Supplementary Information (SI) for Environmental Science: Water Research & Technology.
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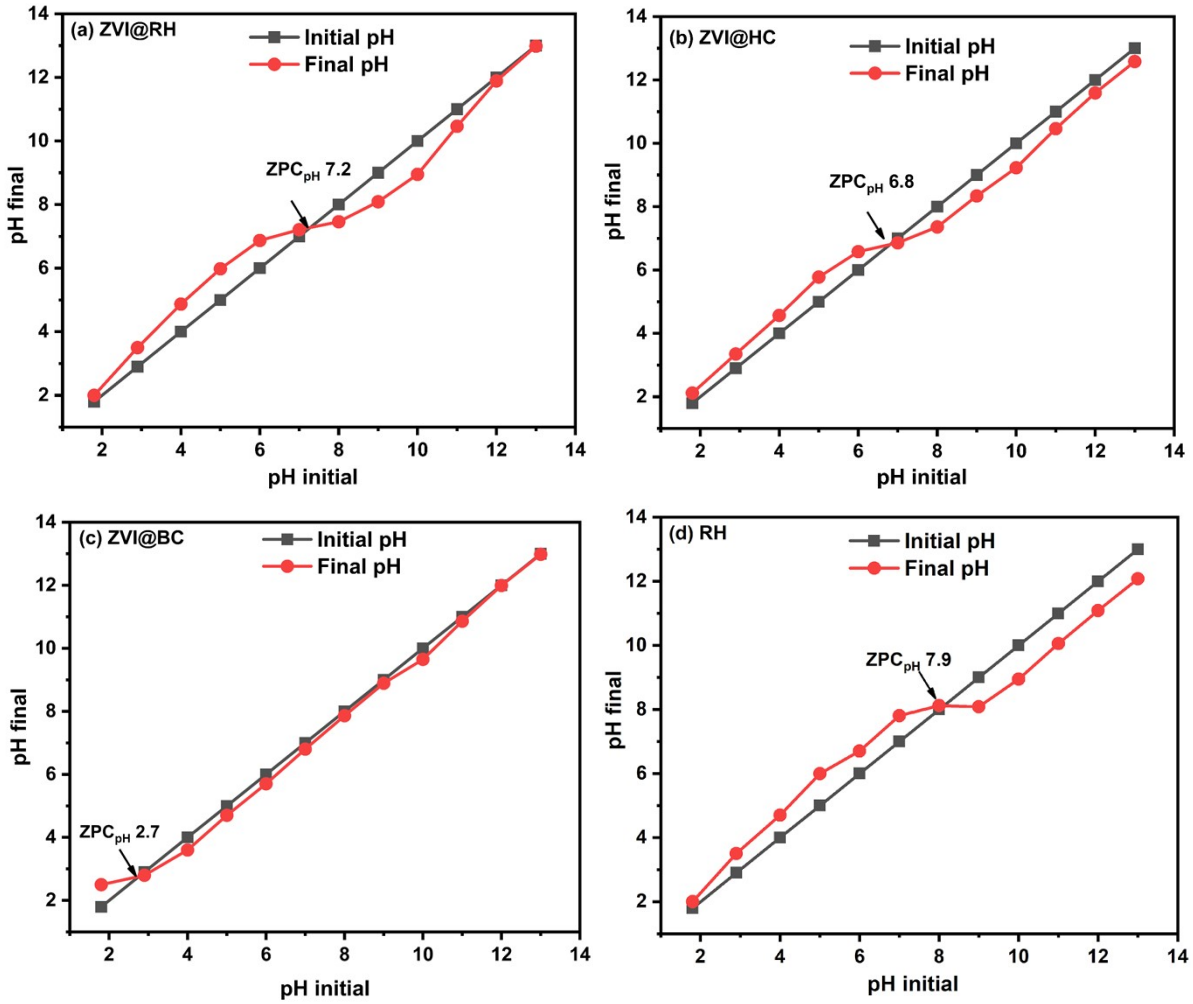
Supporting Information

Synergistic impact of rice husk biomass derived carbon supports on the performance of biogenic Fe^0-catalyzed advanced oxidation processes for oxytetracycline remediation

1. pH_{ZPC} of ZVI@RH, ZVI@HC, and ZVI@BC



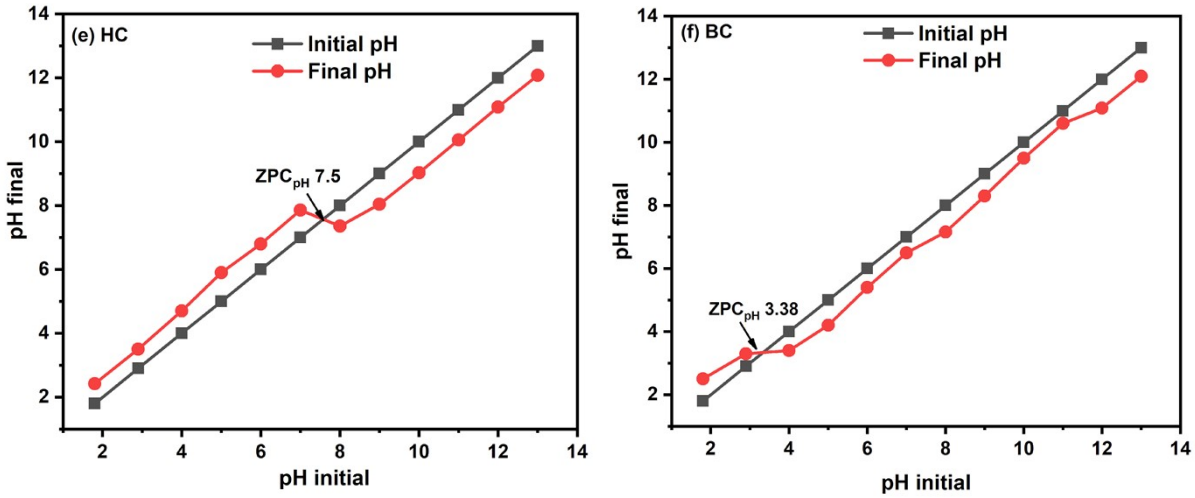


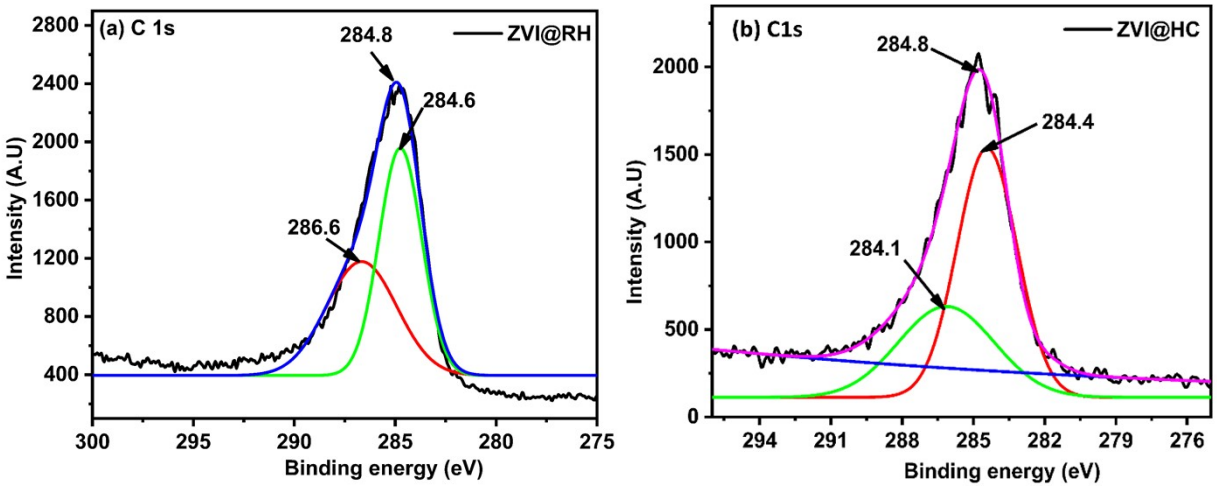
Figure SI 1. Zero-point charge (pHzpc) of (a) ZVI@RH; (b) ZVI@HC; (c) ZVI@BC; (d) RH; (e) HC; (f) BC.

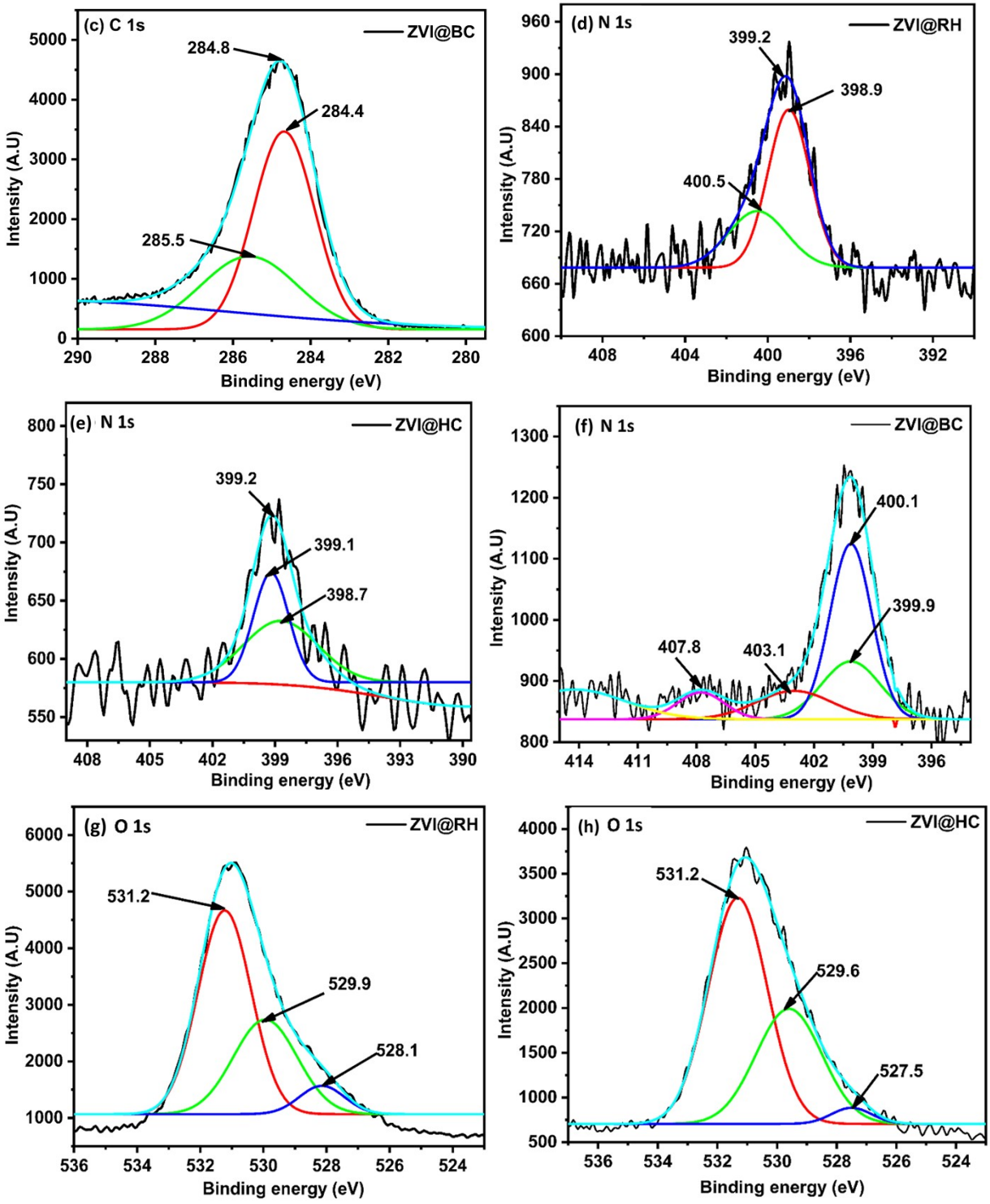
Table SI 1. Information about instrumentation used for studies:

S.N.	Techniques used	Instrumentation Make
1.	FT-IR	Bruker (Tensor 27)
2.	XRD	Empyrean Alpha 1
3.	TGA/DTA	Mettler Toledo and Netzsch
4.	FE-SEM	Carl Zeiss, Germany (Merlin Compact)
5.	HRMS	Waters (QTOF mass spectrometer combined with ESI)
6.	XPS	PHI 5000 Versa Probe II
7.	UV-Vis	Thermofisher (Evolution 220)
8.	TOC	Shimadzu TOC-L (H574056)
9.	Centrifugation	Remi Bench Top

10.	Rotary shaking	Universal Rotary Shaker
11.	Hot air drying	Universal Hot Air Oven
12.	Solution stirring	Remi 5 MLH plus
13.	pH determination	Electronic India Deluxe pH meter (Model-101)

2. XPS analysis:




(c) C 1s
ZVI@BC
284.8
284.4
285.5
Intensity (A.U)
Binding energy (eV)
(d) N 1s
ZVI@RH
399.2
398.9
400.5
Intensity (A.U)
Binding energy (eV)
(e) N 1s
ZVI@HC
399.2
399.1
398.7
Intensity (A.U)
Binding energy (eV)
(f) N 1s
ZVI@BC
400.1
399.9
407.8
403.1
Intensity (A.U)
Binding energy (eV)
(g) O 1s
ZVI@RH
531.2
529.9
528.1
Intensity (A.U)
Binding energy (eV)
(h) O 1s
ZVI@HC
531.2
529.6
527.5
Intensity (A.U)
Binding energy (eV)

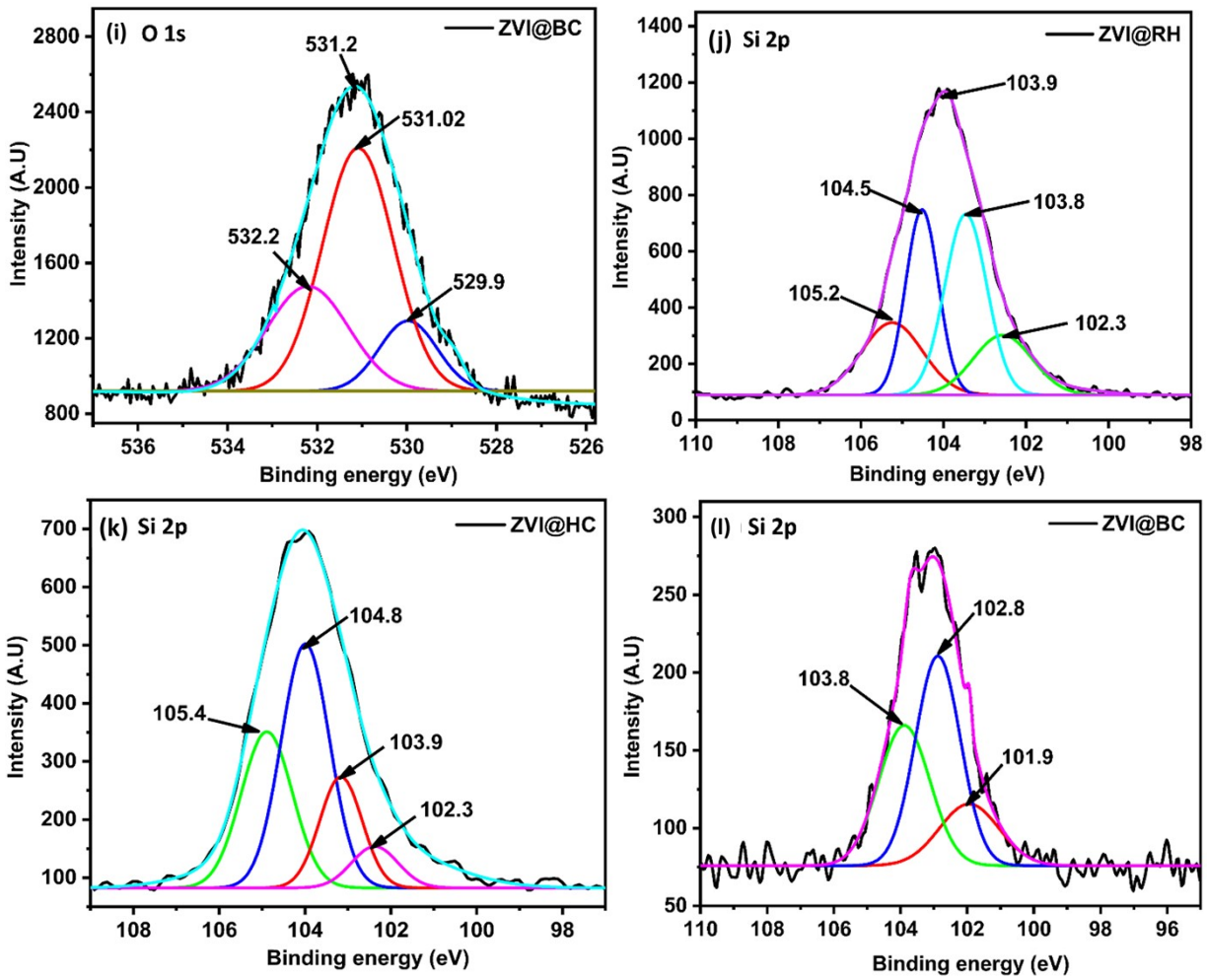


Figure SI 2. X-ray photoelectron spectroscopy survey scans for (a) C 1s spectra for ZVI@RH; (b) C 1s spectra for ZVI@HC; (c) C 1s spectra for ZVI@BC; (d) N 1s spectra for ZVI@RH; (e) N 1s spectra for ZVI@HC; (f) N 1s spectra for ZVI@BC; (g) O 1s spectra for ZVI@RH; (h) O 1s spectra for ZVI@HC; (i) O 1s spectra for ZVI@BC; (j) Si 2p spectra for ZVI@RH; (k) Si 2p spectra for ZVI@HC; (l) Si 2p spectra for ZVI@BC.

3. Water quality parameters

3.1. Chemical Oxygen Demand (COD)

Chemical oxygen demand refers to the amount of oxygen required to chemically degrade pollutants. High levels of COD in wastewater indicate organic and inorganic contamination that can deplete dissolved oxygen in the water, resulting in negative environmental impacts. The COD of samples was determined with standard procedure. Particularly, for COD analysis standard solutions such as potassium dichromate

solution, ferrous ammonium sulfate, sulfuric acid reagent, mercuric sulfate, and phenanthroline ferrous sulfate (ferroin) indicator were required. COD samples were digested with dichromate containing sulfuric acid reagent at 150 °C for 2 h and $HgSO_4$ was used in the digestion solution to remove chlorides that interfere with the COD determination. Titrate the digested samples with standard ferrous ammonium sulfate using a ferroin indicator[1].

$$\text{COD (mg·L}^{-1}) = \frac{(blank - B.R) \times N \times 8000}{Volume\ of\ sample} \quad \text{(Eq. SI 1)}$$

Here, Blank is the burette reading of a blank sample (distilled water), and B.R. is the burette reading of COD samples, N is the normality of standard ferrous ammonium sulfate solution.

COD removal efficiencies:

The percentage COD removal efficiency for TCH is calculated using the formula:

$$\text{COD \% Removal} = [1 - \frac{y}{yo}] \times 100 \quad \text{(Eq. SI 2)}$$

Here, y is final COD value after degradation and y_0 is the initial COD value of contaminant.

3.2. Biological oxygen demand (BOD)

BOD is a method used for indirect measurement of water quality. BOD is the amount of oxygen required for the degradation of biodegradable organic matter at 20 °C for a specific time. The higher the BOD value, the greater the amount of organic matter for oxygen-consuming bacteria which causes depletion of dissolved oxygen (DO) that increases the stress on aquatic organisms, making the environment unsuitable for life. For BOD analysis of wastewater standard method was used in which dissolved oxygen was measured, for the measurement of dissolved oxygen standard solutions were required as sodium thiosulfate, alkaline KI solution, $MnSO_4$ solution, concentration H_2SO_4, and starch indicator. The BOD bottle was filled with 20 ml of given sample ensuring no air bubbles trapped inside. 1 mL of $MnSO_4$ and alkaline KI solution was added to this. The appearance of brown precipitates indicates the presence of oxygen. To this was added conc. H_2SO_4 was used to dissolve the residue, and then it was titrated with thiosulfate using a starch indicator. Dissolved oxygen was calculated and marked as the initial reading. Another bottle containing a wastewater sample was taken, and the mouth of the BOD bottle was sealed to prevent any air movement in or out. After five days, the dissolved oxygen was measured and marked as the final reading. The difference between the initial and final oxygen levels was recorded as the BOD of the sample[2].

Dissolved oxygen as $mg \cdot L^{-1}$ = $\frac{(ml \times N)\ of\ Na_2S_2O_3 \times 8 \times 1000}{Volume\ of\ sample}$ (Eq. SI 3)

BOD ($mg \cdot L^{-1}$) = $[(D_1-D_2)-(B_1-B_2)]f/p$ (Eq. SI 4)

Here, D_1 is oxygen diluted level in the diluted sample at initial time ($mg \cdot L^{-1}$); D_2 is oxygen diluted level in the diluted sample after 5 days ($mg \cdot L^{-1}$); B_1 is oxygen diluted level in the dilution water at initial time ($mg \cdot L^{-1}$); B_2 is oxygen diluted level in the dilution water after 5 days ($mg \cdot L^{-1}$); p is the volume of wastewater sampled for dilution (10 mL) and f is the volume of diluted sample (250 mL).

3.3. Total organic carbon (TOC)

The total organic carbon of the sample was determined using a TOC analyzer (Shimadzu TOC-L (H574056)

3.4. Residual PMS

To determine the residual peroxymonosulfate (PMS) concentration using a spectrophotometric method with sodium carbonate and potassium iodide (KI), water samples were collected and filtered as needed. 1M sodium carbonate solution and a fresh 10% KI solution were prepared. In a clean cuvette, 10 mL of the water sample or PMS standard solution was mixed with 1 mL of the sodium carbonate solution and 1 mL of the KI solution. The reaction was allowed to proceed for 5 min at room temperature. The absorbance of the resulting solution was measured at 352 nm using a spectrophotometer, with distilled water used as the blank. A calibration curve was created by plotting the absorbance against known PMS concentrations from standard solutions. The residual PMS concentration in the samples was determined by comparing their absorbance readings to the calibration curve[3].

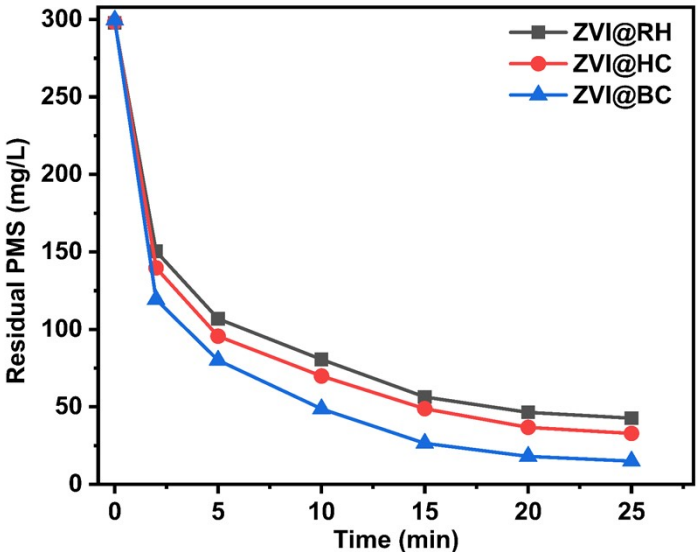


Figure SI 3. Residual PMS concentration in ZVI@RH-PMS; ZVI@HC-PMS and ZVI@BC-PMS activation process for OTC degradation.

3.5. Degradation kinetic

Previous research has suggested that the pseudo-first-order kinetic model was employed to describe the heterogeneous Fenton-like process. This helps us to compare the results of model estimation and experimental data[4]. The following equations can be used to express this model:

$$\frac{[C]}{[C_0]} = e^{-K_{obs}t} \qquad \text{(Eq. SI 5)}$$

Where C is contaminant concentrations at time t; and, C_0 is the contaminant initial concentration ($mg{\cdot}L^{-1}$). Also, t is degradation time (min). K_{obs} is the observed rate constant of pseudo-first-order reaction (min^{-1}), which can be determined from the exponential plot slope of $[C]/[C_0]$ vs t.

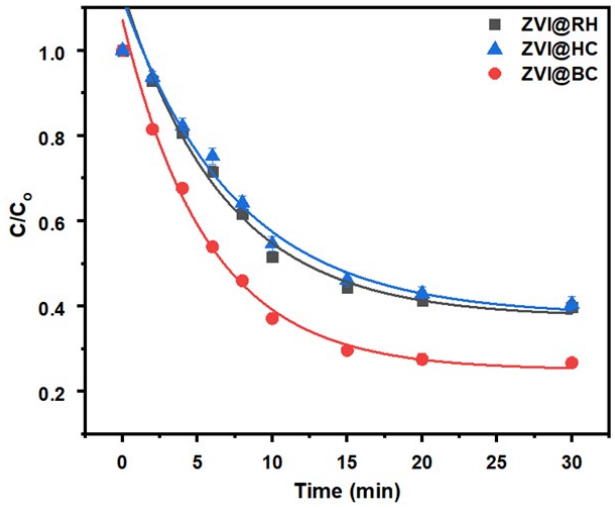


Figure SI 4. Degradation kinetic of OTC by ZVI@RH-PMS and ZVI@HC-PMS and ZVI@BC-PMS process.

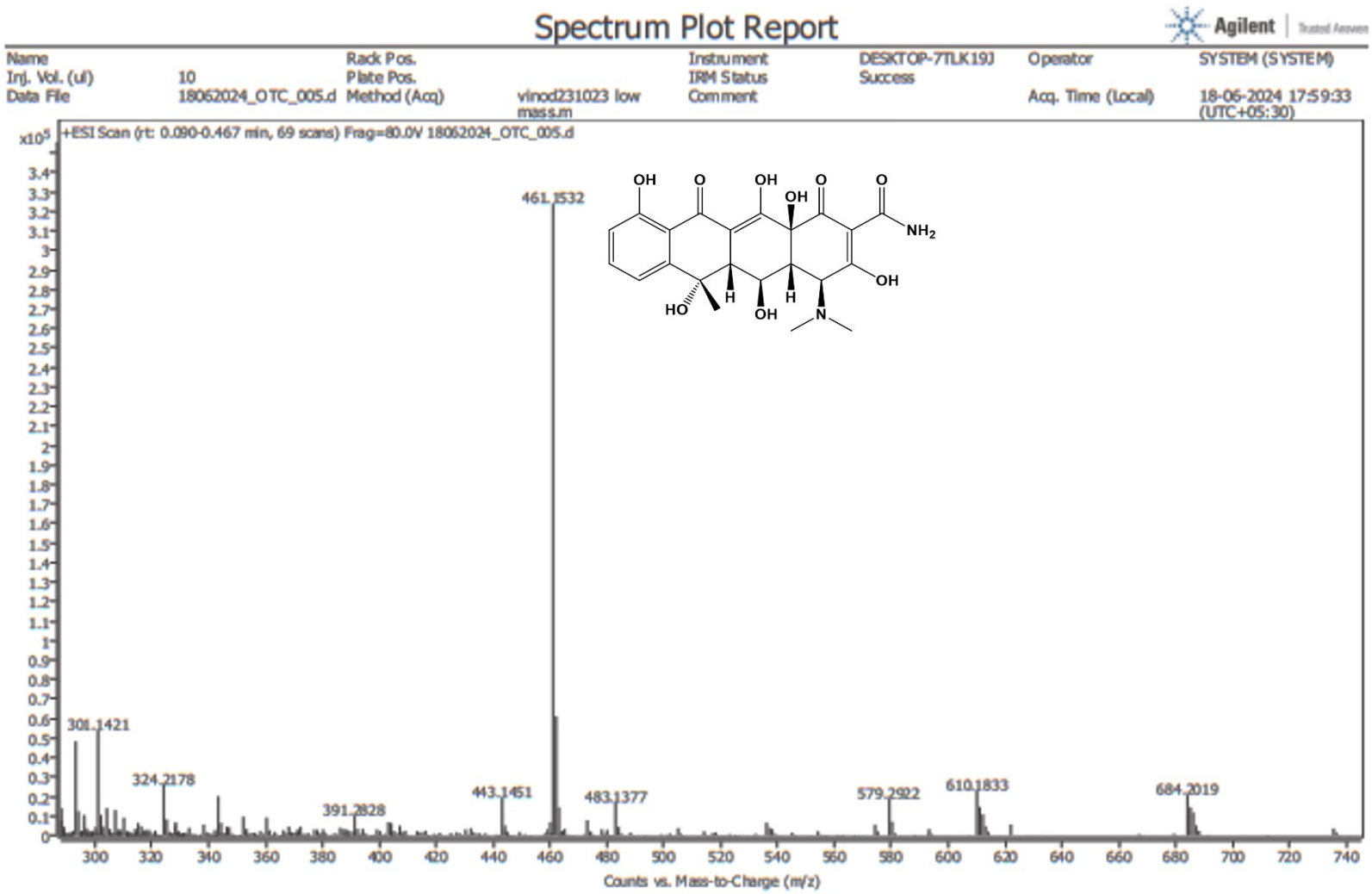


Figure SI 5. High-resolution mass spectrum of OTC.

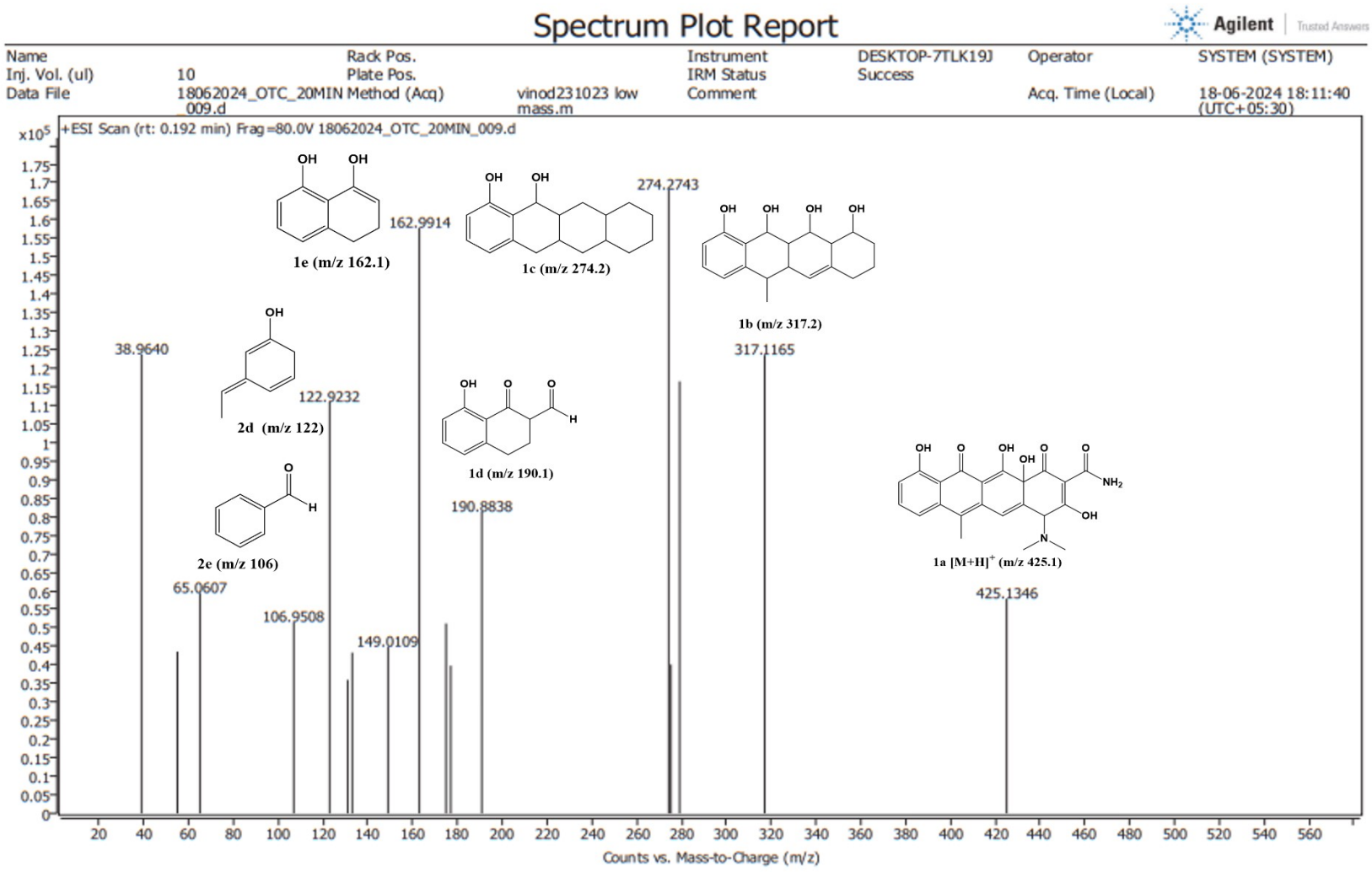


Figure SI 6. High-resolution mass spectrum of intermediates from catalyst-mediated OTC degradation (spectrum is recorded within 5 min of reaction time).

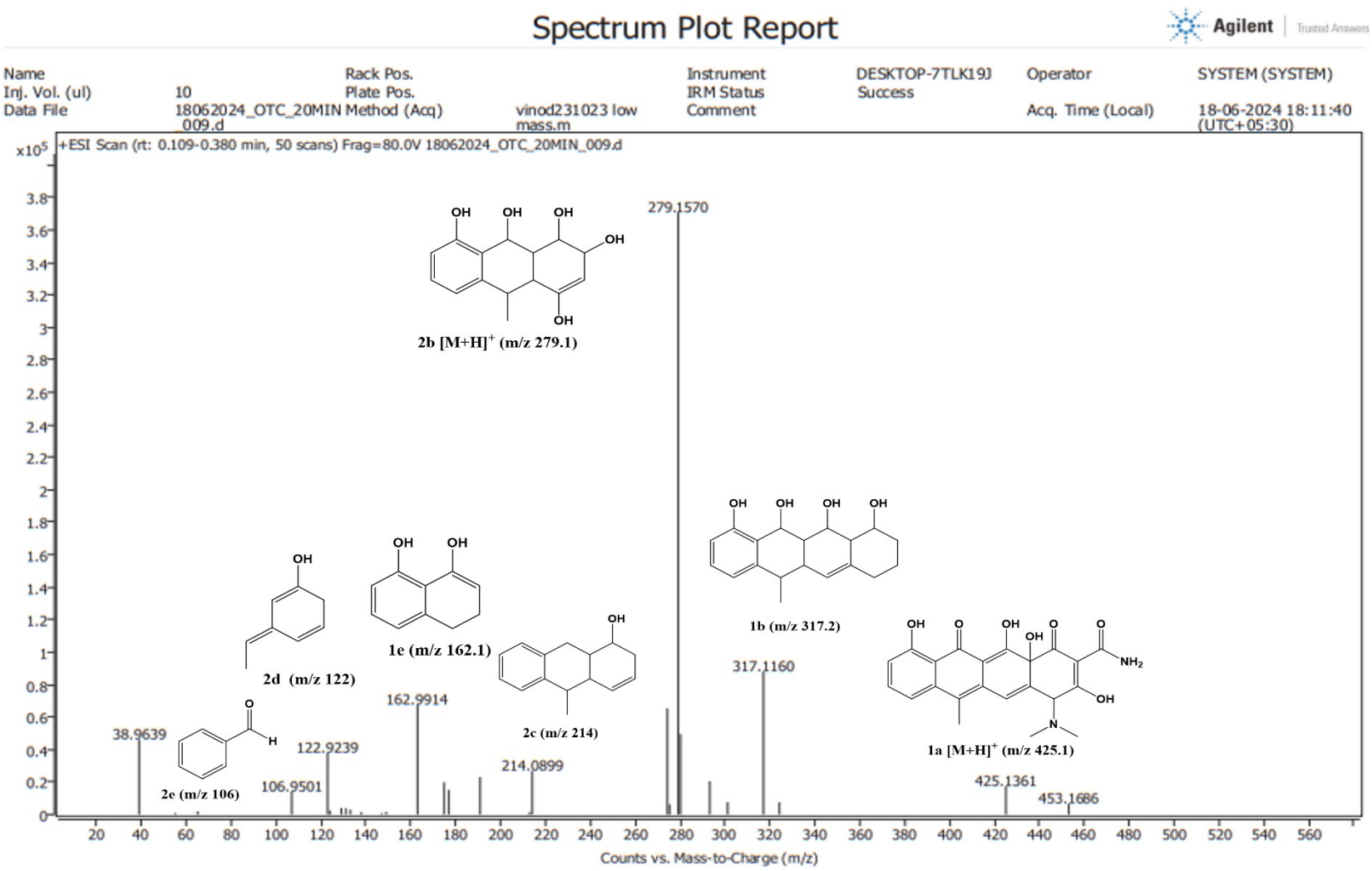


Figure SI 7. High-resolution mass spectrum of intermediates from catalyst-mediated OTC degradation (spectrum is recorded within 10 min of reaction time).

4. Regeneration and Reusability of ZVI@RH, ZVI@HC, and ZVI@BC

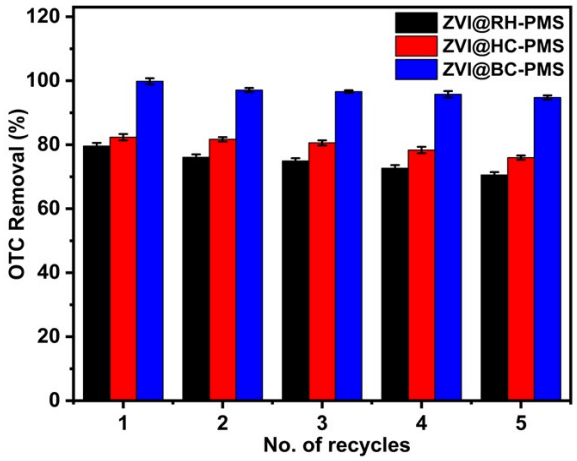


Figure SI 8. Reusability of ZVI@RH, ZVI@HC, and ZVI@BC with PMS-activated for OTC degradation process.

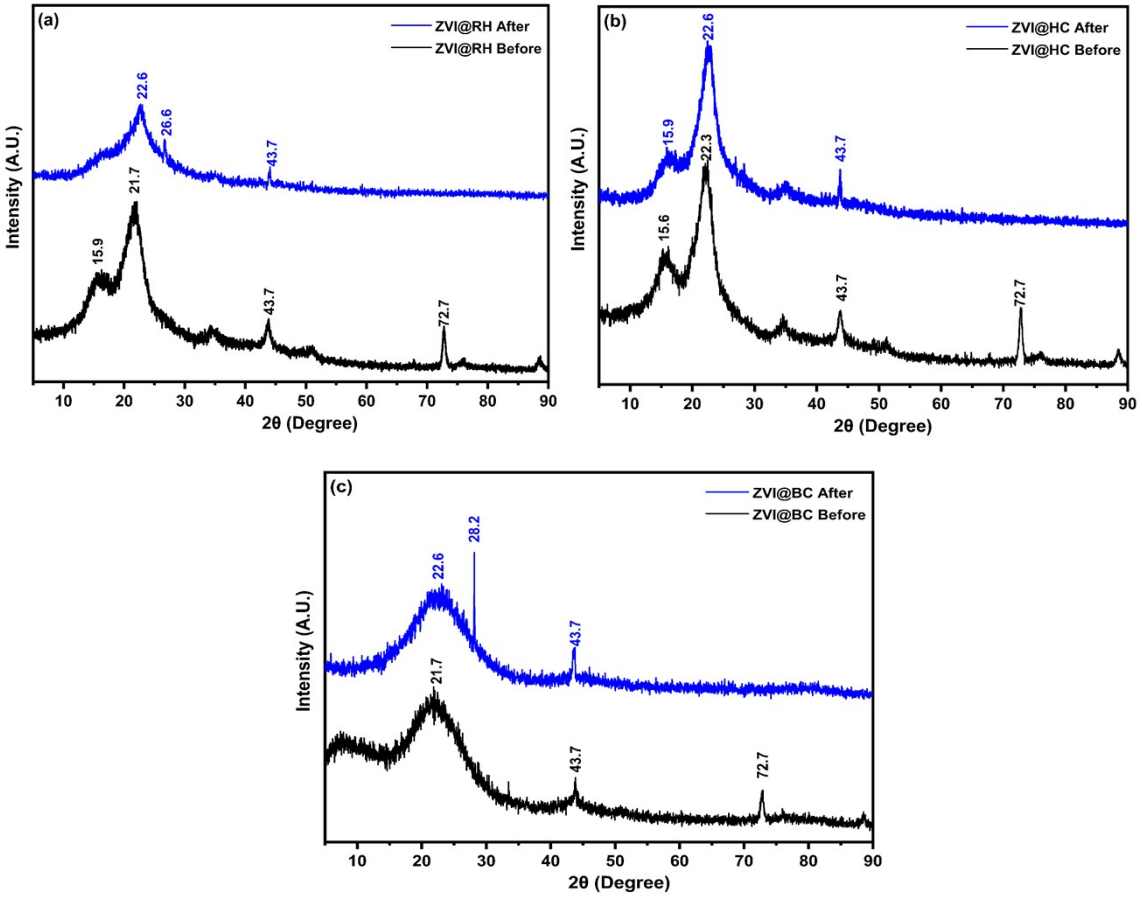


Figure SI 9. XRD pattern analysis of (a) ZVI@RH, (b) ZVI@HC, and (c) ZVI@BC before and after OTC degradation

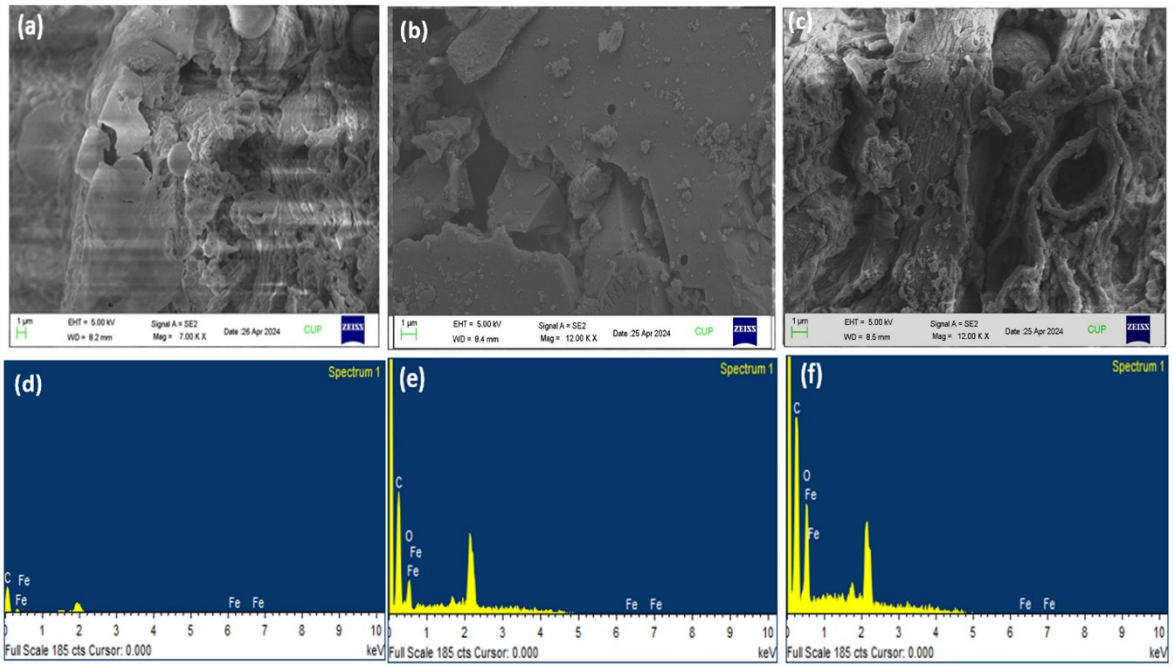


Figure SI 10. (a-c) FESEM pattern and (d-f) EDAX analysis of (a) ZVI@RH, (b) ZVI@HC, and (c) ZVI@BC after OTC degradation

4. Computational Details

To explore the interaction of adsorbent and adsorbate, the density functional theory (DFT) based first principles are performed using NWChem open-source software. To get accurate estimates for the binding energy and electronic structure of molecules, the 6-31G basis sets for C, N, H, O, and Fe atoms with B3LYP functional (Becke's 3-parameter exchange functional with Lee–Yang–Parr correlation energy functional) are used. The structure of molecules built from scratch using Vesta code is fully optimized using default convergence criteria in NWChem. The adsorption energy is calculated using the formula (Eq. SI 6) as given below:

$$E_{Ad} = E_{ABC} - E_A - E_B - E_C \qquad \text{(Eq. SI 6)}$$

Where E_{ABC} represents the total energy of the complex molecule. E_A, E_B, and E_C denote the total energy of the individual optimized molecules.

The HOMO–LUMO energy gap (H) is obtained using the formula (Eq. SI 7) as given below:

$$E = E_L - E_H \qquad \text{(Eq.SI 7)}$$

Where, E_H and E_L represent the energies associated with the HOMO and LUMO orbital, respectively. The indexes such as chemical potential (μ), chemical hardness (η), and electrophilicity index (ω), values have been calculated using the following formulas[5] (Eq. SI 7).

References

(1) Ma J. Determination of chemical oxygen demand in aqueous samples with non-electrochemical methods. Trends in Environmental Analytical Chemistry. 2017 Apr 1;14:37-43. https://doi.org/10.1016/j.teac.2017.05.002.

(2) Jouanneau S, Recoules L, Durand MJ, Boukabache A, Picot V, Primault Y, Lakel A, Sengelin M, Barillon B, Thouand G. Methods for assessing biochemical oxygen demand (BOD): A review. Water research. 2014 Feb 1;49:62-82. https://doi.org/10.1016/j.watres.2013.10.066.

(3) Liu Y, Wang L, Dong Y, Peng W, Fu Y, Li Q, Fan Q, Wang Y, Wang Z. Current analytical methods for the determination of persulfate in aqueous solutions: A historical review. Chemical Engineering Journal. 2021 Jul 15;416:129143. https://doi.org/10.1016/j.cej.2021.129143.

(4) Revellame ED, Fortela DL, Sharp W, Hernandez R, Zappi ME. Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review. Cleaner Engineering and Technology. 2020 Dec 1;1:100032.https://doi.org/10.1016/j.clet.2020.100032.

(5) Tavakol H, Haghshenas H. A DFT study on the interaction of doped carbon nanotubes with H_2S, SO_2 and thiophene. Quantum Reports. 2021 Jul 5;3(3):366-75. https://doi.org/10.3390/quantum3030023.