**Supplementary Material**

Microwave Assisted Synthesis of Copper Loaded Polyamidoxime Brushes as an Efficient Catalytic System for Nitroarene Reduction

Table S1: Main difference between microwave heating and conventional thermal heating

Property	Conventional Heating	Microwave Heating
Heating rate	Slow	Fast
Reaction time	Long time	Short time
Yield	Low	High
Solvent conditions	Difficult to conduct without solvent	Easy to conduct under solvent-free conditions
Homogeinity of Heating	Low	High
Amount of secondary products	High	Low
Reproducibility	Low	High
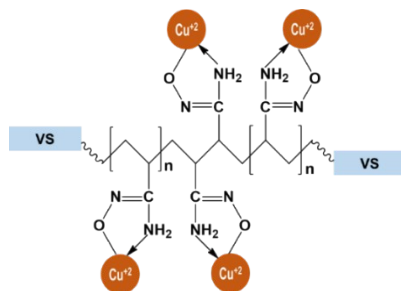
Scheme S1: Copper complexation with polyamidoxime. The amidoxime possesses both basic (NH$_2$) and acidic (OH) sites, making it amphoteric in nature
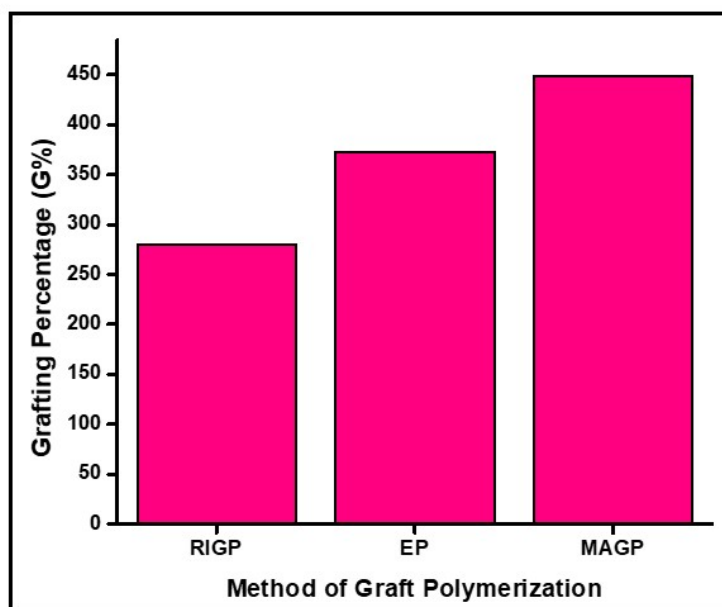
Fig. S1: Comparison of Grafting percentage (G%) in Microwave Assisted Graft Polymerization (MAGP) with Radiation Induced Graft Polymerization (RIGP) and Emulsion Polymerization (EP)

In the previous studies conducted by Taimur et al., grafting percentage of acrylonitrile achieved through Radiation-induced graft polymerization [1] was 280% and by Emulsion Polymerization [2] it was 373%. The comparison presented in Figure 1 reveals that Microwave-assisted graft polymerization (MAGP) in the current study demonstrated the highest grafting percentage (449%). This comparison suggests that all these methods are effective, with MAGP showing superior efficiency by achieving the maximum grafting percentage among the three methods.
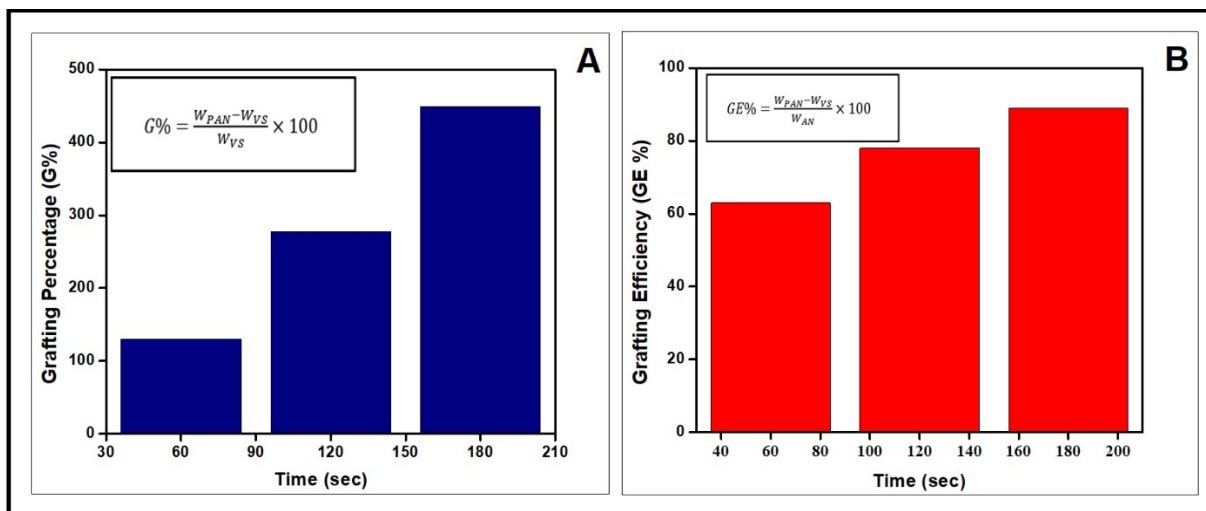
Fig. S2: Effect of microwave irradiation time on (A) grafting percentage, here maximum of 449% is obtained in 180 sec and (B) grafting efficiency, 89% is obtained in 180 sec

Fig. S2 depicts the effect of G% and GE% with time. The maximum of 449 G% and 89 GE% is achieved within 180 seconds that is with respect to substrate (Vinyl Sepiolite) in relation to monomer (Acrylonitrile). These findings accentuate the energy and time efficiency of this approach.

Further explanation of 4-NP adsorption on the surface of Cu-AO-PB by L-H model

The process of adsorption and desorption involving BH^{4-} and 4-NP^{-} takes place rapidly at the surface of the catalyst, yet it does not significantly alter the underlying kinetic equation. The reduction rate of 4-NP is intricately tied to the surface area of the catalyst and can be quantified through equation 1. This approach allows for a detailed understanding of the catalytic process, considering the dynamic interplay between reactants and the polymer brush catalyst surface by following Langmuir–Hinshelwood equation:

$$\frac{-dC_{4-NP}}{dt} = kM\theta_{4-NP}\theta_{BH_4^-} \tag{1}$$

where k is the rate constant, M is the total surface of Cu-AO-PB polymer brush proportional to the apparent kinetic constant, and $\theta_{4\text{-NP}}$ and θ_{BH4^-} designate the surface coverage of 4-NP and BH_4^- respectively, which can be articulated by a Langmuir-Freundlich isotherm: The surface rate

constant (k), adsorption equilibrium constants ($K_{4\text{-}NP}$ and $K_{BH4–}$), and other relevant parameters can be determined by equations 2, 3 and 4 after fitting the data to the Langmuir-Hinshelwood equation which we have planned to accomplish it in future.

$$\theta_j = \frac{(K_j C_j)^{n_j}}{1 + \sum_{n=1}^{n} (K_j C_j)^{n_j}}$$

(2)

Where θ_j is the surface coverage of substance j , K_j is known as adsorption equilibrium constant, C_j denotes concentration and n represents the Langmuir–Freundlich exponent. The surface coverage of BH_4^- and 4-NP can be determined by the following equations [3]

$$\theta_{BH_4^-} = \frac{(K_{BH_4^-} . C_{BH_4^-})^a}{1 + (K_{BH_4^-} . C_{BH_4^-})^a + (K_{4-NP} . C_{4-NP})^b}$$

(3)

$$\theta_{4-NP} = \frac{(K_{4-NP} . C_{4-NP})^b}{1 + (K_{BH_4^-} . C_{BH_4^-})^a + (K_{4-NP} . C_{4-NP})^b}$$

(4)

Putting the surface coverage values of BH_4^- and 4-NP in eq 1:

$$\frac{-dC_{4-NP}}{dt} = k_{app} . C_{4-NP}$$

$$= \frac{kS(K_{BH_4^-} . C_{BH_4^-})^a (K_{4-NP} . C_{4-NP})^b}{\{1 + (K_{BH_4^-} . C_{BH_4^-})^a + (K_{4-NP} . C_{4-NP})^b\}^2}$$

(5)

$$k_{app} = \frac{kS(K_{BH_4^-}.C_{BH_4^-})^a K_{4-NP}{}^b C_{4-NP}{}^{b-1}}{\{1 + (K_{BH_4^-}.C_{BH_4^-})^a + (K_{4-NP}.C_{4-NP})^b\}^2}$$

(6)

Catalytic Study of 4-NP reduction by 1:4 (VS:AN conc) in Cu-AO-PB

The Cu-AO-PB with 1:4 VS to AN conc with 339 G% was also examined as a catalyst for this reduction reaction. When this system was used, complete reduction took place in 450 sec. In contrast, with our optimized 1:5 VS to AN conc (449 G%), complete reduction occurred in 360 seconds. This difference is attributed to the higher grafting percentage, providing a greater number of active sites for the reaction to proceed efficiently.
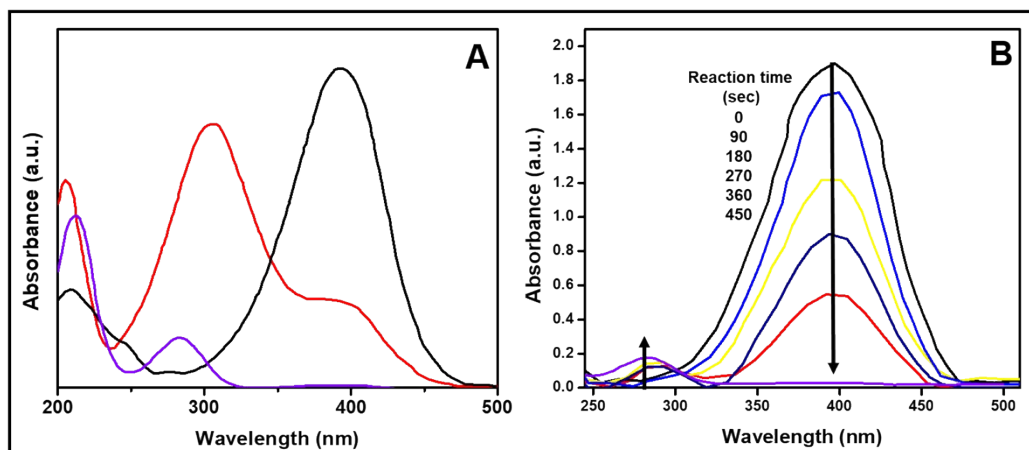

Fig. S3: (A) Time dependent UV-visible study of 4-NP to 4-AP, (B) Kinetic study of 4-NP reduction by 1:4 irradiated sample of Cu-AO-PB polymer brush catalyst

References:

[1]   S. Taimur, M. I. Hassan, and T. Yasin, Removal of copper using novel amidoxime based chelating nanohybrid adsorbent, Eur. Polym. J. 95 (2017) 93–104, https://doi.org/10.1016/j.eurpolymj.2017.08.004.

[2]   S. Taimur and T. Yasin, Influence of the synthesis parameters on the properties of amidoxime grafted sepiolite nanocomposites, Appl. Surf. Sci. 422 (2017) 239–246, https://doi.org/10.1016/j.apsusc.2017.05.263.

[3] M. Bagheri, M. Y. Masoomi, A. Forneli, & H, García, A quasi-metal–organic framework based on cobalt for improved catalytic conversion of aquatic pollutant 4-nitrophenol, J. Phys. Chem. C. 126 (2021) 683-692, https://doi.org/10.1021/acs.jpcc.1c08658.