Doped carbons derived from ZIF-67 for adsorption and electro-oxidative removal of dyes

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1. Introduction – The global issue of water contamination is still not adequately addressed as there is a variety of pollutants that need different remediation approaches. Whether we are employing physical or chemical techniques, material science makes advances in the design of adsorbents and catalysts to assist with the complete removal of pollutants [1]. To explore the potential of carbonised cZIF and its composites with polyaniline cZIF/P for pollutant removal, adsorption and electrochemical degradation methods were employed. The tested organic dyes were methylene blue (MB) and methyl orange (MO) removal to cover representatives of nitrogen/sulphur-containing, anionic and cationic pollutants.

2. Experimental - Novel hydrothermal method in aqueous solutions at room temperature was employed to successfully synthesize ZIF-67 nanocrystals, eliminating the need for toxic organic solvents and reducing costs. The carbonization procedure was conducted in argon flow at 800 °C (cZIF). Additional functionalisation of materials was introduced by conducting polymer addition (polyaniline) before carbonisation (cZIF/P). Adsorption was tested in a batch adsorption system (100 ppm of dye and 1mg/mL adsorbent dose), while the reaction mixture in the electrooxidation experiment contained 15 ppm dye, reaction kinetics was monitored in a 240 min time frame and quantified by UV-Vis spectrophotometry. Degradation of MB/MO was conducted under alkaline conditions using chronoamperometry, with a potential set at -0.8 V for the desired period. Under these conditions, reactive oxygen species are generated which are responsible for dye degradation [1].

3. Results and Discussion - In our investigation, we observed a progressive enhancement in dye adsorption from the original ZIF-67 to its carbonised forms. The prolonged carbonisation at 800 °C proved beneficial for the textural properties of the sample, yielding 65 mg/g retention of MB, and 52 mg/g of MO. Interestingly, contrary to what was expected, the introduction of polyaniline did not induce a higher affinity of nitrogen/sulphur-doped carbons for dye retention resulting in moderate 15-16 mg/g for both dyes. As remediation techniques require the complete degradation of pollutants, we tested the potential intrinsic catalytic activity of doped carbons through electrooxidation in basic conditions. Their applicability in electro-assisted pollutant removal is tested for MB/MO degradation via electrochemical oxygen reduction. The cZIF demonstrated impressive efficiency, achieving 84% degradation for MB and 56% for MO within 4 hours. Notably, cZIF/P exhibited the same degree of MB degradation as cZIF but in just 3 hours, while in the case of MO, the composite displayed a slight 1% improvement over the cZIF sample.

4. Conclusions - The results highlight the efficacy of the ZIF-derived carbons in both physical and chemical processes pertinent to water remediation.

5. References

[1] Milojević-Rakić, M.; Bajuk-Bogdanović, D. Recent Advances in Zeolites and Porous Materials Applications in Catalysis and Adsorption Processes. *Catalysts*, **13**, (2023) 863.
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