**Supplementary material**

# Eco-Friendly Synthesis of $TiO_2$/ZIF-8 Composites: Characterization and Application for the Removal of Imidacloprid from Wastewater

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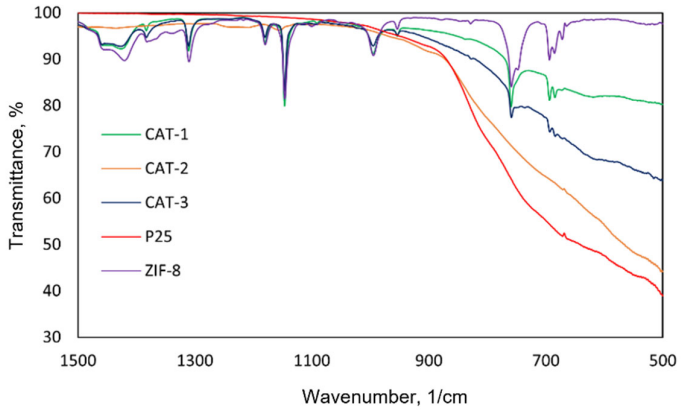


**Figure S1** IR spectra of the studied series of samples

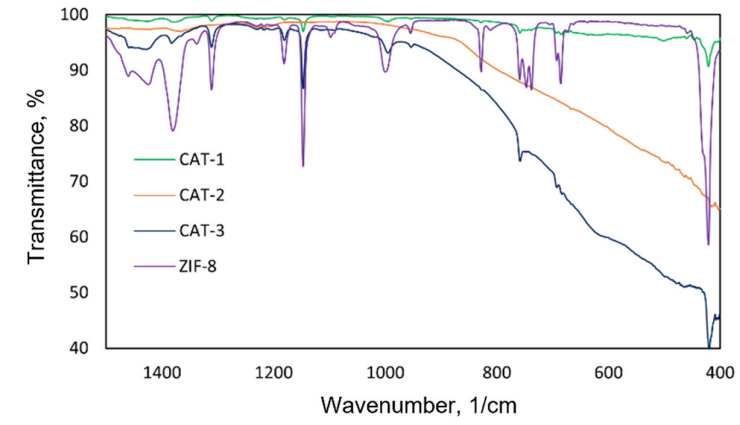


**Figure S2** IR spectra of the samples after imidacloprid adsorption

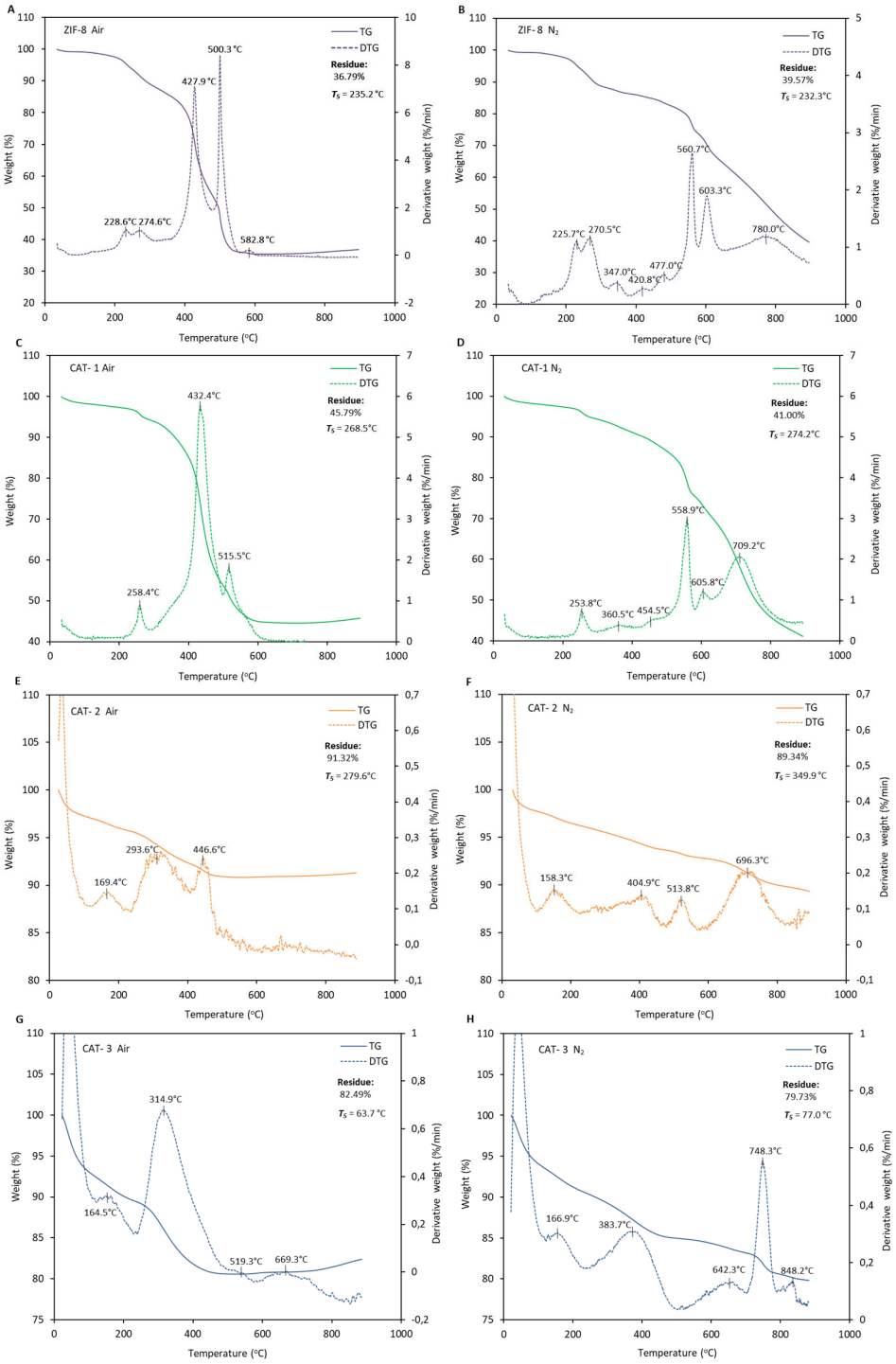


**Figure S3** TGA curves of the samples in nitrogen (A, C, E, G) and air (B, D, F, H) for mechanochemically synthesized ZIF-8 (A, B), CAT-1 (C, D), CAT-2 (E, F) and CAT-3 (G, H)

ZIF-8 looses 5% of its mass at approximately 230 °C in air and in an inert atmosphere. At the end of the analysis in both gas streams, approximately the same mass remains (~ 37% of the initial mass of the ZIF-8 sample). During heating in a stream of nitrogen, several stages of decomposition are observed, which are assumed to be the result of the loss of water and smaller organic molecules present during the synthesis process. In Figures 6A and B two significant peaks attributed to the decomposition of ZIF-8 in two stages are visible, i.e. the first one assigned to the conversion of ZIF-8 into starting components, i.e. 2-methylimidazole and zinc oxide, and the second one to the decomposition of 2-methylimidazole [72,73]. The described process was observed regardless of the atmosphere in which the TG analysis was performed, however, in the nitrogen stream it occurs at higher temperatures (560.73 °C and 603.27 °C) than in the air stream (427.94 °C and 500.31 °C). It follows that ZIF-8 is thermally stable and applicable in a wide range of temperatures up to 400 °C.

In Figures S3 C-H are presented the TGA curves for the synthesized composite photocatalysts. The remaining mass after the analysis depends on the composition of the composite, that is, CAT-1 retains ~ 45% of the mass at the end of the analysis, given that it includes 95% of ZIF-8. After the analysis, a mixture of $TiO_2$ and ZnO remains, which, as inorganic oxides, are stable at temperatures higher than 900 °C. Accordingly, CAT-2 retains ~ 90% of the initial mass, and CAT-3 ~ 80% upon TG analysis. Due to the high thermal stability of the inorganic components of the analyzed samples, it is assumed that water and smaller organic molecules remaining after the synthesis were removed in the early stages of the analysis, followed by the decomposition of ZIF-8 and 2-methylimidazole.

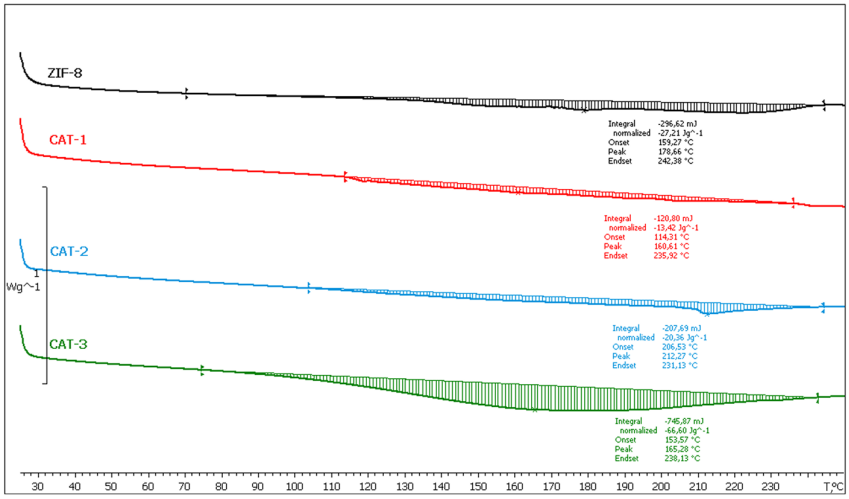


**Figure S4** DSC curves of the studied series of samples

The highest crystallinity is shown by the CAT-3 composite with a latent heat of fusion of 66.60 Jg-1, while the lowest crystallinity is shown by the CAT-1 composite with a latent heat of fusion of 13.42 Jg-1. Melting temperatures (Tm) were also recorded for each sample. The highest melting temperature was achieved for the sample CAT-2 and is 212.27 °C, and the lowest for CAT-1 with the value of 160.61 °C.

## Adsorption experiments

The adsorption capacity ($Q$, mg g-1) is calculated by the following formula:

$$Q = \frac{(C_{A_0} - C_A) \cdot V}{m}$$

where $C_{A0}$ and $C_A$ are the initial imidacloprid concentration and the concentration in the solution (mg L-1 ) at reaction time t, respectively, $V$ represents the volume of the reactant solution (L), and $m$ denotes the mass of the adsorbens. The equilibrium concentration in a given system depends on the concentration of imidacloprid in the solution, the mass of the adsorbent, and the temperature. If the adsorption is carried out in a closed reaction system (batch system) until the appropriate reaction time, i.e. until the time when the concentration of imidacloprid in the solution no longer changes, then this final concentration is the equilibrium concentration.

According to the literature, the mechanism of adsorption can be explained in different ways, including electrostatic interaction, π–π interaction/stacking, hydrogen bonding, acid-base interaction or combination of different interactions [87,88] Understanding the adsorption mechanism is very important for future applications and developments of these materials. The comparison of the results obtained in this work with those published in the literature is very difficult, especially when neonicotinoid insecticides are used as model compounds. Mahmoud et al. [89] gave a comprehensive review and comparison of various MOFs such as OPA-MOF, MIL -100, $NH_2$- MIL -101, Fe-MOF, PCN-224, UiO-66, UiO-66-$NH_2$, HKUST-1, etc. as potential candidates for adsorption and controlled removal of pesticides for agricultural applications. It is noted that the adsorption capacity or percentage eliminated for the corresponding pesticide depends on the formulation of MOFs, the class of pesticide to which adsorption is applied (organophosphates, chlorophenoxy pesticides, neonicotinoids, and miscellaneous), and the conditions under which adsorption is performed, with pH playing a particularly important role. Furthermore, Mahmoud et. al. [89] have considered some challenges related to the use of MOFs, such as modification of linkers that may alter some factors essential for incorporating guest molecules, like the surface charge limiting the pH range for optimal adsorption/loading conditions, synthesis method, etc.

Table S1. An overview of the adsorption capacities of MOF composites found in literature.

| MOFs | Model compound | Adsorption capacity, mg g-1 | Operating condition | Reference |
|---|---|---|---|---|
| $Fe_3O_4$-ZIF-8@ZIF-67 | Fipronil<br>Fipronil desulfiny<br>Fipronil sulfide<br>Fipronil sulone | 3.24 -5.73 | 45 min, 0-20 mg L-1, 15 mg, pH 6, mixture of 4 pesticides | [84] |
| ZIF-8/magnetic multi-walved carbon nanotubes (MWCNT) | Ethoprop<br>Diazinon<br>Isazofos<br>Methidathion<br>Phosalone<br>Profenofos<br>Sulfotep<br>Triazophos | 2.34 -3.89 | 15 min, 8 mg L-1, 15 mg, pH 4, mixture of 8 pesticides | [85] |
| Cu-HKUST-1/$Fe_3O_4$-GO-β-CD | Acetamiprid<br>Clothianidin<br>Dinotefuran<br>Imidacloprid<br>Nitenpyram<br>Thiacloprid<br>Thiamethoxam | 1.77 -3.20 | 60 min, 100 mg L-1, 5 mg, mixture of 7 neonicotinoid pesticides | [86] |
| ZIF-8<br>$TiO_2$(5, 50 wt%)/ZIF-8 | Imidacloprid | 0.3842<br>0.0016-0.030 | 120 min, 1 g L-1, 80 mg, pH 6.5 | This work |

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