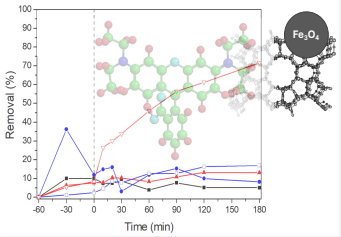
Rhodamine B Removal Applying The Heterogeneous Fenton Process With HZSM-5 Zeolite Obtained From Rice Husk Ash

ORAL/POSTER
Ph.D. Student: Y/N
Journal: NONE

***D.S. Lima[1,*]**, V.P. Drugg[2], A.C.S. Boeira[2], F.M. Mayer[2], M.C. Rangel[2], I.C. Tessaro[1], N.R. Marcílio[1]. (1) Department of Chemical Engineering, Engineering School, Federal University of Rio Grande do Sul (UFRGS), Ramiro Barcelos Street, 2777, CEP90035-007 (2) Department of Inorganic Chemistry, Institute of Chemistry, UFRGS, Bento Gonçalves Avenue, 9500, CEP91501-970 Porto Alegre, RS, Brazil. *dirleia.lima@ufrgs.br*



This study investigates the removal of Rhodamine B dye from aqueous effluents by heterogeneous Fenton method, over iron oxide supported on HZSM-5 zeolite, synthesized from rice husk ash as a silicon source. The prepared zeolite proved efficient as a support for iron catalysts, resulting in high catalytic activity. The catalyst with 5% iron showed the best performance, achieving 71.5% removal of Rhodamine B after 180 min of reaction. The formation of magnetite (Fe_3O_4) provided high availability of ferrous ions (Fe^{2+}), essential for the Fenton reaction. These results highlight the viability of the heterogeneous Fenton process over iron-impregnated HZSM-5 as a promising and sustainable technique for treating industrial effluents containing dyes, contributing to reducing agro-industrial waste and offering an efficient and economical means of wastewater treatment.

Introduction

Rapid population growth and industrial development have generated significant environmental concerns, especially regarding the pollution of water resources. Industries from different sectors discard large amounts of effluents, contributing to water scarcity and environmental degradation. Among industrial pollutants, dyes represent a challenge due to their stability and resistance to degradation. Rhodamine B, widely used in various industries, is particularly problematic due to its toxic and carcinogenic properties.

Advanced oxidative processes (AOPs), such as the Fenton reaction, effectively degrade organic pollutants. The heterogeneous Fenton process, which uses iron-based catalysts offers advantages in removing iron after treatment.

Therefore, this work investigates the removal of Rhodamine B dye from an aqueous effluent using the heterogeneous Fenton method over magnetite supported on HZSM-5 zeolite, obtained using rice husk ash (RHA) as a silicon source.

Material and Methods

HZSM-5 zeolite was synthesized according to the methodology adapted from Bortolini et al. [1], starting from a mixture of a basic dispersion (water, NaOH P.A., and RHA) with an acidic dispersion (water, aluminum sulfate P.A., and sulfuric acid P.A.). The mixture was kept under constant stirring at 25 °C for 60 min (aging step). Ultrasound was employed to obtain the basic dispersion. After aging, the obtained hydrogel was transferred to a Teflon container containing the seed (ZSM-5 - CBV 2314 Zeolyst). This container was placed in an autoclave and the system was kept in an oven for 24 h at 190 °C. Subsequently, the material was vacuum-filtered and washed with deionized water. Afterward, the sample was dried in an oven at 80 °C for 12 h. Ion exchange was carried out with an ammonium nitrate solution and the sample was calcined in a muffle furnace for 2 h at 600 °C. The catalysts were prepared using the synthesized HZSM-5 as a support. The metal (3 or 5 wt%) was impregnated by the excess solvent method using iron nitrate as precursor. Finally, they were calcined in a muffle furnace for 2 h at 600 °C. The sample was then reduced in two steps, the first one at 350 °C for 4 h and the second step at 400 °C for 2h. These temperatures were elected by the temperature-programmed reduction experiments. In both stages, the rate heating was 10 °C/min, and the reducing gas flow was 50 mL/min (10% H_2/Ar).

The catalysts were characterized by X-ray diffraction, nitrogen physisorption measurements, and temperature-programmed reduction.

The catalysts evaluation was carried out at room temperature under constant magnetic stirring. In a 250 mL beaker, 10 mg of catalyst were dispersed in 100 mL of Rhodamine B (RhB) solution at a concentration of 15 mg/L and pH 4. After 60 min of reaction, 1000 µL of hydrogen peroxide was added, starting the Fenton reaction, which is called time zero of reaction. The experiment took place for another 180 min, totaling 4 h. For UV-Vis analyses, aliquots were collected at the following intervals: -60, -30, 0, 10, 20, 30, 60, 90, 120 and 180 minutes. The maximum wavelength of 552.942 was considered to quantify dye degradation.

Results and Discussion

Table 1 presents the prepared samples, the nomenclature adopted and the results of specific surface area, and pore volume. Pure HZSM-5 zeolite (sample HZU) shows the greatest specific surface area, micropores volume and total pore volume. Impregnation with iron nitrate, generating magnetite after calcination/reduction, decreases the specific surface area, the external surface area and consequently, the total surface area for iron catalysts, probably due to the blockage of some pores by iron particles.

Table 1. Sample nomenclature and textural properties.

Sample	Surface área (m^2/g)			Pore volume (cm^3/g)		
	S_{BET}	S_{Ext}	S_{Tot}	V_{micro}	V_{meso}	V_{Tot}
HZU	339	74	413	0.1058	0.0498	0.1555
3%FeHZU	315	89	404	0.0953	0.0580	0.1532
5%FeHZU	308	77	385	0.0927	0.0573	0.1500
3%FeHZU_R	309	67	376	0.0960	0.0517	0.1476
5%FeHZU_R	315	59	374	0.1015	0.0458	0.1473

Figure 1a shows the results of the X-ray diffraction for some prepared samples. The diffractogram of the prepared support, sample HZU, presented the reflections typical of ZSM-5 zeolite at 2Θ between 8 and 10° and between 23 and 26° [2], confirming the formation of the ZSM-5 structure. In samples supported with iron, hematite was present (Fe_2O_3). Still, due to the low impregnated content, it is only possible to observe small characteristic reflections of this oxide at 2Θ equal to 33° and 49°. Due to the low content of impregnated oxide, only a small peak related to magnetite (Fe_3O_4) at 2Θ= 36° was identified in the diffractograms (not shown).

Figure 1b shows the programmed temperature reduction profile carried out for 5%FeHZU sample. Three reduction peaks centered at 403, 576 and 708 °C can be noted, attributed to the reduction of Fe_2O_3 to Fe_3O_4, Fe_3O_4 to FeO and FeO to metallic Fe, respectively [3]. Based on the reduction profile, the catalysts were heated to the maximum reduction temperatures of the catalysts (350 and 400 °C).

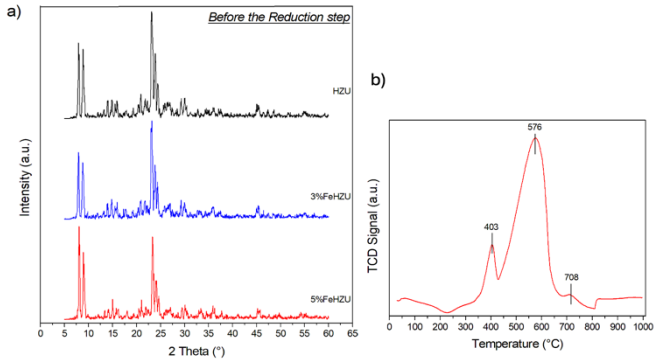


Figure 1. X-ray diffractograms for a) prepared samples and b) TPR analysis for 5%FeHZU sample.

The catalytic efficiency and adsorption performance of the samples were evaluated in the removal of the target contaminant Rhodamine B with H_2O_2 addition. Figure 2 shows that the 5%FeHZU_R sample stood out in removing rhodamine B, reaching 71.5 % after 180 min of reaction. This can be related to the highest content of iron oxide (hematite, α-Fe_2O_3) which, during the reduction stage, is transformed to Fe_3O_4, with availability of ferrous ions (Fe^{2+}).

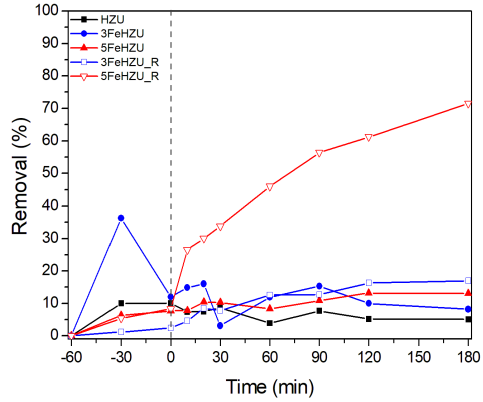


Figure 2. Rhodamine B removal versus reaction time.

Conclusions

This study investigated the removal of Rhodamine B dye from aqueous effluents using the heterogeneous Fenton method. Iron catalysts impregnated in HZSM-5 zeolite, prepared using rice husk ash as a silicon source, were used. The catalyst with 5% iron, which went through the reduction stage, showed the best performance in removing Rhodamine B, reaching 71.5% removal after 180 minutes of reaction. This result can be explained by the formation of magnetite (Fe_3O_4), which has a high availability of ferrous ions (Fe^{2+}), essential for the Fenton reaction. These results highlight the viability of the heterogeneous Fenton process with HZSM-5 zeolite-impregnated iron catalysts as a promising technique for treating dye-containing effluents. The sustainable methodology employing rice husk ash contributes to waste reduction and provides an efficient and economical means of treating industrial wastewater.

Acknowledgments

The authors acknowledge CAPES (Brazilian Agency for Improvement of Graduate Personnel), FAPERGS and CNPq for the financial support to carry out this work.

References

[1] Bortolini, H. R., Lima, D. S., & Perez-Lopez, O. W. *Journal of Crystal Growth*, 532 (2020), 125424.

[2] Lima, D. S., & Perez-Lopez, O. W. *Renewable Energy*, 136 (2019), 828.

[3] Peng, X., Liu, L., Shen, B., Bian, Y., Su, L. *Journal of Fuel Chemistry and Technology*, 51 (2023), 841.