

Supporting Information

A magnetically separable and recyclable $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4$ /porous ruthenium nanocatalyst for the photocatalytic degradation of water-soluble aromatic amines and azo-dyes

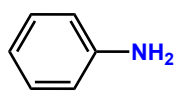
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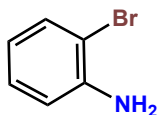
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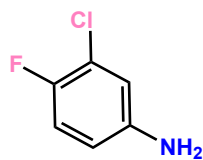
Chart S1. Chemical structure of aromatic amines used in this study.



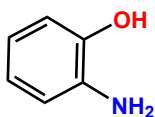
aniline



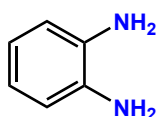
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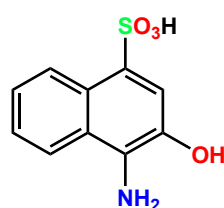
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2-aminophenol

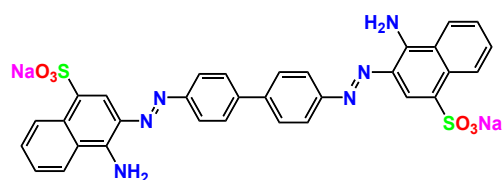


benzene-1,2-diamine

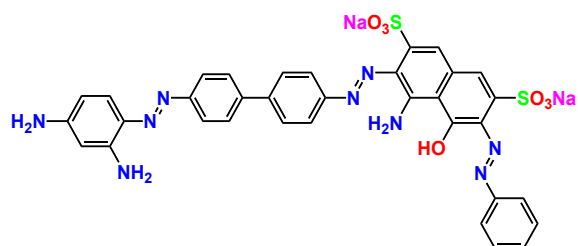


4-amino-3-hydroxynaphthalene-1-sulfonic acid

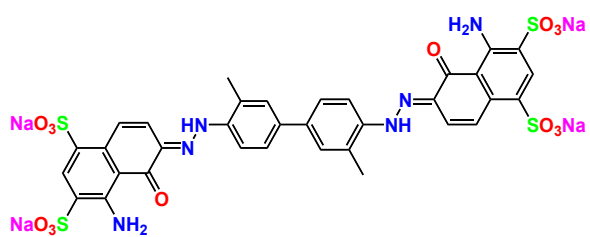
Chart S2. Chemical structure of azo dyes used in this study.



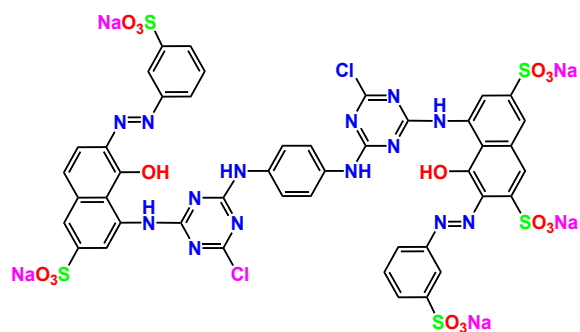
Congo Red (CR)



Chlorazol Black (CB)



Evans Blue (EB)



Reactive Red 120 (RR-120)

Table TS1. Comparison between the present and other related nanocatalysts towards removal of aromatic amines.

Sl. No.	Title	Name of the enzyme/chemical/catalyst	Aromatic amine/hydroxy compounds used	Initial conc. of Dye/Aromatic amines	Medium/Buffer/temperature./pH	% removal
1	Chemical degradation of aromatic amines by Fenton's reagent ¹	Fenton's reagent [Fe(II) + H ₂ O ₂] (100-500 mg/L)	o-dianisidine, 1-naphthylamine, 2-naphthylamine, 3,3'-dichlorobenzidine, p-anisidine, 4-chloroaniline, 2,4-iaminotoluene, o-tolidine and aniline.	0.0003 mM	pH 4.5-5.5	100
2	Removal of aromatic amines and decolourisation of azo dye baths by electrochemical treatment ²	Electrochemical treatment 20 g of diatomaceous earth (90% SiO ₂)	aniline, o-toluidine, 4-chloroaniline and 4-aminobiphenyl	300 mg/L Dye and 10mg/L Aromatic amines		90
3	Chemical coagulation and sonolysis for total aromatic amines removal from anaerobically pre-treated textile wastewater: A comparative study ³	Chemical coagulation, sonolysis Magnesium chloride aided with aluminium chlorohydrate (1800 mg /L)	Azo dyes (CR, RB 5, Disperse blue 3) Aromatic amine: Benzidine, sulfonic acid	200 mg/L	pH 7.0	85 (AAs) 52 (Decolonization of dyes)
4	Horseradish peroxidase for the removal of carcinogenic aromatic amines from water ⁴	Horseradish peroxidase (100U/L) and hydrogen peroxide(1M)	o-tolidine, and 2-naphthylamine; from Aldrich, 1-naphthylamine, 4-aminobiphenyl, pphenylazoaniline, aniline, p-toluidine	100mg/L	pH 5.0	99
5	Removal of direct azo dyes and aromatic amines from aqueous solutions using two - cyclodextrin-based polymers ⁵	b-Cyclodextrin (b-CD) (2.5 g/L)	benzidine, p-chloroaniline and -naphthalamine	0.001 mM	pH 7.0	>85
6	Removal efficiency of a calix[4]arene-based polymer for water-soluble carcinogenic direct azo dyes and aromatic amines ⁶	calix[4]arenes derivative (2.5 g/L)	Azo dyes and aromatic amines (benzidine, p-chloroaniline, -naphthalamine)	0.001 mM	pH 2.0	>90

7	A porous trimetallic Au@Pd@Ru nanoparticle system: synthesis, characterisation and efficient dye degradation and removal ⁷	Porous Au@Pd@Ru Dolochar(150g/L)	Benzidine,benzidine, aminophenol and dimethoxyaniline	4-3,4	Dye and Aromatic amines= 1mM	pH=7.0	>90
8	A Combined Process for the Degradation of Azo-Dyes and Efficient Removal of Aromatic Amines Using Porous Silicon Supported Porous Ruthenium Nanocatalyst ⁸	Porous silicon@porous ruthenium(8 mL in 1 L) and H ₂ O ₂ (1M) (amount of Ru ≈ 3.39 ppm)	Azo dyes and aromatic amines		Dye and Aromatic amines= 1mM	pH=5.0	46-99
9	A magnetically separable and recyclable porous Ruthenium nanocatalyst for the photocatalytic degradation of water-soluble aromatic amines and azo-dyes ^{Present Work}	80 mg/L 100 W, visible LED light (amount of Ru ≈ 3.44 ppm)	Azo dyes and aromatic amines		Dye(200mg /L) Aromatic amines (100-200mg/L)	pH 7.0	The percentage varies from 67-99 And the catalyst is recyclable several times

Table TS2. Catalytic reduction of azo dyes in presence of *g*-C₃N₄/Fe₃O₄/*p*-RuNP nanocomposites and NaBH₄.

Sr. No	Name of the dye/amine	Concentration	Catalyst (per 10 mL)	Time of reaction	Removal efficiency
1	CR	5 mg/L	200 μ L	1 h	100 %
2	CB	5 mg/L	200 μ L	1 h	100 %
3	EB	5 mg/L	200 μ L	18 h	100%
4	RR-120	5 mg/L	200 μ L	2 h	98%

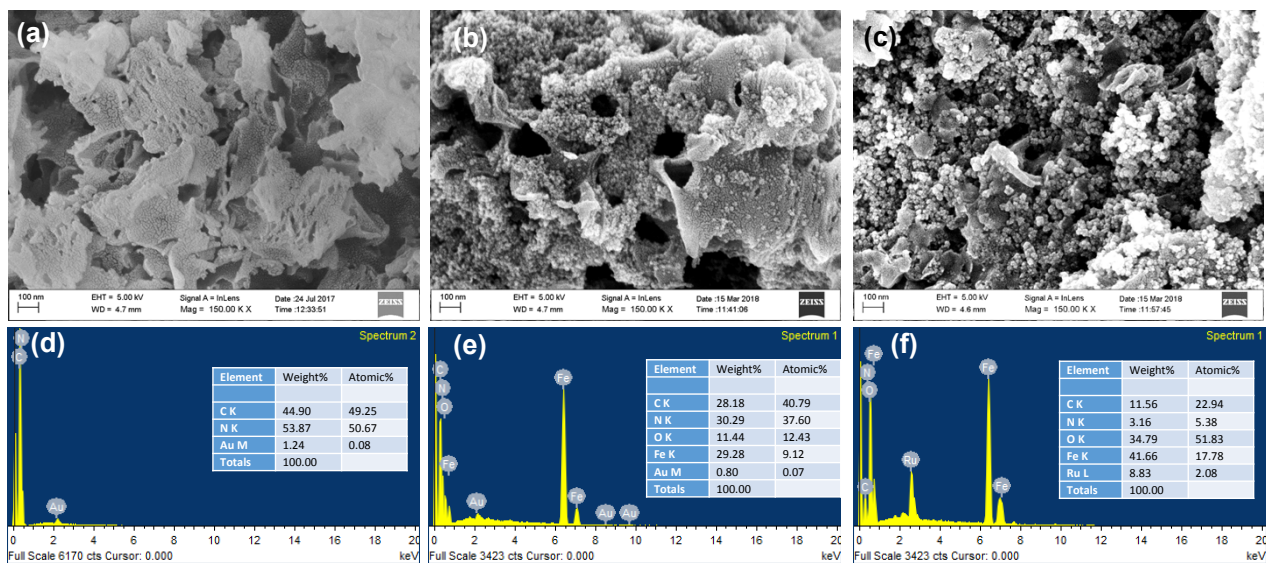


Figure S1. FE-SEM images of (a) $g\text{-C}_3\text{N}_4$ nanosheet, (b) $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4\text{NP}$ and (c) $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocomposites and (d-f) their corresponding EDS spectra, respectively.

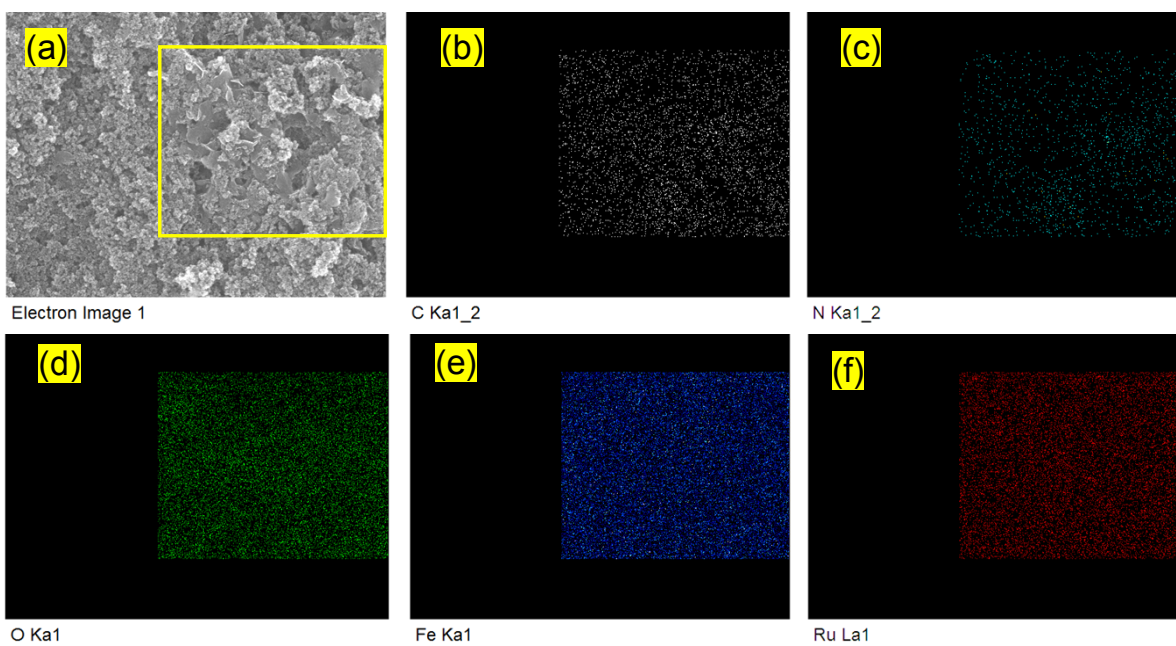


Figure S2. SEM image (a) and mapping of (b) elemental C, (c) elemental N, (d) elemental O (e) elemental Fe and (f) elemental Ru of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocomposite.

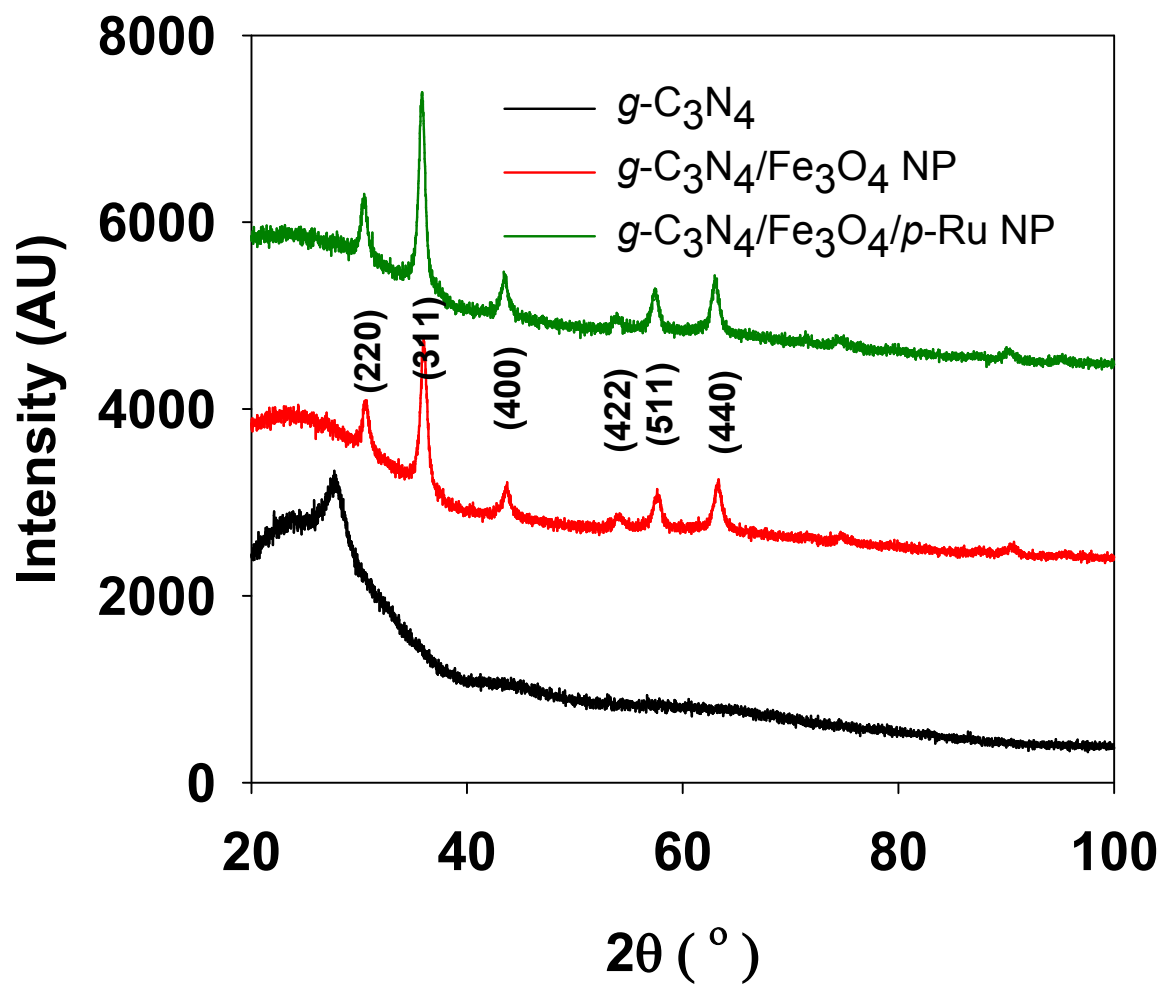


Figure S3. Powder XRD patterns of *g*-C₃N₄ nanosheet, *g*-C₃N₄/Fe₃O₄NP and *g*-C₃N₄/Fe₃O₄/*p*-RuNP nanocomposites.

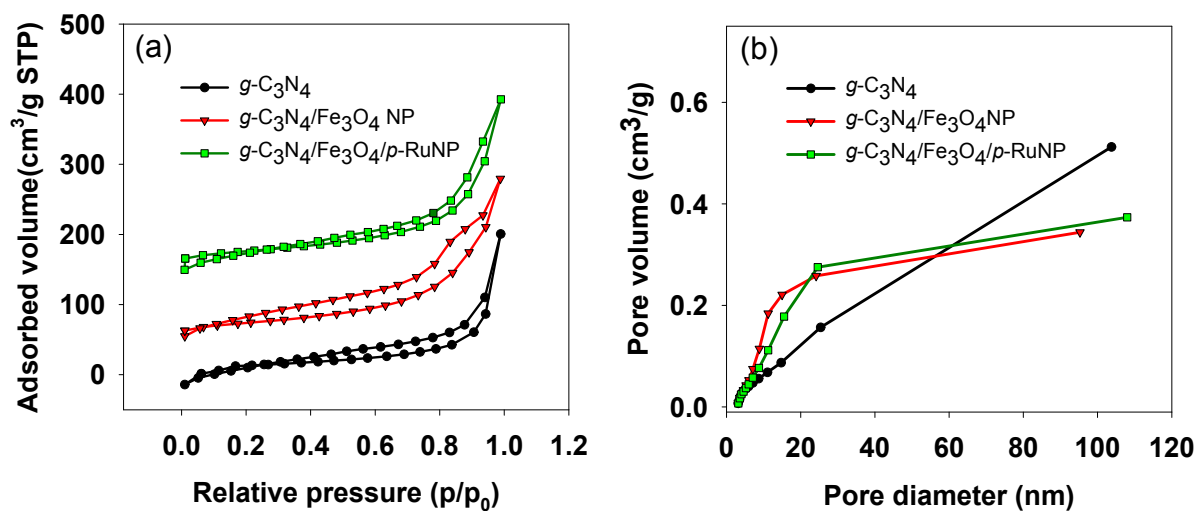


Figure S4. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4\text{NP}$ and $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocomposites.

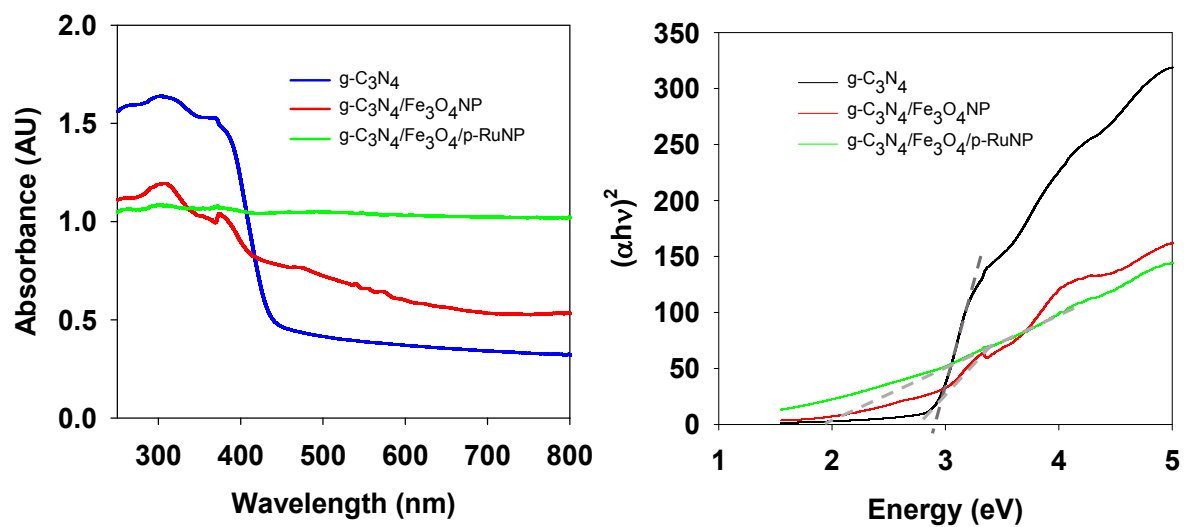


Fig. S5. (a) UV-Vis DRS spectra and (b) Tauc plot of $g\text{-C}_3\text{N}_4$, $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4\text{NP}$ and $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$.

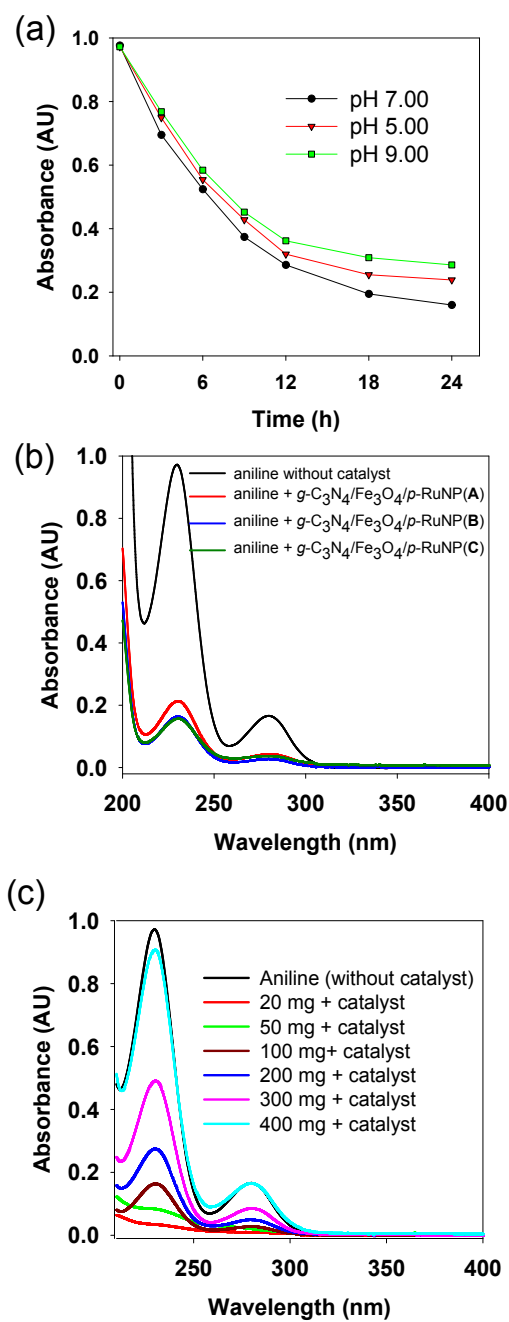


Figure S6. Photocatalytic degradation of aniline (100 mg/L) by $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ at (a) different pH (b) with varying ruthenium concentration and (c) varying aniline concentration after 24 h under LED.

* catalysts were taken 80 mg containing 3.44 ppm of Ru^0 ; The catalysts **A**, **B** and **C** were prepared by taking 5 mM, 10 mM and 20 mM $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$.

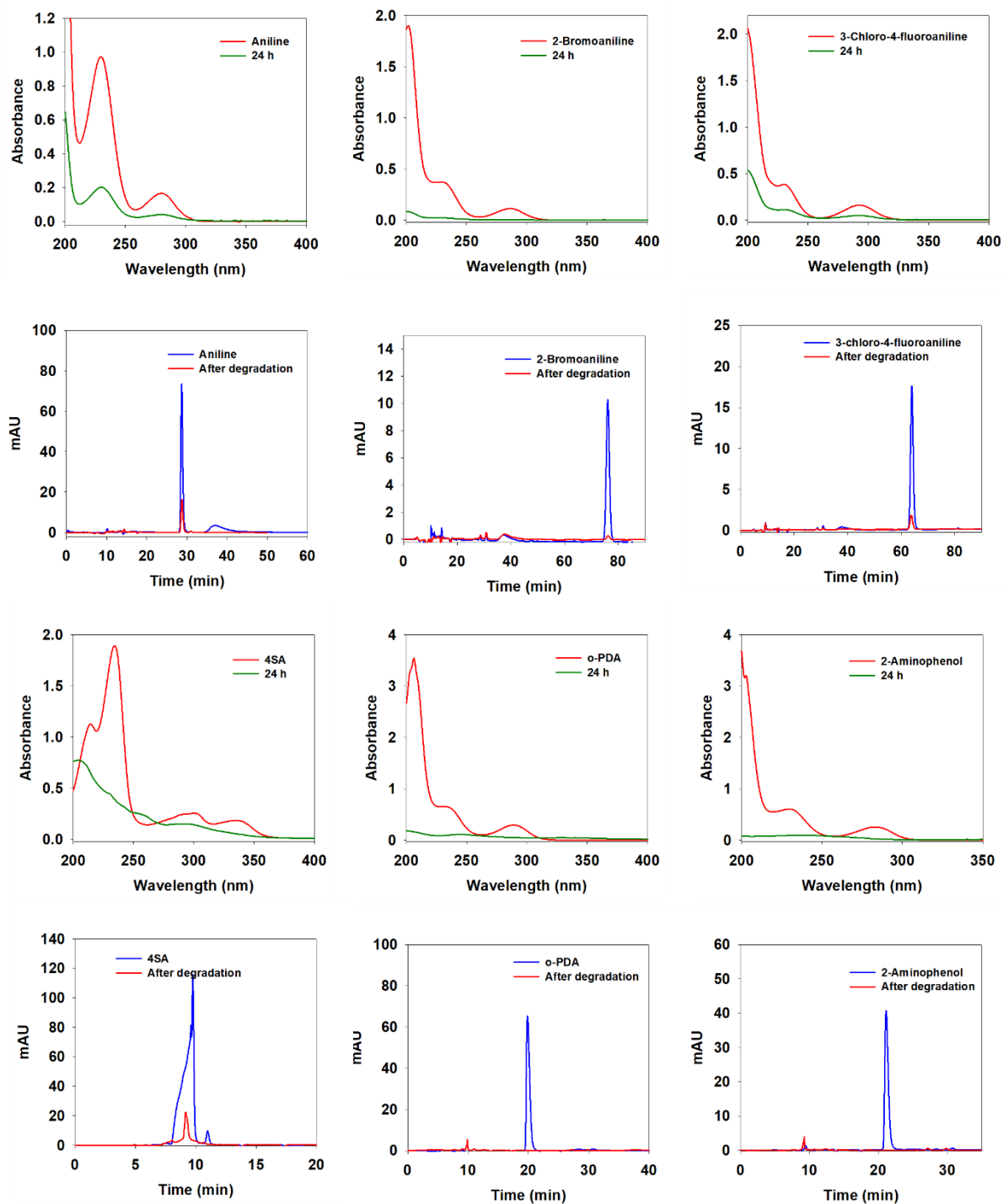


Figure S7. UV-Vis spectra and HPLC of aromatic amines (100 mg/L) and after degradation using visible light at pH 7.0 in presence of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocatalyst (80 mg/L).

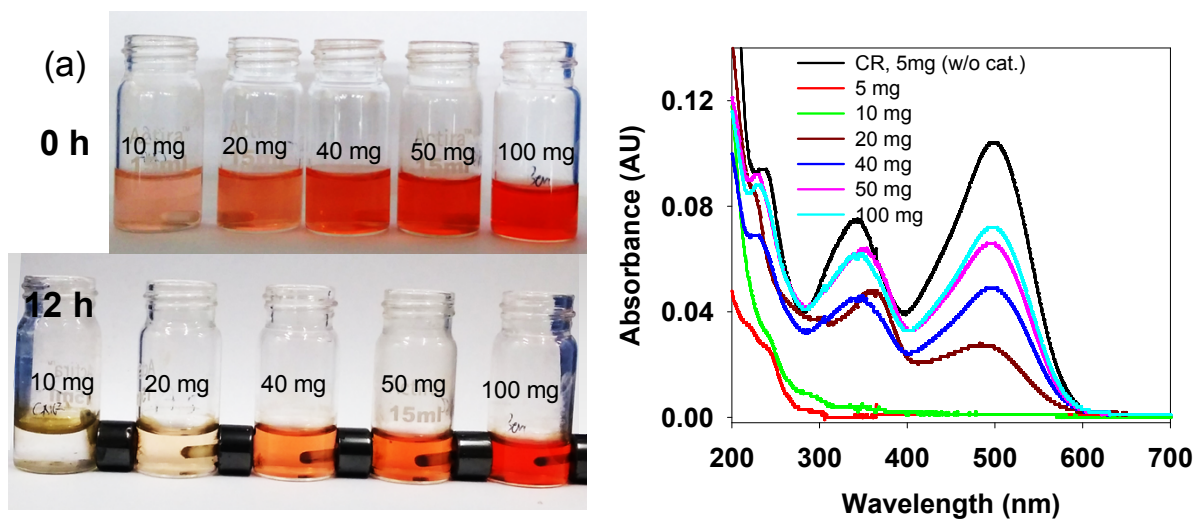


Figure S8. Photograph of CR dye of varying concentration (a) before and (b) after photodegradation (12 h) by $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocomposite and (c) the corresponding UV-Vis spectra.

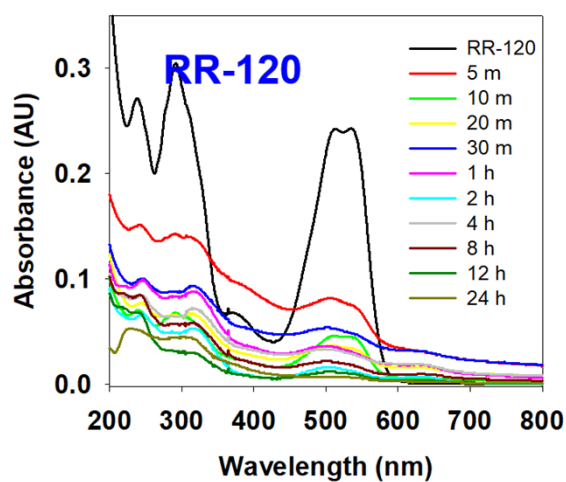
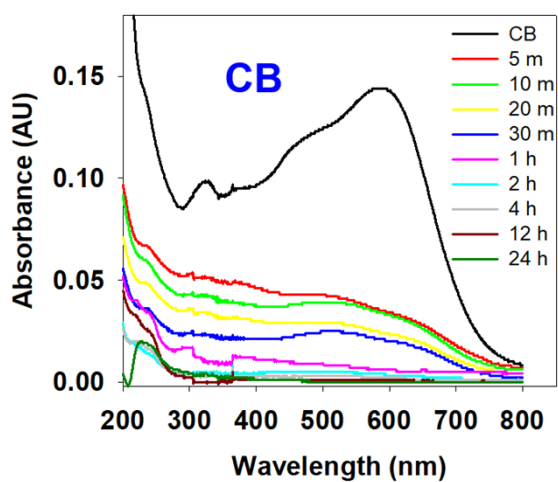
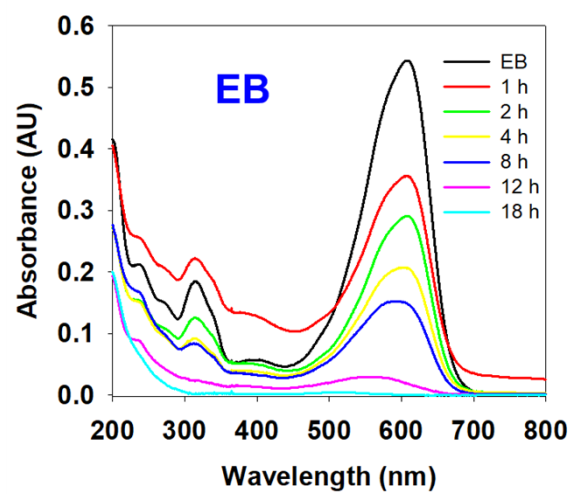


Figure S9. UV-Vis spectra of degradation of various azo dyes (5 mg/L) under LED in presence of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocatalyst (80 mg/L).

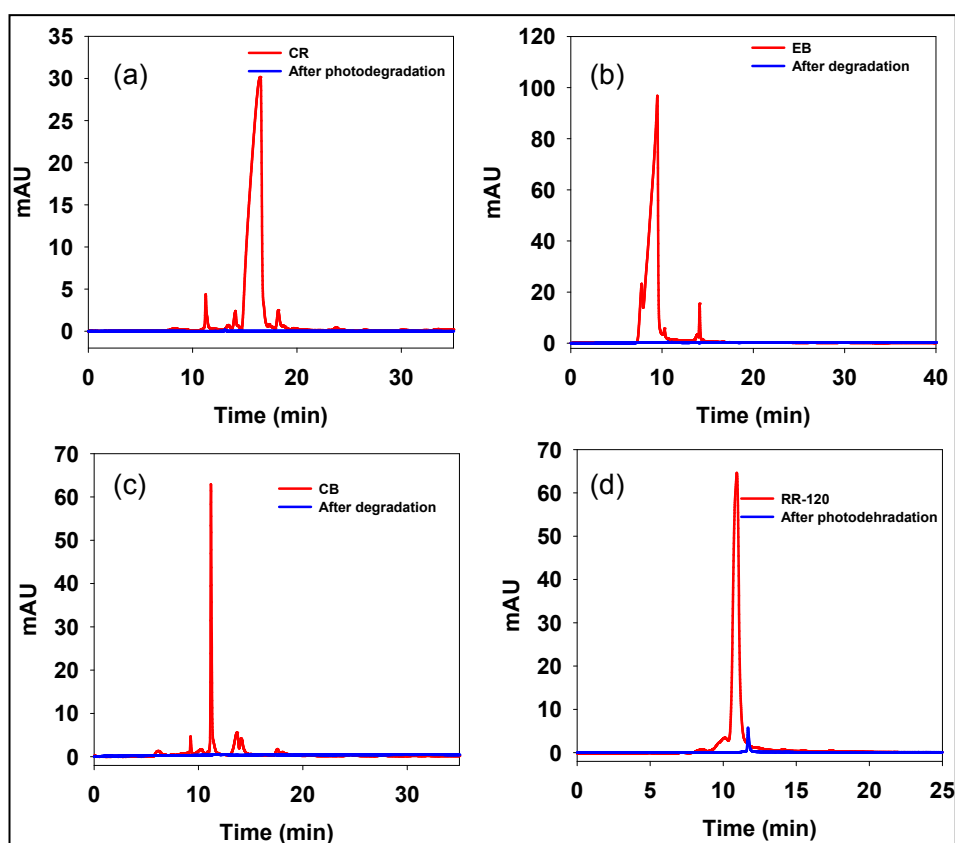


Figure S10. HPLC of azo-dyes (5 mg/L) after and before the degradation using visible light at pH 7.0 in presence of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ (80 mg/L) nanocatalyst.

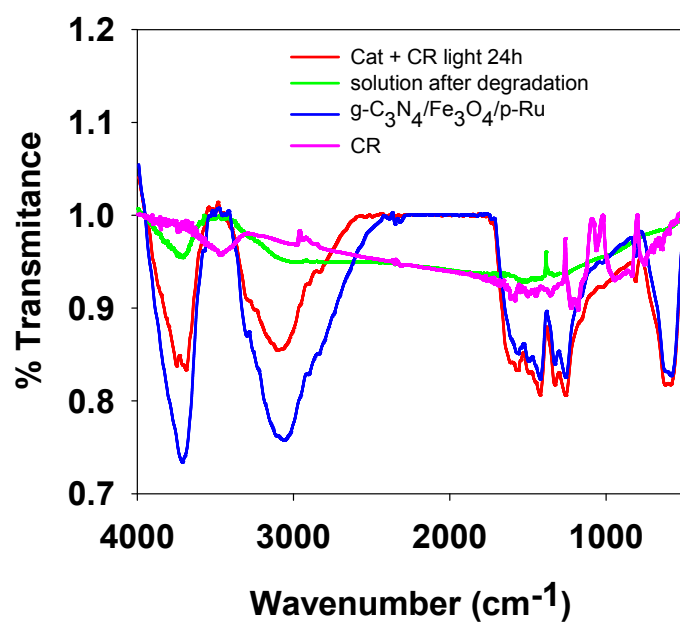


Figure S11. FTIR spectra of CR, *g*-C₃N₄/Fe₃O₄/*p*-RuNP nanocatalyst before and after photo-degradation of CR and the solution after complete degradation of CR.

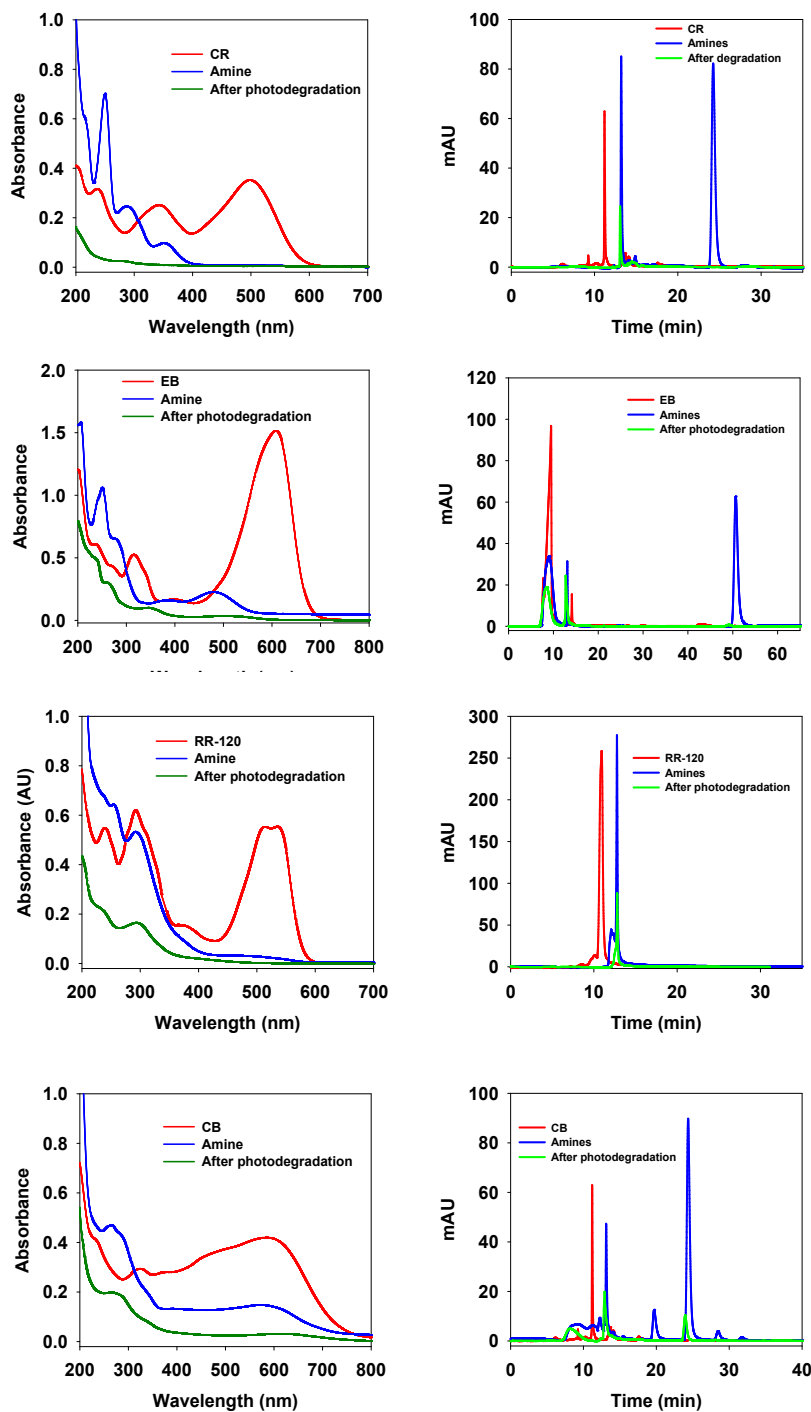


Figure S12. (a, c, e and g) UV-Vis spectra of azo dyes before (i), after(ii) reduction and after photo-degradation (iii); (b, d, f and h) HPLC of aromatic amines of reduced dyes (200 mg/L) after and before degradation using visible light at pH 7.0 in presence of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocatalyst (80 mg/L).

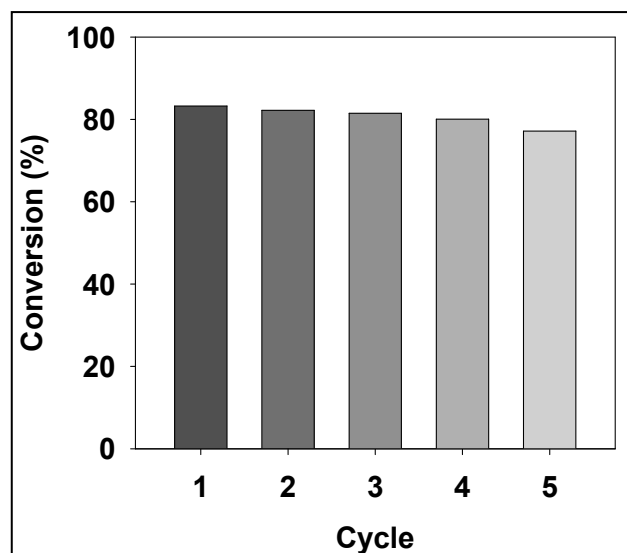


Figure S13. Reusability of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocatalyst towards aniline (100 mg/L) degradation under visible (LED) light.

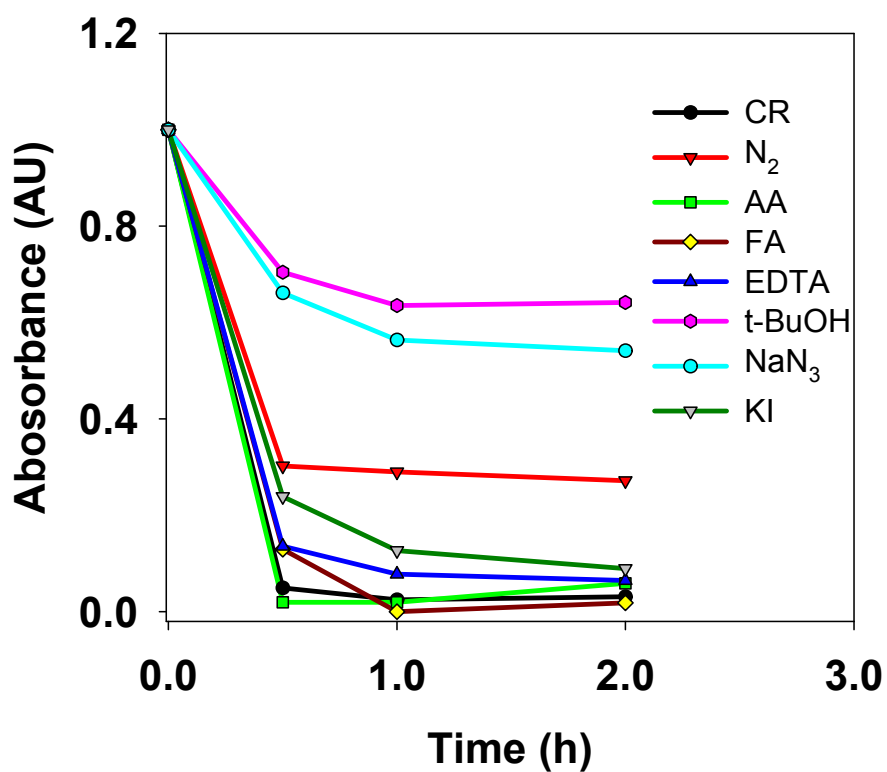


Figure S14. (a) UV-Vis spectra of congo red (CR) after treatment of $g\text{-C}_3\text{N}_4/\text{Fe}_3\text{O}_4/p\text{-RuNP}$ nanocatalyst in the presence of different radical scavengers under LED light.

References:

- 1 I. Casero, D. Sicilia, S. Rubio and D. Pérez-Bendito, *Water Res.*, 1997, **31**, 1985–1995.
- 2 V. López-Grimau, M. Riera-Torres, M. López-Mesas and C. Gutiérrez-Bouzán, *Color. Technol.*, 2013, **129**, 267–273.
- 3 A. Kumar Verma, P. Bhunia, A. K. Verma and R. R. Dash, *Adv. Environ. Res.*, 2014, **3**, 293–306.
- 4 A. M. Klibanov and E. D. Morris, *Enzyme Microb. Technol.*, 1981, **3**, 119–122.
- 5 E. Yilmaz, S. Memon and M. Yilmaz, *J. Hazard. Mater.*, 2010, **174**, 592–597.
- 6 E. Akceylan, M. Bahadir and M. Yilmaz, *J. Hazard. Mater.*, 2009, **162**, 960–966.
- 7 A. Sahoo, S. K. Tripathy, N. Dehury and S. Patra, *J. Mater. Chem. A*, 2015, **3**, 19376–19383.
- 8 A. Sahoo and S. Patra, *ACS Appl. Nano Mater.*, 2018, **1**, 5169–5178.