

Supporting information

Fabrication of a recyclable magnetic halloysite based cobalt nanocatalyst for the efficient degradation of bisphenol A and malachite green.

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1. Experimental

1.1. Chemical and methods

Halloysite nanotubes (HNTs), 3-aminopropyltriethoxysilane (APTES) (>97%), 2-benzoylpyridine (2-BPy), Bisphenol A and Malachite Green were obtained from Sigma Aldrich and TCI chemicals respectively. Ferrous sulphate, ferric sulphate and cobalt chloride hexahydrate were commercially acquired from Sisco Research Laboratory (SRL). All other starting materials and reagents were purchased from Spectrochem Pvt Ltd and are of analytical grade.

1.2. Instrumentation

To gain insights into the functionalization, composition, magnetization, crystallinity and morphology, the newly designed nanocomposites were characterized by using distinctive physico-chemical techniques. P-XRD analysis of all the samples was conducted by using Rigaku XRD Miniflex 600/600-C in 2θ range of $5-80^\circ$ ($\lambda = 0.15405$ nm, 40 kV, 40 mA) at a scanning range of 3° min^{-1} . FTIR spectra were collected through KBr pellet technique from Perkin-Elmer Spectrum II spectrometer within a scanning range of $4000-400 \text{ cm}^{-1}$ at a resolution of 1 cm^{-1} at room temperature. Moreover, by employing Tekmar Sonic Disruptor TM300 sonicator dispersion of agglomerated nanoparticles was carried out. With the aid of EV-9, Microsense, ADE, vibrating sample magnetometer, the magnetic properties of modified and unmodified nanocomposites were studied under atmospheric conditions. To validate the metalation of Co(II)@2-BPy@APTES@MHNTs, energy dispersive X-ray fluorescence (ED-XRF) analysis was executed by Fischerscope X-ray XAN-FAD BC apparatus. In addition, XPS analysis was performed on Thermo Fischer K-alpha+ spectrometer equipped with a monochromator and a 128 channel CCD detector plate. The shape and morphology of synthesized nanocomposites were determined *via* field emission scanning electron microscopy that was performed on Hitachi-SU 8010 FE-SEM. For this, the well-grounded and dried sample was mounted on carbon-taped clean metal stubs which was then coated with gold to make them conductive through a sputter coater. In addition, EDS equipped with FE-SEM was conducted to scrutinize the elemental composition. Apart from that, elemental mapping images of synthesized Co(II)@2-BPy@APTES@MHNTs were acquired on Zeiss EVO40. Besides, to acquire the information pertaining to shape and size, Transmission electron microscopy (TEM) analysis was carried out using Thermo Scientific, Talos instrument. Furthermore, during the

degradation process change in absorption of pollutants was measured by Lab India Analytical UV-3092 UV-Vis spectrophotometer. Besides, F-4700 fluorescence spectrophotometer was utilized to record the fluorescence spectra. Moreover, the N₂ adsorption-desorption isotherm was measured using NOVA touch 4LX [s/n:1050020628] surface area analyzer instrument at liquid nitrogen temperature (77.35 K). The specific surface area was obtained by Brunauer–Emmett–Teller (BET) equation and the pore width distribution was calculated using Density Functional Theory (DFT) method.

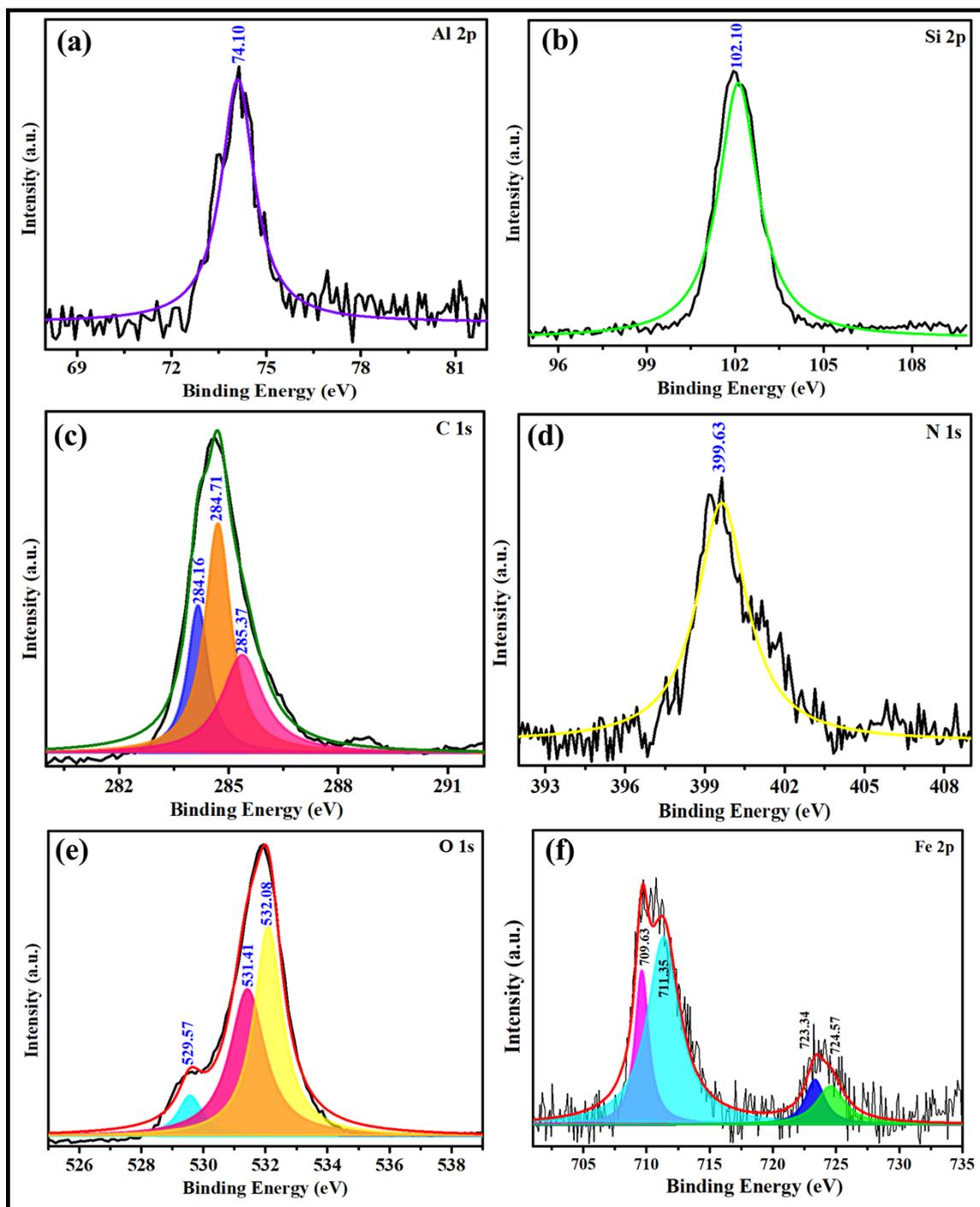


Fig. S1 Core level XPS spectra of (a) Al 2p (b) Si 2p, (c) C 1s (d) N 1s (e) O 1s and (f) Fe 2p.

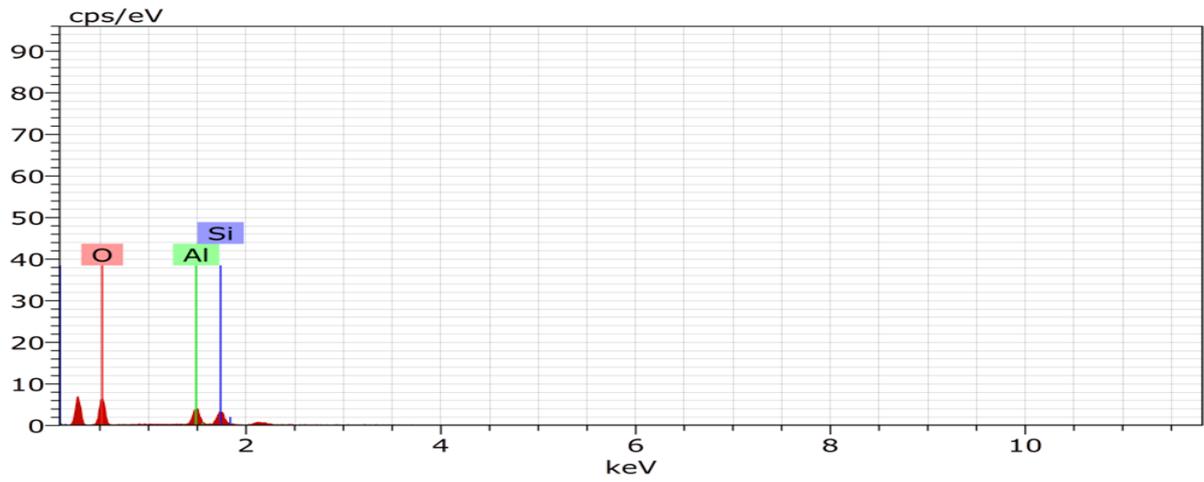


Fig S2. EDS spectrum of HNTs.

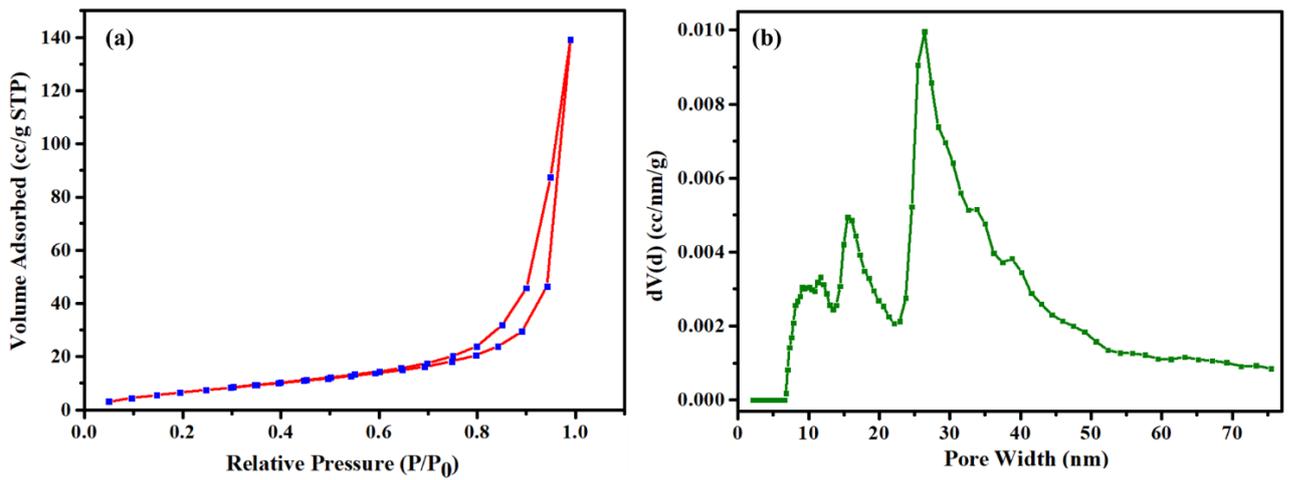


Fig S3. (a) N₂ adsorption-desorption isotherms and (b) the pore width distribution curve obtained using the DFT method.

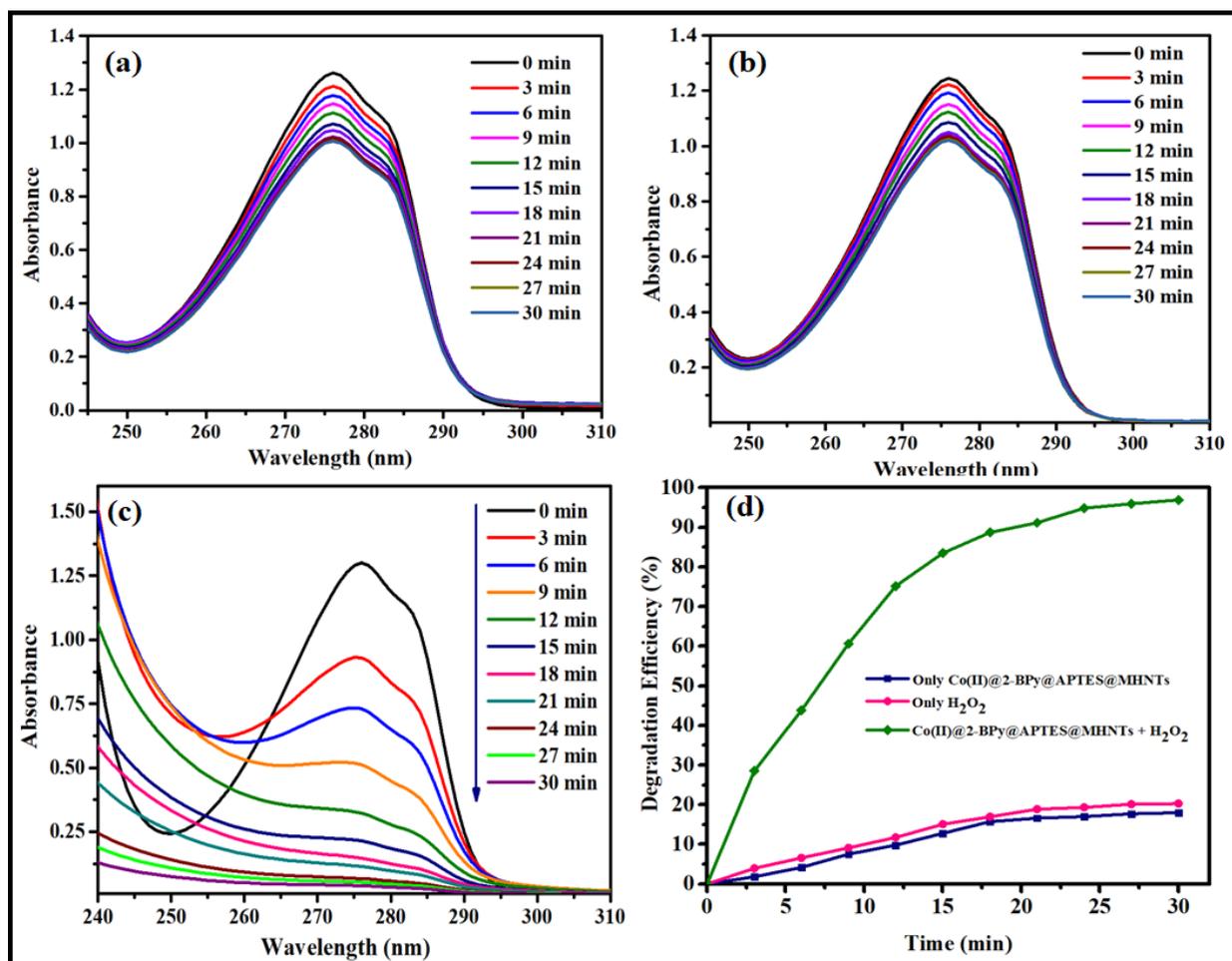


Fig. S4 UV-Vis plot of BPA (68 mg/L), 30 min, r.t., (a) without catalyst (b) oxidant free (c) both catalyst (8 mg) and oxidant (0.5 mL) (d) graph plot of degradation efficiency (%) vs time (min).

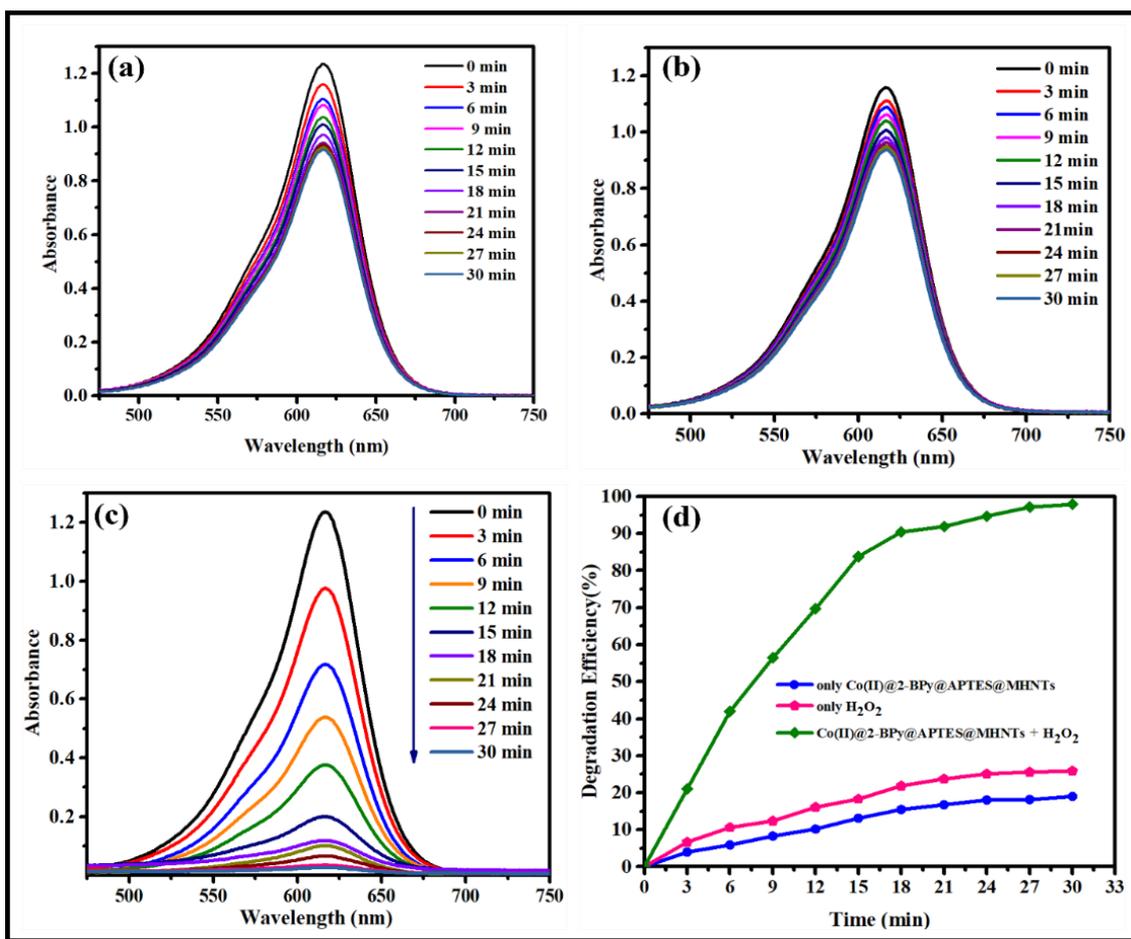


Fig. S5 UV-Vis plot of MG (36 mg/L), 30 min, r.t., (a) without catalyst (b) oxidant free (c) both catalyst (10 mg) and oxidant (0.8 mL) (d) graph plot of degradation efficiency (%) vs time (min).

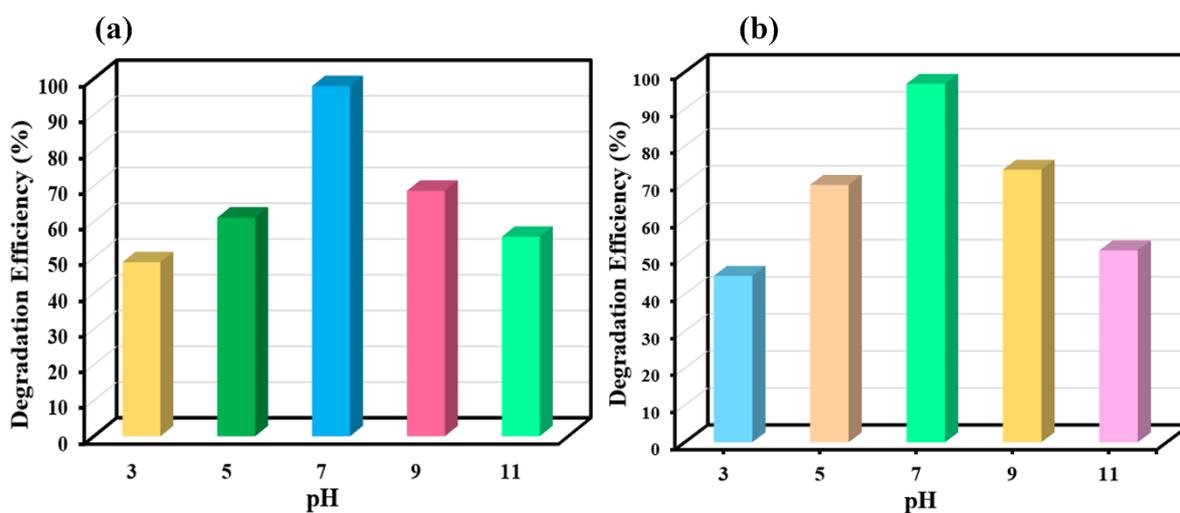


Fig. S6 Effect of pH on the catalytic degradation of (a) 50 mL of BPA stock solution (68 mg/L), 0.5 mL of H₂O₂, 8 mg of catalyst, pH = x, 30 min, r.t., $\lambda_{\text{max}} = 276$ nm and (b) Reaction conditions: 50 mL of MG stock solution (36 mg/L), 0.8 mL of H₂O₂, 10 mg of catalyst, pH = x, 30 min, r.t., $\lambda_{\text{max}} = 617$ nm.

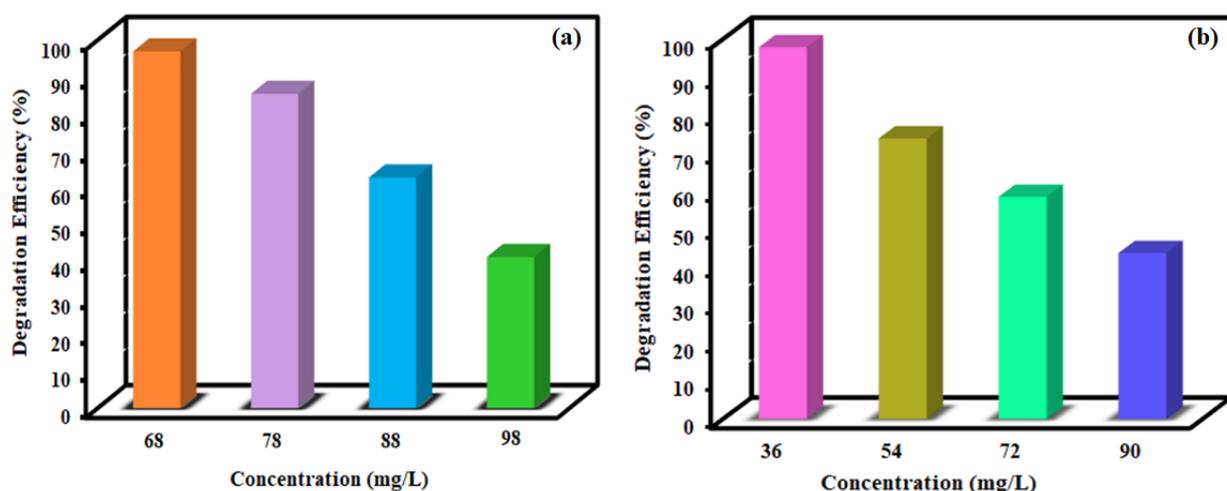


Fig. S7 The effects of the initial concentrations of contaminants present on the catalytic degradation of (a) BPA under optimized conditions (reaction conditions: 50 mL stock solution, 0.5 mL H₂O₂, 8 mg catalyst, 30 min, r.t., $\lambda_{\max} = 276$ nm) and (b) MG (50 mL stock solution, 0.8 mL H₂O₂, 10 mg catalyst, 30 min, r.t., $\lambda_{\max} = 617$ nm).

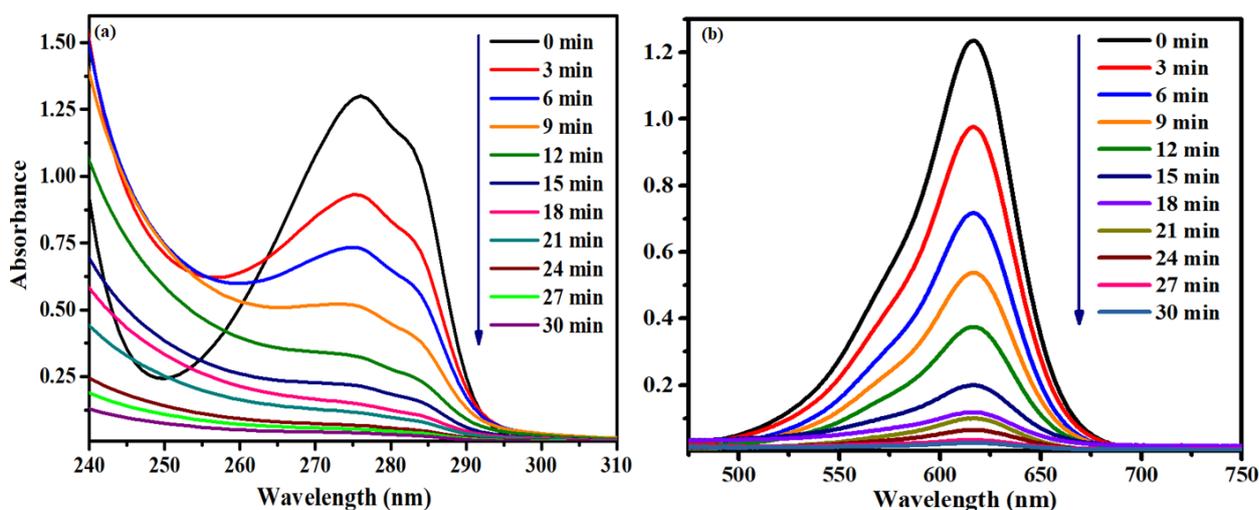


Fig. S8 (a) UV-Vis plot of degradation of (a) BPA under optimized conditions (reaction conditions: 50 mL stock solution (68 mg/L), 0.5 mL H₂O₂, 8 mg catalyst, 30 min, r.t., $\lambda_{\max} = 276$ nm) (b) UV-Vis plot of degradation of MG under optimized reaction conditions (50 mL stock solution (36 mg/L), 0.8 mL H₂O₂, 10 mg catalyst, 30 min, r.t., $\lambda_{\max} = 617$ nm).

TON and TOF is calculated by: [1]

$$\text{TON} = \left[\frac{\text{moles of substrate}}{\text{moles of catalyst}} \right] \times \text{Degradation efficiency (\%)}$$

$$\text{TOF} = \text{TON}/\text{time (h)}$$

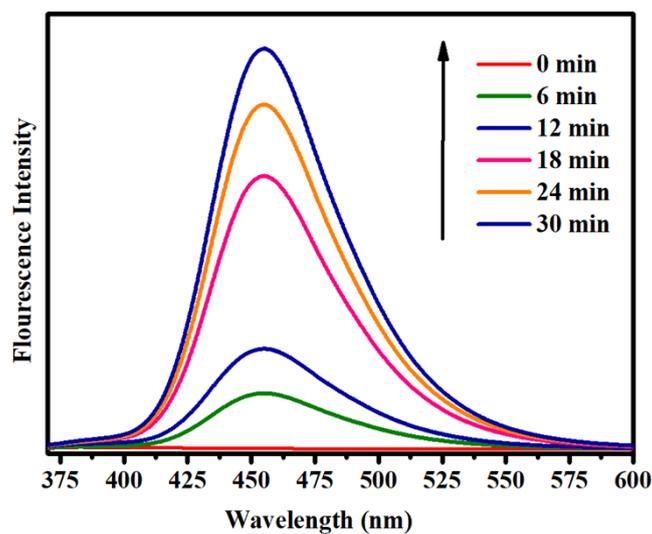


Fig. S9 Fluorescence spectral changes of coumarin solution (1×10^{-3} mol L⁻¹) in the presence of 10 mg of catalyst and 0.8 mL of H₂O₂.

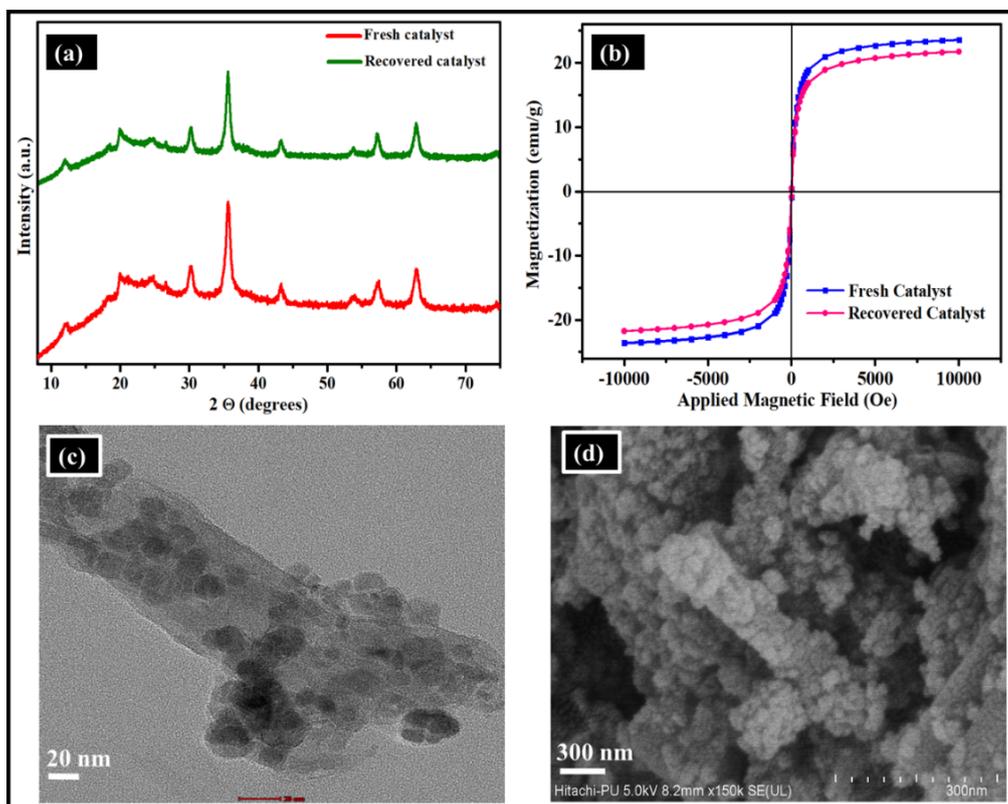
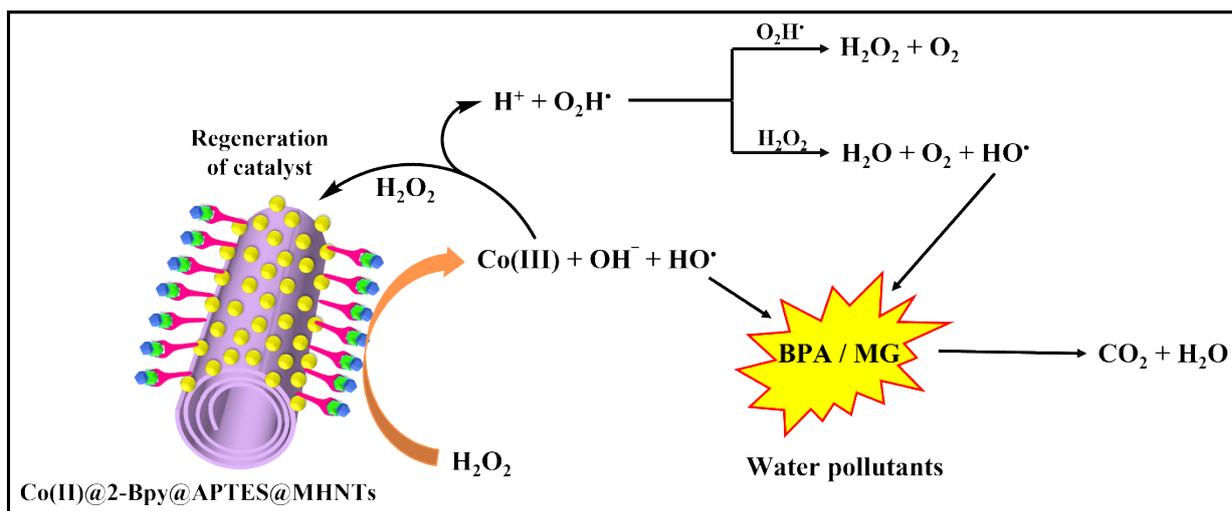


Fig. S10 (a) XRD, (b) VSM, (c) TEM and (d) FE-SEM analyses of the recovered catalyst after six consecutive cycles.



Scheme S1. Proposed mechanism for the degradation of organic pollutants.

Table S1 Comparison of the catalytic potency of the Co(II)@2-BPy@APTES@MHNTs with literature precedents for the degradation of BPA and MG.

BPA				
S.No	Catalyst & catalyst amount	Reaction conditions & time (min)	Degradation efficiency (%)	References
1.	PVP-Ag, 10 mg/L	BPA = 0.1 mol/L, H_2O_2 (0.2 mM), pH = 7, 480 min	95.5	13
2.	Au/SRAC, 125 mg/L	BPA = 113 ppm, H_2O_2 (530 ppm), pH = 3, 720 min	90.91	14
3.	Fe_3O_4 /MWCNT, 50 mg/L	BPA = 0.3mM, H_2O_2 (1.2 mM), pH = 3, 360 min	97	15
4.	TNT/CNT/ Fe_3O_4 , 100 mg/L	BPA = 50 mg/L, H_2O_2 (2.5 g/L), pH = 6.30, 240 min	>99	16
5.	NZVI@bentonite, 0.01 g	BPA = 90 mg/L, H_2O_2 (0.7 mL), pH = 3, 290 min	>99	17
6.	M-nZVI-Da, 0.2 g/L	BPA = 50 mg/L, H_2O_2 (20 mM), pH = 5.75, 1440 min	100	18
7.	GS-Fe-NPs, 0.30 g/L	BPA = 25 mg/L, H_2O_2 (1.0 mol/L), pH = 6.9, 150 min	96.4	19
8.	Cu/TUD-1, 0.1 g	BPA = 100 ppm, H_2O_2 (90 mM), 180 min	90.4	20
9.	$\text{LaCu}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$, 1.0 g/L	BPA = 20 mg/L, H_2O_2 (12 mM), pH = 6, 120 min	92.1	21
10.	CuFeO_2 , 1.0 g/L	BPA = 0.1 mmol/L, H_2O_2 (20 mM), pH = 5, 120 min	> 99	22
11.	Cu-doped AlPO_4 , 1.0 g/L	BPA = 25 mg/L, H_2O_2 (10 mM), pH = 5, 180 min	92	23
12.	Fe_3O_4 @Alg-Fe, 0.7 g/L	BPA = 10 mg/L, H_2O_2 (30 mM), pH = 7, 60 min	52	24
13.	Co(II)@2-BPy@APTES@MHNTs, 8 mg	BPA = 68 mg/L, H_2O_2 (0.5 mL), pH = 7, 30 min	96.83	Present Work

MG				
S.No	Catalyst & Catalyst amount	Reaction conditions & time (min)	Degradation efficiency (%)	References
1.	IO-NPs-Lc-Hap, 1 g/L	MG = 100 mg/L, H ₂ O ₂ (5 mL), pH = 3.3, 240 min	100	25
2.	EDTA-Fe(III), 500 μM	MG = 10 μM, H ₂ O ₂ (20 mM) pH = 7, 60 min	100	26
3.	MnFe ₂ O ₄ , 30 mg	MG = 50 mg/L, H ₂ O ₂ (500 μL), pH = 7, 60 min	100	27
4.	Porous Manganese Oxide Octahedral Molecular Sieve (OMS-2), 7.5 mg	MG = 5 ppm, H ₂ O ₂ (2mL), 60 min	99.00	28
5.	WM-hydrochar, 0.5 g/L	MG = 100 ppm, H ₂ O ₂ (7.96 mM), pH = 6.8, 60 min	94.10	29
6.	DMSNs, 30 mg	MG = 500 mg/L, H ₂ O ₂ = 30 mM, 70 min	93.00	30
7.	Fe(ClO ₄) ₂ , 3.6×10 ⁻⁵ mol dm ⁻³	MG = 1.08 × 10 ⁻⁵ mol dm ⁻³ , H ₂ O ₂ (8.82 × 10 ⁻⁴ mol dm ⁻³), pH = 2.5-2.8, 300 min	98.00	31
8.	MnO ₂ nanosheets, 0.5 g/L	MG = 50 mg/L, pH = 5.5-6.6, 60 min	99.00	32
9.	Fe NPs, 0.3 g/L	MG = 50 mg/L, H ₂ O ₂ = 7.4mM, pH = 4, 60 min	82.80	33
10.	Laccase immobilized Fe ₃ O ₄ @C- Cu ²⁺ NPs, 436 mg/g	MG = 200 mg/L, pH = 4.5, 120 min	99.00	34
11.	Co(II)@2- BPy@APTES@MHNTs, 10 mg	MG = 36 mg/L, H₂O₂ = 0.8 mL, pH = 7, 30 min	97.89	Present Work

Reference

1. T. Günay and Y. Çimen, Degradation of 2,4,6-trichlorophenol with peroxymonosulfate catalyzed by soluble and supported iron porphyrins. *Environ. Pollut.*, 2017, **231**, 1013-1020.