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1	Porous Zinc-Discs as Nanocatalyst for Methylene Blue Dye Treatment in Water: Sensing, Adsorption and Photocatalytic
2	Degradation
3	
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10 1. Materials and methods

11 Zinc nitrate hexahydrate [(ZnNO₃)₂.6H₂O)] (Molychem), 2-aminoterphthalic acid (H₂ATA) (Alfa Aesar), triethylamine (TEA) 12 (Merck), dichloromethane (CH₂Cl₂) (Rankem), Sodium hydroxide (NaOH) pellets (Rankem), ethanol, acetone, 13 dimethylformamide (DMF) (Emplura) andHCl (Rankem) were of analytical grades. Indigo Carmine (IC) (C16H8N2O8S2; Mol.wt. 14 466.36 g/mol; Sisco Research Laboratories Pvt. Ltd.), Methylene blue trihydrate (MB) (C16H18CIN3S.H2O; Mol.wt. 319.85 g/mol; SRL), Crystal Violet (CV) (C₂₅H₃₀N₃Cl; Mol.wt. 407.979 g/mol; SRL), Trypan blue (TB) (_{C34}H₂₄N₆Na₄O₁₄S₄; Mol.wt. 872.88 g/mol; 15 16 SRL), Rhodamine B (RhB) (C₂₈H₃₁ClN₂O₃; Mol.wt. 479.02 g/mol. All the chemicals and reagents were applied without any further 17 purification. Double distilled water (DI H₂O) with a resistivity of 18 MΩcm was used in all experiments as it was received from 18 the Millipore purification system.

19 1.1 Sensing of organic dyes and selectivity study

20 The sensing study of dye was performed using PL spectroscopy. An aqueous stock solution (1000 ppm) of MB, RhB, TB, and IC 21 was prepared in DI water. 1 g of respective dye was dissolved in 1 L DI water to generate the stock solution. A series of aqueous 22 solutions with a distinct concentration of MB dye were prepared from the stock solution. To determine the surface charge of 23 the as-prepared0.1 mg/ml ZD samples, the pH 2-12 was adjusted using 0.1 M HCl and 0.1 M NaOH solutions. The effect of pH 24 (2-12) on the absorbance and PI emission properties of as-synthesized ZD were also monitored. The interaction of the dye with 25 ZD was studied at selected pH (i.e.,2, 8, and 12). MB sensing study was performed using the 0.1mg/ml ZD solution as a 26 reference. MB was added into this ZD solution to have its final concentration varying as3.1x10-9 M, 7.8x10-8 M, 1.5x10-7 M, 27 3.1x10⁻⁷ M, 6.2x10⁻⁷ M, 1.2x10⁻⁶ M, 1.8x10⁻⁶ M, 2.5x10⁻⁶ M, 3.1x10⁻⁶ M, 6.2x10⁻⁶ M, 1.2x10⁻⁵ M, 1.8x10⁻⁵ M, 2.5x10⁻⁵ M, 3.1x10⁻⁵ 28 M to 1.5x10⁻⁴ M in the respective sample. The variation in the emission intensity of the reference ZD sample was monitored 29 with PL spectroscopy.

30 1.2 Adsorption of Organic dyes and selectivity study

31 Before the adsorption process, the adsorbent or ZD was dried under vacuum at 80°C and stored in the desiccators. Initially, the

32 10mg/L ZD was used as a reference and studied for the adsorption of 10 mg/L MB in solution. The impact of contact time on the

- 33 adsorption capacity (qe) of ZD (0.025 mg/L) for MB removal (10 mg/L) was read by varying the contact time from 0 to 480
- 34 minutes. Further, the best fitted reaction-order kinetic was also determined. The effect of initial adsorbate concentration on

35 the adsorption efficiency of ZD was studied at 10, 20, 40, 60, 80, and 100 mg/L concentrations of MB in solution. This study was 36 utilized to obtain the adsorption isotherm parameters for this ZD/MB-based adsorption system.

The adsorption experiments were followed through in a 100 ml flask at 25°C. The ZD and MB solutions were mixed well with magnetic stirring at 120 rpm for a specific time interval of contact. After a predetermined time, the reaction mixtures were centrifuged and the adsorbate concentration in the solution was analyzed using a UV-Vis spectrophotometer to find the adsorption capacity and removal efficiency of ZD. To determine the effect of various pHs on the adsorption capability, the pH of ZD was pre-adjusted with 0.1M NaOH and 0.1 M HCl.

42 1.3 Photocatalytic degradation of dye

43 The photocatalytic performance of ZD nanocatalyst was monitored by degrading MB dye and verified with UV-Vis absorption 44 spectroscopy. Under the dark conditions, the 10 mg/L ZD was used as a reference and studied for the photocatalytic 45 degradation of 10 mg/L MB at ambient temperature. Initially, the solution was stirred to attain the adsorption-desorption 46 equilibrium in a 500 ml capacity reactor. Similarly, IC, Rh B, and CV dye solutions were also prepared with the ZD in dark. 47 Thereafter, the photocatalytic reaction of this solution was performed under a 400W metal halide arc lamp. The experimental 48 parameters such as photocatalyst dosage (10 mg/L and 20mg/L ZD) and reaction time were optimized to facilitate the MB 49 removal from the samples. The variation in absorption profile of the respective solutions is monitored and recorded at an 50 increased time interval of 5 min up to 70 minutes. Before recording the data, the treated samples were collected by 51 centrifugation of the samples at 10,000 rpm. Finally, the reaction kinetics along with their respective rate constants and 52 correlation coefficients were calculated. Besides, the selective degradation efficiency of ZD for MB under UV-irradiation was 53 also studied with the different dyes such as IC, RhB, and CV at concentrations as 7.8x10⁻⁸ M, 6.2x10⁻⁷ M, and 6.2x 10⁻⁶ M. The 54 before and after treatment effect of ZD nanocatalyst on the MB concentrations were determined using a UV-Vis 55 spectrophotometer at 663 nm of wavelength.

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57 1.4 Recovery and Reusability

The ZD was recovered from ZD/dye complex by applying the physical and chemical treatments and compared for the effectiveness of the utilized method. Physically, the ZD/dye complexes were subjected to ultrasonic treatment to split the physical/weak interactions between the adsorbed dye molecules from the ZD surface. Chemically, the ZD/dye complex was treated with 5M NaOH to recover the ZD nanocatalyst. The absorption intensity of the ZD/dye complex was assessed before and after the respective treatment to evaluate their efficiency. Thereby, the recovered ZD was reused for 3 cycles to adsorb the dye and evaluated the efficiency using the UV-absorbance data.

64 **2.** Result and Discussion

65 2.1 Hydrodynamic size and Surface potential at pH

Figure S1 and figure S2 show the spectral data of the hydrodynamic size and zeta potential, respectively of the as-synthesized ZD at different pH values. It can be observed that with the increase in pH from 2 to 12, there is a decrease in the hydrodynamic size of ZD (Fig S3a). It can be credited to the possible involvement of –COOH groups of ZD to form –COO⁻ at higher pH which might have resulted in the distortion of superficial layers of ZD up to a margin. The zeta potential of ZD is pH-dependent and can be attributed to the existence of the –NH₂ group at ZD (Fig. S3b). At pH 2, a highly positive charge, +28.4 mV, is acquired by ZD due to the presence of excessive H⁺ ions in the solvent which induces the formation of -NH₃⁺ of ZD. With an increase in pH from 4 to 12, the negative surface charge indicates the removal of hydrogen ions owing to the presence of OH- ions in the solvent. It tends to form a stern layer and a slipping plane around the dispersed ZD particles. The magnitude of the zeta potential shows the degree of electrostatic repulsion between adjacent, similarly charged particles. Therefore, the ZD particles are well stable in dispersion at pH 8-10. The results indicate that NH₂-containing ZD could easily adsorb and interact with cationic pollutants, MB, at this pH range of 8-10 through electrostatic attraction. Beyond pH 10, there could be elevated alkalimediated interference in MB structure which had resulted in its degradation at pH12 [1].

78





87 Fig. S3: the variation in (a) hydrodynamic size and (b) zeta potential of as-synthesized ZD at pH 2, 4, 6, 8, 10 and 12.

- 88 89
- 0)
- 90

91 2.2 Optical Characteristics



Fig. S4: (a) UV-Vis absorbance spectra, (b) absorbance wavelength, (c) PL emission spectra, and (d) variation in PL emissionintensities, excitation wavelength, and emission wavelengths of the as-synthesized ZD at pH 2, 4, 6, 8, 10 and 12.

95



97 Fig. S5: The PL emission spectra of as-synthesized ZD at pH 2, 4, 6, 8, 10, and 12 at different excitation wavelengths.

99 2.3 FTIR and RAMAN characterization

100 Figure S6a presents the FT-IR spectra of MB, ZD and ZD/MB complex. In the FTIR spectrum of ZD, peaks at 3430 and 3300 cm⁻¹ 101 correspond to the amino groups while the peaks at 1550 and 1400 cm⁻¹can be ascribed to the asymmetric and symmetric C-O 102 vibrations of carboxylate linker, respectively. Further, the broadband at 1053 cm⁻¹ corresponds to C-O stretching vibrations [2]. 103 In the FTIR spectrum of MB, the characteristic peaks appear at 3400, 2920, 1618, 1380, and 1100 cm⁻¹ which are assigned to O-104 H stretching, C-H stretching, N-H bending of amines, and aromatic amines and C-N stretching, respectively. It coincides well 105 with the reported MB spectrum [3]. In the FTIR spectrum of the ZD-MB complex, the peaks at 1630 (N-H bending vibration), 106 1380 and 1030 cm⁻¹ confirmed the adsorption of MB on the ZD surface. It might be due to the H-bonding and electrostatic 107 interaction as supported by the disappearance of the peak at 3300 cm⁻¹(-OH group). 108 Figure S6b illustrates the Raman spectra of MB, ZD, and ZD-MB complex after the instant addition of dye in ZD. The RAMAN

right Sob indictates the Raman spectra of MB, 2D, and 2D-MB complex after the instant addition of dye in 2D. The RAMAN spectrum of MB exhibits the peaks at 1604 cm⁻¹ and 1563 cm⁻¹ due to C-C stretching: 1486 cm⁻¹ from C-N asymmetric stretching and 1395 cm⁻¹by C-H in-plane ring deformation [4]. In the RAMAN spectrum of ZD, the characteristic peak at 1621 cm⁻¹ confirmed the presence of functional group >C=O mixed with NH deformation. The multiple peaks ranging from 800- 1000 cm⁻¹ denote the multi-substituted aromatic ring of aminobenzene dicarboxylic acid in ZD. The high-intensity peak at 1430 cm⁻¹ can be ascribed to CH₂ deformations [5]. Peaks near 696 and 816 cm⁻¹ correspond to C-O and C-O-C, respectively. The diminished peak intensity at 1430 and 805- 867 cm⁻¹ resulted from the interaction between the MB and ZD particles. The unaltered peak intensity at 1621 cm⁻¹ denotes the stable structural bonding even after MB interaction.



- 117 Fig. S6: (a) The FTIR and (b) RAMAN spectra of only MB, only ZD, and ZD/MB complex.











124 Fig. S8: The variation in PL emission intensity of ZD with increased concentration of MB.



126 **2.5 Selectivity Study for MB sensing**



- 129 Stern-Volmer plots and (f) Q% for the variation in PL emission intensity of ZD in presence pf MB, IC, RhB and TB dyes.
- 130
- 131 To further strengthen the sensing performance of ZD for MB, the selective activity of this material is also conducted as shown in
- 132 figure S9. It is evident that the ZD selectively interacts with MB dye but not with any other counterparts such as IC, RhB, and TB.
- 133 The quenching effect of these dyes was monitored at their three different concentrations i.e., 7.8x10⁻⁸ M, 6.2x10⁻⁷ M, and 6.2x
- 134 10⁻⁶ M. In the presence of 6.2x 10⁻⁶ M concentration of MB, IC, RhB and TB, the net quenching was attained to be 93.32%,

135 13.23%, 13.03%, and 6.01% respectively (Fig. S9f). MB resulted in approximately seven times higher than the second-highest 136 quenching that occurred in the presence of IC. This data points to the ultra-selectivity of ZD particles towards MB dye. 137 Furthermore, this outcome was supported by the Stern-Volmer quenching constants of these respective dyes as shown in figure 138 S9e. The *Ksv* of ZD particles for MB, IC, RhB, and TB is calculated to be 2.3x10⁶ M⁻¹, 6.8x10³ M⁻¹, 6x10³ M⁻¹and 3.5x10³ M⁻¹ 139 respectively. It shows that ZD possesses a thousand times higher affinity for MB than that for IC, RhB, and TB dyes. The 140 ultrasensitive and selective performances of ZD particles render them a highly potent sensing material for MB dye detection.

141



Fig. S10:(a) The variation in the absorbance intensity and (b) the % change in absorption intensity of MB at wavelength 664 nm
during adsorption onto ZD concerning the contact time; (c) the removal efficiency and (d) adsorption capacity of ZD for MB
adsorption concerning the contact time.

146

147 2.6 Photocatalytic degradation of MB in absence of ZD

148 The photo-degradation activity of ZD for MB dye was executed to assess the photocatalytic efficiency of ZD nanoparticles at pH 149 8. For reference purposes, only 10 mg/L MB solution (without ZD) was irradiated under UV-illumination for 1 hour at an interval 150 of 5 min (Fig. S11). It can be observed that even after the 1 hr. of irradiation, there is a very negligible change in the UV-151 absorbance intensity (A) of MB (Fig. S11a). At all the three main SPR band positions i.e., 246 nm, 291 nm, and 663 nm, there is

- 152 no notice worthy variation in absorbance (A₀-A), here A₀ and A are the initial and the final absorbance intensities of ZD before
- 153 and after the UV-irradiation, respectively (Fig. S11b). The full width at half maximum (FWHM) of the absorbance bands of MB at
- 154 these three wavelengths is minimally affected after instant UV exposure but remains almost unaltered thereafter up to 60
- 155 minutes (Fig. S11c).



Fig. S11: (a) The variation in the absorbance intensity, (b) the change in the absorption intensity, and (c) the FWHM of only MBat wavelengths 246 nm, 292 nm, and 664 nm concerning the UV-irradiation time for degradation evaluation.



Fig. S12: (a) The % change in absorption intensity, and (b) FWHM of MB at wavelength 663 nm in the absence and presence ofZD concerning the UV-irradiation time for photocatalytic degradation efficiency evaluation.



Fig. S13: (a) Variation in MB concentration in presence of 10mg/L and 20 mg/L ZD dosage concerning irradiation time; and (b)
 Photocatalytic removal efficiency of 10mg/L and 20 mg/L ZD for MB degradation against irradiation time.

$169\quad$ 2.7 Colorimetric Analysis of Photocatalytic degradation

170 The colorimetric change in the 10 mg/L MB dye solution irradiated with UV-light in the presence and the absence of ZD catalyst

- 171 is represented in the pictures shown in figures S14 and S15, respectively. In figure S14, there is a sharp change in the blue color
- 172 of MB solution treated with ZD at time t=0 min of UV-exposure to greenish color at time t=70 min. But this alteration in MB
- 173 solution color has not occurred in the absence of ZD even up to 1 hr. of the UV light treatment (Fig. S15).



- 175 Fig. S14: Photograph of MB reference (left: without UV-irradiation) and ZD/MB complex solution (right: at different time
- 176 intervals, t= 0, 5, 01, 15, 20, 25, 30, 35, 40, 45, 50, 60, 65 and 70 minutes of UV-irradiation).
- 177



- 0 min 178
- 179 Fig. S15: Photograph of MB solution (left: without UV-irradiation and right: at different time intervals, t= 0, 5, 01, 15, 20, 25, and
- 180 30 minutes of UV-irradiation).
- 181

182 2.8 Selectivity Study

- 183 To monitor the selective interaction of the ZD particles as adsorbent and photocatalyst for MB dye removal in water, the
- 184 experiments were also executed with other dyes such as RhB, CV, and IC. The effect of ZD in the respective dye solutions with
- 185 and without UV light irradiation was investigated using UV-Vis absorption spectroscopy and the data is presented in figure S16.
- 186





Fig. S16: The variation in the absorbance intensity of (a) CV, (b) IC, and (c) RhB dyes in the presence of ZD concerning the UVirradiation time; (d) the % change in absorption intensities of CV, IC, RhB and MB dyes in the presence of ZD concerning the UVirradiation time; and (e) the plot of C_t/C_o versus UV-irradiation time for these dyes in ZD.

192 It can be noted that there is negligible change in the absorption intensities of CV and RhB dyes in the presence of ZD. The 193 negligible adsorption, as well as photocatalytic degradation effect, was observed in these dyes' concentrations (fig. S16d). 194 Although, IC could have interacted with ZD particles to some extent resulting in noticeable adsorption and a little degradation 195 in the presence of UV light, but after 10 min of UV treatment, the saturation in degradability of IC dye was documented (Fig. 196 S16b). A net 32% of absorption change is noticed even after the UV treatment for 30 minutes which is comparatively very low 197 than that of MB dye (80%) (Fig. S16d). The decrease in the final concentration of MB (R²= 0.98) in presence of ZD under UV-198 irradiation for a total period of 70 minutes was very high than that of RhB (R²= 0.477), CV (R²= 0.531), and IC (R²= 0.729) as 199 shown in figure S16e. As studied from literature, Mantasa et. al, 2020, reported that the reason for high adsorption of MB is not 200 only the cationic nature, but also the linearity of the dye [6]. The linear structure of MB enhances the adsorption as it can 201 access the available adsorbent sites more easily. IC also should have made a swift approach to the adsorbent sites due to the 202 linear structure and resulted in its 32% net adsorption. CV being a cationic dye show electrostatic interaction towards the ZD 203 while, the adsorption is declined due to its non-linear and bulky structure in comparison to MB. Therefore, it can be 204 summarized that ZD nanoparticles selectively possess photocatalytic activity for MB degradation in water under UV-light 205 exposure.

$206\,$ 2.9 The mechanism of MB dye sensing, adsorption, and photocatalysis degradation

The prominent adsorption mechanisms proposed during adsorptive interplay between the solid ZD-aqueous MB interfaces are represented in the schematic in figure S17. The mechanism of the specific and selective sensing behavior of ZD for MB can be explained by the electrostatic interaction between the lone pairs of amino groups of ZD and MB. The $-NH_2$ group on ZD readily

210 accepts hydrogen proton and acquires positively charged $-NH_3^+$, accelerating the interaction with MB. The types of interactions

that might present between ZD and MB include electrostatic interaction, hydrogen bonding, and π - π stacking. Hydrogen bonding involves polar interaction or extreme dipole-dipole interaction of NH₂ functional group on ZD with complementary groups of MB. Besides, the π - π staking between aromatic rings of both the MB dye and ZD particles is also responsible for the enhancement in the energy transfer between ZD and MB [7]. These interactions ultimately lead to the pore filling of ZD with MB which further results in the adsorption of MB out of the contaminated water. ZD possesses the negatively charged surface at this experimental pH 8 (Fig. S3b) with water as a dispersant which can easily interplay with oppositely charged cationic MB



Additionally, the prevalent mechanism of ZD-derived photocatalytic degradation and discoloration of MB dye is established on the semiconductor theory (Fig. S18). When ZD is illuminated with UV light having photons equal to the energy of the band gap, the electronic excitation occurs. The electrons (e⁻) are excited from the highest filled orbital (HOMO) to the lowest vacant orbital (LUMO) and generate the electron-hole pairs (e⁻/h⁺). The holes and electrons are further involved with the formation of reactive charge species due to the photo excitation of ZD nanoparticles. The holes behave as photo-oxidants and participated in the redox reactions to oxidize the MB to CO₂ and H₂O by forming OH[•] radicals. The possible mechanism of this photocatalytic degradation activity of ZD can be represented as follow [7]:

$$ZD + hv \rightarrow ZD \; (e_{CB}^- + h_{VB}^+) \tag{1}$$

$$e_{CB}^{-} + O_2 \rightarrow O_2^{-}$$
 (2)

230
$$O_2^- + H_2 O \to OH^- + OOH^-$$
 (3)

231
$$h_{VB}^+ + H_2 O \to OH^- + H^+$$
 (4)



236

237 2.10 Recovery and Reusability

238 The recovery and reusability of an adsorption or degradation system is a crucial factor for its real field applicability and 239 industrial setups. As explained in hydrodynamic size and surface potential studies, that there are elevated electrostatic 240 interactions and alkali mediated interference resulting in MB degradation. According to this finding, the ZD was regenerated by 241 easy degradation of MB at high pH [1]. It is evident from figure S19a, the maximum decrement in the absorption intensity of 242 MB (10 mg/L) at 664 nm occurred at pH 12 as compared to pH 2 or 8. The adsorption capacity and removal efficiency of ZD; and 243 the %variation in absorbance intensity of MB dye at pH 2, 8, and 12 are shown in figure S19b, and parameters are summarized 244 in table S8. The highest adsorption capacity (377.6 mg/g) and removal efficiency (94.4 %) was achieved by ZD at pH 12. Also, the 245 maximum % change in absorption intensity (88.04 %) was achieved in this alkaline condition. This trend might have occurred 246 due to the produced ·OH (hydroxyl radicals) that electrophilically attacked the cleavage of C-S+=C of MB in alkaline conditions 247 which can be represented as follows [8]:

²³⁵ Fig. S18: The schematic representation of ZD mediated photocatalytic degradation of MB.

(6)

249 Besides, the dispersed dye is cationic (basic type) in nature and gets easily dissolved in organic media having a low dielectric 250 constant [9]. This desorption was achieved by breaking the electrostatic interaction between dye molecules and reactive sites 251 of ZD adsorbent in the presence of NaOH. While at acidic pH, the positively charged ZD surface repelled this cationic dye, which 252 completely justifies the low rate of MB removal by ZD at acidic pH. With the increase in pH, the negative charge of the ZD 253 surface is increased, hence, more attractive forces occur between the photocatalyst and the dye in aqueous solutions, leading 254 to a higher MB removal. Additionally, the hypochromic shift in the absorption wavelength at pH 12 indicates the structural 255 degeneration of MB. Therefore, it can be concluded that the higher pH (alkaline) was most effective for MB removal from ZD. 256 This mechanism of pH-mediated behavior of ZD and MB interaction is represented in the scheme in figure S20.



258 Fig. S19: (a) The UV-Vis absorption spectra of ZD/MB complex; and (b) adsorption capacities of ZD, removal efficiencies of ZD,

- and % change in absorption intensities of ZD/MB complex at pH 2, 8, 12; (c) The UV-Vis absorption spectra of MB in presence of
- 260 $\,$ NaOH and ZD for MB (after 24 hr and 48 hr).
- 261



- 263 Fig. S20: The schematic representation of ZD/MB interaction at different pH (acidic to alkaline).
- 264

These findings are further utilized for the degradation of MB from ZD/MB complex to regenerate the ZD afresh. It can be observed from figure S19c that approximately 55.3 % Mb dye was degraded in the presence of only NaOH. While in the presence of ZD, NaOH was utilized to degrade up to 91 % within 24 hrs which is further increased up to approx. 98% in the next 24 hrs. This data confirms the complete restoration of ZD from the ZD/MB complex by treating it with NaOH solution (Fig. S19c). After this highly commendable MB degradation, the ZD material was centrifuged and collected in a pellet by removing the degenerated MB dye solution in the supernatant.

271 Thereafter, this collected ZD was characterized using FTIR and RAMAN spectroscopies for any alteration in its functional 272 structure as shown in figures S21a and S21b respectively. It can be noticed that the characteristic FTIR peaks of recovered ZD 273 remain unaffected and completely match with the bare ZD spectrum as represented in figure S6a. The RAMAN spectrum of 274 these recovered-ZD particles is also completely restored as to the bare ZD shown in figure S6b. Therefore, these findings 275 describe the successful degradation of MB dye from the ZD/MB complex and the successful recycling of the ZD with well 276 retained functional characteristics. Further, this recovered ZD was reused for MB adsorption as shown in figure S21c. It can be 277 observed the empty sites of recovered ZD successfully reabsorbed the MB out of the contaminated water sample. The 278 characteristic absorption band of MB at 664 nm confirms the presence of MB onto the reused ZD. To strengthen the reusability 279 of ZD, the recovery study was conducted in four cycles for MB adsorption onto ZD (Fig. S21d). Although, the percentage 280 recovery decreased continuously with successive cycles yet was brilliant enough as even in the fourth cycle, the best desorption 281 capacity was found to be 58% for MB dye.

Therefore, this study well verse about the applicability of zinc-disc nanomaterial as an excellent sensor, adsorbent, and photocatalyst with high recovery and reusability. It can be suggested that these luminescent, porous, and readily to be functionalized ZD nanoparticles can be applied for various other applications such as sensing, cell-imaging, drug delivery, adsorption, removal of various other organic/inorganic contaminants, etc.



Fig. S21: (a) FTIR and (b) RAMAN spectra of recovered ZD; (c) the absorbance spectra of recovered and reused ZD for MBpresence; and (d) the % recovery assessment of ZD up to four cycles.

291 Table S1: The summarized XRD parameters for ZD.

S.No	20	d-spacing	FWHM	Hkl
1	38.2	2.35	0.2160	111
2	44.4	2.03	0.1680	200
3	64.8	1.43	0.3840	220
4	77.8	1.22	0.2400	311
2				

$\,$ Table S2: The surface area data of ZD and ZD/MB $\,$

Property	ZD	ZD/MB
MultiPoint BET	1.598e+02 m ² /g	4.113e+01 m²/g
BJH method cumulative adsorption surface area	2.197e+01 m²/g	1.585e+01 m²/g
BJH method cumulative desorption surface area	1.867e+01 m²/g	1.264e+01 m²/g
DH method cumulative adsorption surface area	2.251e+01 m²/g	1.624e+01 m²/g
DH method cumulative desorption surface area	1.911e+01 m²/g	1.294e+01 m²/g
DFT cumulative surface area	1.994e+02 m²/g	3.703e+01 m²/g

$\,$ Table S3: The pore volume data of ZD and ZD/MB $\,$

Property	ZD	ZD/MB
Total pore volume for pores with Radius less than 1963.17 Å at P/Po	9.592e-02 cc/g	3.781e-02 cc/g
= 0.995		
BJH method cumulative adsorption pore volume	3.388e-02 cc/g	2.357e-02 cc/g
BJH method cumulative desorption pore volume	2.970e-02 cc/g	2.023e-02 cc/g
DH method cumulative adsorption pore volume	3.333e-02 cc/g	2.320e-02 cc/g
DH method cumulative desorption pore volume	2.923e-02 cc/g	1.992e-02 cc/g
		<i>-</i>
DFT method cumulative pore volume	8.811e-02 cc/g	3.498e-02 cc/g

$\,$ Table S4: The data of equilibrium models studied for adsorption $\,$

Model	Equation	Ра	rameters	
		q _m (mg g ⁻¹)	207.0	
Langmuir	C_{e} 1 C_{e}	K _L (L mg ⁻¹)	0.2445	
	$\frac{\overline{q_e}}{\overline{q_e}} - \frac{\overline{k_L q_m}}{\overline{k_L q_m}} + \frac{\overline{q_m}}{\overline{q_m}}$	RL	0.039	
		R ²	0.9890	
Freundlich		K _F (mg g ⁻¹)	1.49	

	$\ln a = \frac{1}{-\ln c} + \ln k$	n	5.15
	$mq_e = n mc_e + mc_F$	R ²	0.8772
Temkin	$\ln q_e = \frac{1}{-\ln c_e} + \ln k_E$	K _⊤ (L mg ⁻¹)	7.725
	n e r	RT/b _T (kJ/mol)	31.09
		R ²	0.8787

Table S5: Kinetic parameters for the adsorption of MB onto ZD

Model	Linear Equation	Parameters	
First Order	$\frac{1}{q_t} = \frac{1}{q_t} + \frac{k_1}{q_e t}$	k ₁ (min ⁻¹) q _{e,calc} (mg g ⁻¹) R ²	16.12 337.83 0.69836
Second Order	$\frac{1}{C_e} - \frac{1}{C_0} = k_2 t$	k ₂ (gmg ⁻¹ min ⁻¹) R ²	0.00237 0.68534
Pseudo-Second Order	$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$	k ₂ (gmg ⁻¹ min ⁻¹) q _{e,calc} (mg g ⁻¹) R ²	0.00011 386.1 0.99
Elovich	$q_t = \frac{\ln\left(a * b\right)}{b} + \frac{\ln t}{b}$	a (mg g ⁻¹ min ⁻¹) b (gmg ⁻¹) R ²	124.74 0.0137 0.83135
Intraparticle Diffusion	$q_t = k_p t^{1/2} + c$	k _p (mg g ⁻¹ min ^{-1/2}) C R ²	13.45 143.52 0.6861

³⁰³

³⁰⁴ Table S6: Comparison of the maximum uptake/ adsorption of MB onto ZD with that of various adsorbents

S. No.	Adsorbent	<i>q_{max}</i> (mg g ⁻¹)	Reference
1	Cedar cone	4.55	[10]
2	Baker's yeast	25	[11]
3	Jute stick powder	87.7	[12]
4	Kaolinite	46.08	[13]
5	Acid-treated dika nut	232	[14]
6	Fly ash	10	[15]
7	Natural coal	40.82	[16]

8	Microwave-treated nilotica leaf	24.39	[17]
9	Sugarcane baggas	51.5	[18]
10	Modified coir pit	14.9	[19]
11	HM-MIL-101	21.0	[20]
12	MIL-100 (Fe)	736.2	[20]
13	MIL-100 (Cr)	645.3	[21]
14	MOF-235	252.0	[22]
15	Zinc-disc	386.1	This work

³⁰⁵

306 $\,$ Table S7: Kinetic parameters for the photocatalytic degradation of MB with ZD nanocatalyst

Model	Linear plot scale parameters	Parameters		
			10 mg/L ZD	20 mg/L ZD
Pseudo Zero Order	C (mg L ⁻¹) <i>vs</i> t (min.)	k (mgL ⁻¹ min ⁻¹)	0.02566	0.008141
		R ²	0.93151	0.98151
Pseudo First Order	-In C _t /C _o vs t (min.)	k (min ⁻¹⁾	0.015	0.011
		R ²	0.99	0.989
Pseudo-Second	1/Ct (L mg ⁻¹) <i>vs</i> t (min.)	k (Lmg ⁻¹ min ⁻¹)	0.03488	0.00969
Order		R ²	0.90681	0.93303

307

308 Table S8: The comparison of adsorption capacities, removal efficiencies and absorption intensity change of ZD for MB at

309 various pH

рН	Co-Ce*v/m	Co-Ce/Co*100	A ₀ -A/A ₀ *100
2	280.14792	70.03698	18.42308
8	281.06367	70.26592	19.07692
12	377.65898	94.41474	88.04808

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311 References:

312 1. M. Zamouche and O. Hamdaoui, *Energy Procedia*, 2012, **18**, 1228.

313 2. S. Devi, S. Shaswat, V. Kumar, A. Sachdev, P. Gopinath, and S. Tyagi, Microchimica Acta, 2020, 187, 1-10.

314 <u>https://doi.org/10.1007/s00604-020-04496-0</u>

315 3. D.L. Pavia, G.M. Lampman, G.S. Kriz and J.A. Vyvyan, Introduction to spectroscopy Cengage learning, 2014.

- 316 4. M. del Pilar Rodríguez-Torres, L.A. Díaz-Torres and S. Romero-Servin, International Journal of Molecular Sciences, 2014, 15,
- 317 19239. <u>https://doi.org/10.3390/ijms151019239</u>
- 318 5. D.Y. Siberio-Pérez, A.G. Wong-Foy, O.M. Yaghi and A.J. Matzger, *Chemistry of materials*, 2007, **19**, 3681.
 <u>https://doi.org/10.1021/cm070542g</u>
- 320 6. I. Mantasha, H.A. Saleh, K.M. Qasem, M. Shahid, M. Mehtab and M. Ahmad, *Inorganica Chimica Acta*, 2020, **511**, 119787.
 321 <u>https://doi.org/10.1016/j.ica.2020.119787</u>
- 322 7. C. Van Tran, D.D. La, P.N.T. Hoai, H.D. Ninh, P.N.T. Hong, T.H.T. Vu, A.K. Nadda, X.C. Nguyen, D.D. Nguyen and H.H. Ngo,
 323 *Journal of hazardous materials*, 2021, **420**, 126636. <u>https://doi.org/10.1016/j.jhazmat.2021.126636</u>
- T.A. Kurniawan, Z. Mengting, D. Fu, S.K. Yeap, M.H.D. Othman, R. Avtar and T. Ouyang, *Journal of environmental management*, 2020, 270, 110871. <u>https://doi.org/10.1016/j.jenvman.2020.110871</u>
- 326 9. S.P. Shukla and N. Dhiman, Environmental Earth Sciences, 2017, 76, 1-12. https://doi.org/10.1007/s12665-017-7030-x
- J.T. da Fontoura, G.S. Rolim, B. Mella, M. Farenzena and M. Gutterres, *Journal of environmental chemical engineering*,
 2017, 5, 5076. <u>https://doi.org/10.1016/j.egypro.2012.05.138</u>
- 329 11. J.X. Yu, B.H. Li, X.M. Sun, Y. Jun and R.A. Chi, *Biochemical Engineering Journal*, 2009, 45, 145.
 330 <u>https://doi.org/10.1016/j.bej.2009.03.007</u>
- 331 12. G.C. Panda, S.K. Das, and A.K. Guha, 2009, 374. Journal of Hazardous Materials, 164, 332 https://doi.org/10.1016/j.jhazmat.2008.08.015
- 333 13. T.A. Khan, S. Dahiya, and I. Ali, Applied Clay Science, 2012, 69, 58. <u>https://doi.org/10.1016/j.clay.2012.09.001</u>
- 334 14. Z. Tong, P. Zheng, B. Bai, H Wang, and Y. Suo, Catalysts, 2016, 6, 58. https://doi.org/10.3390/catal6040058
- 335 15. S.H. Chang, K.S. Wang, H.C. Li, M.Y. Wey and J.D. Chou, *Journal of hazardous materials*, 2009, **172**, 1131.
 <u>https://doi.org/10.1016/j.jhazmat.2009.07.106</u>
- 337 16. N. Hasani, T. Selimi, A. Mele, V. Thaçi, J. Halili, A. Berisha and M. Sadiku, *Molecules*, 2022, 27, 1856.
 338 <u>https://doi.org/10.3390/molecules27061856</u>
- 339 17. T. Santhi, A.L. Prasad and S. Manonmani, *Arabian Journal of Chemistry*, 2014, 7, 494.
 340 <u>https://doi.org/10.1016/j.arabjc.2010.11.008</u>
- 341
 18. Z. Zhang, I.M. O'Hara, G.A. Kent and W.O. Doherty, Industrial Crops and Products, 2013, 42, 41.

 342
 https://doi.org/10.1016/j.indcrop.2012.05.008
- M.V. Sureshkumar and C. Namasivayam, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2008, 317,
 277. https://doi.org/10.1016/j.colsurfa.2007.10.026
- 345 20. X.X. Huang, L.G. Qiu, W. Zhang, Y.P. Yuan, X. Jiang, A.J. Xie, Y.H. Shen and J.F. Zhu, *CrystEngComm*, 2012, 14, 1613.<u>https://doi.org/10.1039/C1CE06138K</u>
- M. Tong, D. Liu, Q. Yang, S. Devautour-Vinot, G. Maurin and C. Zhong, *Journal of Materials Chemistry A*, 2013, 1, 8534.
 <u>https://doi.org/10.1039/C3TA11807J</u>
- 349
 22. E. Haque, J.W. Junand and S.H. Jhung, Journal of Hazardous materials, 2011, 185, 507.

 350
 https://doi.org/10.1016/j.jhazmat.2010.09.035
- 351
- 352 Supplementary figure captions:
- 353 Fig. S1: The hydrodynamic size of as-synthesized ZD at pH 2, 4, 6, 8, 10, and 12.
- 354 Fig. S2: The zeta potential of as-synthesized ZD at pH 2, 4, 6, 8, 10, and 12.

- 355 Fig. S3: The variation in (a) hydrodynamic size and (b) zeta potential of as-synthesized ZD at pH 2, 4, 6, 8, 10 and 12.
- 356 Fig. S4: (a) UV-Vis absorbance spectra, (b) absorbance wavelength, (c) PL emission spectra, and (d) variation in PL emission
- intensities, excitation wavelength, and emission wavelengths of the as-synthesized ZD at pH 2, 4, 6, 8, 10 and 12.
- 358 Fig. S5: The PL emission spectra of as-synthesized ZD at pH 2, 4, 6, 8, 10, and 12 at different excitation wavelengths.
- 359 Fig. S6: (a) The FTIR and (b) RAMAN spectra of only MB, only ZD, and ZD/MB complex.
- 360 $\,$ Fig. S7: The BET surface area (a) and pore data of ZD and ZD/MB complex.
- 361 Fig. S8: The variation in PL emission intensity of ZD with increased concentration of MB.
- 362 Fig. S9: The variation in PL emission intensity of ZD with increased concentration of (a) MB, (b) IC, (c) RhB, and (d) TB; the (e)
- 363 Stern-Volmer plots and (f) Q% for the variation in PL emission intensity of ZD in presence pf MB, IC, RhB and TB dyes.
- 364 Fig. S10:(a) The variation in the absorbance intensity and (b) the % change in absorption intensity of MB at wavelength 664 nm
- 365 during adsorption onto ZD concerning the contact time; (c) the removal efficiency and (d) adsorption capacity of ZD for MB
- $366 \quad \text{adsorption concerning the contact time.}$
- 367 Fig. S11: (a) The variation in the absorbance intensity, (b) the change in the absorption intensity, and (c) the FWHM of only MB
- 368 $\,$ at wavelengths 246 nm, 292 nm, and 664 nm concerning the UV-irradiation time for degradation evaluation.
- 369 Fig. S12: (a) The % change in absorption intensity, and (b) FWHM of MB at wavelength 663 nm in the absence and presence of
- 370 ZD concerning the UV-irradiation time for photocatalytic degradation efficiency evaluation.
- 371 Fig. S13: (a) Variation in MB concentration in presence of 10mg/L and 20 mg/L ZD dosage concerning irradiation time; and (b)
- 372 Photocatalytic removal efficiency of 10mg/L and 20 mg/L ZD for MB degradation against irradiation time.
- 373 Fig. S14: Photograph of MB reference (left: without UV-irradiation) and ZD/MB complex solution (right: at different time
- 374 intervals, t= 0, 5, 01, 15, 20, 25, 30, 35, 40, 45, 50, 60, 65 and 70 minutes of UV-irradiation).
- 375 Fig. S15: Photograph of MB solution (left: without UV-irradiation and right: at different time intervals, t= 0, 5, 01, 15, 20, 25, and
- 376 30 minutes of UV-irradiation).
- 377 Fig. S16: The variation in the absorbance intensity of (a) CV, (b) IC, and (c) RhB dyes in the presence of ZD concerning the UV-
- 378 irradiation time; (d) the % change in absorption intensities of CV, IC, RhB and MB dyes in the presence of ZD concerning the UV-
- 379 irradiation time; and (e) the plot of C_t/C_o versus UV-irradiation time for these dyes in ZD.
- 380 $\,$ Fig. S17: The schematic representation of MB adsorption mechanism onto ZD.
- 381 Fig. S18: The schematic representation of ZD mediated photocatalytic degradation of MB.
- 382 Fig. S19: (a) The UV-Vis absorption spectra of ZD/MB complex; and (b) adsorption capacities of ZD, removal efficiencies of ZD,
- 383 and % change in absorption intensities of ZD/MB complex at pH 2, 8, 12; (c) The UV-Vis absorption spectra of MB in presence of
- 384 NaOH and ZD for MB (after 24 hr and 48 hr).
- 385 Fig. S20: The schematic representation of ZD/MB interaction at different pH (acidic to alkaline).
- 386 Fig. S21: (a) FTIR and (b) RAMAN spectra of recovered ZD; (c) the absorbance spectra of recovered and reused ZD for MB
- 387 $\,$ presence; and (d) the % recovery assessment of ZD up to four cycles.
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389 Table Captions:

- 390 Table S1: The summarized XRD parameters for ZD.
- 391 Table S2: The surface area data of ZD and ZD/MB.
- 392 Table S3: The pore volume data of ZD and ZD/MB.
- $393 \quad \text{Table S4: The data of equilibrium models studied for adsorption.}$
- 394 Table S5: Kinetic parameters for the adsorption of MB onto ZD.

- 395 Table S6: Comparison of the maximum uptake/ adsorption of MB onto ZD with that of various adsorbents.
- 396 $\,$ Table S7: Kinetic parameters for the photocatalytic degradation of MB with ZD nanocatalyst.
- 397 Table S8: The comparison of adsorption capacities, removal efficiencies, and absorption intensity change of ZD for MB at

398 various pHs.