

Journal Name

ARTICLE

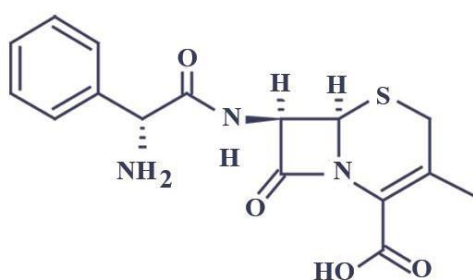


Fig. SI1. Scheme of cephalexin monohydrate

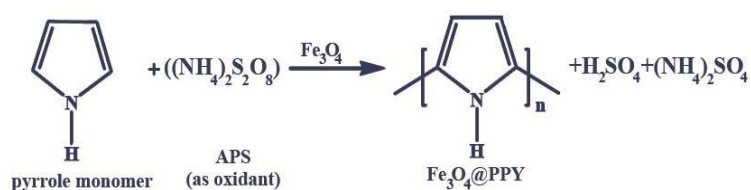


Fig. SI2. Mechanism of formation polypyrrole

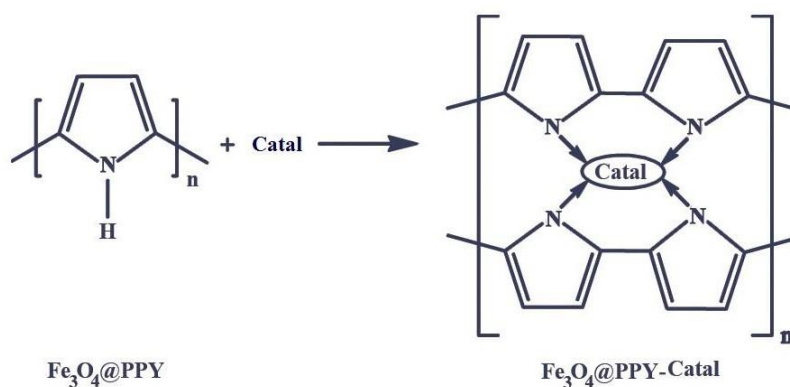


Fig. SI3. Mechanism immobilization of catalyst on polypyrrole magnetically

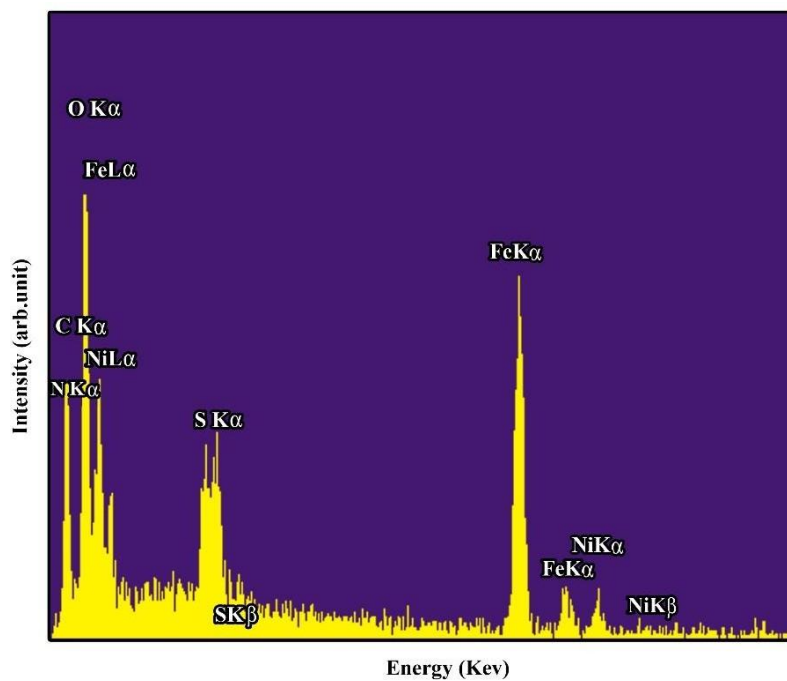


Fig. S14. EDAX spectra Fe₃O₄@PPY-NiO-NiS

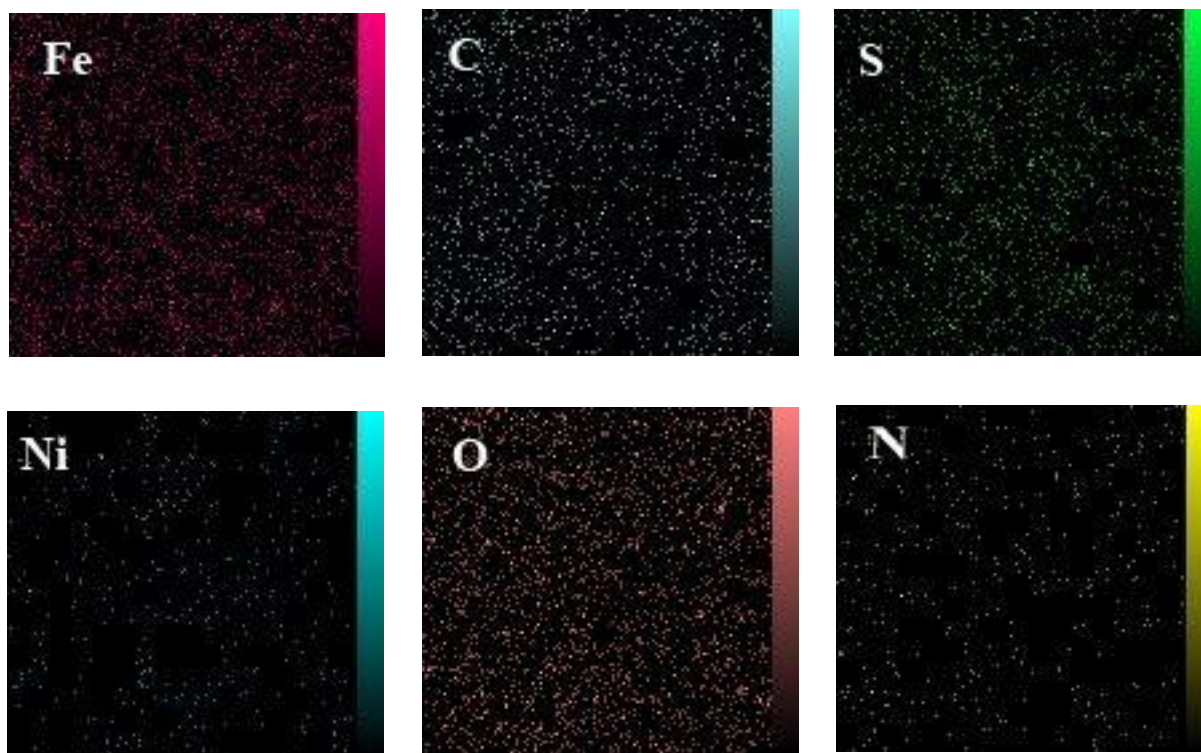


Fig. SI5. Map of elements abundance in sample $\text{Fe}_3\text{O}_4@\text{PPY-NiO-NiS}$

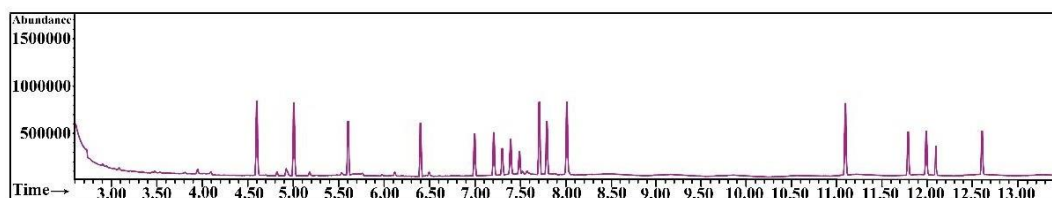
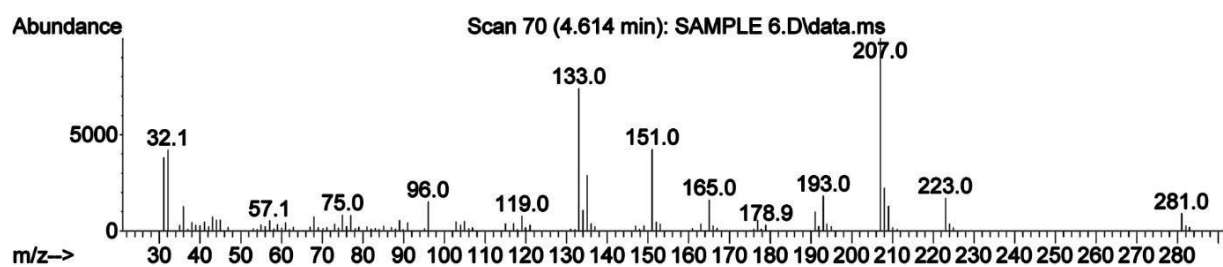
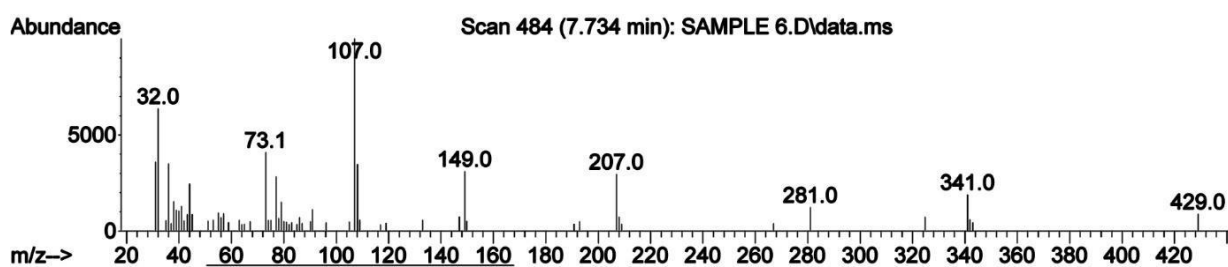
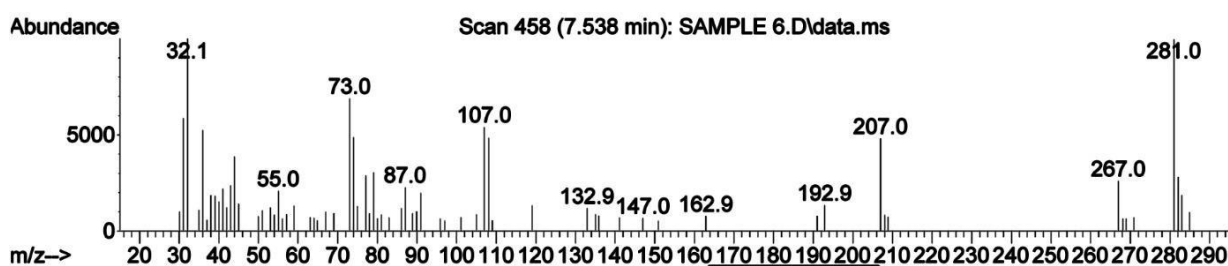
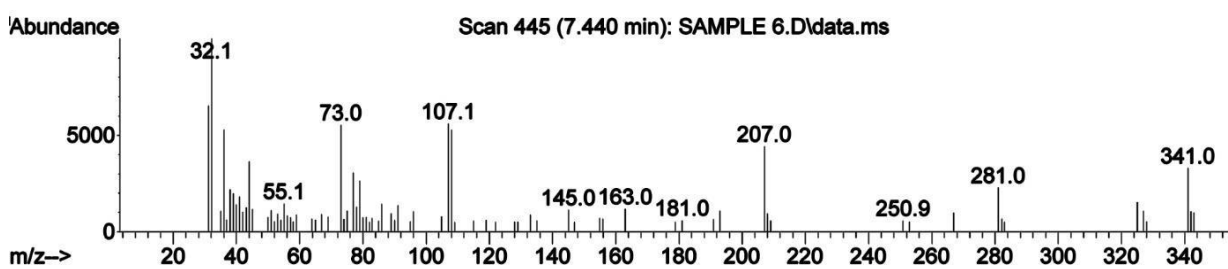
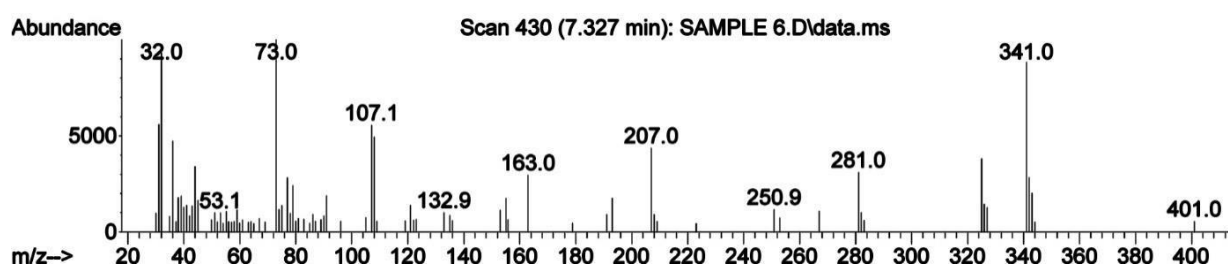
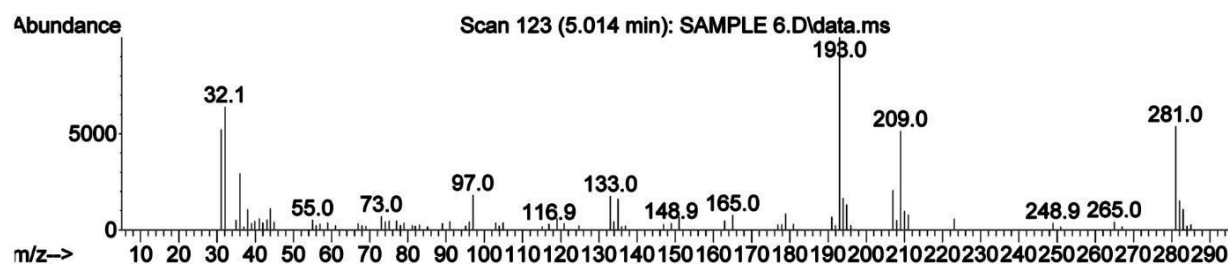


Fig. SI6. GC spectrum of cephalixin after degradation by $\text{Fe}_3\text{O}_4@\text{PPY-NiO-NiS}$





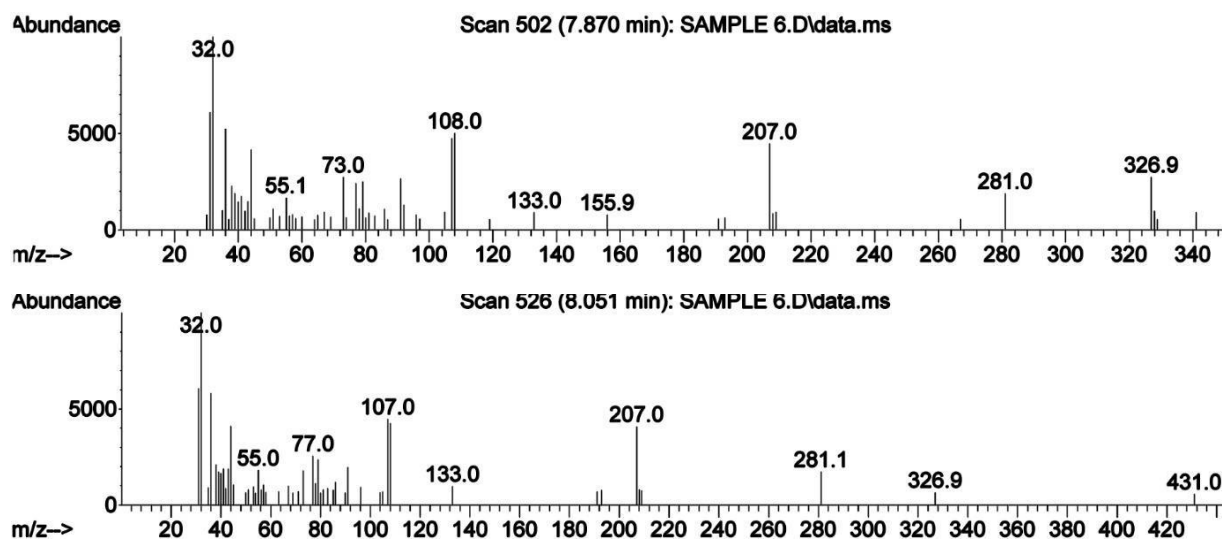


Fig. S17. MS spectrum of cephalixin degradation products arranged by RT.

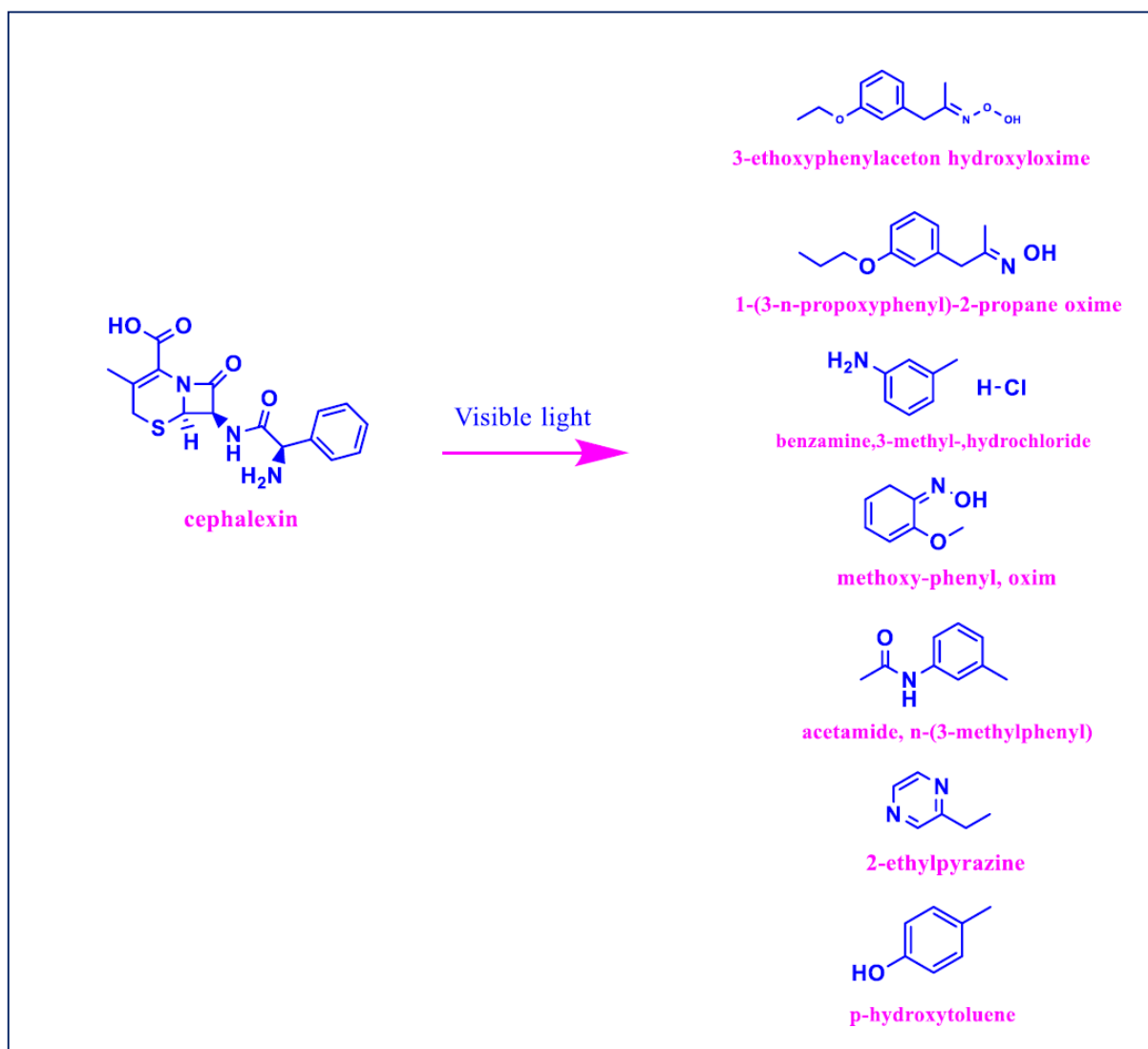


Fig. S18. Schematic of degradation products

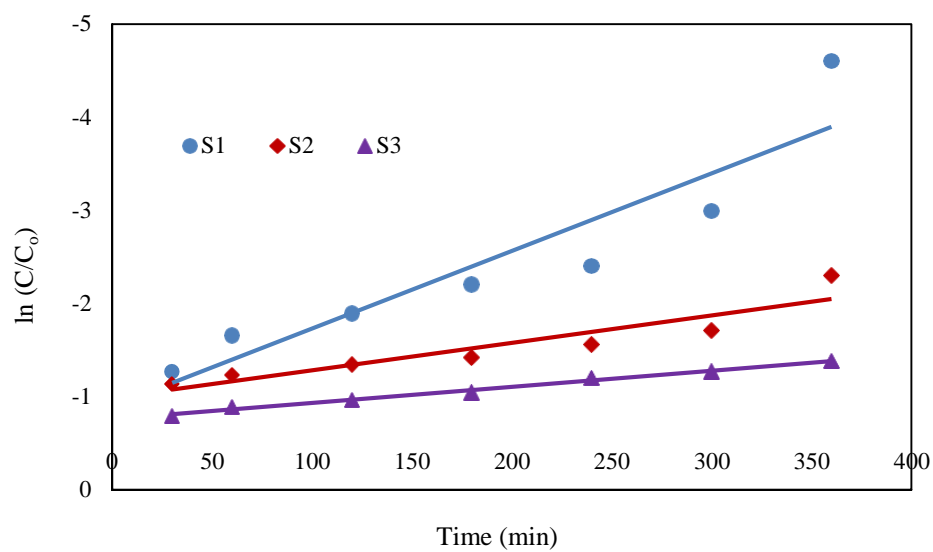


Fig. S19. Linear plots of Pseudo-first-order kinetic model

Table SI1. Synthesis condition of Fe₃O₄@PPY

No	Fe ₃ O ₄ (g)	APS (g)	pyrrole (ml)	Magnetic property
1	0.5	5.0	1.5	Not observed
2	1.0	5.0	1.5	Not observed
3	1.0	2.5	1.5	Not observed
4	1.0	0.5	0.5	Observed

Table SI2. Statistical parameters

Parameters	Results
Working Range	10-1000 mg.L ⁻¹
Dynamic Range	30-700 mg.L ⁻¹
Correlation Coefficient (R ²)	0.9902
Regression Equation	Y=16.066X + 1940.6
RSD%	2.5
Intra-day (%RSD)	3.2
Inter-day (%RSD)	6.9
LOD	1.6
LOQ	4.5

Table SI3. Elementary analysis of Fe₃O₄@PPY-NiO-NiS

Element	% weight	% Atomic
C	30.54	39.51
N	12.48	13.84
O	43.94	42.67
S	1.80	0.87
Fe	10.15	2.82
Ni	1.09	0.29
	100.00	100.00

Table SI4. List of compounds obtained from GC-MS analysis of Fe₃O₄@PPY-NiO-NiS

No	RT	m/z	Degradation Compounds
1	4.6	133.0, 32.1, 151.0 96.0, 165.0, 193.0, 207	Oxime-, methoxy-phenyl
2	5.0	32, 193, 209.0, 281.0	3-ethoxyphenylacetone hydroxyl oxime
3	7.3	32.0, 73.0, 341.0, ,107.1,207.0,163.0, 281.0	9H-pyrrolo[3',4':3,4]pyrrolo[2,1-a]phthalazine-9,11(10H)- dione,10-ethyl-8-phenyl
4	7.4	32.1, 73.0, 107.1 207.0, 341.0, 281.0	2-Ethylpyrazine
5	7.5	32.1, 281.0, 73.0, 107.0 207.0	p-Hydroxytoluene
6	7.7	107.0, 32.0, 73.1, 149.0, 207.0, 281.0, 341.0	Acetamide, n-(3-methylphenyl)-
7	7.8	32.0, 108.0, 207.0, 73.0 326.9, 55.1, 281.0	Benzenamine, 3-methyl-, hydrochloride
8	8.0	32.0, 107.0, 207.0, 55.0 77.0, 281.1	1-(3-n-propoxyphenyl)-2-propane oxim

3.4.3. Optimizing of photocatalyst dosage and NiS and NiO loading

Degradation of cephalexin was studied with different photocatalysts dosage (0.2-4 g.L⁻¹). The C/C₀ ratio inversely proportional to the degradation efficiency was firstly decreased with increasing of photocatalyst dose and then remained constant (Fig. SI10). An advantageous of catalyst coupling on support is decreased of catalyst dosage that observed by S1. In the S1 photocatalyst by using of 1 g.L⁻¹ catalyst concentration, degradation efficiency increased clearly and then remained constant. But by using of S2 and S3 highest efficiency is at 2 g.L⁻¹ catalyst dosage. By increasing of photocatalyst dose, the number of adsorption active sites increased and more pollutant molecules were adsorbed on the surface of catalyst and hence interaction between OH radicals and the pollutant molecules facilitated. At higher dose, the aggregation of nanoparticles lowered the surface area and increased light scattering both causing lower degradation efficiency (Homayoon F., Faghihian H., Torki F., , Environ. Sci. Pollut. Res. 2017).

To study the effect of NiS and NiO contents of the photocatalyst on the degradation efficiency, several Fe₃O₄@PPY-NiO-NiS photocatalysts were prepared in which the content of NiO and NiS were changed from (10 to 80 W%, 5 to 40 W% of each). It was concluded that the maximal efficiency was obtained for the 50 W% loading (25% of NiS and 25% of NiO (Fig.SI11). For synthesis of photocatalysts Fe₃O₄@PPY-NiS and Fe₃O₄@PPY-NiO, procedure explained in previous work were used [13]. When the photocatalyst loading was low, limited OH radicals were generated and consequently lower degradation was observed. By increasing the NiS and NiO content the activity of the photocatalyst was firstly increased and when the loading exceeded to 50%, the aggregation of nano-sized particles lowered the surface area, increased the light scattering and consequently the number of adsorbed pollutant molecules and incident photons was deceased. Pourtaheri et al. prepared a photocatalyst by immobilization of NiO on the clinoptilolite support for degradation of cefixim. They reported that the degradation efficiency was 72% for 20 mg.L⁻¹ cefixim solution (A. Pourtaheri, A.N. Ejhieh, Chem. Eng. Res. Design. 2015, 104, 835). Higher catalyst loading compared to literature was mainly structure of the photocatalyst which prevented of e⁻/h⁺ pair recombination (Fig. SI3).

In this work, the degradation efficiency of 100, 90 and 75% were obtained respectively for S1, S2 and S3 samples by visible light. These were very advantageous for the prepared photocatalysts; first, decreased of catalyst dosage and second, increased degradation efficiency after coupling of catalysts, NiO and NiS, onto the catalyst suport.

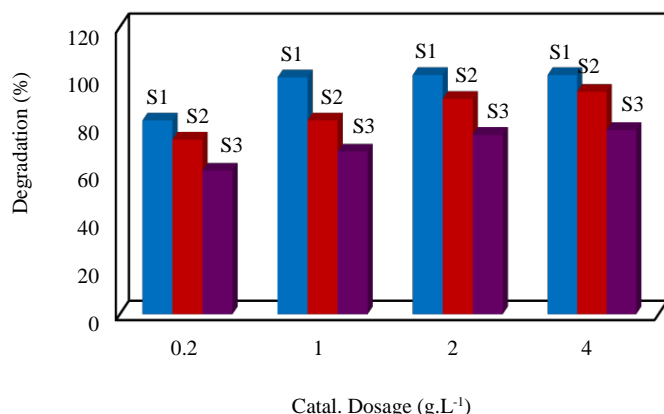


Figure SI10. Effect of photocatalyst dosage on cephalexin degradation by $\text{Fe}_3\text{O}_4@\text{PPY-NiO-NiS}$ (S1), $\text{Fe}_3\text{O}_4@\text{PPY-NiS}$ (S2), $\text{Fe}_3\text{O}_4@\text{PPY-NiO}$ (S3)

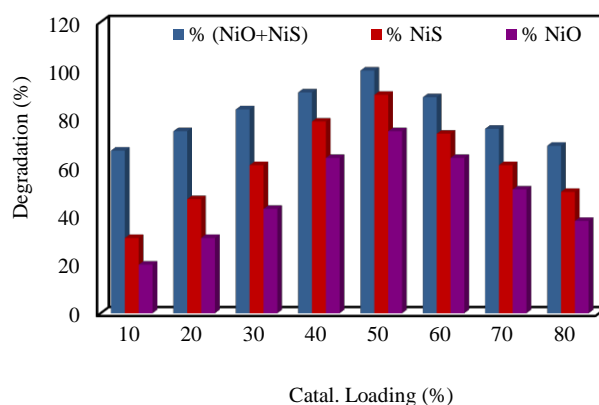


Figure SI11. %loading NiS and NiO on magnetically support

3.4.8. Effect of initial concentration of pollutant

The degradation efficiency was measured in the solutions with different concentration of pollutant (30–700 mg.L⁻¹). At low concentration, the pollutant molecules were adsorbed on the surface of catalyst where interacted with the generated OH radicals. At high concentration of cephalexin the surface of catalysts was properly engaged and the remaining excess cephalexin molecules in the solution caused lower penetration of the incident photons to the catalyst surface (S. Naeimi, H. Faghihian, Sep. Purif. Technol. 2017, 175, 255). However, at the highest concentration of pollutant, (700 mg.L⁻¹) the degradation efficiency of 69, 62 and 49% were obtained respectively by S1, S2 and S3 were obtained (Fig. SI12).

3.4.9. Effect of irradiation time

The time needed for degradation process for equilibrium establishment is one of the most important parameters that should be optimized. From the result of kinetic study, it was concluded that the process was preceded fast and the degradation percentage of 80 and 68 and 55% was obtained within 30 min respectively for S1, S2 and S3 samples. The degradation efficiency increased respectively to 100, 90 and 75% after equilibrium was attained in 360 min (Fig.SI13). The rate constants were calculated by the straight line constructed by plotting $\ln(C/C_0)$ versus time. The rate constants of 8.3×10^{-3} ($R^2=0.8602$), 2.9×10^{-3} ($R^2=0.8634$), 1.7×10^{-3} ($R^2=0.9918$) were obtained for S1, S2 and S3 respectively (Fig. SI9) and confirmed that the experimental data fit to the pseudo-first order kinetics.

The degradation kinetic was faster in the S1 sample. The coupled photocatalyst confirmed that simultaneous coupled grafting NiS and NiS NiO on the surface of the support ($\text{Fe}_3\text{O}_4@\text{PPY-NiO-NiS}$) give much and faster degradation efficiency compared to the photocatalysts prepared by single immobilization of NiO and NiS (S2 and S3). The degradation in small irradiation time of 30 min is very advantageous for a photocatalyst under visible light irradiation. The slower rate of degradation efficiency after 30 min was due to the deposition of intermediate degradation products on the catalyst surface which limited the number of pollutant molecules adsorbed by the photocatalyst (Naeimi S., Faghihian H., Sep. Purif. Technol. 2017, 175, 255). The fast and effectiveness step time obtained in this work was lower than the reported values for similar catalysts. For example, Choina et al. reported 85% degradation of ibuprofen (10 mg.L⁻¹) after 180 min UV irradiation in the presence of TiO_2 (Choina J. et al. Appl. Catal. B: Environ. 2013, 129, 589). Saadati et al. reported that 73% of tetracycline (15 mg.L⁻¹) was degraded by using Cl-TiO_2 and UV irradiation after 60 min (Saadati F. et al. Crit. Rev. Env. Sci. Tec. 2016, 46, 757]. Sayed et al.

studied degradation of metronidazole (1mg.L^{-1}) by use of CuO and up to 97% degradation reported after 120 min of UV radiation (Sayed G.O.E. et al. Basic. Environ. Sciences. 2014, 1, 102). The most advantageous result of this work is that the short equilibration time was obtained with visible light.

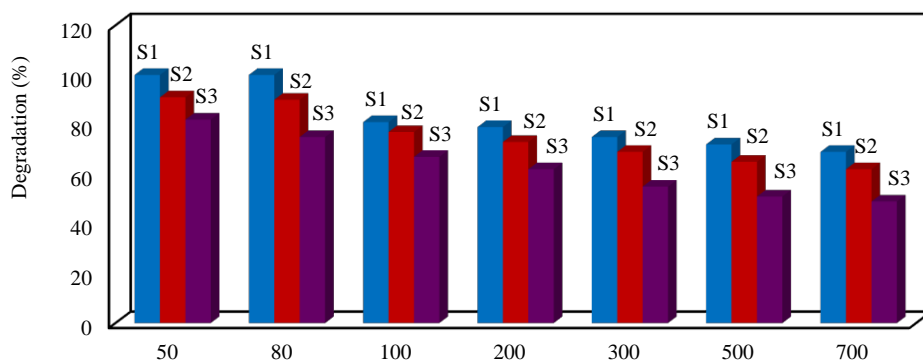


Fig. S112. Effect of the initial concentration on cephalixin degradation

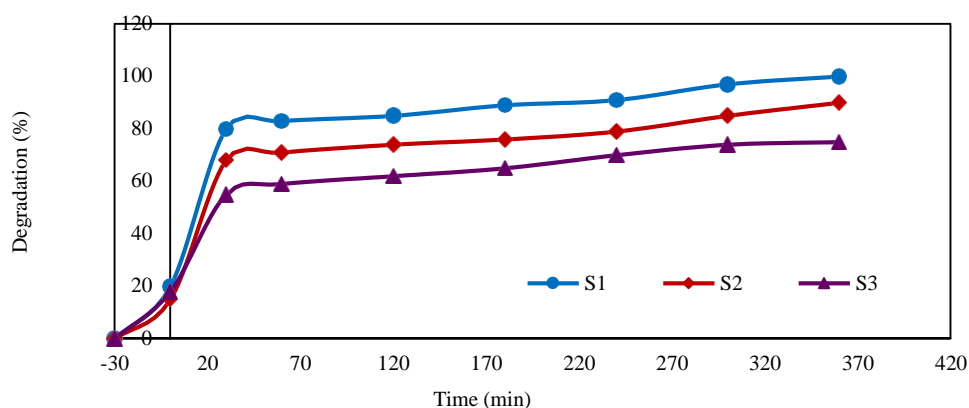


Fig. S113. Effect of irradiation time on cephalixin degradation