

ELECTRONIC SUPPORTING INFORMATION

Indigenous north eastern India fern mediated fabrication of spherical silver and anisotropic gold nano structured materials and their efficacy for the abatement of perilous organic compounds from waste water-A green approach

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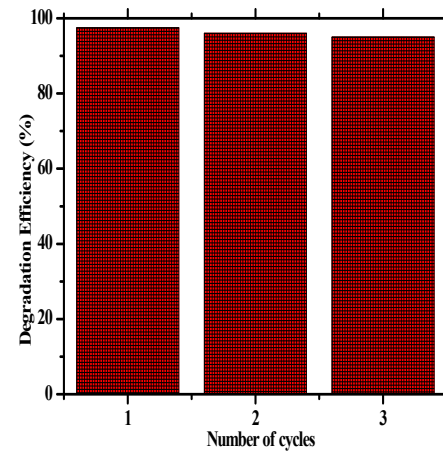
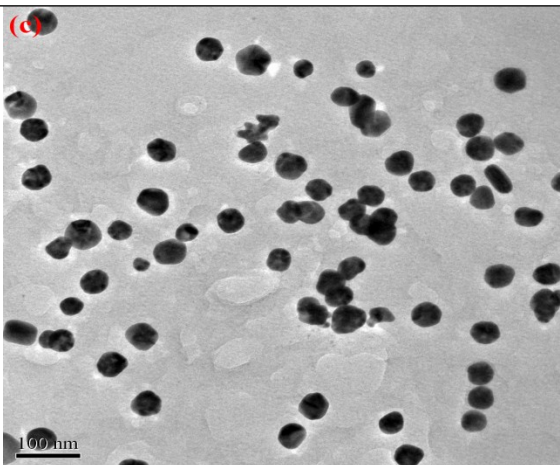
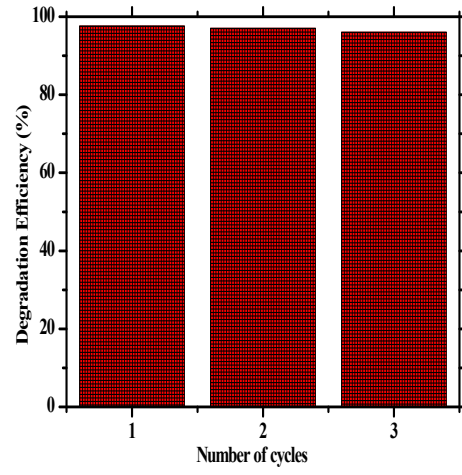
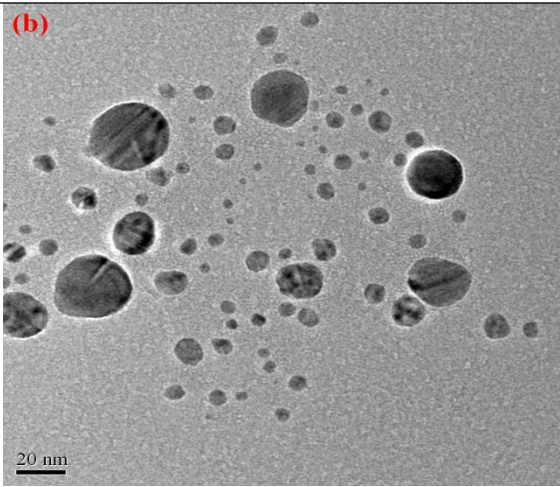
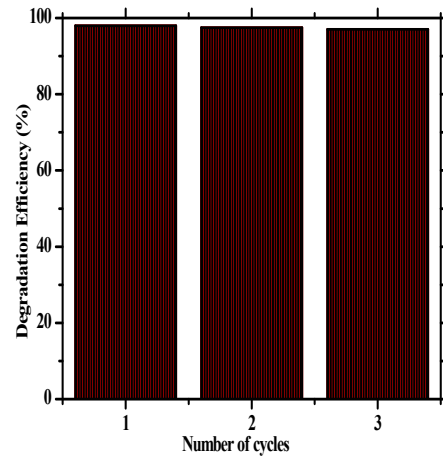
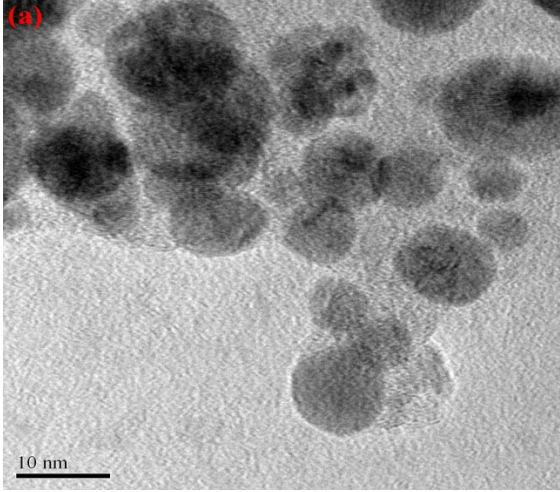
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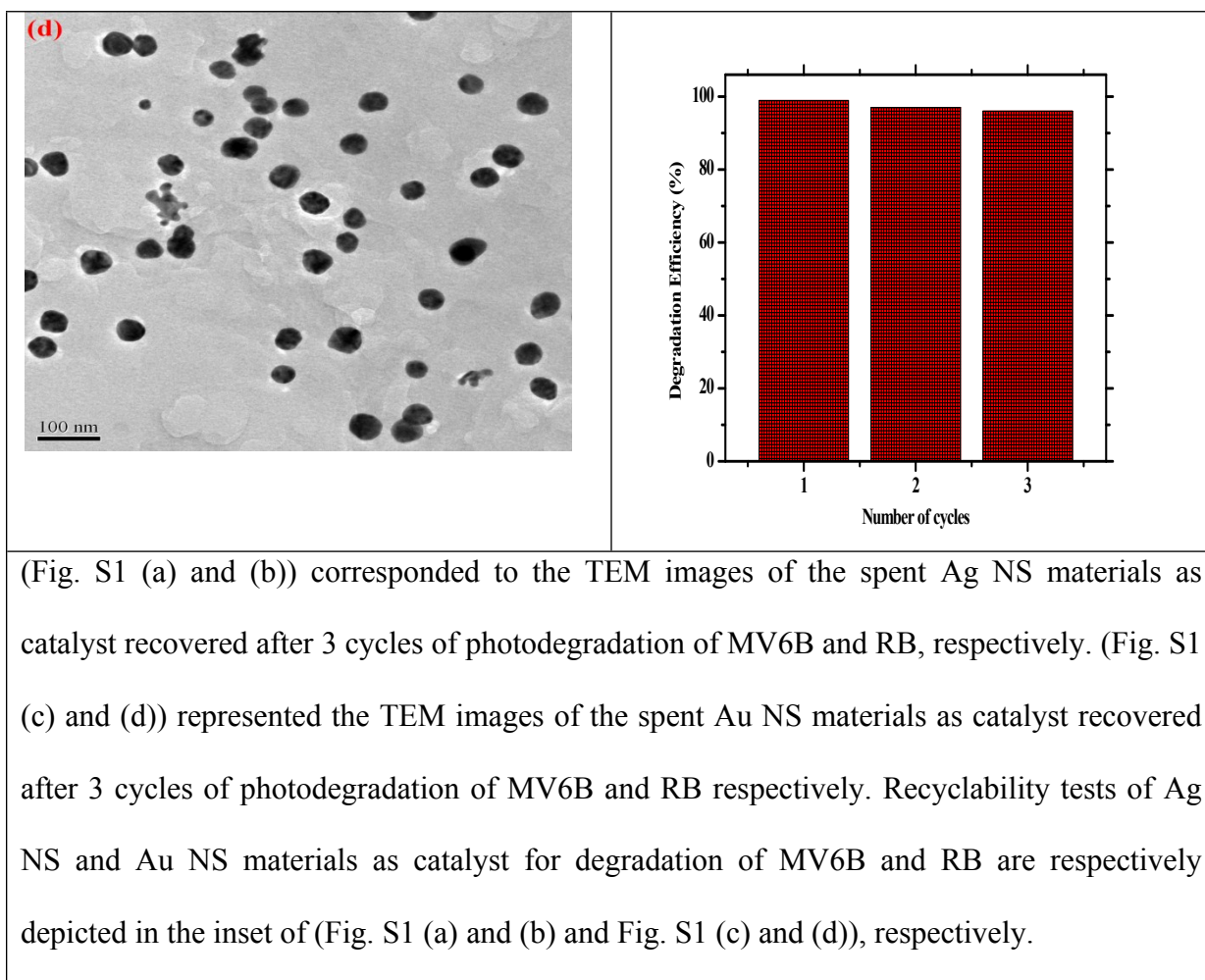
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S1 Photostability of the NS materials:

(Fig. S1 (a) and (b)) represented the TEM image of the spent catalyst recovered after 3 cycles of photodegradation of MV6B and RB employing Ag NS materials while (Fig. S1 (c) and (d)) respectively represented the TEM micrographs of the spent catalyst recovered after 3 cycles of photodegradation of MV6B and RB employing Au NS as catalyst. The TEM images revealed that the particles morphology is almost similar instead the particle morphology has been slightly increased (11-20nm) in case of MV6B and (12-24 nm) in case of RB employing Ag NS materials (Fig. S1(a) and (b)) respectively. While in case of Au NS materials as catalyst the particle size enhanced from 10-18 nm and 12-20 nm in case of MV6B and RB (Fig.S1 (c) and (d)) respectively.

The results of the recyclability test for MV6B and RB are respectively shown in the inset of (Fig. S1 (a) and (c) and Fig. S1 (b) and (d)), respectively. Thus, it was relevant that the NS materials exhibited excellent photostability under solar irradiation even after 3 cycles of recovery with unaltered morphology of the catalyst.





S2 Identification of the intermediate products of dye degradation:

The intermediates generated during the degradation process were analyzed using LC-MS technique and were identified by comparison with commercial standards and by interpretation of their fragment ions in the mass spectra.

Fig. S2 (a) displayed the LC-MS of RB dye solution with NS materials initially. The figure depicts a prominent mass signal at $m/z = 1022$ which is very close to the formula mass of RB dye. Noticeably, no mass signals corresponding to the formula of reaction intermediates were found. Fig. S2 (b) showed the LC-MS of RB dye solution with NS materials finally. Here, it was observed that the signal at $m/z = 1022$ was weakened and multiple signals corresponding to the reaction intermediates were found. The molecular structures of the possible reaction intermediates from fragmentation of the main skeleton of RB which have the oxy groups in

their rings were represented in Fig. S2 (c). It was believed that the formations of these reaction intermediates are very important to determine the degree of degradation of the organic compounds to complete the mineralization process [1].

Fig. S2(d) depicted the LC-MS of MV6B dye solution with NS materials initially. The figure clearly displayed a prominent peak at $m/z = 344$ which is very close to the formula mass of MV6B dye. Noticeably, no signals corresponding to the formation of reaction intermediates were observed. Fig. S2(e) represented the LC-MS of MV6B dye solution with NS materials after complete degradation. Here, it was found that the multiple mass signals corresponding to reaction intermediates have appeared. The molecular structures of the possible reaction intermediates from fragmentation of the main skeleton of MV6B dye were shown in Fig. S2(f). It was supposed that the formation of the reaction intermediates take place by cleavage of one or more of the methylene groups substituent on the amine group. For example, the formation of N-methyl-N''-methyl-N''-methyl pararosiline, N-methyl-N''-methyl pararosiline, N-methyl-methyl pararosiline and pararosiline (Fig.S2(f)) occurred through the demethylation cleavage during the photocatalytic degradation has been reported in the literature [2]. The pararosiline then undergoes cleavage to form 4,4'-bis-amino benophenone and 4-amino phenol which then undergoes fragmentation to furnish 4-amino benzoic acid and amino benzene (Fig.S2(g)). These then produces acetic acid and 1-hydroxy-2- propanone which then produces the mineralization products [2].

Henceforth, it could be concluded that the synthesized NS materials showed marvellous photocatalytic activity because of high surface area to volume ratio, which provided maximum exposure for the reactant to the active surface. As a whole, the photodegradation of dyes using synthesized NPs in the visible light can be explained because of the excitation of surface plasmon resonance, which is actually the oscillation of charge density that can propagate at the interface between the metal and the dielectric medium.

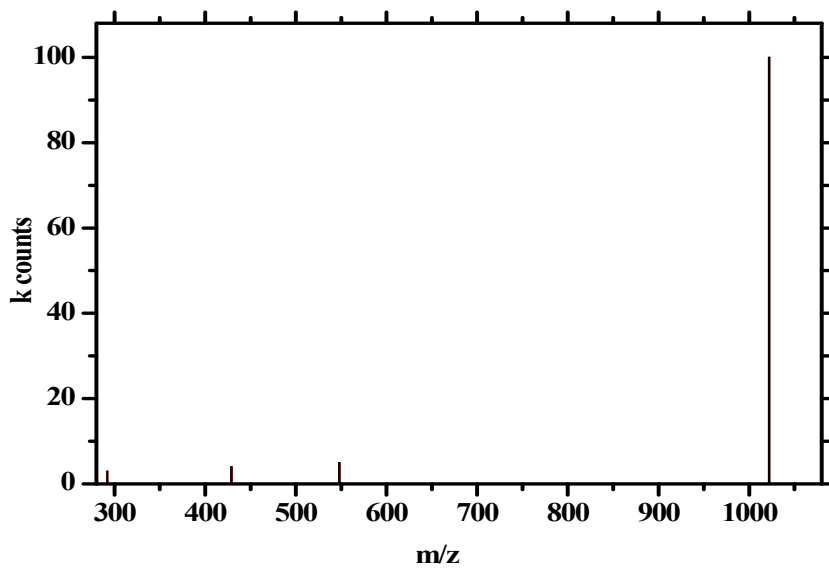


Fig. S2 (a) represented the LC-MS of RB dye solution with NS materials after 0 minutes.

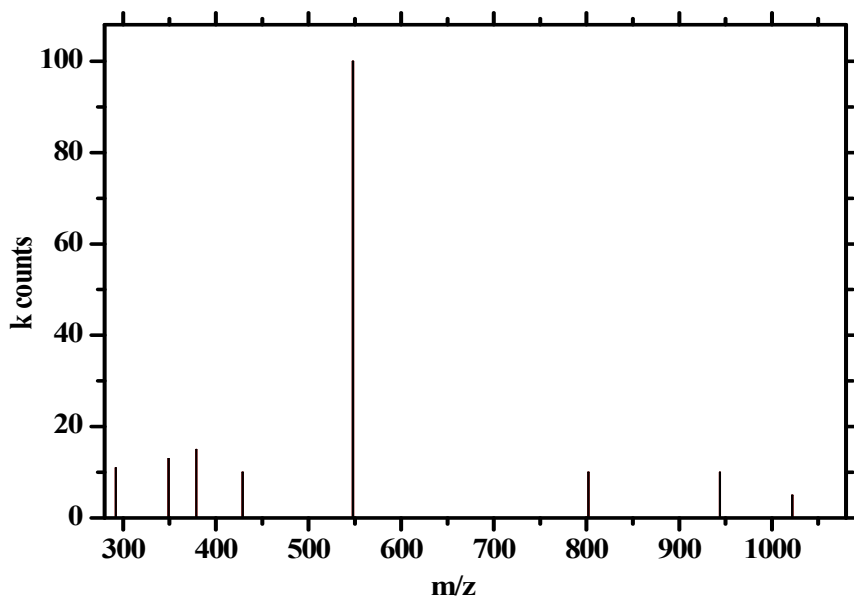


Fig. S2 (b) represented the LC-MS of RB dye solution with NS materials after complete degradation.

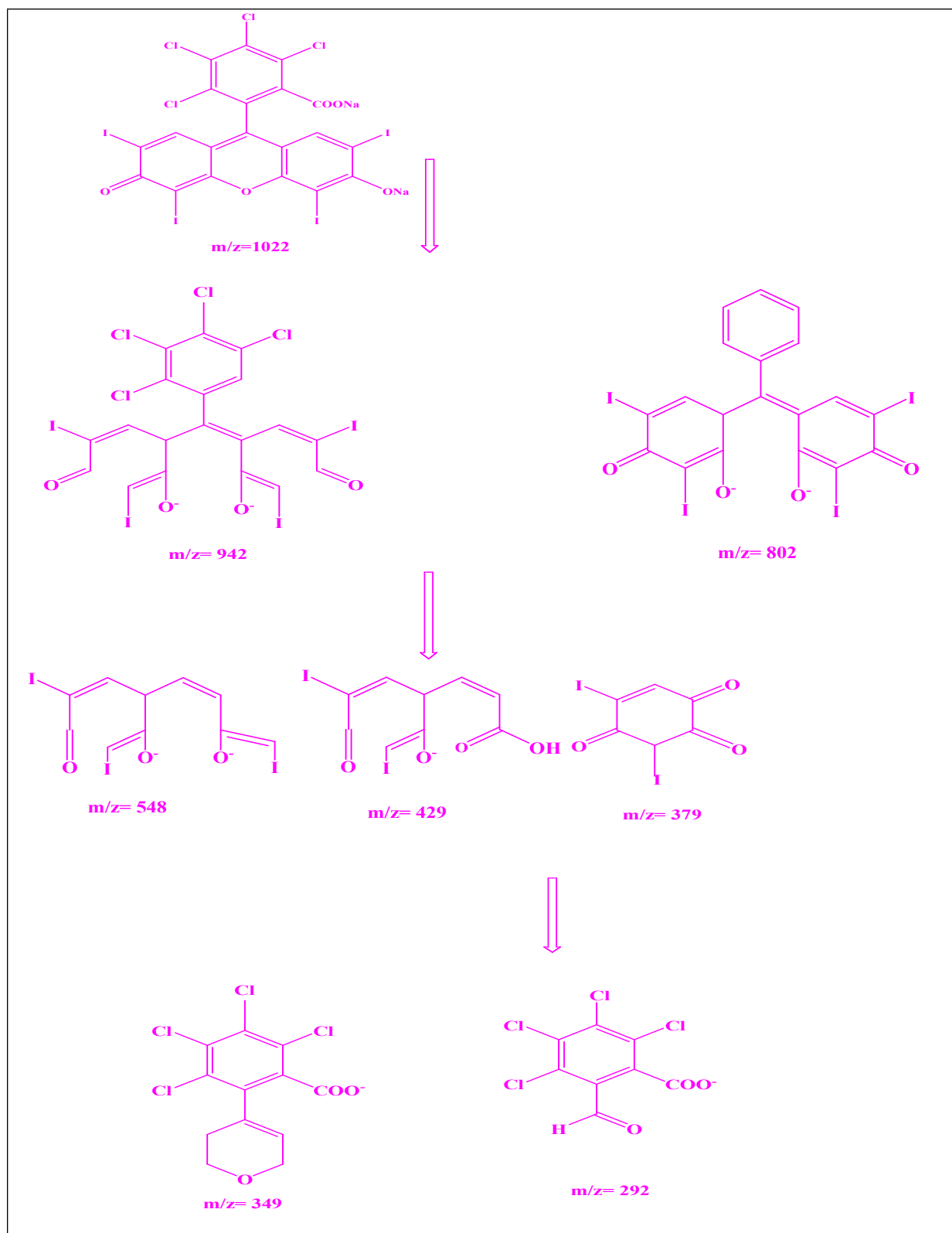


Fig.S2(c) depicted the molecular structures of the possible reaction intermediates from fragmentation of the main skeleton of RB dye.

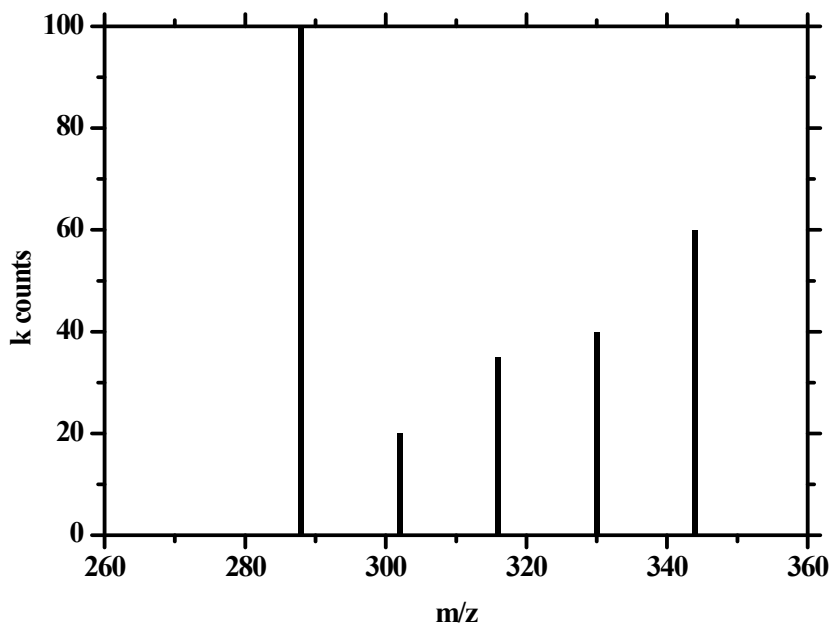


Fig. S2 (d) Showed the LC-MS of MV6B dye solution with NS materials after 0 minutes.

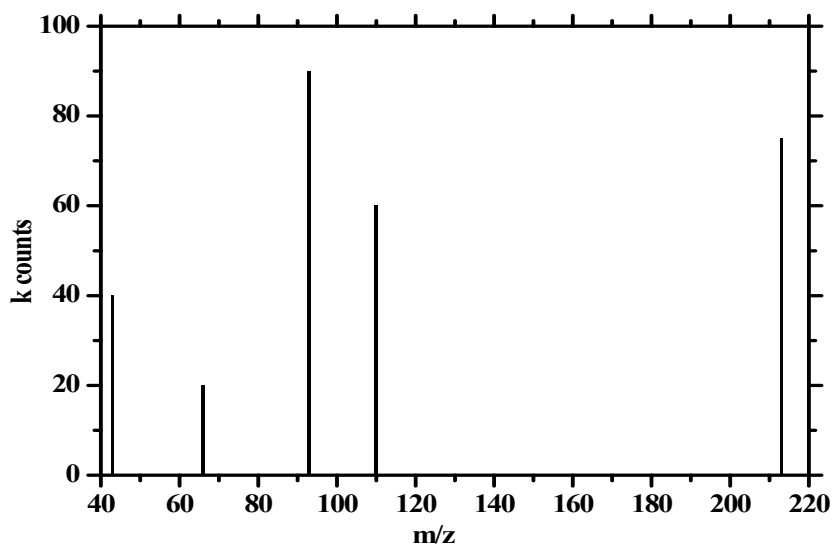


Fig. S2 (e) Depicted the LC-MS of MV6B dye solution with NS materials after complete degradation.

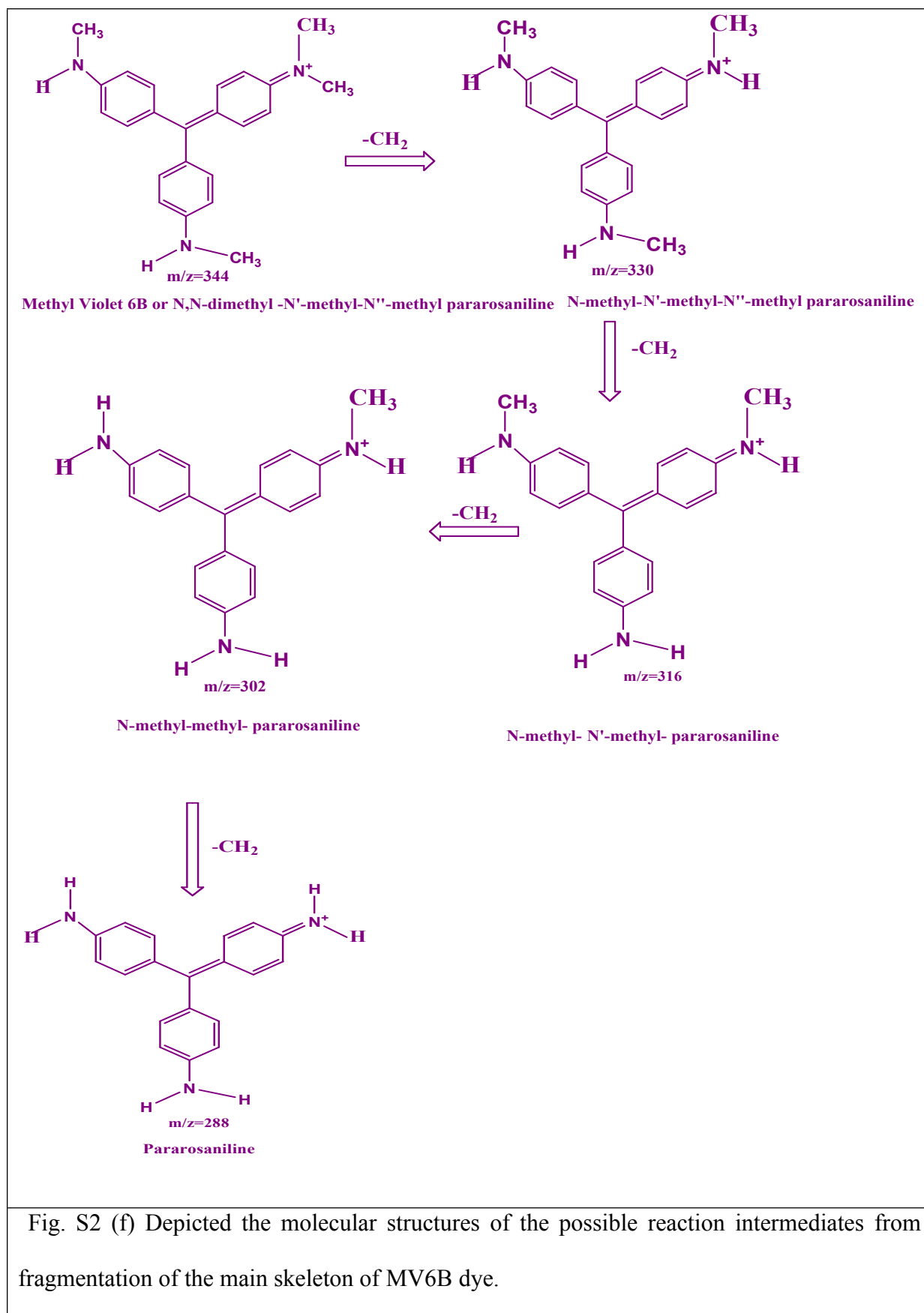
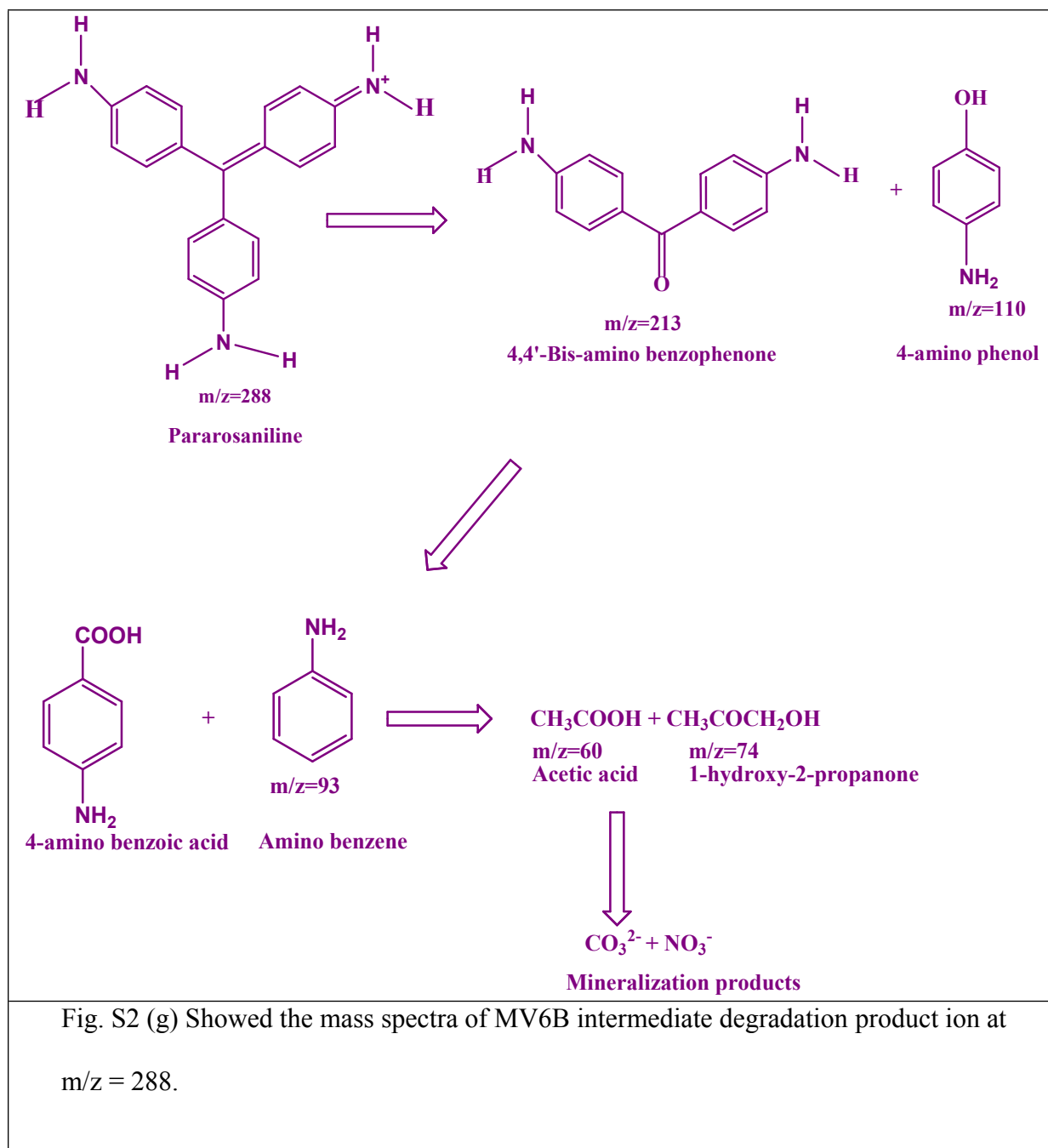


Fig. S2 (f) Depicted the molecular structures of the possible reaction intermediates from fragmentation of the main skeleton of MV6B dye.



S3.Catalytic reduction of 4-NP to 4-AP employing NS materials as catalyst in aqueous medium:

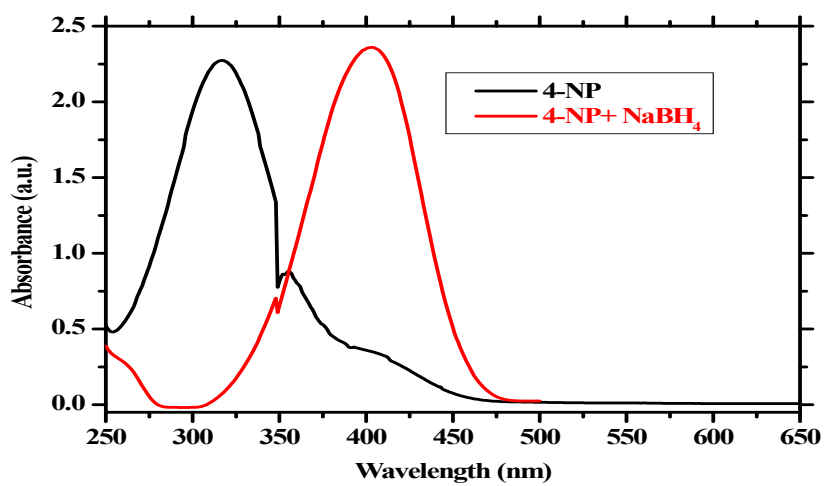
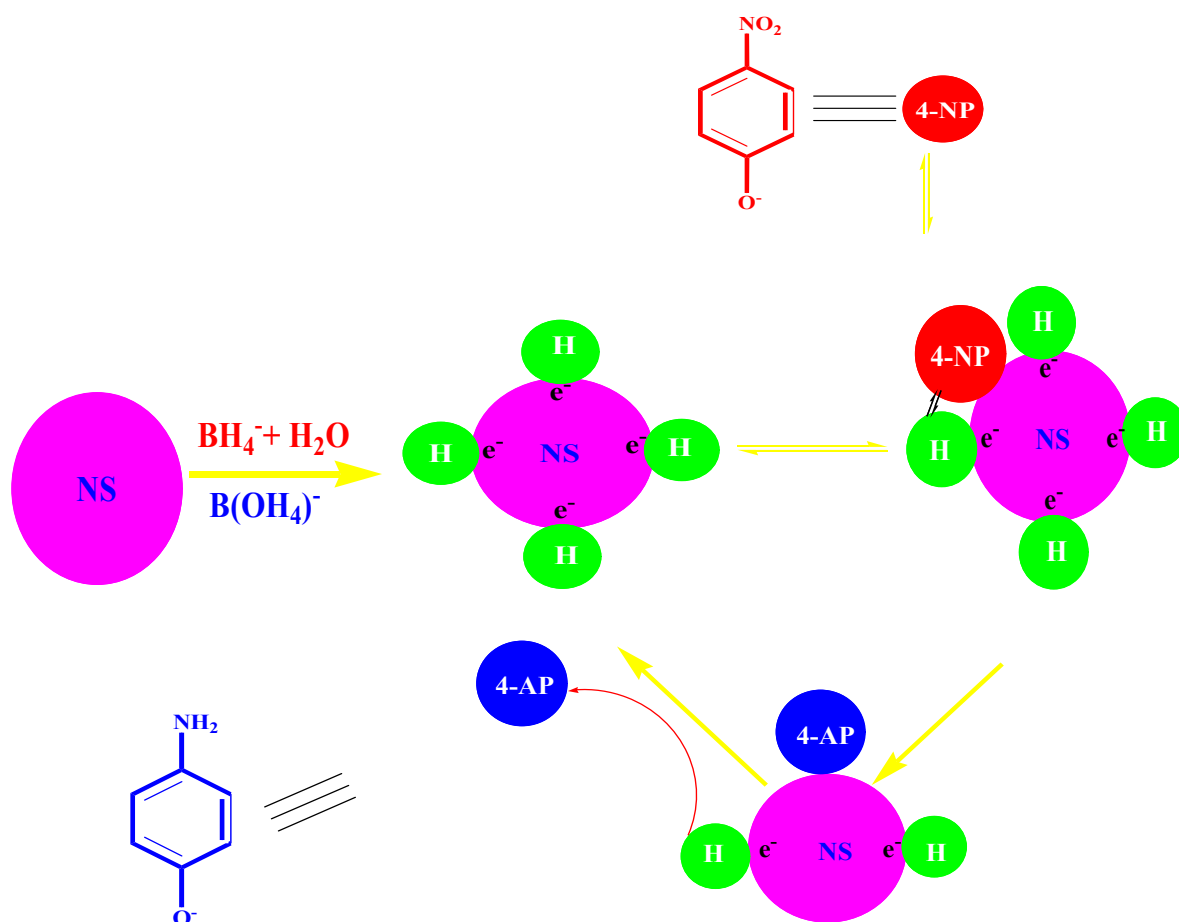


Fig. S3(a) represented the absorbance spectra of 4-NP and 4-NP + NaBH₄ in aqueous medium.

S4 Mechanism of reduction of 4-NP to 4-AP:

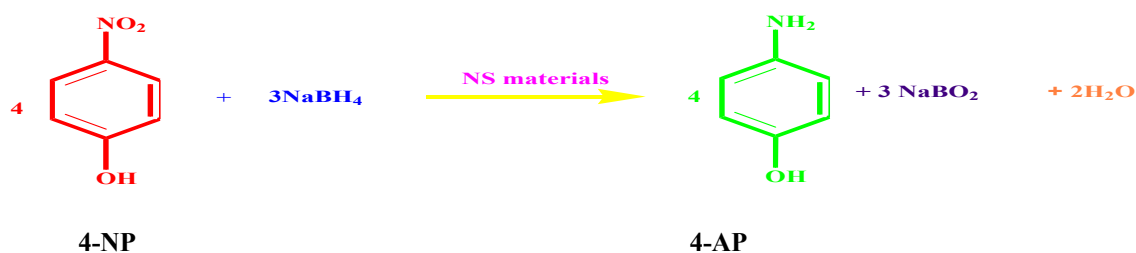
The mechanism of reduction of 4-NP to 4-AP can be illustrated in terms of Langmuir Hinshelwood model (Scheme S1) [3].



Scheme S1. Mechanism of reduction of 4-NP to 4-AP

Initially on the surface on the surface of the NS materials, the adsorption of boride ions and transfer of a surface-H specie takes place. Simultaneously, 4-NP is also adsorbed on the cluster surface. Finally, the H atom at the NS materials surface react with 4-NP to yield the product 4-AP. 4-AP then undergoes desorption. Thus, making the catalyst surface free and

the catalytic cycle can begin again. Henceforth, the reduction reaction could be summarized by the following equation:



REFERENCES:

- [1] S. Ameen, H.K.Seo, M.S.Akhtar, H.S.Shin, Novel graphene/polyaniline nanocomposites and its photocatalytic activity toward the degradation of rose Bengal dye, *Chem. Eng. J.*, 2012, 210, 220-228.
- [2] H.J. Fan, S.T Huang, W.H. Chung, J.L. Jan, W.Y. Lin, C.C. Chen, Degradation pathways of crystal violet by Fenton and Fenton-like systems:Condition optimization and intermediate separation and identification. *J. Hazard.Mater.*, 2009, 171, 1032-1044.
- [3] S. Wunder, F. Polzer, Y. Lu, Y. Mei, M. Ballauff, Kinetic Analysis of Catalytic Reduction of 4-Nitrophenol by Metallic Nanoparticles Immobilized in Spherical Polyelectrolyte Brushes, *J. Phys. Chem. C.*, 114 (2010) 8814–8820.

