Title: Enhanced Photocatalytic Degradation of Methylene Blue in Water Using Modified Clinoptilolite

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Abstract

This study investigates the performance of modified natural clinoptilolite in the photocatalytic removal of the model dye methylene blue. By comparing the effectiveness of zeolites in the degradation by photo-Fenton process, we demonstrate the significant role of the zeolite modifications on the kinetic constant and overall removal efficiency of the dye. The findings highlight the potential of zeolites as effective catalysts and adsorbents in water treatment for environmental applications.

Clinoptilolite is one of the most abundant natural zeolites; aluminosilicate minerals with a rigid anionic framework containing a two-dimensional channel system and with two well-defined cavities that host exchangeable metal cations [1]. In this way, metal that are relevant in Fenton reactions can be incorporated into the zeolites in an attempt to provide the material with catalytic applications for water treatment. The catalytic process involves the transformation of hydrogen peroxide to hydroxyl radical, which thus is capable of oxidizes organic matter in water.

0.1 g of NZ-Cu were dispersed in 100 mL of a methylene blue solution (3 mg/L). After allowing the system to stabilize for 1 h, hydrogen peroxide was added to the solution (100 mg/L). The photoreactor was then exposed, uncovered, to visible light (wavelength range of 410-710 nm, light intensity of 9 W/m²). To prevent overheating of the solution during the irradiation process, a cooling jacket was employed to maintain the temperature within a controlled range, ensuring that the reaction proceeded under optimal thermal conditions.

Two experiments were conducted to evaluate the effectiveness of the zeolites in enhancing the degradation of methylene blue via Fenton reactions. In the first experiment, a solution of methylene blue was treated solely with hydrogen peroxide and visible light radiation. In the second experiment, methylene blue was treated with hydrogen peroxide and visible light radiation in the presence of zeolites. The percentage reduction of methylene blue was calculated by comparing the concentrations remaining after treatment in both experiments. This approach allowed to assess the additional impact of the zeolites on the degradation process. The removal values of methylene blue indicate a significant improvement due to the use of zeolites, reaching a final removal of 65% (17 % without catalyst) and doubling the degradation rate, with a kinetic constant of $k=0.007 \text{ s}^{-1}$ and 0.0140 s^{-1} for the test without and with zeolite, respectively. This suggests that the zeolites greatly enhance the degradation of methylene blue compared to hydrogen peroxide alone, highlighting their effective role as catalysts and adsorbent. Further work is underway for removing emergent contaminant and pathogens.

References

[1] Kraljević Pavelić S, Simović Medica J, Gumbarević D, Filošević A, Pržulj N, Pavelić K. Critical Review on Zeolite Clinoptilolite Safety and Medical Applications *in vivo*. Front Pharmacol. 2018 Nov 27;9:1350. doi: 10.3389/fphar.2018.01350. PMID: 30538633; PMCID: PMC6277462.