

Highly efficient recyclable bismuth nanocatalyst fabricated by using a facile one-step aqueous method for faster reduction of azo dye contaminants

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Table S1: The recipes for the aqueous in situ preparation of Bi/TANPs and their respective average hydrodynamic diameters (D_h).

No. of batch	Amount of ingredients				D_h of Bi/TANPs (nm)
	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (g)	TA (g)	Glycerin (g)	Water (g)	
1	0.100	0.800	0.200	18	369
2	0.500	0.800	0.200	18	261
3	1.000	0.800	0.200	18	209
4	1.500	0.800	0.200	18	278
5	0.10	0.800	0.20	18	308
6	0.10	0.800	0.10	18	209
7	0.10	0.800	0.05	18	245
8	0.10	0.800	0.20	16	278
9	0.10	0.300	0.20	16	727
10	0.10	0.600	0.20	16	786
11	0.10	0.800	0.20	16	299
12	0.10	0.800	0.20	16	360

Reaction conditions: 80 °C, 5 h, bubbling N_2 gas.

Surface composition and elemental mapping

The energy-dispersive spectroscopy (EDS) scan was used to determine the chemical composition and purity of the Bi/TANPs. Energy-dispersive X-ray spectrum showed that Bi/TANPs are composed of Bi, C, and O as elements, which is shown in Fig. S1a. The highest intense peak appeared at a corresponding energy of 2.5 keV indicates the presence of Bi. The other peaks for C and O at their corresponding energy of 0.25 and 0.5 keV are derived from TA.¹ This spectrum also showed the presence of sodium at 1 keV, which indicates that phenolic groups of TA and gallic acid units are converted into sodium phenoxides that remained on the surface of Bi/TANPs. To investigate the elemental distributions on the surface of synthesized Bi/TANPs elemental mapping analyses were performed. Fig. S1b clearly indicates the combined existence of Bi, O, and C as elemental components as well as ensure purity of the formed product. The distributions of individual elements namely, Bi, C, and O present on the surface of Bi/TANPs are clearly depicted in Fig. S1c-e, respectively. The red dot map indicated the presence of metallic-Bi in Bi/TANPs. The green dot and yellow dot maps represented the distributive information of C and O in Bi/TANPs.

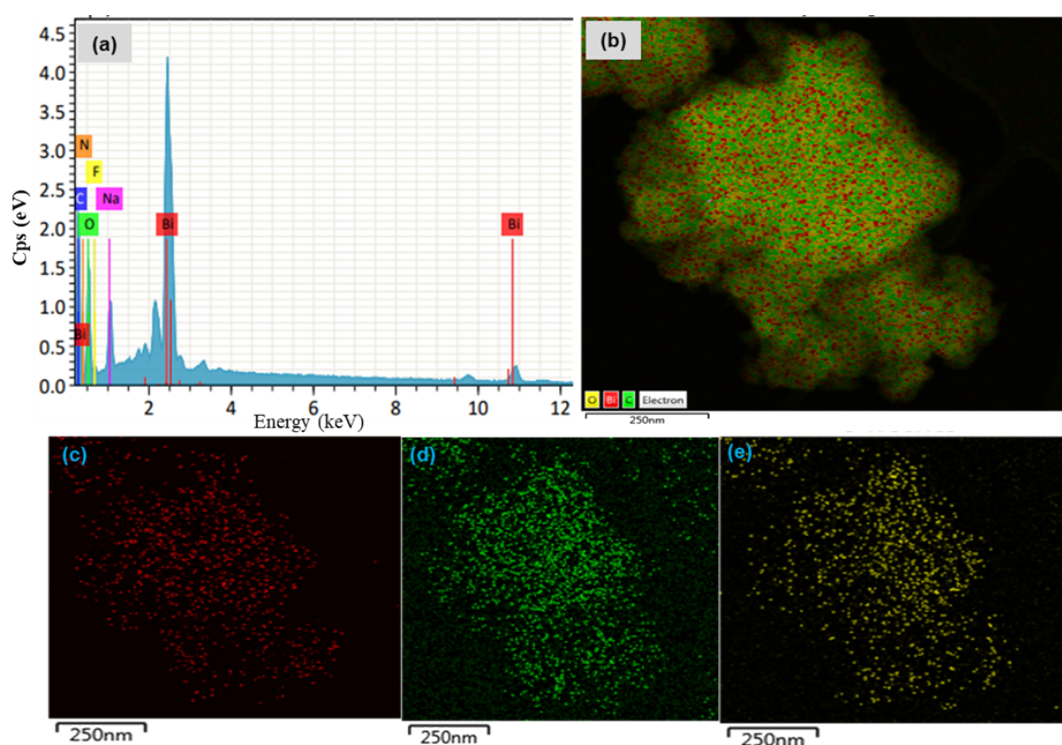


Fig. S1: (a) EDS spectrum of Bi/TANPs; (b) combined elemental mapping of Bi/TANPs; and (c-e) individual elemental maps of Bi (c); C (d); and O (e) measured on the surface of Bi/TANPs.

Effect of initial dye concentration on reduction

The initial dose of dye highly affects the reaction time and overall degradative reduction of the organic pollutants. As can be seen in Fig. S2a,b, the reduction time is just 40 s, and 60 s for MB, CR respectively when the respective dye concentration is 40 mg/L. The reaction time increased when the amount of initial dye is increased. Reasonable catalytic sites exist at lower dye concentrations, which allow reduction of the MB, and CR dyes at a maximum speed. As more and more dyes are added, the catalyst surface turned saturated with dye molecules and hence, hindering of the electron transfer process lengthened the time for dye conversion. This is to mention that with regard to reduction efficiency, Bi/TANPs reduced 99.77% of added MB (Fig. S2c), and 99.37% of added CR (Fig. S2d) within 40 s and 60 s. However, this efficiency of Bi/TANPs is gradually decreased with increasing dye concentration.

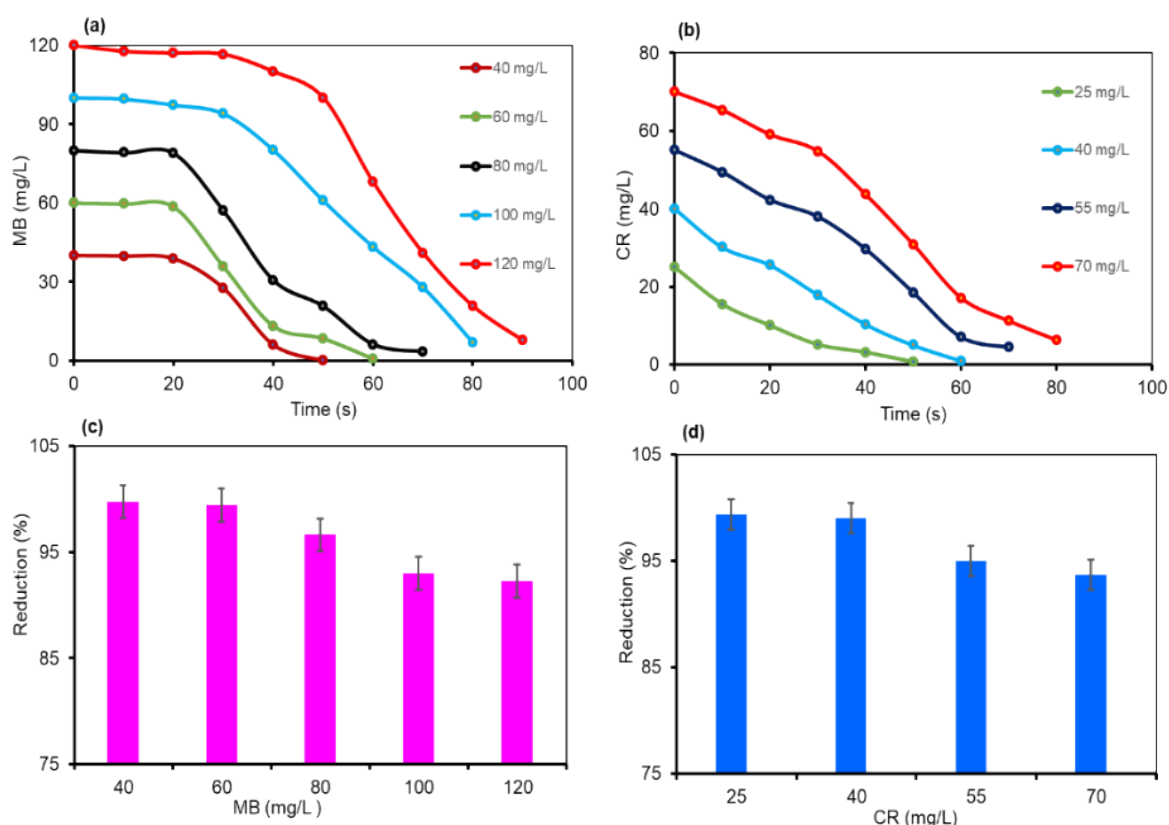


Fig. S2: Concentration dependent changes in catalytic reduction rate and reduction efficiency of Bi/TANPs against MB (a,c) and CR (b,d) in presence of NaBH_4 . Conditions: room temperature, reducing agent 1 mg, catalyst 0.2 mg, and total volume of 50 mL.

Effect of solution pH, and catalyst contact time on catalytic reduction of azo dyes

The surface charge of any substrates and catalysts easily influenced by the pH variations of the reaction medium, plays an important role during adsorption/desorption process on the catalyst surface. The surface charge of Bi/TANPs is highly negative and the catalytical activity of this system can be described by the adsorption/desorption mechanism.² Figure S3a,b shows the effect of pH on the reduction percentages of respective aqueous dye solution at specific concentrations of MB (40 mg/L) and CR (40 mg/L), catalyst, Bi/TANPs (0.2 mg/L), and reducing agent, NaBH₄ (1 mg). The pH-dependent catalytic reduction of MB was carried out at a pH range of 2 to 12 (Figure S3a). At lower pH, protonated-MBH²⁺ was produced from MB, where finally MB was catalytically reduced to form the Leuco-MB.³⁻⁵ The catalytic reduction of MB was thus proceeded by the electrostatic interaction of MBH²⁺ ions with the negative surface of the catalyst resulted in higher catalytic efficacy of the reductive degradation. Above pH 7, the MB molecules were demethylated and formed a negative charge in the nitrogen atom and a positive charge in the methyl group from the CH₃-N band.³⁻⁵ In the alkaline medium, the demethylated-MB with a negative charge was associated with the lower adsorption on the catalyst surface due to the electrostatic repulsions resulted in least amount degradation. At pH 2, the reduction of MB to LMB was thus occurred within few seconds, showed the highest efficiency of the reduction due to the electrostatic attraction between the catalyst and dye. On the contrary, the reduction percentage of CR was studied between pH 6 to 10. The reduction study at < pH 6 was avoided because CR forms aggregate and tautomer's in aqueous acidic medium.⁵⁻⁶ At pH 6, CR is protonated and increased electrostatic interaction between the negatively charged catalyst and the positively charged dye molecules. At increasing pH, electrostatic repulsion increased between the adsorption sites of the catalyst and dye molecules, slowed down the adsorption of the dye molecules and reduced the reduction rate resulted minimal reduction efficacy. The maximum reduction percentage was observed at pH 2 for MB (99.77%) within 20 s and for CR (99.37%) within 40 s at pH 6.

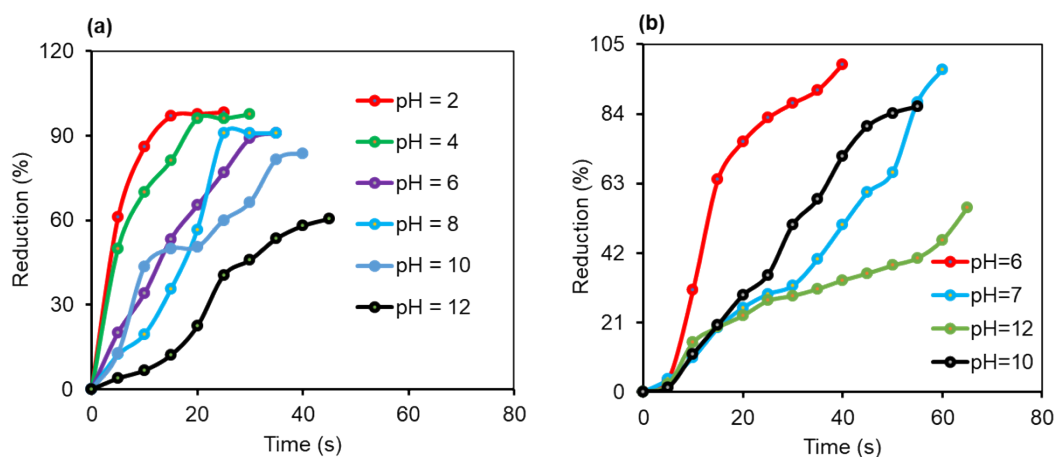


Fig. S3 Effect of pH on catalytic reductive reductions of (a) MB and (b) CR by Bi/TANPs. Conditions: room temperature, reducing agent 1 mg, catalyst 0.2 mg, and total volume 20 mL.

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