Diminishing of Biological Oxygen Demand during Wastewater Depollution by Oxidation with Nanostructured Catalysts

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The high content of organic matter of surface waters represents a real danger for aquatic fauna, even if their toxicity is low. Such a high rate of biodegradation leads to oxygen depletion of the waters in question and thus the suffocation of aquatic fauna. The elimination of these disadvantages by using purge technologies of catalytic oxidation may be a viable solution. The oxidation process of pollutants in wastewater that contain glycerol or molasses was performed on nanostructured catalysts based on Fe, Mn and Fe-Mn mixed. The catalysts were prepared by precipitation-coprecipitation of selected precursors and they were characterized by determination of particle size distribution. Measurements for the determination of particle size distribution were carried out using the method of dynamic light scattering. The oxidation process was conducted in a batch reactor equipped with air bubbling system, in suspension of catalysts. Efficiency of oxidation process of wastewater loaded with glycerol or molasses is expressed by biochemical oxygen demand. Compared to Mn or Fe catalyst, the Fe-Mn catalyst favors an advanced treatment of wastewater that contain glycerol or molasses by oxidation with air.

Keywords: catalyst, nanoparticles, wastewater, oxidation, biological oxygen demand, glycerol, molasses

The assessment of current disposal methods of glycerol from wastewater obtained at biodiesel production and of molasses from wastewater resulting from the sugar manufacturing industry was the basis of numerous studies that have proposed new purge treatment technologies [1-3].

The treatment of water loaded with a high content of molasses can be achieved by anaerobic or aerobic treatment, adsorption or physico-chemical methods depending on the concentration of molasses in wastewater [4, 5]. Due to high turbidity of wastewater, using bleaching processes represents currently the last step of treatment. As such purification technology applied is quite expensive [5, 6].

Biodiesel production is another important process in which results high concentrations of organic matter in wastewater. The amount of wastewater is usually higher and BOD (biochemical oxygen demand) can reach up to 75,000 ppm. Current treatment methods are anaerobic or aerobic treatment, MBR technologies (membrane bioreactor technologies), physico-chemical treatment [7].

By analyzing the data existing in the literature for the above processes, the degree of purification is more than 80% in BOD, at up to 3% of content in glycerol or molasses in the wastewater.

Wastewater treatment using nanotechnologies represent an advantageous solution but insufficiently studied. Contaminants advanced recovery, process selectivity and low amount of obtained sludge are the main advantages of using this technique. The nanoparticles used in these methods of treatment are based on zeolites [8], noble metal oxide [9] and Fe compounds [10].

This paper proposes for wastewater treatment resulting from sugar and glycerol industry the use of nanoparticles like Fe, Mn oxide and mixtures thereof. Catalyst nanoparticles in suspension can reduce BOD concentration by applying catalytic oxidation process, up to the limit allowed by law.

Experimental part

Raw materials used in the study are glycerol and molasses resulting from the manufacture of biodiesel and sugar. Analysis of physico-chemical parameters was done respecting the standardized methods [11]. The reagents used in the preparation of the catalysts were manganese acetate $Mn(CH_3COO)_2$, PEG 300, ammonium hydroxide solution 25%, ferric chloride anhydrous and ferrous chloride 98%, Sigma-Aldrich reagents.

Mn-based nanoparticles have been prepared by precipitation of a 0.2M solution of $Mn(CH_3COO)_2$ under intense stirring, at room temperature, with a 10% solution of NaOH at a molar ratio of $Mn(CH_3COO)_2/NaOH$ 1/2. The obtained precipitate was separated by centrifugation, washed three times with distilled water and dried. Iron catalyst used in this study were prepared by coprecipitation of 0.1M $FeCl_3$ and 0.1M $FeCl_2$ solution in a volume ratio of $FeCl_3/FeCl_2$ 2/1 in the presence of 10% polyethylene glycol (% by weight, to the total mass of the reaction) with a 25% NH_3 solution at a molar ratio of $NH_3/FeCl_3$ 4/1. The precipitate obtained was washed three times with distilled water and dried. The catalyst type Fe - Mn was prepared by a previously submitted recipe [12].

The distribution of particle sizes of iron and manganese catalysts was measured with a particle size measurement by dynamic light scattering (DLS). The instrument used for measuring is a Nano ZS (Red badge).

Experimental installation used to study the catalytic oxidation process contains a column-type reactor made of glass, equipped with thermostating jacket and fitted with a frit for dispersing air bubbles.

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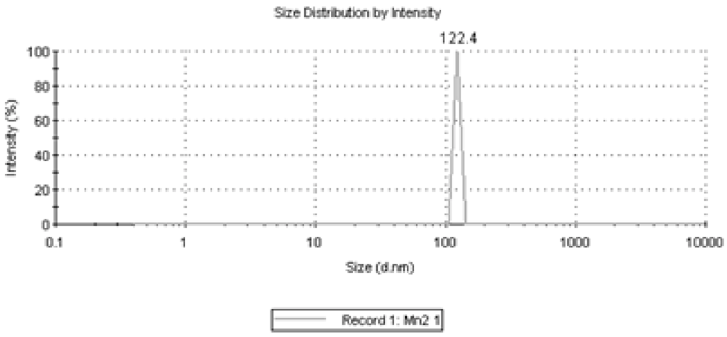

Fig. 1. DLS analysis of Mn catalyst

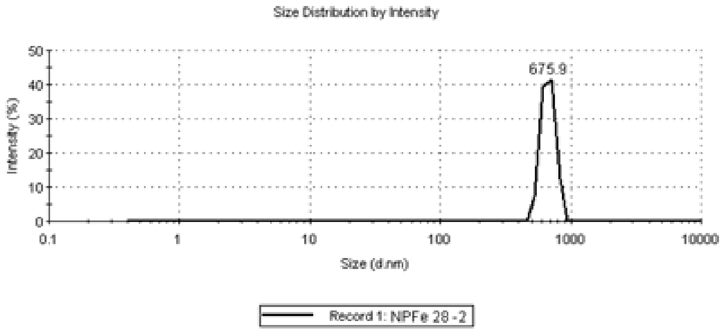

Fig. 2. DLS analysis of Fe catalyst

The suspended catalyst concentration was 1% and the reactions were conducted at 85°C and a initially *p*H of 10. The reaction time varied from four to ten hours and the volume hourly space velocities of air was 500 h^{-1}. The oxidation efficiency of water loaded with glycerol or molasses is expressed by biochemical oxygen demand to five days and the action of oxidants on organic matter in the wastewater was highlighted by measuring ORP (Oxidation Reduction Potential).

Results and discussions

Figure 1 shows the DLS analysis of Mn-based catalyst. There is a mean size of catalyst particle of 122.4 nm and a variation range of particle size of between approx. 102 and 200 nm.

Figure 2 shows the DLS analysis of Fe-based catalyst. The average particle size of the catalyst was 675.9 nm and the minimum size approx. 450.

The DLS analysis of catalyst type Fe - Mn was presented in a previously article [12].

The content glycerol or molasses of water used in the experiment was between 1% and 3%. Characterization of water loaded with glycerol and molasses is presented in table 1.

The results of catalytic oxidation for the three type nanoparticles catalysts are shown in figures 3-8. In the case of 1% glycerol content, after the oxidation with air, biochemical oxygen demand of the waste water decreases with reaction time by a similar curve for all catalysts, for less than 4-5 h of the duration of oxidation process. Catalysts type Mn-Fe nanoparticles exhibit a better activity in the glycerol oxidation, BOD decreasing approx. 7 times after eight hours reaction. Fe-type catalyst shows a lower activity than the other two in the oxidation process, especially at longer reaction durations of 4 h (fig. 3).

Increasing of the glycerol concentration in the wastewater at 2% resulted in a activity decrease of the all catalysts at durations less than 4 h of reaction. For reaction times greater than 4 h , catalyst activity increases, the increase being more pronounced for Fe-Mn catalyst and less pronounced for Fe catalysts. Thus, after 10 h of reaction, BOD decreases for more than 4 times for all the catalysts tested (fig. 4).

Table 1
CHARACTERIZATION OF WASTEWATER CONTAINING GLYCEROL AND MOLASSES

Contents, wt%	BOD, mg/L	
	Glycerol	Molasses
1	3380	5124
2	4415	6957
3	5253	8689

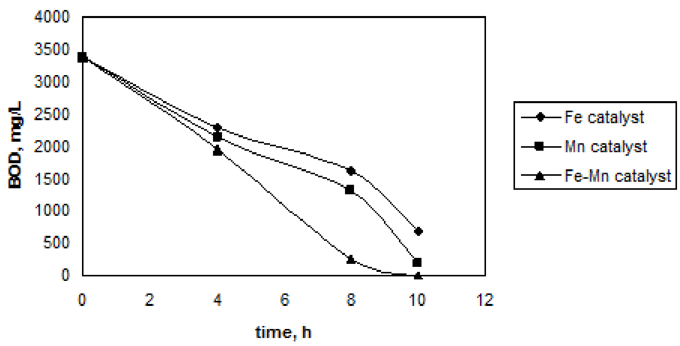

Fig. 3. BOD variation of 1% glycerol in wastewater with mixing time

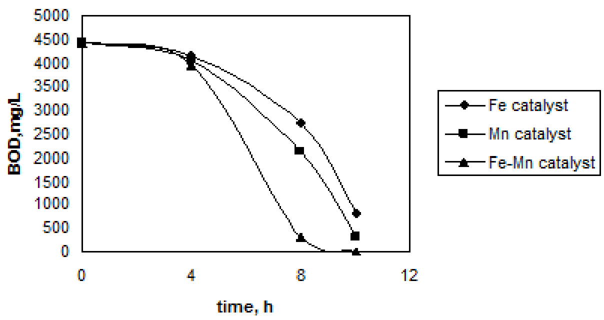

Fig. 4. BOD variation of 2% glycerol in wastewater with mixing time

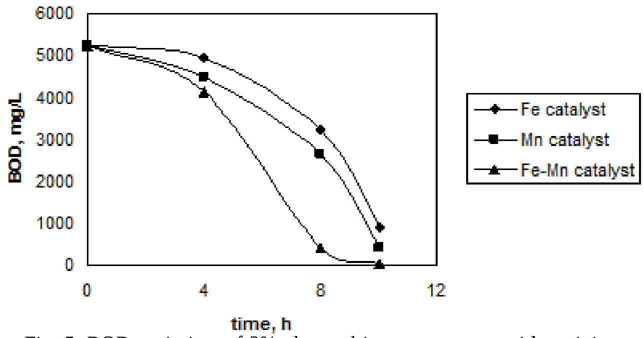

Fig. 5. BOD variation of 3% glycerol in wastewater with mixing time

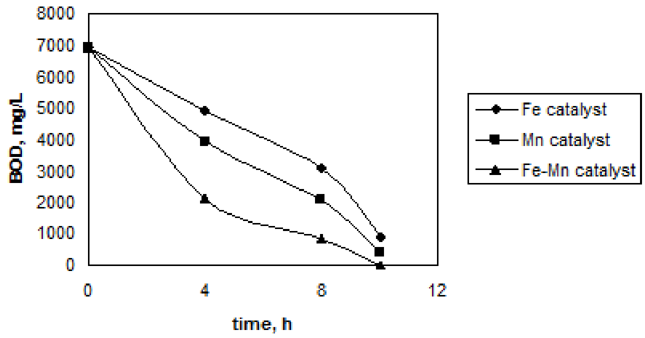

Fig. 7. BOD variation of 2% molasses in wastewater with mixing time

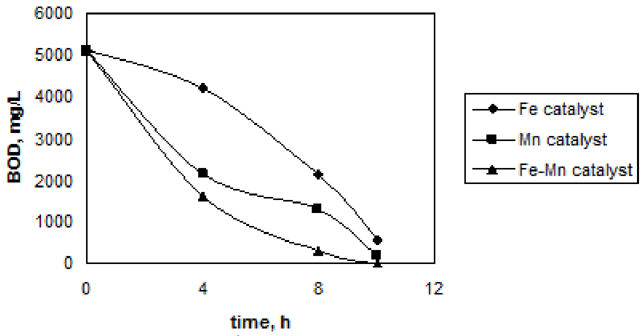

Fig. 6. BOD variation of 1% molasses in wastewater with mixing time

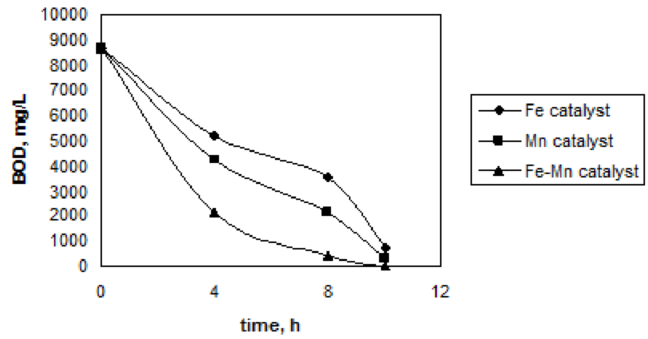

Fig. 8. BOD variation of 3% molasses in wastewater with mixing time

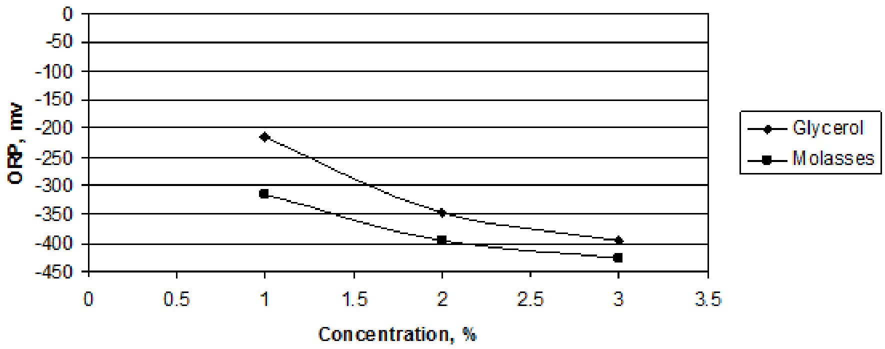

Fig. 9. ORP variation for glycerol and molasses at 10 hours mixing time in the presence of Fe-Mn catalyst mixture

In the case of wastewater containing 3% glycerol, the results from oxidation are similar to those obtained for 2% glycerol content, the slope of the variation curves of BOD with time is greater at the reaction times greater than 4 hours (fig. 5). Also Fe-Mn catalyst showed a higher activity than the other two and the Fe catalyst showed a lower activity than the other two.

The efficiency of all three catalysts was very good in case of water containing molasses at a 1%, 2% and 3% concentration. Such, BOD variation curves with reaction time, shows a similar shape for the three concentrations of molasses, with a slope greater the reaction times of less than 4 h for Fe-Mn catalyst and a lower slope for Fe catalyst at the reaction time lower than 4 h.

Such, for 1% molasses, at ten hours reaction time, BOD value decreased from 5124 mg/L up to 561 mg /L in the Fe catalyst case and respectively of 14 mg L value in the Fe-Mn catalyst case (fig. 6). For a content of 2% molasses and a reaction time of 10 h, BOD value decreased from 6957 mg /L up to 924 mg /L value in the Fe catalyst case and up to 22 mg /L in the case of the Fe-Mn catalyst (fig. 7). In the case of wastewater with 3% molasses, BOD decreases from 8689 mg /L up to 741 m /L (Fe catalyst), up to 314mg/ L (Mn catalyst) and up to 21 mg/L (Fe - Mn catalyst) for a 10 h reaction time (fig. 8).

Evaluation of the catalyst which showed a better activity, respectively Fe-Mn catalyst, was achieved by determining ORP variation, which shows the stage for both chemical reactions, the probability of subsequent formation of biogas and the catalyst consumption in the reaction medium. Thus for 10 h reaction time Fe-Mn catalyst, shows a significant ORP variation (fig. 9). On the basis of these results it can be proposed a pre-treatment step of the water loaded with glycerol or molasses. Thus, the catalytic oxidation step, being followed by recovery of the biogas.

Conclusions

Wastewater treatment with a high content of BOD is a current problem whose solution must take into account of the need to protect aquatic fauna and to obtaining an advanced degrees of treatment while reducing the amount of sludge.

The oxidation process of pollutants in wastewater that contain glycerol or molasses was performed on nanostructured catalysts based on Fe, Mn and Fe-Mn mixed.

The catalysts were prepared by precipitation-coprecipitation of select precursors and they were characterized by determination of particle size distribution.

Measurements for the determination of particle size distribution were carried out using the method of dynamic light scattering.

The oxidation process was conducted in a batch reactor equipped with air bubbling system, in suspension of catalysts at a concentration of 1%, at temperature of 85^{o} C, *p*H 10, for a period of 4 h, 8h and 10 h respectively.

The oxidation efficiency of water loaded with glycerol or molasses is expressed by biochemical oxygen demand.

For a glycerol or molasses content up to 3% using Fe-Mn catalyst nanoparticles favors an advanced treatment of wastewater by oxidation with atmospheric oxygen.

The implementation of this method in industry can be achieved by coupling classic treatment with the catalytic oxidation.

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