***Neutral pH Fenton and Photo-Fenton activity of Mo-doped iron-pyrite particles.***

by

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## 1. Result and discussion

**Table M1.** Lattice parameter of synthesized sample and their error calculations.

| S. No | Sample | Instrument precision % | Reading error % | Calculation error % |
|---|---|---|---|---|
| 1. | Py | 0.0253 | 0.0017 | 0.0059 |
| 2. | $Py_1$ | 0.0253 | 0.0003 | 0.0009 |
| 3. | $Py_4$ | 0.0253 | 0.0010 | 0.0035 |
| 4. | $Py_8$ | 0.0253 | 0.0005 | 0.0016 |

Instrument precision %= (Standard deviation / Mean) *100

All errors are negligible in the lattice parameter calculation.

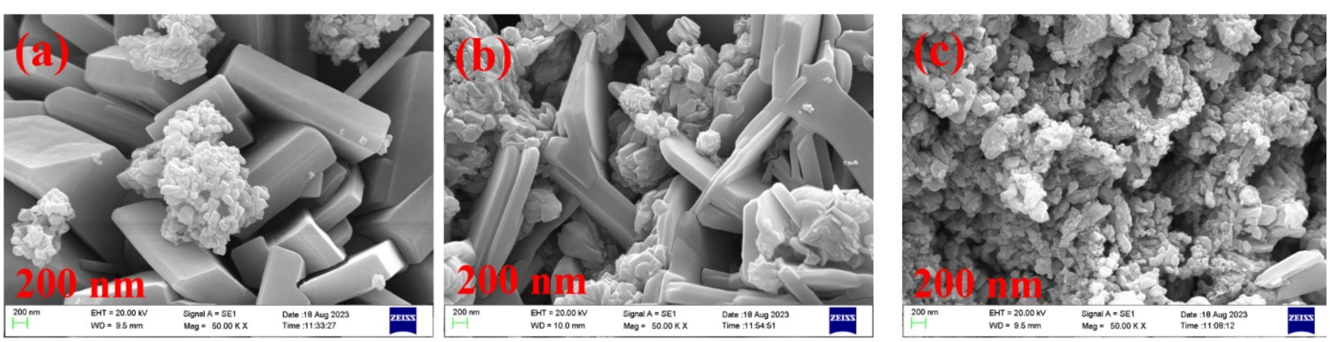


**Figure M1.** SEM images of (a) Py, (b) $Py_1$, and (c) $Py_8$ samples.

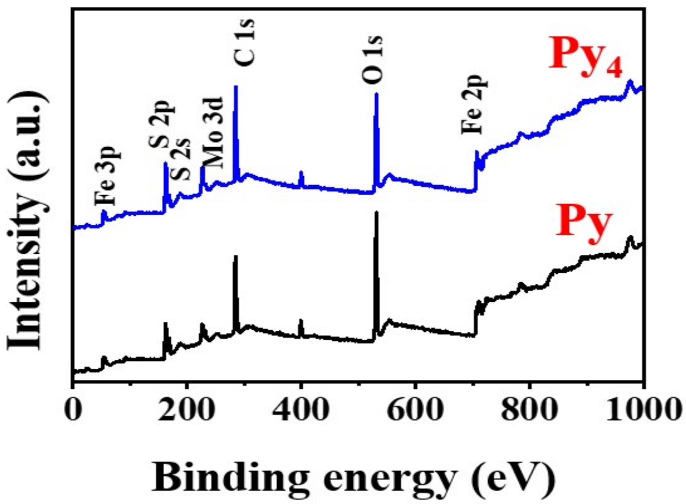


**Figure M2.** XPS Survey spectrum of Py and Py$_4$ samples.

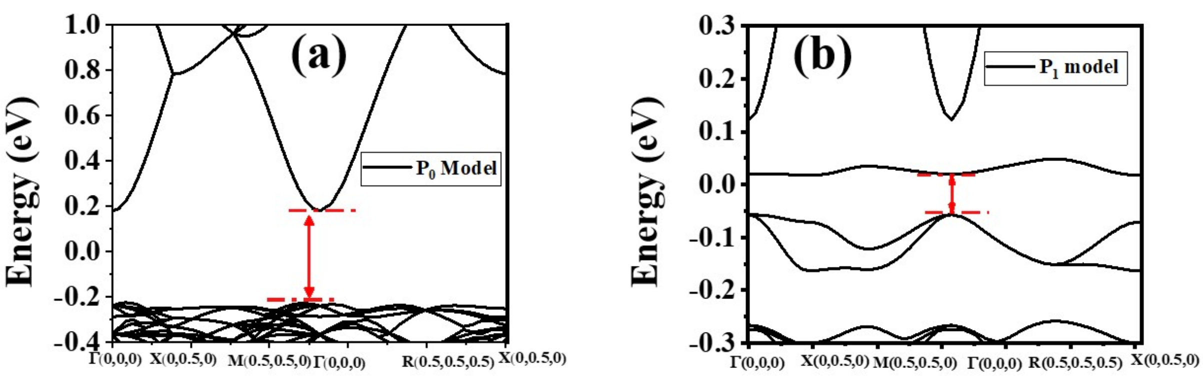


**Figure M3.** Band structure of (a) P$_0$ and (b) P$_1$ models.

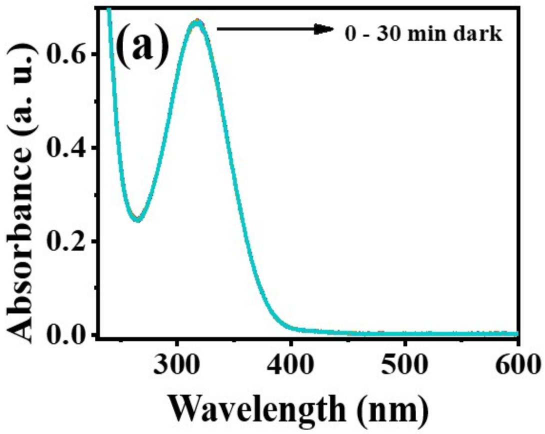


**Figure M4.** The effect of $H_2O_2$ on PNP (a) in dark and (b) in light conditions without catalysts.

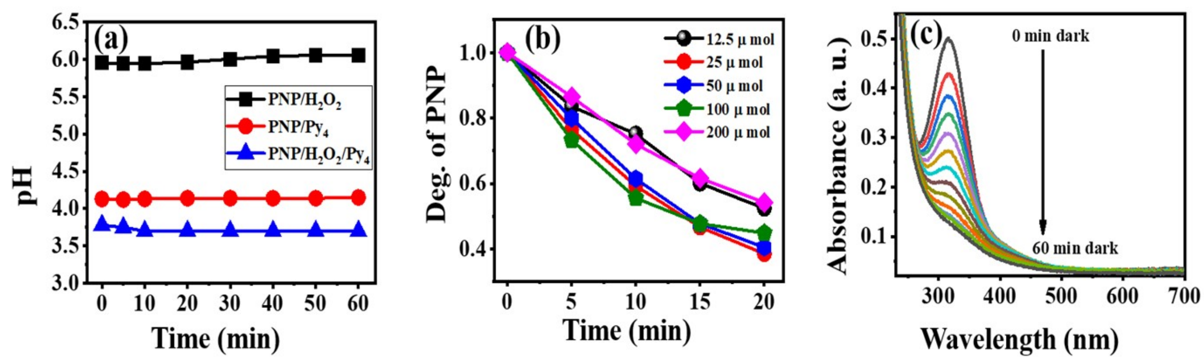


**Figure M5.** (a) pH v/s time plot of the degradation of PNP in the Fenton reaction, (b) degradation v/s time plot of PNP degradation in the Fenton reaction in the presence of different amounts of $H_2O_2$, and (c) UV-visible absorbance plot of PNP degradation in the presence of the Py catalyst.

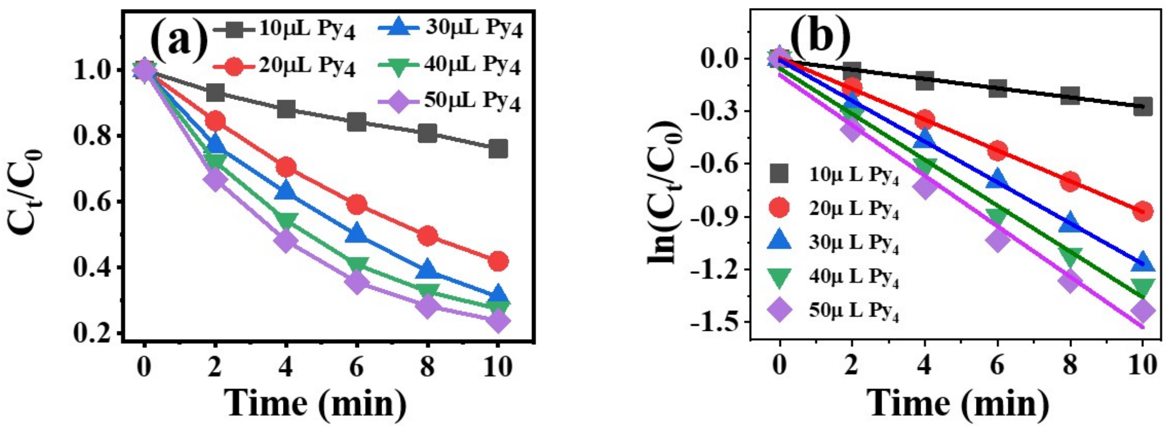


**Figure M6.** (a) degradation v/s time plot of PNP degradation in the photo-Fenton reaction in the presence of different amounts of $Py_4$ catalyst, and (b) kinetic plot of photo-Fenton reaction catalyst optimization, reaction conditions [PNP]=10 mg/L, $[H_2O_2]$ = 25 μmol, $[Py_4]$ = 10, 20, 30, 40, and 50 μL of 2mg/2ml.

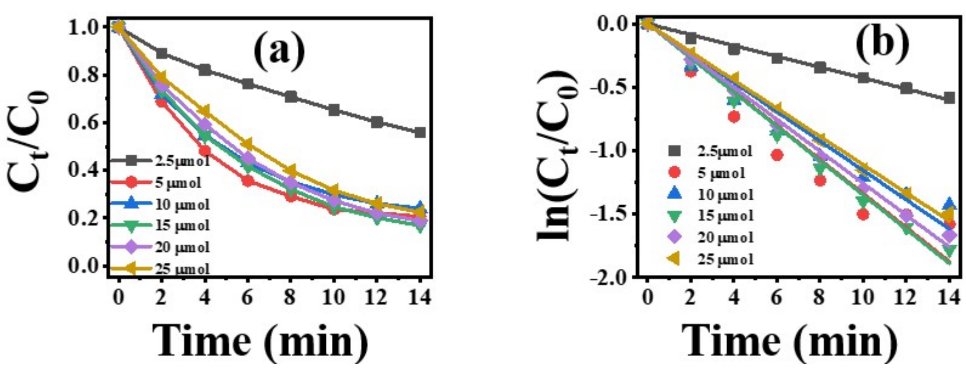


**Figure M7.** (a) Photo-Fenton PNP degradation versus time plots in the presence of different amounts of $H_2O_2$, and (b) photo-Fenton reaction with different amounts of $H_2O_2$ follow first-order-kinetics (reaction condition [PNP]=10 mg/L, $[Py_4]$ = 30μL of 2 mg/2ml).

## Kinetic studies

The pseudo-order kinetics equations were used because the concentration of $H_2O_2$ was in excess (23.09 times higher than the PNP concentration) and accordingly treated as a constant during the reaction. The kinetics of a reaction can change with the catalyst. The different kinetics exhibited under Fenton and photo-Fenton conditions point to dissimilar mechanisms followed by the two types of reactions. Moreover, rate constants do not take in account the amount of catalysts used. Hence, rate constants cannot be used for comparing or evaluating the activity of a catalyst/photocatalyst. It must be mentioned here that TOF is a much better parameter for comparing and evaluating the activity of a catalyst/photocatalyst. TOF values give the reactant consumed in unit time per moles (or grams) of the catalyst. The data in Table M2 (supporting information) confirms that Pseudo-first-order kinetics plot fitting was considerable in PNP degradation in the photo-Fenton reaction [1,2].

**Table M2.** Correlation coefficients of ($R^2$) of the fitting of the PNP photo-Fenton degradation kinetics data to zero-order, first-order, and second-order kinetics equations.

| S. No | Photocatalyst | Zero-order | First-order | Second-order |
|---|---|---|---|---|
| 1. | Py | 0.8468 | 0.9957 | 0.9989 |
| 2. | $Py_1$ | 0.8878 | 0.9825 | 0.9950 |
| 3. | $Py_4$ | 0.9425 | 0.9873 | 0.9972 |
| 4. | $Py_8$ | 0.9956 | 0.9963 | 0.9992 |

**Table M3.** Normalized recyclability and TOF of PNP degradation in Fenton and photo-Fenton reactions.

| **Cycles of $Py_4$** | **Fenton degradation (%)** | **TOF (µmol $g^{-1}$ $min^{-1}$)** | **Photo-Fenton degradation (%)** | **TOF (µmol $g^{-1}$ $min^{-1}$)** |
|---|---|---|---|---|
| 1 | 68.00 | 6.52 | 93.39 | 13.37 |
| 2 | 64.75 | 6.46 | 88.87 | 12.91 |
| 3 | 50.10 | 6.40 | 84.15 | 12.90 |
| 4 | 21.69 | 4.16 | 76.63 | 12.81 |

Table M3, in the supporting information of the revised manuscript, gives the complete recyclability data for sample $Py_4$. Columns 2 and 4 give the percentage PNP degradation on the catalyst under (dark) Fenton and (visible light) photo-Fenton conditions. Note that the data in columns 2 and 4 give the percentage degradation due to the catalyst recovered after each cycle of use. There is some catalyst loss during the washing and drying of the recovered catalyst. Hence, the decrease in columns 2 and 4 (Fenton and photo-Fenton) activity is also due to catalyst loss. In contrast, columns 3 and 5 give the PNP degradation TOF values obtained on the $Py_4$ catalyst under Fenton and photo-Fenton conditions respectively. The TOF has µmol. $g^{-1}.min^{-1}$ unit and it is giving the PNP degradation activity per gram of the catalyst. The TOF catalyst activity is considerably better than those displayed in columns 2 and 4.

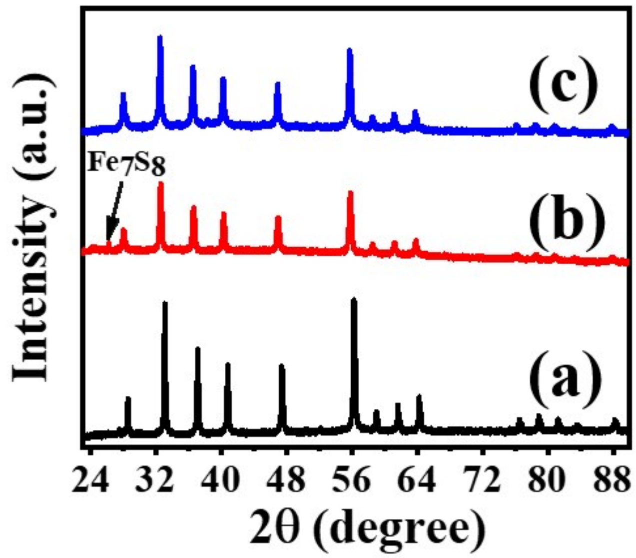


**Figure M8.** XRD pattern of **(a)** $Py_4$ **(b)** and **(c)** are after the 4th cycle $Py_4$ in Fenton and photo-Fenton reaction respectively**.**

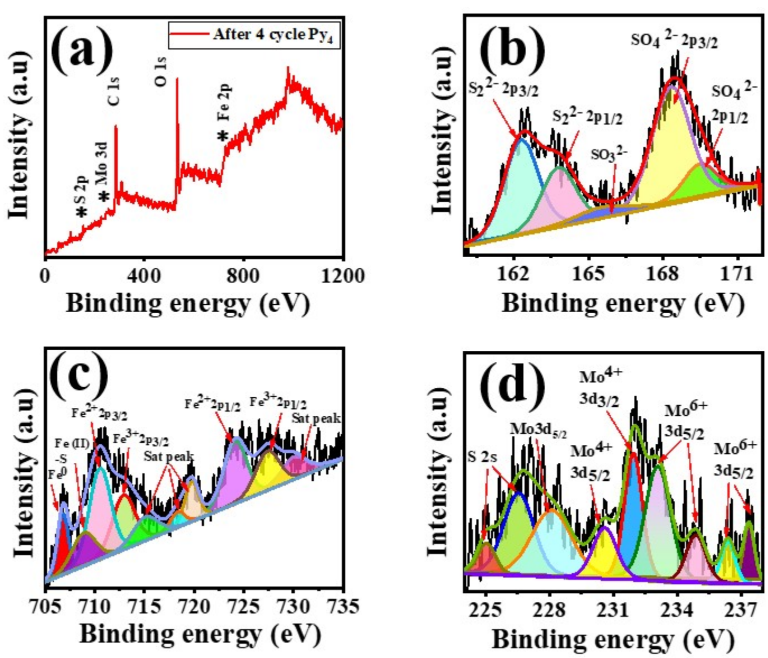


**Figure M 9.** After 4 cycles used $Py_4$ photocatalyst XPS spectra, (a) survey spectrum, core level XPS spectra of (b) S 2p, (c) Fe 2p, and (d) Mo 3d.

| S. No | Sample | TOF (μ mole $g^{-1}$ $min^{-1}$) | $H_2O_2$ Normalized TOF (HTOF) ($mg^{-1}min^{-1}$ L) | $H_2O_2$ (mM) | Reusability | Ref. |
|---|---|---|---|---|---|---|
| 1 | Pyrite (pH=7) | *71.88 | 8.98 | 8.00 | 30 % in 3rd cycle | 3 |
| 2 | $Mn_3O_4$.CuO (pH~7) | *8.53 | 0.08 | 100 | 78 % in 5th cycle | 4 |
| 3. | $Py_4$ (pH~7) | 113.16 | 13.58 | 8.33 | 65.88 % in 4th cycle | This work |

**Table M4.** PNP Fenton degradation comparison with different catalysts.

**Table M5.** A comparison of PNP photo-Fenton degradation over different catalysts.

| S. No | Sample | TOF (μmol $g^{-1}$ $min^{-1}$) | $H_2O_2$ Normalized TOF (HTOF) ($mg^{-1}min^{-1}$ L) | Light source | $H_2O_2$ (mM) | Reusability | Ref |
|---|---|---|---|---|---|---|---|
| 1 | $Zn_{1-1.5x}Fe_xS$ /g-$C_3N_4$ (pH=6.1) | *1.43 | 1.43 | 500-W Xenon lamp (29.3mWcm$^{-2}$) | 1.00 | 76.90 % in 5th cycle | 5 |
| 2 | MIL-100 | *95.84 | 114.09 | 300 W Mercury Lamp | 0.84 | 100 % in | 6 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | /Fe (pH=7) | | | | | $5^{th}$ cycle | |
| 3 | Pyrite (pH=7) | *179.71 | 22.46 | 300W Xenon lamp with light cut filter (λ >400 or λ > 420 nm) | 8.00 | 85 % in $3^{rd}$ cycle | 1 |
| 4 | Fe–$TiO_2$ | *23.96 | 4.89 | UV lamp, 340 nm (100 μW $cm^{-2}$) | 4.90 | 90 % in $4^{th}$ cycle | 7 |
| 5 | $Py_4$ (pH=7) | 254.50 | 152.39 | White cool LED | 1.67 | 95.12 % in $4^{th}$ cycle | This work |

*All catalyst turnover frequency was calculated by the information given in the cited research articles.

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