Application of Ferric Zeolite as catalytic material in PAO for Restoration of Water Quality in the Chignahuapan Lagoon.

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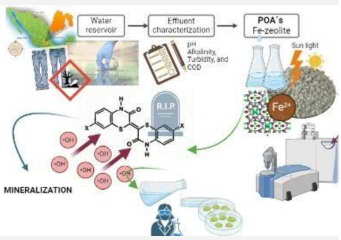

The Chignahuapan Lagoon (Almoloya del Río, Estado of Mexico) is nowadays contaminated due to textile activity, posing highly alarming concerns at both local and national levels. Advanced Oxidation Processes (AOPs) have achieved removal and mineralization of contaminants from the textile industry. This study characterized effluents following the methods of current Mexican official standards and evaluated the homogeneous and heterogeneous photo-Fenton processes using iron-modified zeolites as an alternative for water restoration in the lagoon. The water from the lagoon that mainly proceeds from industrial and domestic wastewater was restored to its original pH~7 in a span of 5 hours ([H_2O_2] 45 mmol). The raw water taken from the source achieved an 80% color removal (pH=5, [H_2O_2] 90 mmol, 5 hours). Heterogeneous photo-Fenton processes did not generate residual sludge, which is attractive to local stakeholders considering the installation of Water treatment plants. Phytotoxicity tests on the treated effluents yielded a 95% germination rate.

Introduction

Indigo dye has been used for centuries in the coloring of blue textiles, currently the global indigo carmine market is expected to reach a valuation of more than US$ 70.0 million in 2031. It is also well acknowledged that under experimental conditions, Advanced Oxidation Processes (AOPs) are effective due to the formation of powerful oxidizing agents such as hydroxyl radicals (HO•)[1] which can oxidize contaminating organic matter, including textile dyes. This project involved the sampling of real contaminated surface waters with textile dyes from Chignahuapan Lagoon and assessing the removal of the present dyes using ferric zeolites. Sampling was conducted over four periods. The samples were characterized by determining physicochemical parameters following the methods of official Mexican standards for waters[2]. This approach was proposed for water restoration and reuse at the site, aiming to establish estable conditions for a plant operation in the locality.

Material and Methods

The sampling of polluted water was conducted at four specific points within the lagoon, as well as at the source of raw water, during both dry and rainy seasons. For homogeneous and heterogeneous photo Fenton treatment (FFHomog and FFHeterg), pH was adjusted with 0.01M HCl, 30% H_2O_2 was used and the metal salt employed was $FeCl_3$ 0.1M, using direct sunlight exposure in a batch reactor. The natural zeolite clipnotilolite was characterized by various techniques and modified under the hydrothermal method to FFHeterg. Color removal monitoring was determined by Uv-vis absorbance turbidity. Different concentrations of ZeFe catalyst and H_2O_2 doses were tested to investigate the effect of the operating parameters. Toxicity determination of the treated aqueous solution was evaluated using lettuce seeds (acceptance>90%).

Results and Discussion

An initial monitoring via UV/Vis absorption in the range of 580-620 nm (Figure 1a,1b) reveals the presence of blue dyes (mixed with black ones, according to the textile workshop source). Table 1 displays the parameters for both raw and treated water samples. The alkalinity ranging from medium to highly alkaline in the lagoon water samples indicates strong hydrolysis of organic matter and turbidity indicative of planktonic life. Chemical oxygen demand and does not demonstrate any desirable conditions for aquatic life[3]. The application of FFHomog and FFHeteg photo Fenton-like processes leads to an effective proposal before discharge and a restorative nature over the lagoon. The application of PAOs in the Laguna sample achieves positive effects on turbidity (Table 1). The characterization of the catalyst was carried out for FFHeterg through Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). In Figure 1d, bright areas indicative of iron in the conditioned zeolite (ZeFe) are observed, which is confirmed by EDS compared to natural zeolite (ZNat), where ZeFe obtains 20% iron enrichment starting from 1.26% in ZNat. Sodium is not reported in ZeFe (ZNat %Na= 0.71), due to the desirable cation exchange of the synthesis process. Other elements reported in the materials are %C 18, 20, %Si 12, 13, %O 54, 48, %Al 3, 3, %K 2, 2, and %Ca 5, 1; for ZNat and ZeFe respectively, intrinsic to the zeolite structure. FTIR provides tracking of the modification from ZNat to ZeFe (Fig. 1d). Bands found at around ~3000 cm^{-1} are associated with Si-OH groups. The band observed at ~1400 cm^{-1} could possibly be attributed to the ONa linkage, which is absent in the ZeFe sample but present in ZNa, as supported by EDS. Regarding the specific surface area (BET), it increases in ZeFe to 110.62 compared to ZNat 25.31 m^2/g, for materials before and after synthesis. Regarding Catalytic Performance,the effect of pH level and H_2O_2 concentration to 5 hours. It is acclaimed that the optimal pH range in processes similar to Fenton's ONE is between 2 and 5. From Figure 1c, we can observe that the FFHomog treatment is favored at pH=5 and [H_2O_2] 45 mmol (97%) in the lagoon samples, while the application of the same treatment on samples from the raw water source resulted in the highest removal at pH=5 with [H_2O_2] 90 mmol (79%). It is noteworthy that at pH around 7 (original), color removal was not favorable with FFHomog (lagoon 58% and raw water source 66% [H_2O_2 90 mmol]). The application effect of the FFHeterg treatments on the lagoon water sample can be carried out at around pH 7 (original), achieving a 98% color removal rate with [H_2O_2] 45 mmol. The samples from the raw water source do not show any effect superior to 80% for FFHeterg compared to the homogeneous treatment (79%); however, the principal advantage that the FFHeterg treatment haves is that it does not generate residual sludge (200 mg/L dry basis). These color removal efficiencies are explained by the presence of species from the dyeing process such as washing surfactants and greases, which are molecules subject to electrostatic repulsion. Therefore this results in low efficiencies of the applied treatments. Additionally, the decomposition of H_2O_2 into O_2 and H_2O at pH>5

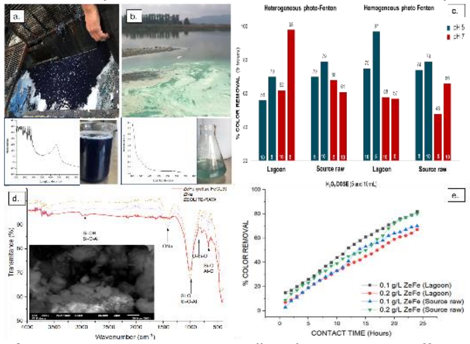

Figure 1. a. Raw water sampling, b. Lagoon, c. Effect of dose and pH on treatments (raw water sample and lagoon), d. FTIR for materials and ZeFe micrograph, e. Evaluation of mass effect on heterogeneous photo Fenton.

reduces the oxidation capacity for HO• radicals. Consequently, a thorough study is required for raw water samples of unknown and variable origin. The effect on the mass with the highest color removal was observed at 0.1g/L after 5 hours of contact.

Table 1. *Physicochemical characterization of water samples for source raw water and lagoon before and after AOP's.*

Treatment	Homogeneous photo-Fenton				Heterogeneous photo-Fenton			
site	*Source raw water*		*Lagoon*		*Source raw water*		*Lagoon*	
	raw	treated	raw	treated	raw	treated	raw	treated
pH	7.3	5.2	7.6	5.4	7.3	6.9	7.6	7.4
Alkalinity (mg/L $CaCO_3$)	186	162	234	171	186	154	234	156
Turbidity	13.54	4.5	12.9	2.2	13.54	2.3	12.9	2.3
COD (mg/L O_2)	581	ND	715	ND	581	208	715	1454
Absorbance (u.a.)	2.46	0.68	0.209	0.004	2.46	0.218	0.209	0.122

ND: Undeterminated

Conclusions

Such is the pollution caused by dyeing dyes in real water effluents that, as it matters to the concentrations of the substances used, that they are unknown in the effluents. The application of heterogeneous photo Fenton-like processes (FFHeterg) using zeolite-based catalysts can represent a real and potential approach to minimize and mitigate the contaminating effects. Through the employment of FFHeterg, a color removal of 98% was achieved in water samples from Chignahuapan Lagoon at their original state of pH~7 in 5 hour. An 80% color removal was achieved for the source waters under the same conditions using iron-modified zeolite.

Acknowledgments

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