Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts

SUPPLEMENTARY DATA

Photodegradation Routes of the Herbicide Bromoxynilin Solution and Sorbed on Silica Nanoparticles.

1.- Characterization of the nanoparticles:

1.1 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectra in the range from 4000 to 400 cm^{-1} were recorded on a Bruker EQUINOX 55 apparatus with a resolution of 2 cm^{-1}, using a KBr disk. To obtain a high signal-to-noise ratio 128 scans were accumulated for each sample.

The FTIR spectra of BXN and NP-BXN are compared in Table S1.

Table S1: Bands observed in FTIR spectra of BXN and NP-BXN.

BXN	NP-BXN
2928.7	2928.8
2868.1	2860.1 / 2872.9
2229.7	2233.7
1465.2	1468.6
1548.5	1545.1
717.6	704.2

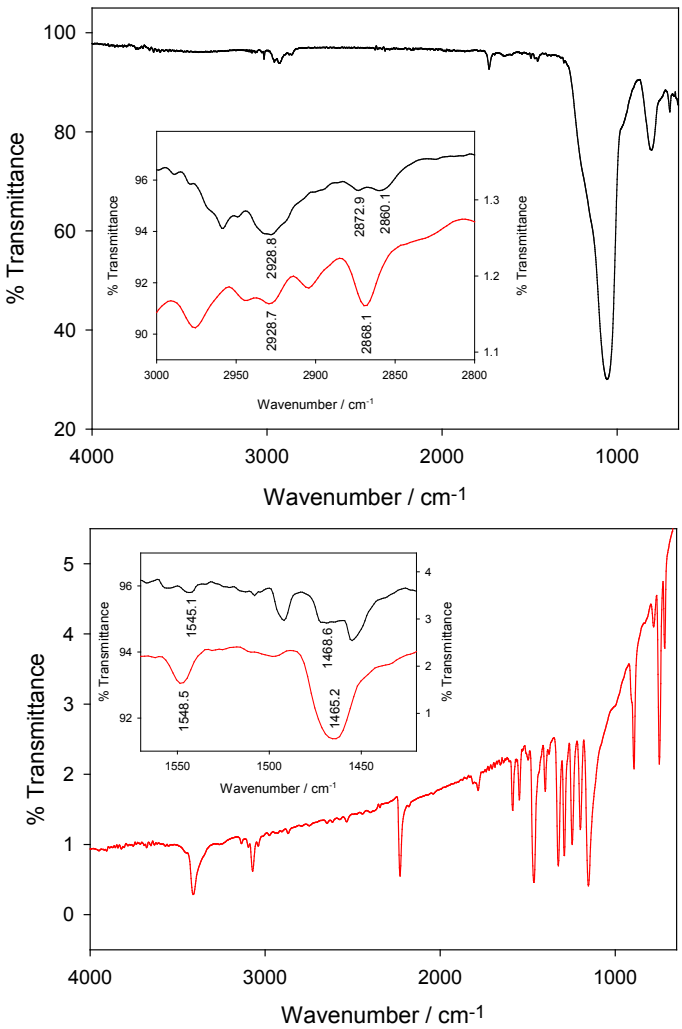

Figure S1: FTIR spectra of BXN (red) and NP-BXN (black).

1.2 Brunauer-Emmett-Teller (BET) analysis

The specific surface area (SSA) was determined via nitrogen (N_2) adsorption isothemsat 77 K in the reduced pressure range from 0.04 to 0.12 using the Brunauer-Emmett-Teller (BET) method (1). For this puropose a gas adsorption apparatus (Micromeritics ASAP 2020 V1.04 E) was employed.

1.3 Thermogravimetry (TG)

The thermogravimetric curve was performed with a Shimadzu TA-50 thermogravimeter analyzer, under He atmosphere with heating rate of 0.17 Ks^{-1}. The instrument was calibrated with $CaC_2O_4.3H_2O$.

1.4 UV-Visible Spectroscopy

The absorption spectra were taken with a computer-controlled Hewlett Packard 8453 spectrophotometer.

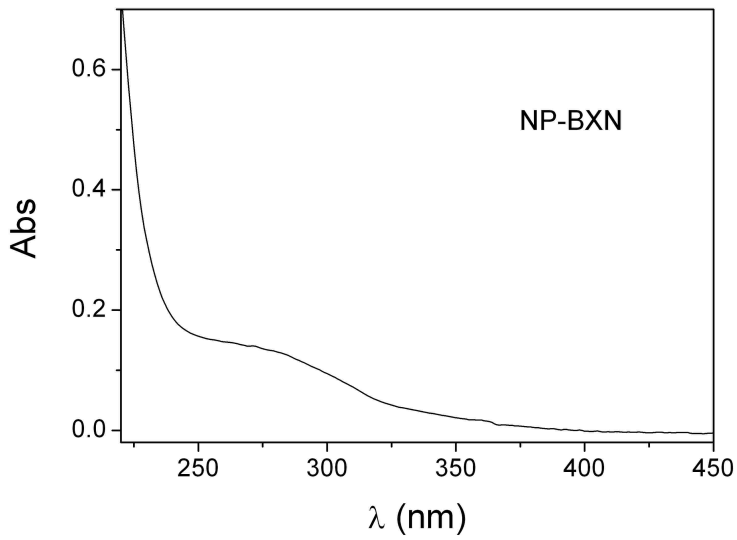

Figure S2: Absorption component of the UV-visible spectrum of NP-BXN.

1.5 Dynamic light scattering

The hydrodynamic diameter and size distribution of particles was measured by dynamic light scattering using a Malvern 4700 goniometer and 7132 correlator with an argon-ion laser operating at 488 nm. All measurements were made at a scattering angle of 90◦ at temperature of 25 ◦C. The measurements were analyzed by triplicate and the results were analyzed with Zetasizer software (provided by the manufacturer).

2.- Kinetics of Bromide Ion Formation

From Scheme 1:

$$-\frac{d[BXN]}{dt} = k_4 \times [BXN] \quad \text{(S1)}$$

$$\frac{d[DHBN]}{dt} = k_4 \times [BXN] - k_5 \times [DHBN] \quad \text{(S2)}$$

$$\frac{d[Br^-]}{dt} = k_4 \times [BXN] + k_5 \times [DHBN] \quad \text{(S3)}$$

Integration of eq. (S1) yields eq. (S4).

$$[BXN] = [BXN]_o \times e^{-k_4 \times t} \quad \text{(S4)}$$

From eqs. (S2) and (S4), eq. (S5) is obtained.

$$\frac{d[DHBN]}{dt} = k_4 \times [BXN]_o \times e^{-k_4 \times t} - k_5 \times [DHBN] \quad \text{(S5)}$$

Integration of eq. (S5) leads to eq. (S6).

$$[DHBN] = \frac{k_4 \times [BXN]_o}{(k_5 - k_4)} \times \left(e^{-k_4 \times t} - e^{-k_5 \times t}\right) \quad \text{(S6)}$$

From eqs. (S3), (S4), and (S6), we can write eq. (S7).

$$\frac{d[Br^-]}{dt} = k_4 \times [BXN]_o \times e^{-k_4 \times t} + \frac{k_4 \times k_5 \times [BXN]_o}{(k_5 - k_4)} \times \left(e^{-k_4 \times t} - e^{-k_5 \times t}\right) \qquad \text{(S7)}$$

Rearrangement and integration of eq. (S7) leads to eq. (S8).

$$[Br^-] = \frac{(2k_5 - k_4) \times [BXN]_o}{(k_5 - k_4)} \times \left(1 - e^{-k_4 \times t}\right) - \frac{k_4 \times [BXN]_o}{(k_5 - k_4)} \times \left(1 - e^{-k_5 t}\right) \qquad \text{(S8)}$$

If k5 >> k4, eq. (S9) is obtained from eq. (S8).

$$[Br^-] \approx 2 \times [BXN]_o \times \left(1 - e^{-k_4 \times t}\right) \qquad \text{(S9)}$$

3.- Calculation of k_a.

The photolysis rate of aqueous BXN can be expressed as:

$$-\frac{d[BXN]}{dt} = k_a \Phi [BXN] \qquad \text{eq. (S10)}$$

Where Φ is the photolysis quantum yield and k_a is the specific rate of light absorption.

The rate constant k_a was calculated from equation (S11) as recommended by Zepp (3).

$$k_a = \frac{2.303}{6.02 \times 10^{20}} \times \sum \bar{\varepsilon}_\lambda Z_\lambda \qquad \text{eq. (S11)}$$

Where $\bar{\varepsilon}_\lambda$ is the average absorption coefficient at a wavelength interval centered at λ and Z_λ is the underwater solar irradiance in this wavelength interval. Table S2 lists the values of $\bar{\varepsilon}_\lambda$ and Z_λ employed in the calculations.

From the data shown in Table S2 and eq. (S2) the calculated value of k_a is 7.92×10^{-3} s^{-1} and the photolysis rate $k_a \times \Phi$ yields 5.07×10^{-4} s^{-1} for BXN and 1.66×10^{-5} s^{-1} for NP-BXN.

Table S2: The values of $\bar{\varepsilon}_\lambda$ from this work and Z_λ in water midday, midsummer, latitude 40°N from ref. (2).

λ(nm)	**$\bar{\varepsilon}_\lambda$ ($M^{-1}cm^{-1}$)**	**Z_λ(photons/cm^2s) ×10^{-14}**
297.5	10709.8	7.1600×10^{-3}
300.0	9948.1	0.0240
302.5	9048.5	0.0723
305.0	8020.7	0.1810
307.5	6886.7	0.3050
310.0	5682.4	0.4950
312.5	4456.2	0.7170
315.0	3266.9	0.9330
317.5	2179.3	1.1500
320.0	1258.4	1.3500
323.0	455.8	2.5200
330.0	210.0	8.4600

References

1.- S. Brunauer, P.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309-319.

2.- R.G. Zepp, *Environ. Sci. Technol.*, 1978, **12**, 327–329.