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# Doxycycline detection and degradation in aqueous media via simultaneous synthesis of Fe-N@Carbon dots and $Fe_3O_4$-Carbon dot hybrid nanoparticles: One arrow two hawk approach

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## Experimental Section

### S1. Benesi-Hildebrand plot

The binding affinity of doxycycline to the Fe-N@CDs was confirmed using the Benesi-Hildebrand plot [1–3] for the quantitative determination of association constant from fluorescence data. To determine the binding constant, the following equation has been employed

$$1/(F_o - F) = 1/K_a(F_{max} - F_o)[\text{Doxycycline}] + 1/(F_{max} - F_o)$$

Where, $K_a$ = binding constant, $F_{max}$ = maximum fluorescence intensity, $F_0$ = Initial fluorescence intensity. The binding constant calculated from the Benesi-Hildebrand equation is $2.8 \times 10^6\ M^{-1}$.

**Table. 1** Comparison of pharmaceutical degradation reported methods with this work.

| Catalyst | Pharmaceuticals | Conc. | Volume used | Reaction time (min) | % Degradation achieved | Methods used | Ref. |
|---|---|---|---|---|---|---|---|
| Ag@LiNbO3/ PVDF | Tetracycline | 0.2 mM | 10 ml | 120 | 69% | Ultra-sonication | 4 |
| Laccase | chlortetracycline | 2mg | 1L | 120 | 80% | Ultra-sonication | 5 |
| p-n BiOI/ $Bi_3O_4Cl$ | Tetracycline | - | - | 180 | 73.5% | Photo-catalytic | 6 |
| Mn-doped $CeO_2$ | Tetracycline, chlortetracycline, oxytetracycline. | - | - | 60 | 98.6 %, 97.4%, 88.1 % | Fenton like photo catalytic reaction | 7 |
| $Fe_3O_4$-CDs | Tetracycline | 50mg | 500ml | 5 | 70.26% | Kitchen blender | **This work** |

**Table. 2** Comparison of reported Doxycycline sensing methods with this work.

| S.No. | Material | Method of sensing | LOD | Linearity Range | Ref. |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 1. | NCQDs | Fluorometric assay | 87 nM | 5 to 50 µM | [8] |
| 2. | CuNCs | Fluorescence | 270 nM | 1–1000 µM | [9] |
| 3. | BiOBr nanosheets | Photo-electrochemical | 0.14 µM | 0.50 µM to 1 mM | [10] |
| 4. | CDs@MOF(Eu) | Fluorescence | 0.1665 µg/mL | 0–60 µM | [11] |
| 5. | AOT-AgNPs | Chemosensing | 0.2 µM | 0.1 to 140 µM | [12] |
| 6. | ZIF-8/NH2-MIL-53(Al) | Fluorescence | 1.2 µg $L^{-1}$ | NA | [13] |
| 7. | CDs | Fluorescence | 16.35 µM | 10–1000 µM | [14] |
| 8. | Fe-N@CDs | Fluorescence | 66 ng/mL 148nm | 0 mg $mL^{-1}$ to 50 mg $mL^{-1}$ | *This work* |

**Table. 3** Doxycycline determination in milk samples after 2 h incubation with doxycycline (n=3)

| Sample | Spiked (µM) | Detected (µM) | Recovery (%) | SD |
|---|---|---|---|---|
| **1** | **0** | **ND*** | | |
| **2** | **20** | **20.6** | **103** | **1.08** |
| **3** | **30** | **28.9** | **96.3** | **1.97** |
| **4** | **40** | **40.89** | **102.2** | **0.87** |

**Table. 4** Doxycycline determination in milk samples after 24 h incubation with doxycycline (n=3)

| Sample | Spiked (µM) | Detected (µM) | Recovery (%) | SD |
|---|---|---|---|---|
| **1** | **0** | **ND*** | | |
| **2** | **20** | **18.7** | **93.5** | **2.03** |
| **3** | **30** | **27.9** | **93** | **1.33** |
| **4** | **40** | **39.1** | **97.75** | **1.62** |

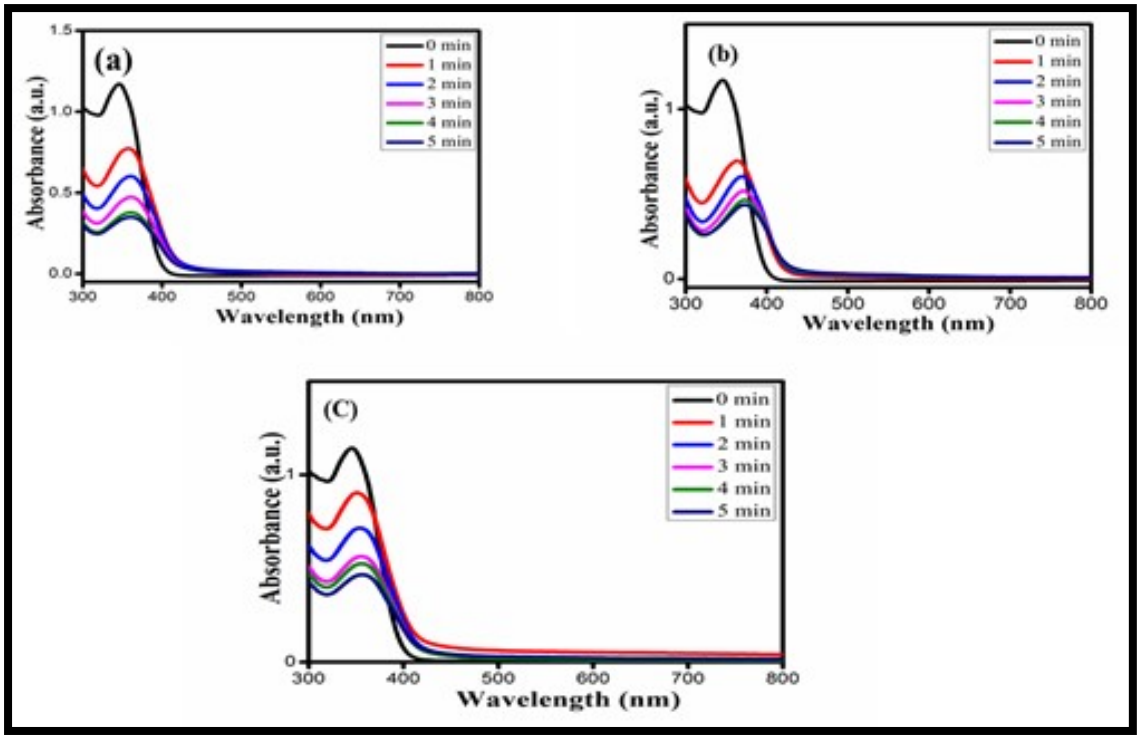


**Fig. S1** The recyclability of doxycycline by $Fe_3O_4$-CDs (a) First cycle (b) second cycle (c) Third cycle.

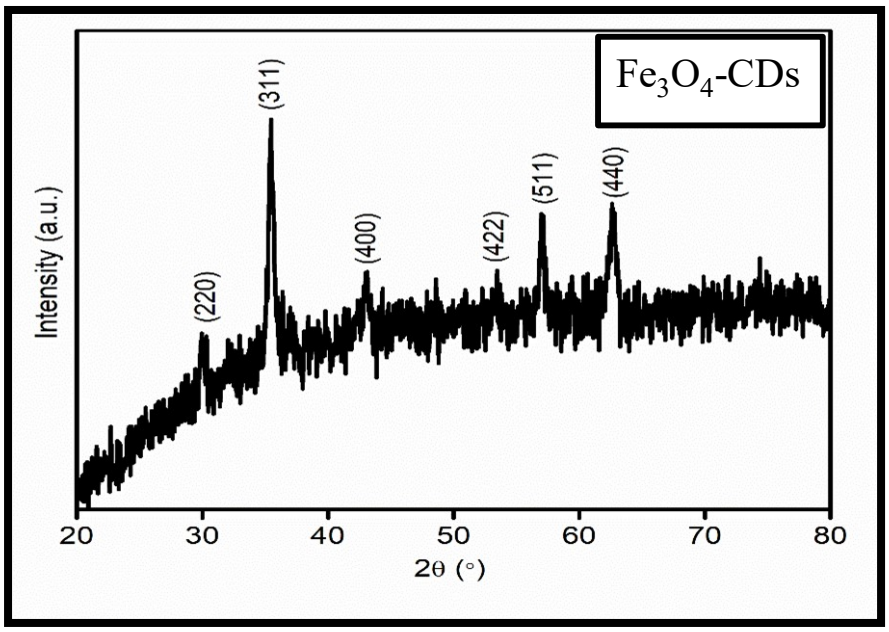


**Fig. S2** PXRD pattern of $Fe_3O_4$-CDs after three consecutive cycles.

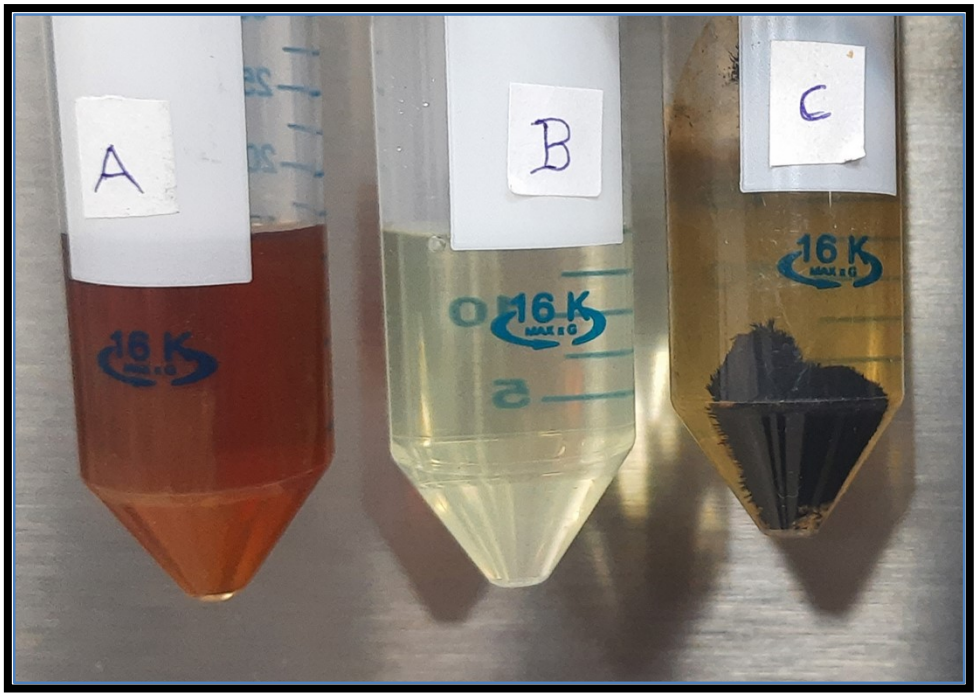


**Fig. S3** Images of the samples prepared under different reaction conditions.

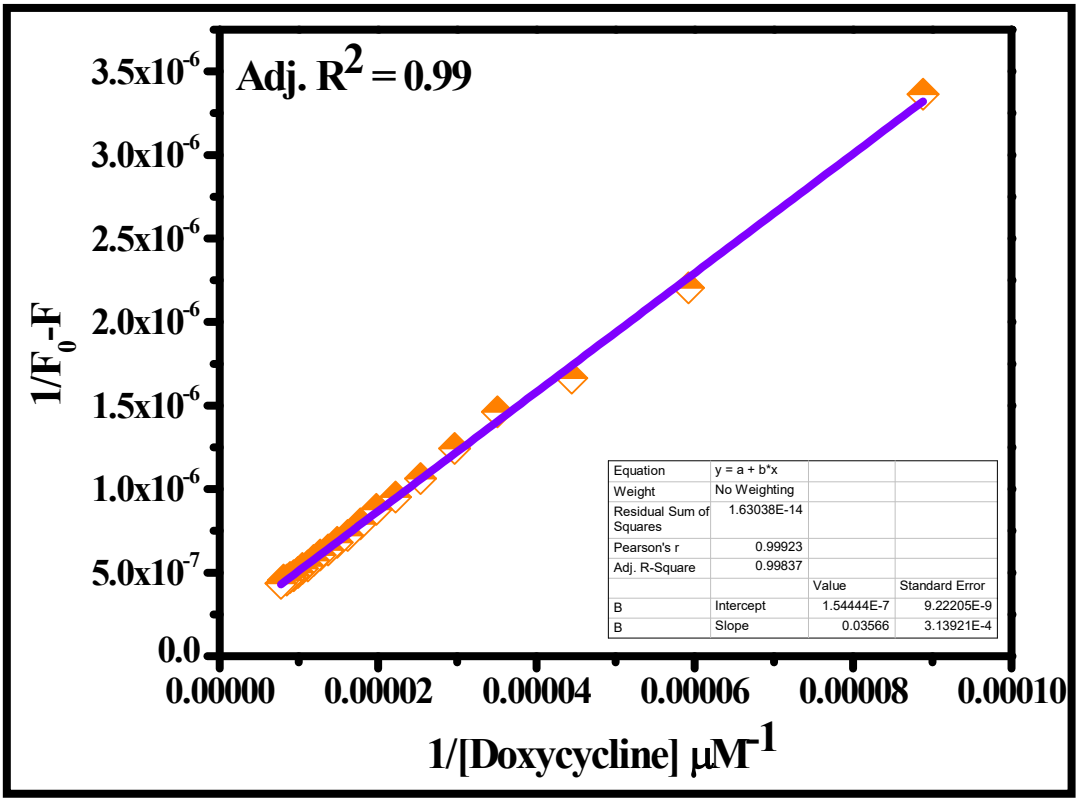


**Fig. S4** Benesi-Hildebrand plot of Fe-N@CDs:Doxycycline.

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