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Evaluation of ZnO Catalyst Supported on Zeolite NaA in the Photocatalytic Degradation of Vinasse Pretreated by Coagulation/Flocculation

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The research for a proper disposal of vinasse is a serious concern for countries that produce ethanol from sugar cane such as Brazil. The wastewater of its production process is generated with an extremely high toxic load. In this work, samples of *in natura* vinasse were submitted to a pre-treatment by coagulation/flocculation process, applying the Tanfloc® SG in order to obtain a clarified vinasse and improve the performance of photocatalytic degradation. The pre-treated vinasse (clarified) was characterized by chemical oxygen demand (COD), colour, turbidity and absorbance reductions. Coagulation/flocculation reduced 80 % of colour, 70 % of turbidity, 40 % of COD and 43 % of absorbance at 270 nm (region of maximal absorption of vinasse). The sludge obtained from this process was submitted to thermogravimetric and differential thermal analysis (TGA/DTA), verifying its potential for use as fuel in furnaces of boilers in power plants. Catalysts based on zinc oxide supported on commercial zeolite NaA under the following compositions were prepared by wet impregnation: 5 % ZnO/NaA and 10 % ZnO/NaA (wt%). The catalysts were characterized by X-ray diffraction (XRD), N_2 physical adsorption (BET), atomic absorption (AA), photoacoustic spectroscopy (PAS), infrared spectroscopy (FTIR), energy dispersive X-ray (EDX), scanning electron microscopy (SEM), and then applied in photocatalytic reactions of clarified vinasse. The efficiency of the combined treatment coagulation/flocculation/photocatalysis was evaluated by means of COD and UV-Vis absorbance reductions. It was found that 10 % ZnO/NaA showed better activity, with an increase of 50 % and 36 % reduction in COD and absorbance, respectively, when compared to plain zeolite NaA.

1. Introduction

The research for a proper disposal of vinasse is a serious concern for countries that produce ethanol from sugar cane such as Brazil. With the increase in demand for cleaner energy sources, ethanol consumption has increased substantially all over the world. Among the methods of harnessing, treatment and disposal of vinasse which is considered 100 times more polluting than domestic wastewater (Freire and Cortez, 2000) can stand out a fertirrigation, the launching of vinasse in plantations of sugarcane despite the risks of alteration of the quality groundwater (Lelis Neto, 2009).
An alternative method to degradation of vinasse that has large amount of organic compounds which are resistant to conventional physicochemical and biological treatments is the use of advanced oxidation processes (Esplugas et al. 2002). These promote mineralization of pollutants or conversion into compounds of smaller chains and non-toxic (Andreozzi et. al. 1999), through the production of highly

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reactive free radicals that oxidize many organic pollutants using solar and UV irradiation (Santana and Fernandes-Machado, 2008).

When a semiconductor is subjected to radiation whose energy is equal to or greater than its band gap energy, the excitation promotes a valence band electron to the conduction band, creating a gap in the valence band with enough positive potential to generate •OH radicals from adsorbed water molecules. These radicals are highly oxidising and react with organic compounds mineralising them (Ferrari-Lima et. al., 2012). The most used semiconductor as photocatalyst is titanium dioxide, which is activated in the UV radiation.

As alternative, some researchers have tested zinc oxide (Ferrari-Lima et. al., 2012) which has band gap energies similar to that of titanium dioxide. However, the practical application of titanium dioxide in aqueous media is limited because TiO_2 has a polar surface and is not a good adsorbent by itself for nonpolar organic molecules. So that the addition of suitable supporting matrix may enhance catalytic activity of semiconductors (Amereh and Afshar, 2010). The, the aim of this work was to evaluate the activity of the catalyst ZnO supported on zeolite NaA in the photocatalytic degradation of vinasse pre-treated by coagulation/flocculation process using a tannin-based coagulant.

2. Experimental

2.1 Materials

Sample of vinasse was obtained from a power plant, located in the northwest of Paraná, Brazil. It was collected directly from the distillation column (temperature around 100°C) and characterized following the Standard Methods for Examination of Water and Wastewater (APHA, 1998). The natural coagulant tannin (Tanfloc®) type SG was furnished by the manufacturer Tanac S/A in liquid state.

2.2 Preparation and characterization of photocatalyst

The catalysts 5 % ZnO and 10 % ZnO (wt%) supported on zeolite NaA (Baylith from Bayer) were prepared by wet impregnation from zinc nitrate. After impregnation, the obtained catalysts (5 % ZnO/NaA and 10 % ZnO/NaA) were calcined at 400 ºC for 5 h. The impregnated photocatalysts were characterized by X-ray diffraction (XRD), N_2 physical adsorption (BET), atomic absorption (AA), photoacoustic spectroscopy (PAS), Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), and then applied in photocatalytic reactions of clarified vinasse.

2.3 Coagulation/flocculation

The coagulation/flocculation process was conducted in jar test equip Milan JT 101 at room temperature. The best experimental parameters for clarification were previously determined (Souza et. al., 2013). Sample of 1000 mL of vinasse *in natura* were mixed with 250 mL Tanfloc® SG solution of 10 % (v/v) at 100 rpm during 1 min, followed by 30 min of slow agitation (50 rpm). The experiment was performed at the natural pH of the vinasse (pH ~ 4.8). The parameters of clarification analysis were colour (PtCo-APHA), turbidity (FTU) and COD (mg O_2 L^{-1}) (APHA, 1998). The sludge obtained from this process was separated, dried at 110 ºC to constant weight and it was submitted to TGA/DTA analysis and also the calorific capacity was determined, verifying its potential for use as fuel in furnaces of boilers in power plants, since this sludge generated is an organic material easy to burn.

2.4 Photocatalytic degradation

The photodegradation experiments were performed with samples of vinasse pre-treated (coagulation/flocculation) employing artificial UV irradiation. In all experiments used 2.0 g of catalyst dispersed in 500 mL of effluent in a glass batch photo-reactor. The temperature was controlled around at 25 °C. The illumination was provided by five germicide mercury lamps (total 75 W). The photo-illumination processes were carried out for 48 h with aliquots retired in 1 h intervals (first day) and 2 h (second day). The collected aliquots were analyzed: pH, COD and colour (APHA, 1998). The photodegradation were also monitored by UV-Vis electronic absorption at: 270 nm, 254 nm, 284 nm, 310 nm and 500 nm (BOROSKI et. al., 2009).

3. Results and discussions

3.1 Vinasse characterization and coagulation/flocculation

In the Table 1 are shown the results of the characterization of the vinasse *in natura* in conjunction with the vinasse pre-treated after coagulation/flocculation process. The values of COD and pH are near to those found by other authors (Souza et. al., 2013). Coagulation/flocculation process removed 80 % and 70 % of colour and turbidity respectively, indicating that besides the compounds responsible for the colour and turbidity (inorganic and organic) are also present yeasts that eventually flocculated and adhered to the sludge. There wasn't change in the pH value (4.86). In this work, as also reported by Souza et. al. (2013), the tannin proved to be effective in reducing the COD, turbidity and colour of the effluent.

Table 1: Characterization of vinasse in natura and pre-treated after coagulation/flocculation

Initial values	Colour (PtCo)	Turbidity (FTU)	COD (mg O_2 L^{-1})
In natura	23.800	1.200	32.480
	% Reduction		
	Colour (455 nm)	Turbidity (860 nm)	COD (600 nm)
Pre-treated	80	70	40

The reduction of the absorbance was evaluated by means of absorption spectra UV-Vis (Figure 1), for the sample of vinasse *in natura* and after pre-treatment by coagulation/flocculation. In terms of absorption at 270 nm, the efficiency of the clarification showed 42.5 % of reduction in absorbance.

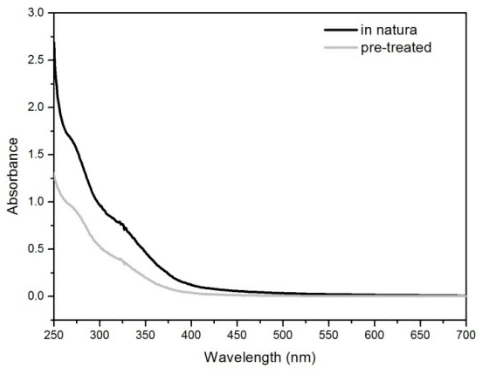

Figure 1: UV-Vis spectra of vinasse in natura and pre-treated with Tanfloc®.

The generation of sludge in the pre-treatment employing Tanfloc®, was approximately 600 mL/L. It's generated due to the waste of the effluent and also of the coagulant. Studies have been performed to evaluate the possibility of using the dried sludge as fuel or to incorporate it in the production of bricks for use in construction (Kushwaha et. al, 2010). The dry sludge showed 90 % humidity, was found by TGA/DTA analysis a mass loss of 70 % indicating that it may be subjected to thermal decomposition. The calorific capacity determined was -3.356 k cal g^{-1}, value near to found for the cane bagasse which is already used in boilers in Brazil. That corresponds to a significant calorific capacity and may be tested as a fuel in boilers.

3.2 Catalysts characterization

By atomic absorption analysis it was found 4.5 and 8.5 % of impregnation for 5 and 10 % of ZnO on zeolite NaA, respectively. Textural analysis of the catalysts supported on zeolite and pure support is shown in Table 2. The zeolite NaA presented specific surface area of 28.4 m^2 g^{-1}, being possible verify a reduction in surface area of approximately 59 and 83 % after impregnation of 5 to 10 % of ZnO, respectively. This is due to the partial obstruction of the pores by small clusters generated during the calcination. Evaluating the average pore diameter there has been a gradual increase, showing that the oxides were impregnated in all ranges of pore size, being distributed throughout the exposed surface.

Table 2: Textural analysis of the catalysts

Catalyst	Surface area (m^2 g^{-1})	Micropore area (m^2 g^{-1})	External surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (Å)
NaA	28.4	22.8	6.5	0.023	16.2
5%ZnO/NaA	11.7	5.5	6.2	0.013	22.8
10%ZnO/NaA	4.7	0.1	4.6	0.008	34.1

X-ray diffraction analysis showed that zeolite is crystalline (Figure 2). The appearance of a peak at 2θ of 12° and around 14-15° indicate the presence of ZnO impregnated into the zeolite NaA. Already for the catalyst containing 10 % ZnO/NaA there was an increase in intensity of these peaks due to the increase in the content of oxide impregnated. It's noticed the appearance of another peak when 2θ is around 20^o.

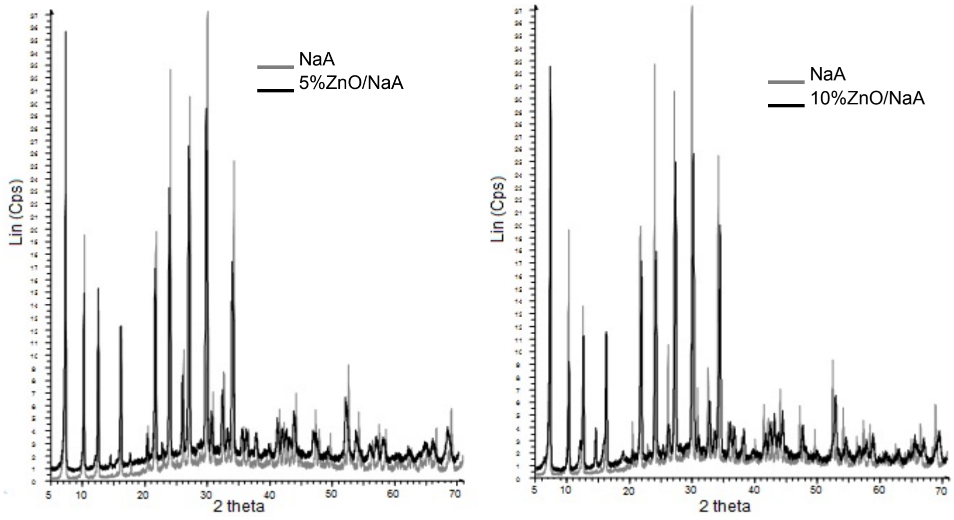

Figure 2: Diffractograms of pure zeolite NaA and supported catalyst.

PAS analysis showed that the supported catalysts had an increase in band gap energies (3.7 eV) compared to ZnO band gap around 3.1 eV. It means that the supported catalysts require the similar amount of energy to be activated by the lamp that emits a main peak at 400 nm and other of lesser intensity at 360 and 430 nm.

The infrared spectra of the catalysts showed that supported ZnO exhibited similar followed the characteristic of pure zeolite (Figure 3-A). It was observed the peaks near to 900 cm^{-1} and another around 1400 cm^{-1} for the supported catalysts, peaks characteristic of zinc oxide. In the infrared spectra for NaA before and after photodegradation of vinasse (Figure 3-B) the same profile is verified, it means that there wasn't residual vinasse/intermediates and that the degradation is due the photocatalytic process and not the transfer by adsorption. The same result was found for the supported catalysts.

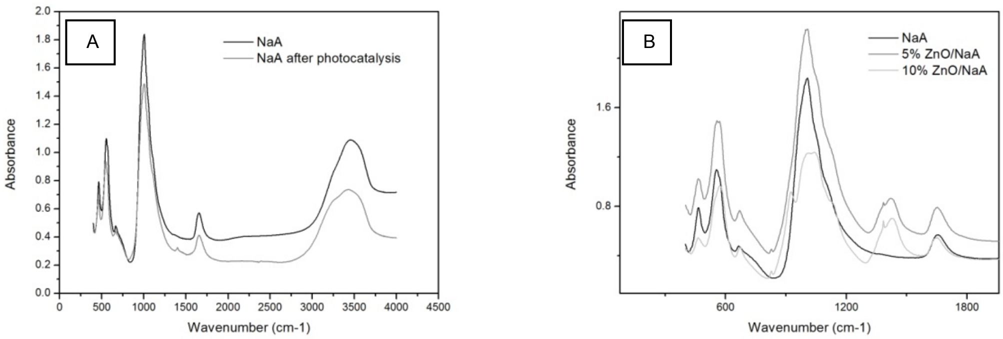

Figure 3: Infrared spectra of pure zeolite (A) and supported catalysts (B).

Based on the micrographs, it was verified that the pure zeolite before the reaction had well defined solids in the cubic format and solids that haven't gone through a good formation or are presented in the form of grains (Figure 4-A). After the reaction, was verified adsorption of vinasse, losing its original shape (Figure 4-B).

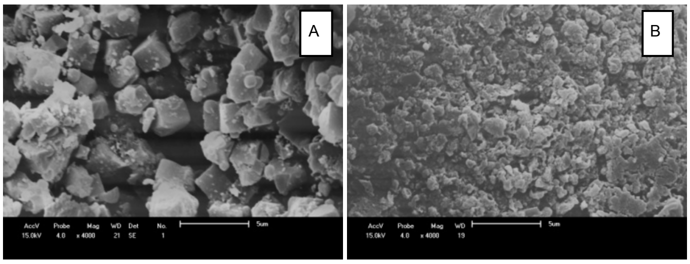

Figure 4: Micrograph of pure zeolite NaA (magnification 4000x).

The impregnation of the 5 % of oxide on the zeolite maintained its original cubic shape and can be visualized small grains of ZnO accumulated between the cubes of the zeolite (Figure 5-A), however the presence of 10 % ZnO resulted in a morphological change in the structure of zeolite, undoing its original cubic shape (Figure 5-B). Both catalysts after the reactions, suffered structural changes due to adsorption of vinasse on its surface (Figure 6-C and 6-D).

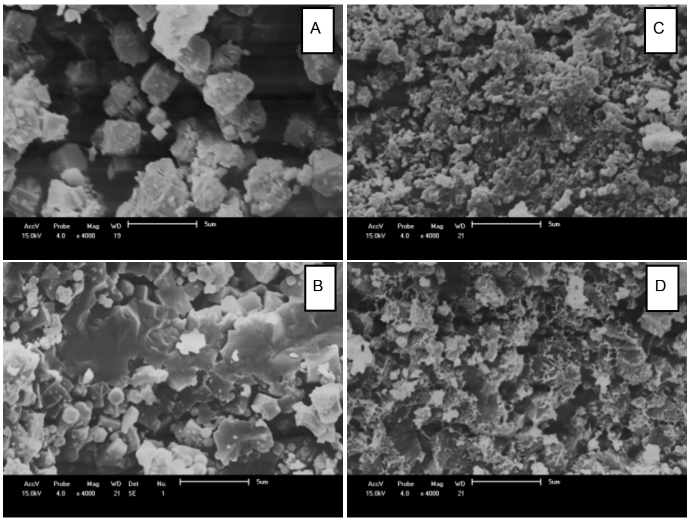

Figure 5: Micrograph of supported catalysts (magnification 4000x).

The surface composition was determined by EDX, which confirmed the presence of Si, Al constituent of zeolite and also the presence of Zn by impregnation of ZnO on the support.

3.3 Photocatalytic degradation

It was observed in Table 3 that the supported catalyst containing 10 % ZnO showed better activity, with an increase of 50 % and 36 % of reduction in COD and absorbance, respectively, relative to the pure support.

Table 3: Results of photodegradation of vinasse pre-treated by coagulation/flocculation

Catalysts	% Reduction	
	Abs (270 nm)	COD (600 nm)
NaA	10.8	9.3
5%ZnO/NaA	12.8	14.9
10%ZnO/NaA	16.9	18.5

Through the UV-Vis spectra (Figure 6), it's possible to evaluate the efficiency of several catalysts employed. Note that the catalyst with 10 % ZnO/NaA showed the greatest reduction in absorbance across the range investigated.

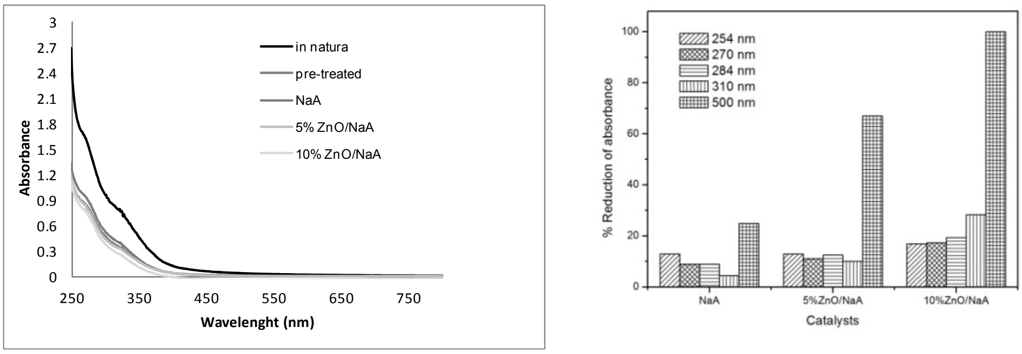

Figure 6: UV-Vis spectra and reduction of absorbance: vinasse in natura, pre-treated and photocatalysis.

The presence of the support (zeolite NaA) showed high photocatalytic activity due to its high aluminum content, which favours the adsorption of water (Brites et. al., 2011). The hydrophilic nature of the zeolite probably increases the formation of hydroxyl radicals from OH^- (on the catalyst surface).

4. Conclusions

Inorganic coagulants can be replaced by the organic coagulant Tanfloc® which leads to reduction of colloidal matter with no changes on pH. Combined treatment by coagulation/flocculation/photocatalysis allows the reduction of pollutants and toxic compounds. The presence of the support (zeolite NaA) showed high photocatalytic activity due to its high aluminum content, which favors the adsorption of water and the formation of hydroxyl radicals.

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