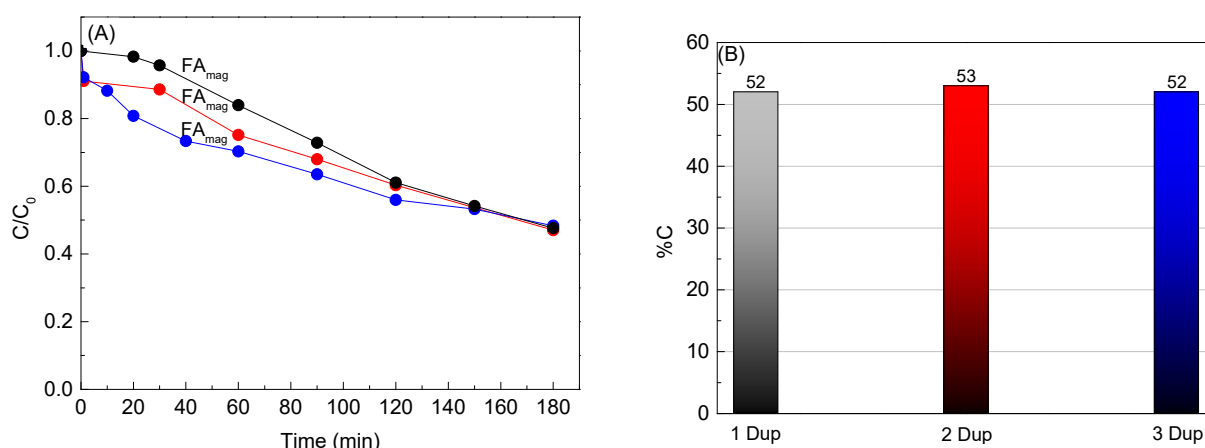


Figure 6. The results of catalytic reduction of 4-NPh using FA_{mag} as catalyst, triplicate test (A) kinetic curves and (B) conversion of 4-NPh during the catalytic reduction process, 1-3Dup—the number of experiment duplications. Conditions: $m_{catalyst} = 100$ mg, $c_{4-NPh} = 5 \times 10^{-5}$ M, 30 mL, 56.7 mg of $NaBH_4$.

Kinetic studies of the catalytic reduction of 4-NPh were performed. The reactions were performed using a significant excess of $NaBH_4$ compared to the substrate concentration, under the assumption that the BH_4^- concentration remains constant during the reaction cycle. These studies were assessed using pseudo-first-order kinetics. The rate constants obtained from linear correlation of $\ln(C/C_0)$ vs. time for 4-NPh reduction were 1.98 min^{-1} , 1.02 min^{-1} , 0.0818 min^{-1} , 0.004 min^{-1} and 0.0005 min^{-1} for $FA_{mag}@CS@CuFe$, $CuFe$, $FA_{mag}@CS@Cu$, FA and $FA@CS$ catalysts, respectively (Figure 5B). The calculated activity parameter (reaction rate constant per unit mass) was $19.800 \text{ min}^{-1}\text{g}^{-1}$, $10.200 \text{ min}^{-1}\text{g}^{-1}$, $0.818 \text{ min}^{-1}\text{g}^{-1}$, $0.040 \text{ min}^{-1}\text{g}^{-1}$ and $0.005 \text{ min}^{-1}\text{g}^{-1}$, respectively (Table 2). Using $FA_{mag}@CS@CuFe$ as catalyst, the reaction rate and catalyst activity increased 495 times in comparison with FA_{mag} , 24 times in comparison with $FA_{mag}@CS@Cu$, and 2 times in comparison with bare $CuFe$. These high activities may derive from abundant amine and primary and secondary hydroxyl groups on chitosan that prevented $CuFe$ nanoparticle aggregation on the material surface (Figure 3G,H). A similar effect was observed using polydopamine-graphene/Ag-Pd nanocomposite as the catalyst for reduction of nitrophenol in the presence of $NaBH_4$ as reducing agent. The high activity of the catalyst originated from numerous amine and catechol groups on polydopamine, which ensured the dispersion of bimetallic Ag/Pd nanoparticles on the surface of the nanocomposite [53].

The details of 4-NPh reduction reaction conditions along with the catalytic rate constants are summarized in Table S1 (Supplementary Material). The $FA_{mag}@CS@CuFe$ catalyst exhibited superior catalytic activity compared with the other FA-based catalysts, even those containing noble metals. For example, FA-supported Pd-Ag bimetallic nanoparticles led to faster 4-NP reduction in the presence of $NaBH_4$ in water ($K_1 = 0.7176 \text{ min}^{-1}$) than their monometallic analogues FA-Pd ($K_1 = 0.5449 \text{ min}^{-1}$) and FA-Ag ($K_1 = 0.5572 \text{ min}^{-1}$), as well as their physical mixture ($K_1 = 0.4075 \text{ min}^{-1}$) [54], which was 2.7 times slower than the rate obtained with $FA_{mag}@CS@CuFe$ ($K_1 = 1.9761 \text{ min}^{-1}$) in this work. Furthermore, the rate constant of 4-NPh reduction over core-shell fly ash@polypyrrole/Au composite microspheres ($K_1 = 0.474 \text{ min}^{-1}$) [55] was 4.2 times lower than the one obtained for $FA_{mag}@CS@CuFe$ ($K_1 = 1.9761 \text{ min}^{-1}$).

Similarly, the $FA_{mag}@CS@CuFe$ catalyst exhibited enhanced catalytic activity compared to the core-shell structured $CuFe_2O_4/Ag@COF$ nanocomposites ($K_1 = 0.77 \text{ min}^{-1}$) as well as its two-component composite $CuFe_2O_4/Ag$ ($K_1 = 0.25 \text{ min}^{-1}$) or $CuFe_2O_4@COF$ ($K_1 = 0.15 \text{ min}^{-1}$) [56], eggshell membrane- $CuFe_2O_4$ nanocomposite ($K_1 = 0.748 \text{ min}^{-1}$) [57], cellulose nanocrystal (CNC)-supported magnetic $CuFe_2O_4@Ag@ZIF-8$ nanospheres ($K_1 = 0.64 \text{ min}^{-1}$) [58] or reduced graphene oxide (RGO) nanocomposite with the best catalytic performance among other RGO/ $CuFe_2O_4$ composites, i.e., material consisting of 96 wt.% $CuFe_2O_4$ and 4 wt.% RGO ($K_1 = 1.032 \text{ min}^{-1}$) [59] vs. $K_1 = 1.9761 \text{ min}^{-1}$ obtained

in this work. The superior activities of FA_{mag}@CS@CuFe can be ascribed to the synergistic effect of CuFe₂O₄, CS and FA_{mag} and the homogeneous distribution of CuFe nanoparticles.

Other examples with good performance in 4-NPh reduction were found for the nanocomposite catalysts consist of carbon dots and CuFe nanoparticles [60], possibly due to the smaller particle size of CuFe₂O₄ in composite than pure CuFe₂O₄, and consequently the larger surface area of the composite and better adsorption of the substrate and reductant and good electron-transport properties of the C-dot shell [61,62]. However, carbon dot preparation is complex and demands high energy-consuming hydrothermal conditions for coating [62] and core-shell [61] catalysts.

Stability of Catalysts

The recycling of the catalysts is essential to make the process more attractive for application at industrial scale. In this sense, to assess the reusability of the best performing catalyst (FA_{mag}@CS@CuFe), trials were conducted under the same reaction conditions in a sealed quartz cell (optical path $l = 1$ cm, $V = 3$ mL). After the first cycle, the catalyst was fixed at the cuvette bottom using an external magnet, the reaction mixture was removed by decantation, and a new portion of 4-NPh and NaBH₄ was added to the remaining catalyst. This process was repeated four times. The results are summarized in Figure 7, and the corresponding UV-Vis spectra are shown in Figure S5 (Supporting Materials).

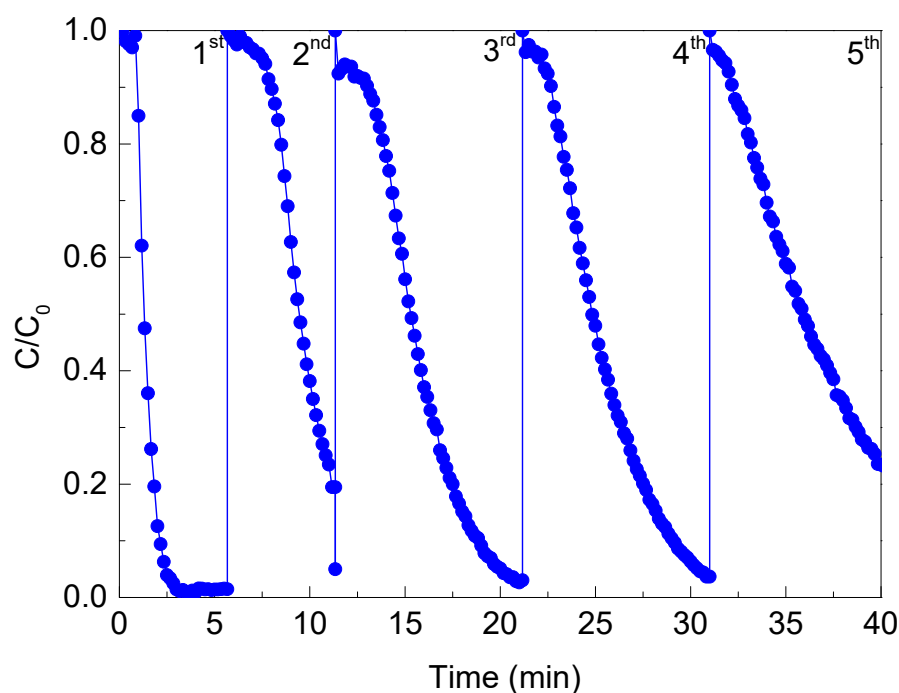


Figure 7. Plot of five consecutive cycles for reduction of 4-NPh over FA_{mag}@CS@CuFe.

The FA_{mag}@CS@CuFe catalyst was highly active during five consecutive cycles and led to 85% conversion of 4-NPh in the first 10 min. However, the apparent K_1 gradually decreased in each cycle (from K_1 1st_{cycle} = 1.98 min^{-1} to K_1 5th_{cycle} = $1.82 \times 10^{-1} \text{ min}^{-1}$), which may have been due to some leaching of CuFe. The XRD pattern of the recycled catalyst (Figure S6, Supporting Material) was similar to that of the as-prepared sample, suggesting that the spinel structure of the oxides did not change during five consecutive cycles. However, after the last catalytic cycle, the copper content of the FA_{mag}@CS@CuFe composite was significantly reduced (14.34 wt.% for the as-prepared sample vs. 0.84 wt.% after the fifth cycle), suggesting Cu leaching from the sample (Table 1), whereas the Fe concentration did not change (61.68 wt.% vs. 61.64 wt.%). However, the Raman spectrum of the FA_{mag}@CS@CuFe catalyst after the fifth reaction cycle showed no features pertaining to Cu- or Fe-oxides, indicating their partial conversion into metallic Cu⁰ or Fe⁰, respec-

tively [60]. Another possibility is the adsorption of borohydride on the particle surface (Cu^0), decreasing the reduction potential of the metallic nanoparticle [63]. This can promote the oxidative dissolution of reduced Cu^0 due to high susceptibility toward oxidation by oxygen, and may cause the copper leaching.

Figure 8 displays the results of room-temperature magnetization vs. applied magnetic field curves for all samples. All samples followed a soft ferromagnetic-like behavior where magnetization reached saturation at relatively low fields (<5 kOe), and small remanence magnetization and coercive field values (<3 emu g^{-1} and 58 Oe) were observed. Such behavior is consistent with the presence of both CuFe_2O_4 and Fe_3O_4 magnetic phases. The two most striking features were (i) the larger saturation magnetization displayed by the $\text{FA}_{\text{mag}}@\text{CS}@\text{CuFe}$ material after the last catalytic cycle, particularly in comparison with the as-prepared $\text{FA}_{\text{mag}}@\text{CS}@\text{CuFe}$ (blue curve), and (ii) the larger paramagnetic-like linear behavior exhibited by CuFe nanoparticles. The latter can typically be attributed to the linear susceptibility associated with uncompensated spins at the nanoparticle surface [64]. More importantly, the former feature can be explained by the enhancement of the higher-saturation magnetization Fe_3O_4 phase at the expense of the lower-saturation magnetization CuFe_2O_4 phase—leading to an overall increase in the saturation magnetization of the sample [65,66]. These results corroborate the XRF results (Table 1) and support the hypothesis of Cu leaching from the sample during catalytic cycles.

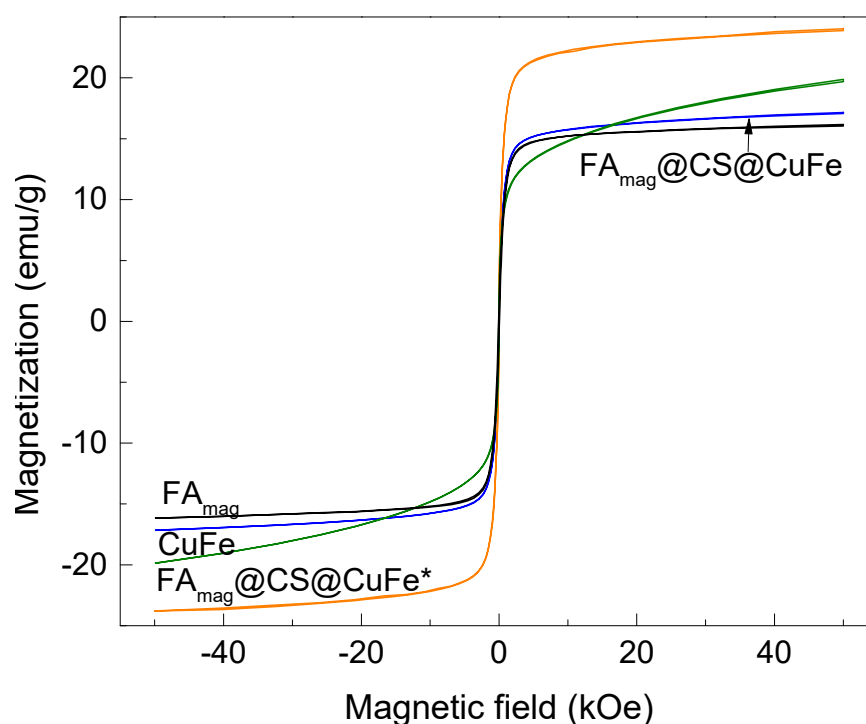


Figure 8. Room-temperature magnetization vs. magnetic field curves of CuFe nanoparticles, and bare FA_{mag} and composite $\text{FA}_{\text{mag}}@\text{CS}@\text{CuFe}$, where $\text{FA}_{\text{mag}}@\text{CS}@\text{CuFe}^*$ is the catalyst after the last catalytic cycle.

The formation of Cu^0 was observed by Kang et al. [67] during reductive decomposition of CuFe nanoparticles in a methane atmosphere, where Cu segregation and simultaneous formation of magnetic Fe_3O_4 occurred in the first reduction step of CuFe . The Cu^{2+} reduction to metallic Cu^0 was also observed by Park et al. [68] for water-washed coal fly ash-supported copper catalysts in the presence of NaBH_4 . The authors suggested that the $\text{Cu}^0/\text{Fe}^{3+}$ and $\text{Cu}^0/\text{Fe}^{2+}$ were the active species that led to the enhanced reduction of 4-NPh. This conclusion suggests that the catalysts should be more active in consecutive cycles, and it agrees with the results from the second cycle of $\text{FA}_{\text{mag}}@\text{CS}@\text{Cu}$ (Table 2), where the apparent K_1 increased in the second cycle from 8.18×10^{-2} to $1.22 \times 10^{-1} \text{ min}^{-1}$.

Summarizing, the Raman spectrum of the FA_{mag}@CS@CuFe material after the catalytic cycle suggests partial reduction of Cu²⁺ to Cu⁰ (from CuFe) and Fe²⁺ or Fe³⁺ to Fe⁰ (from CuFe or from ferrospheres, i.e., Fe₂O₃ or Fe₃O₄). The study of magnetic properties of FA_{mag}@CS@CuFe suggests the formation of Fe₃O₄ from CuFe₂O₄. All of these data support the statement that Cu⁰ is formed. In aqueous solution, the BH₄[−] ions (from NaBH₄) are adsorbed on the surface of the catalysts, and the active species acts as intermediate for electron transfer from BH₄[−] (donor) to substrate 4-NPh (acceptor). During this process, Cu²⁺ can be partially converted into Cu⁰ and induce the changes in the valence state between Cu⁺–Cu²⁺ and Fe²⁺–Fe³⁺ ion pairs in CuFe₂O₄, which can enhance catalytic activity, which was suggested by H Zheng et al. [69]. Thus, the presence of Cu⁰ plays a key role in enhancing the catalytic reduction of 4-NPh, as it can boost the electron transfers of CuFe₂O₄ and directly transfer electrons from BH₄[−] ions to 4-NPh. Thus, the oxidative leaching of Cu⁰ to solution causes that activity of FA_{mag}@CS@CuFe to decrease in the following cycles.

3. Materials and Methods

3.1. Reagents and Materials

In this work, the following reagents were used: chitosan (CS, medium molecular weight, 75–85% deacetylated, Merck KGaA, Darmstadt, Germany), sodium tripolyphosphate (TPP, technical grade, 85%, Merck KGaA, Darmstadt, Germany), iron(III) chloride hexahydrate (FeCl₃ × 6H₂O, for analysis, Merck KGaA, Darmstadt, Germany), copper(II) chloride dihydrate (CuCl₂ × 4H₂O, ACS reagent, ≥99.0%, Merck KGaA, Darmstadt, Germany), potassium bromide (≥99%, FTIR grade, Merck KGaA, Darmstadt, Germany), 4-nitrophenol (4-NPh, >99%, Merck KGaA, Darmstadt, Germany), sodium borohydride (NaBH₄, >99%, Merck KGaA, Darmstadt, Germany), 4-aminophenol (≥99%, Merck KGaA, Darmstadt, Germany), sodium hydroxide (NaOH, ≥99.5%, Merck KGaA, Darmstadt, Germany), potassium carbonate (K₂CO₃, 98%, VWR Chemicals, Carnaxide, Portugal). All experiments were conducted using ultrapure water (Millipore, specific resistivity 18 MΩ · cm^{−1}, Merck Millipore, Darmstadt, Germany).

The Fe-rich fraction (sample FA_{mag}) was magnetically recovered from a fly ash sample from a pulverized coal-fired thermal power plant (Abrantes, Portugal) [45].

3.2. Preparation of Materials

3.2.1. Synthesis of CuFe₂O₄ Nanoparticles

The CuFe₂O₄ nanoparticles were prepared by an aqueous coprecipitation method described elsewhere [70]. Briefly, 4.0 mmol CuCl₂ × 4H₂O and 8 mmol FeCl₃ × 6H₂O were dissolved in 100 mL distilled water, then 15 mL of NaOH solution (5.0 M) was added dropwise (1.5 mL min^{−1}). The mixture was heated at 100 °C and mechanically stirred for 5 h. The obtained dark brown precipitate was separated by external magnet, washed with water until pH 7, then washed with ethanol and acetone, and then dried at 80 °C for 12 h. Henceforward, this sample will be denominated as “CuFe”.

3.2.2. Preparation of Chitosan-Coated Fe-Rich Morphotypes

The sample of “chitosan-coated Fe-rich morphotypes” was prepared according to a modification of a method described by Calvo et al. based on the ionic gelation of CS with TPP anions [71]. An acetic acid solution (0.5%, *v/v*, 25 mL), stirred at RT for 1 h, was used to disperse 0.5 g of FA_{mag} sample while dissolving CS (0.7 g). The TPP solution (2.5 g/L, 50 mL) was injected dropwise into the CS solution by using a syringe pump with 1 mL/min injection rate. After the complete addition of TPP, the mixture was mechanically stirred at 1000 rpm for 1 h. The formed powder product was then collected with an external magnet, washed with water until pH 7, and dried under vacuum at RT for 24 h. Henceforward, this sample will be denominated as “FA_{mag}@CS”.

3.2.3. Modification of FA_{mag}@CS with CuCl₂

Briefly, 0.5 g FA_{mag} was dispersed in 0.5% acetic acid together with CuCl₂ × 4H₂O (0.3 mmol) and CS (0.7 g), and mechanically stirred for 1 h. Then, 50 mL of TPP solution (2.5 g/L) was injected dropwise, and the mixture was stirred for 1 h. The powder product was separated with an external magnet, washed with water and dried under vacuum at RT for 24 h. Henceforward, this sample will be denominated as “FA_{mag}@CS@Cu”.

3.2.4. Modification of FA_{mag}@CS with CuFe₂O₄

One three-component composite was prepared by wet impregnation based on ionic gelation using sodium tripolyphosphate as cross-linking agent. Briefly, 1.0 g FA_{mag} was dispersed in 0.5% acetic acid together with freshly prepared CuFe nanoparticles (0.5 g) and CS (1.3 g) and mechanically stirred for 1 h. Then, 100 mL of TPP solution (2.5 g/L) was injected dropwise, and after complete addition, the mixture was stirred for 1 h. The powder product was separated with an external magnet and washed with water and dried under vacuum at RT for 24 h. Henceforward, this sample will be denominated as “FA_{mag}@CS@CuFe”.

3.3. Sample Characterization Methods

The chemical characterization of FA_{mag}, FA_{mag}@CS, FA_{mag}@CS@Cu and FA_{mag}@CS@CuFe included elemental analysis using a portable X-ray fluorescence analyzer (X-MET7500, Oxford Instruments, Bristol, UK) equipped with a 45 kV Rh tube and a high-resolution silicon-drift detector (SDD). Element contents were presented as an average value calculated by the analyzer based on three separate measurements for each sample (20 s per measure).

For the detailed imaging and semi-quantitative chemical analysis, experiments were carried out in a Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM/EDS) FEI Quanta 400 FEGESEM/EDAX Genesis X4M at the Materials Centre of the University of Porto—CEMUP, Porto, Portugal.

The FTIR spectra were obtained in KBr pellets (Merck, KGaA, Darmstadt, Germany, spectroscopic grade) containing 0.4 wt.% material, 1:250 sample KBr ratio using a Jasco, (Tokyo, Japan) FT-IR 460 Plus spectrometer. All spectra were collected at room temperature, in the 400–4000 cm^{−1} range using a resolution of 4 cm^{−1} and 32 scans.

Raman analyses were performed on powder samples at room temperature using a Jobin–Yvon LabRaman spectrometer (Horiba, France) equipped with a CCD camera and a He–Ne laser at an excitation wavelength of 632.8 nm. An optical microscope from Olympus (Tokyo, Japan) with a 100× objective lens was used to focus the laser beam on the sample surface and to collect the scattered radiation. A neutral density filter was used to reduce the power of the laser by 75% (D.06) to avoid laser-induced transformation of the Fe-bearing phases. Scans from 100 cm^{−1} to 1000 cm^{−1} were performed on the particles' surface. The acquisition time and respective accumulations were individually adjusted to acquire an optimized spectrum at spectral resolutions near 1 cm^{−1}.

X-ray diffraction (XRD) analyses were performed at IFIMUP (Departamento de Física e Astronomia da Universidade do Porto, Portugal) on a Rigaku Smartlab diffractometer (Tokyo, Japan). The XRD measurements were performed at room temperature over the range 2θ = 15–80° using Cu Kα radiation (λ = 1.5406 Å) and the Bragg–Brentano θ/2θ configuration.

Measurements of the magnetic properties of materials were investigated by using a commercial Quantum Design MPMS 3 SQUID magnetometer. The magnetization (M), as a function of the applied magnetic field (H) measurement, was performed at 300 K for a maximum H of 50 kOe.

3.4. Catalytic Reduction

The catalytic reduction of 4-NPh to 4-APh was carried out at room temperature using NaBH₄ as the reducing agent. During the experiments, 30.0 mL of a 5.0 × 10^{−5} M stock solution of 4-NPh and 56.7 mg of NaBH₄ were constantly stirred. With the addition of NaBH₄, the pale-yellow color of the solution turned to bright yellow due to the formation

of nitrophenolate ions. After addition of FA_{mag}-based catalysts, the yellow color of the solution progressively vanished, following the reduction of 4-NPh. The samples were collected at fixed intervals of time and centrifuged. The conversion of the substrate to the 4-APh was monitored by UV-Vis spectroscopy measurements of the absorption spectra in the range 200–500 nm, using a quartz cell (*l* = 1 cm).

After each catalytic cycle, the catalysts were separated using an external magnet and washed with water to remove potential traces of substrate product and reductant adsorbed on the catalyst surface. The recovered catalysts were dried at 60 °C for 12 h under vacuum and reused in a new reaction cycle under identical experimental conditions. Adsorption experiments were carried out in the presence of the catalysts in the dark, and a blank experiment in the absence of catalyst was also performed. Reusability of the material with the best catalytic performance was evaluated for five continuous cycles.

4. Conclusions

Catalysts based on coal fly ash, a coal combustion residue, were prepared by an efficient method using a bio-degradable polymer (chitosan) as linker and CuFe as catalytic active sites, avoiding the use of noble metal-based catalysts. Multi-technique characterizations (XRF, FTIR, SEM-EDS and RAMAN) confirmed the successful preparation of the target tri-component composite, FA_{mag}@CS@CuFe, which exhibited catalytic activity superior to that of the other catalysts studied and, to some extent, those described in the literature, which can be ascribed to the specific characteristics of its structure and the synergistic effect of CuFe and chitosan. The recyclability of this composite is remarkable, although with some negligible losses after the fifth cycle, showing that the reported catalyst is very promising for the industrial-scale use of coal fly ash as support for active transition-metal oxides to be used in the reduction of nitro compounds or other typical catalytic reduction reactions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal14010003/s1>, Figure S1: Detailed imaging and X-ray microanalysis of the FA_{mag}@CS@Cu sample; Figure S2: Elemental area-mappings for FA_{mag}@CS@Cu sample; Figure S3: Change of UV-Vis spectrum of 4-NPh during the reduction of 4-NPh by NaBH₄ in the presence of: A—FA_{mag}@CS@CuFe, B—CuFe, C—FA_{mag}@CS@Cu, D—FA_{mag} and E—FA_{mag}@CS catalysts (initial 4-NPh concentration *c* = 5.5 × 10^{−5} M, catalyst dose = 3.3 mg L^{−1}, NaBH₄ concentration *c* = 0.05 M); Figure S4: Reproducibility tests of FA_{mag} catalyst (initial 4-NPh concentration *c* = 5.5 × 10^{−5} M, catalyst dose = 3.3 mg L^{−1}, NaBH₄ concentration *c* = 0.05 M); Figure S5: Stability tests of FA_{mag}@CS@CuFe catalyst (initial 4-NPh concentration *c* = 5.5 × 10^{−5} M, catalyst dose = 3.3 mg L^{−1}, NaBH₄ concentration *c* = 0.05 M); Figure S6: XRD patterns of CuFe nanoparticles, samples FA_{mag}, and composite FA_{mag}@CS@CuFe, where FA_{mag}@CS@CuFe* is the catalyst after the last catalytic cycle, Table S1: Comparison of catalytic conditions and apparent first-order rate constants for reduction of 4-NPh by FA_{mag}@CS@CuFe and similar catalytic systems recently reported.

Author Contributions: I.K.-B.: Conceptualization, Investigation, Validation, Data curation, Writing—Original draft, review and editing, Project Administration and Funding Acquisition; I.F.: Investigation; M.M.: Investigation; A.C.S.: Investigation, Data curation, Writing—Original draft, review and editing, B.V.: Conceptualization, Validation, Data curation, Writing—Original draft, review and editing, Project Administration and Funding Acquisition; A.G.: Investigation, Validation, Review and editing; J.H.B.: Investigation, Data curation, Writing—Original draft; J.P.A.: Investigation, Data curation, Writing—Original draft; C.F.: Project Administration and Funding Acquisition, Review and editing; A.F.P.: Conceptualization, Review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by project PhotoBioTrans (FCT ref. EXPL/CTM-CTM/0790/2021, <http://doi.org/10.54499/EXPL/CTM-CTM/0790/2021>).

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Acknowledgments: The authors thank Fundação para a Ciência e Tecnologia (FCT) and Ministério da Ciência, Tecnologia e Ensino Superior (MCTES) for support of this work through the projects UIDB/50006/2020, UIDB/04683/2020, UIDP/04683/2020, UIDB/04968/2020, UIDP/04968/2020,

PTDC/EME-TED/3099/2020, INSUB (FCT ref. DRI-India/0315/2020), PINFRA/22096/NECL/2016, and authors I.K.-B. for contract funding through program DL 57/2016—Norma transitória REQUIMTE/EEC2018/14, A.C.S. for PhD scholarship Ref: SFRH/BD/131713/2017 and COVID/BD/151941/2021) J. H. Belo for his contract DL57/2016 reference SFRH-BPD-87430/2012 and A.F. P. for contract funding under the Scientific Employment Stimulus (FCT ref: 2020.01614.CEECIND/CP1596/CT0007). The authors also thank Pego power plant (Portugal) for the fly ash samples.

Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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