Removing of Pollutants from Catalytic Cracking Wastewater by Oxidation with Nanostructured Catalysts

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The literature highlights the use of nanoparticles for the treatment of wastewaters containing organic compounds such as hydrocarbons, phenols, etc. The oxidation process of pollutants in wastewater from catalytic cracking was performed on nanostructured catalysts based on Fe, Mn and Fe-Mn mixed. The catalysts were prepared by precipitation-coprecipitation in the presence of anti-caking. 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%, a temperature of 85-90° C, pH 9.2, for a period of 2h, 4h and 6h respectively. The best results were obtained in the presence of Fe - Mn catalyst at 6 hours reaction time. Degree of contaminant removal for this catalyst had maximum values of 72.80% for COD, 77.97% for extractible, 74.4% for phenol, 67.53% for ammonium and 67.57 % for sulfides,. Better behavior of Fe - Mn catalyst in the oxidation reaction was due both to the nature of the catalyst, as to well as the smaller size of this catalyst particles.

Keywords: nanoparticles, wastewater, catalytic cracking, chemical oxygen demand, phenol

The amount of waste generated lately is growing. These issues are reflected in the large number of articles published in the literature in which it is addressed the issue of waste [1-3]. Among these wastes, wastewater is a priority given the effects of environmental pollution with them. Industrial and municipal wastewater treatment is a necessity of modern society in permanent development. At present it known a large number of wastewater pollutants, their diversity is closely linked to the diversity of industrial processes [4].

The treatment of refinery wastewater is imposed by new EU rules on environment. So, are sought solutions to remove undesirable compounds from the wastewater that can reach in groundwater and rivers, leading to the destruction of fauna and flora [5-7]. The need for wastewater pretreatment or advanced treatment of this, led to the identification of treatment processes based on chemical reaction in the catalysts presence [8-10].

Implementation of advanced purification in the presence of nanoparticles represent a trend in this field and has the advantages of low prices and high degrees of treatment [11, 12]. In a recent article [13] presented a study with the scope to determine the effectiveness of iron nanoparticles to reduce the chemical oxygen demand (COD), biological oxygen consumption (BOD5), total solids content (TS) and waste levigated. The experiments were carried out in a batch reactor, the main factors investigated being pH, reaction time and the concentration of iron nanoparticles. On the basis of the results it was observed that after the treatment with iron nanoparticles could be removed in the proportion of 53% for the levigate, COD, BOD5 and TS, in a short contact time (10 min). The increasing of pH up to 6.5, increase the efficiency of the process, while the increasing of pH to 8.5 decrease the efficiency of the depollution process. Increasing the dose of nanoparticles to 2.5 g / L, increase the efficiency of the process. High compatibility and efficiency of this process can be a solution for treating of municipal waste landfills.

The use of Mn nanoparticles for preconcentration of salt solutions [14] highlights the advantages of using catalytic conversion process in water treatment. Decontamination of surface and deep water by catalytic oxidation with Mn nanoparticles are another option for depollution by catalytic oxidation [15, 16]. In all of these processes emphasizes the importance of the preparation method of the nanoparticles, in determining the morphology and chemical properties of their [17]. So, nanoparticles characteristics and reaction conditions are the parameters which define the efficiency of treatment process [18,19].

Waters from catalytic cracker unit represents a significant proportion of the total water resulting in refinery. This paper proposes the use of catalytic oxidation process for treatment of these waters. Charging with pollutants of wastewater from catalytic cracker unit comes from the condensate resulting from steam used in catalyst stripping at the reactor outlet, from the condensed water resulting at combustion of hydrocarbons present in the coke deposited on the used catalyst and from the condensation of steam from stripping of column fractionation. The oxidation was carried out in suspension of the nanostructured catalysts on the Fe and Mn basis .

Experimental part
The Mn and Fe catalysts preparation

Catalysts used in this study were prepared by precipitation - coprecipitation method in the presence of anti-caking. Thus, the manganese oxide catalyst was prepared by precipitation of a 0.2 molar manganese acetate $Mn(CH_3COO)_2$ (Sigma-Aldrich reagents) solution in the presence of 1% Pluronic - P123 (mass percentage to the reaction mass) under vigorous stirring at room temperature with a 10% NaOH solution and the 1:2 molar ratio

Parameter	Methods	Equipment used
pH	SR ISO 10523 -2009	pH-meter TOLEDO
Phenols, mg/L	STAS 7884-91	DR 5000
Sulfides, mg/L	SR EN 7510:1997	DR 5000
Chemical Oxygen Demand (COD), mg/L	SR ISO 6060/96	DR 5000
Extractable organic matter, mg/L	SR ISO 7587:1996	Dean-Starck device
Amonium, mg/L	SR ISO 5315:1994	DR 5000

Table 1
ANALYTICAL METHODS AND EQUIPMENT USED TO DETERMINE THE WASTEWATER CHARACTERISTICS

$Mn(CH_3COO)_2$:NaOH. The resulting precipitate was separated by centrifugation, and then washed with distilled water and dried.

The Fe-based catalyst was prepared by co-precipitation of a solution 1 M Fe Cl_3 and 1M $FeSO_4$ (reagents Sigma-Aldrich) at a 2:1volume ratio, with a 25% aqueous ammonia solution (molar ratio of $FeCl_3$: NH_3 = 1: 5), in the presence of 0.5% Pluronic, under vigorous stirring at 60°C. Postreaction time under the same stirring and temperature conditions was 0.5 h. The precipitate was washed with distilled water and dried at 80° C for 24 h.

Preparation of mixed nanoparticles based on Fe-Mn has been made by co-precipitating of a mixture of 0.5M $FeCl_3$ and 0.5M Mn $(CH_3COO)_2$ solution (Sigma-Aldrich reagents), in a molar ratio Fe: Mn 1: 1 with a 2M NaOH solution in a molar ratio Mn $(CH_3COO)_2$ / NaOH of 1/2, under intense stirring in the presence of diethyleneglycol monobutyl ether (2% by mass to the reaction mass) at a 60°C. The obtained precipitate was separated by centrifugation, washed three times with distilled water and dried.

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).

The study of the catalytic oxidation process in suspension

Experimental installation used for the catalytic oxidation process was composed of a bubbler provided with a frit to disperse air bubbles. The amount of sample introduced into bubbler was 500 mL and the concentration of the catalyst was 1% compared to the wastewater. The monitoring of pH was done with pH sensor Multiline pH /

Oxi 340i. Temperature range in which the experiment took place was 85-90° C. The reaction time varied between 2 and 6 h and the pH was maintained at 9.2 for all experiments.

Since the composition of waste water samples from the catalytic cracking channel is not constant, 12 samples were taken at intervals of 12 h, which, after being analyzed, were mixed to obtain a mixed sample. Sampling method was appropriate standard [20].

Physico-chemical parameters analyzed for both the 12 wastewater samples and average sample used in the catalytic oxidation, analysis methods and equipment used to perform analyzes are shown in table 1 [21-26].

To implement the process in wastewater treatment is necessary to evaluate degree of contaminant removal according to equation 1:

$$DG = \frac{c_i - c_f}{c_i} \cdot 100, \quad \% \qquad (1)$$

where:
- *DG* is the degree of contaminant removal, %
- c_i initial concentration of contaminant before applying catalytic oxidation process;
- c_f the final concentration of the contaminant after the application of the catalytic oxidation process.

Results and discussions

Figure 1 shows the DLS analysis of Mn-based catalyst. There is a mean size of catalyst particle of 260 nm and a variation range of particle size of between approx. 108 and 300 nm.

Figure 2 shows the DLS analysis of Fe-based catalyst. The average particle size of the catalyst was 251.5 nm and
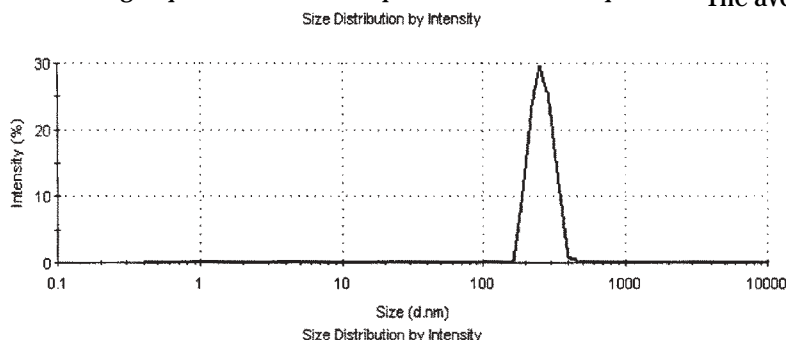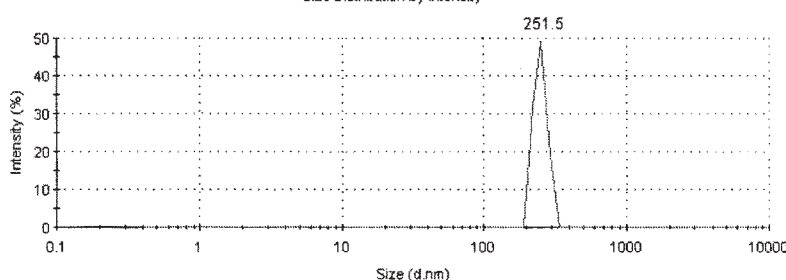

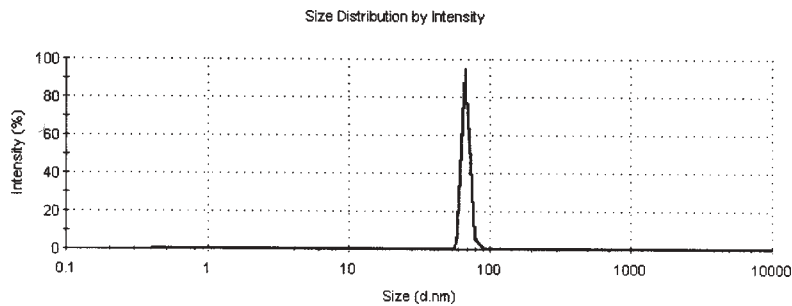Fig.1. DLS analysis of Mn catalyst

Fig.2. DLS analysis of Fe catalyst

Fig.3. DLS analysis of the mixture
Fe-Mn catalyst

SAMPLE	COD, mg/L	PHENOL, mg/L	EXTRACTABLE, mg/L	AMMONIUM, mg/L	SULPHIDES, mg/L
1	509	4.1	110	5.8	5.4
2	512	6.2	112	7.6	6.3
3	583	9.1	114	10.3	9.8
4	621	7.2	116	8.9	7.6
5	478	4.6	118	5.4	4.5
6	750	15.2	130	16.5	10.1
7	535	11.1	124	12.1	9.7
8	514	6.8	123	7.2	6.8
9	678	11.7	108	10.1	8.9
10	712	10.2	113	9.8	5.4
11	673	12.4	114	11.1	6.2
12	680	14.3	127	13.2	8.3
AVERAGE	603.7	9.4	117.4	9.8	7.4

Table 2
CHARACTERISTICS OF
WASTEWATER SAMPLES COLLECTED
FROM CATALYTIC CRACKER UNIT

the particle size variation of between approx. 190 and 330 nm.

From the DLS analysis catalyst of particles based on Fe-Mn, it is observed a mean particle size of 68.61 nm and a variation range of particle size of between approx. 70 and 90 nm (fig. 3).

Wastewater samples characteristics collected are presented in table 2.

The analysis of wastewater samples collected from sewerage of catalytic cracking unit highlights a variation of COD between 478 and 750 mg/L, ammonium concentration varied between 5.4 and 16.5 mg/L, the concentration of sulfides varied between 4.5 and 10.1 mg/L, the concentration of extractable varied between 108 and 130 mg / L and the concentration of phenol varied between 4.1 and 15.2 mg / L. The experimental program was conducted using samples of the average wastewater. The results of the catalytic oxidation process are shown in figures 4- 8.

Using catalyst of Mn and of mixture Mn - Fe leads to advanced removal of COD in wastewater from catalytic cracker unit (fig. 4). Thus for Fe catalyst, at a reaction time of two hours, the COD concentration decreases from 603 mg / L to 518 mg / L and for Mn catalyst the COD concentration lowers to 498 mg / L. Using Fe - Mn catalyst, COD decrease to 411 mg / L for the same reaction time. Increasing the reaction time to four and six hours lead to intensification of removal of COD, thus as the reaction time of six hours, for Fe catalyst the COD concentration decrease to 289 mg / L, for Mn catalyst to 210 mg / L, and for the Fe - Mn catalyst to 164 mg /L.

The removal of extractible present in this waste water are more efficient for Fe - Mn catalyst (fig. 5). Thus, for a maximum time of reaction of six hours, the concentration of extractible decreased to 66.1 mg / L in the case of Fe
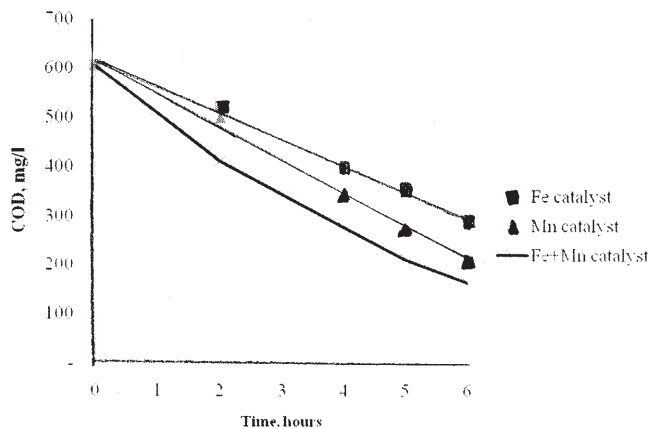

Fig. 4. Variation of COD with duration of the process for the three catalysts tested
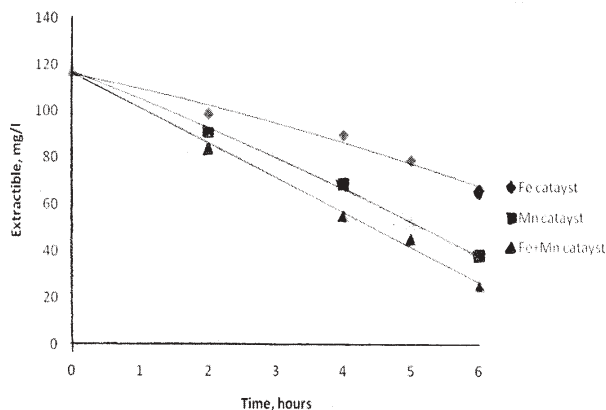

Fig. 5. Variation of extractable organic matter with duration of the process for the three catalysts tested
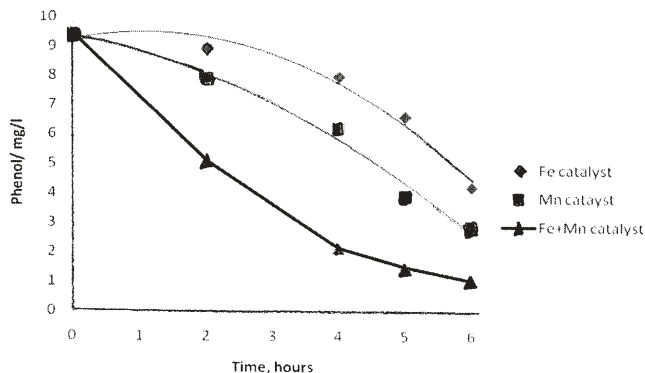
Fig. 6. Variation of phenols concentration with duration of the process for the three catalysts tested
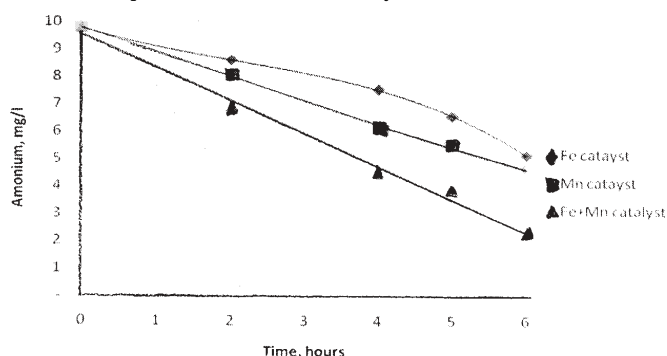

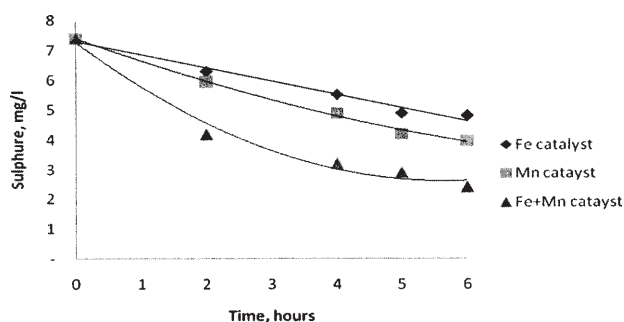Fig.7. Variation of ammonium concentration with duration of the process for the three catalysts tested

Fig.8. Variation of sulphides concentration with duration of the process for the three catalysts tested
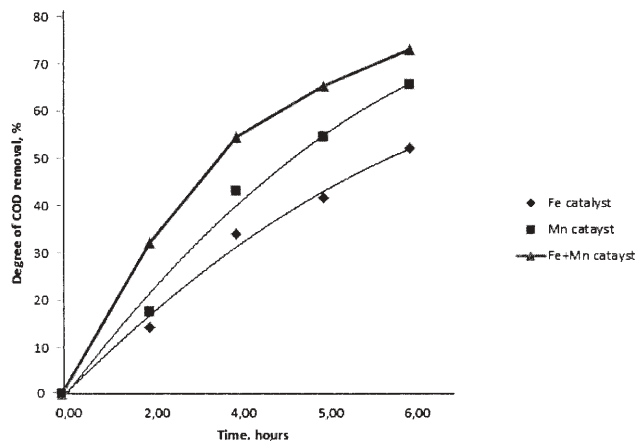

Fig. 9. Degree of COD removal with duration of the process, for the three catalysts tested
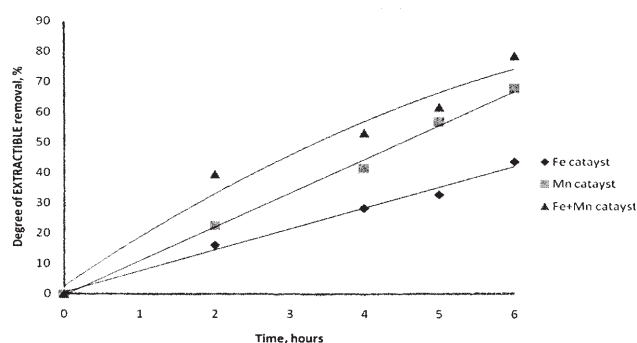

Fig. 10. Degree of extractible removal with duration of the process, for the three catalysts teste
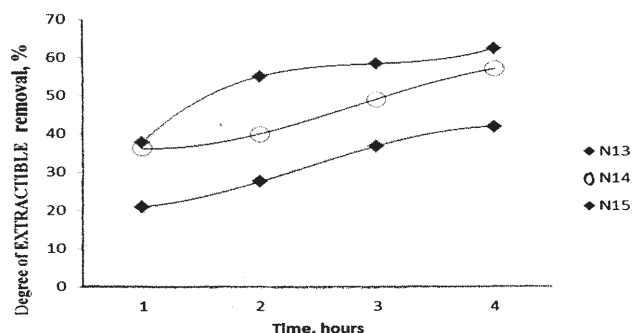

Fig. 11. Degree of phenol removal with duration of the process, for the three catalysts tested

catalyst, up to 85 mg / L in the case of Mn catalyst and up to 25.3 mg / L for Fe - Mn catalyst.

Because phenol is difficult to remove in wastewater treatment plant, selection of a pretreatment processes is most commonly used method in industrial practice. By proposed method the minimum value in the phenol concentration for six hours, was 4.2 mg / L in the case of Fe catalyst, 2.8 mg / L in the case of Mn catalyst and 1.0 mg / L in the case of Fe - Mn catalyst. So, using this process, can be a solution for water treatment loaded with phenol from refinery (fig. 6).

The ammonium concentration decreases with increasing reaction time for all three catalysts (fig. 7). Thus for two-hour reaction, using Fe catalyst leads to a maximum concentration of 8.9 mg / L, while using Mn catalyst leads to a maximum concentration of 8.7 mg / L. The Fe - Mn catalyst gives good results both for small reaction time (6.2 mg / l for two hours) as well as for six hours reaction time (2.3 mg / L).

The sulphides concentration (fig .8) decreases with the reaction time. Thus, for six hours, the sulphides concentration decreases to the value of 4.8 mg / L using Fe catalyst, to 3.97 mg / L when using Mn catalyst and to 2.4 mg / L in the case of using the Fe - Mn mixed catalyst. From the analysis of data presented we can see that the best

results are obtained in the case of reaction time of six hours and of Fe - Mn catalysts.

Degree of contaminant removal appropriate of physico-chemical indicators obtained in the experiments are shown in figure 9-13.

The maximum value of the degree of COD removal was 72.80% for six hours reaction time and Fe - Mn catalyst. The value of extractible removal degree was 77.97% for Fe - Mn catalyst and 58.09% for Fe catalyst at six hours reaction time. The degree of phenol removal by catalytic oxidation in the presence of Fe catalyst at six hours reaction time was 55.21%, while using Fe - Mn catalyst can lead to increasing of removal degree to 74.4% for the same time reaction. The removal degree of ammonium and sulphides for Fe - Mn catalyst was higher than for Fe catalyst and Mn catalyst at the same reaction time. Thus, for the six hours reaction time, the degree of amonium removal was approx. 67.53 % and the degree of sulphures removal was approx. 67.57 %, for this type of catalyst.

Mathematical modeling of experimental data is required in case of implementation in an industrial process. So based on experimental results can be expected intermediate
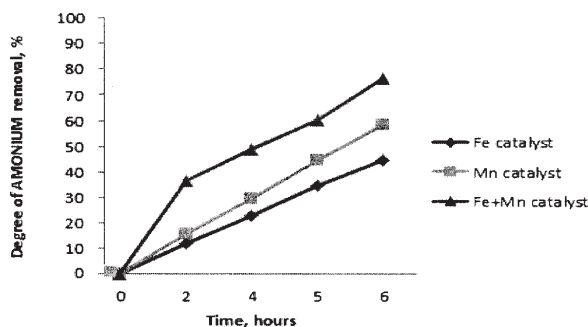
Fig. 12. Degree of ammonium removal with duration of the process, for the three catalysts tested
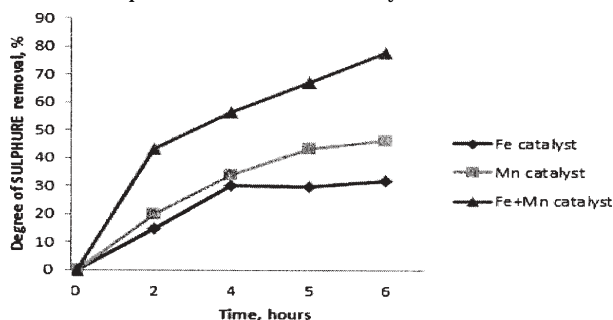

Fig. 13. Degree of sulphides removal with duration of the process, for the three catalysts tested

Fig.14. Variation of ammonium concentration, extractible and COD for Fe - Mn catalyst for a 6 hreaction time

values of the process leading to obtaining an optimal technical and economic standpoint. In this respect the present work was done using a mathematical modeling program MathlabR2013b of the variation of key parameters involved in coupling of the proposed station plant with the classical plants: ammonium, extractible and COD. The results are shown in figure 14.

Conclusions

The literature highlights the use of nanoparticlesfor the treatment of wastewaters containing organic compounds such as hydrocarbons, phenols, etc.

The oxidation process of pollutants in wastewater from catalytic cracking was performed on nanostructured catalysts based on Fe, Mn and Fe-Mn mixed. The catalysts were prepared by precipitation-coprecipitation in the presence of anti-caking. Measurements for the determination of particle size distribution were carried out using the method of dynamic light scattering.

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The best results were obtained in the presence of Fe - Mn catalyst at 6 h reaction time. Degree of contaminant removal for this catalyst had maximum values of 72.80% for COD, of 77.97% for extractible, 74.4% for phenol, 67.53% for ammonium and 67.57 % for sulfides. Better behavior of Fe - Mn catalyst in the oxidation reaction was due both to the nature of the catalyst, as well as the smaller size of this catalyst particles.

The implementation of this method in industry is done either by coupling with the oxidation catalytic classic treatment or by making purification by catalytic oxidation, thus abandoning the classic treatmemt.
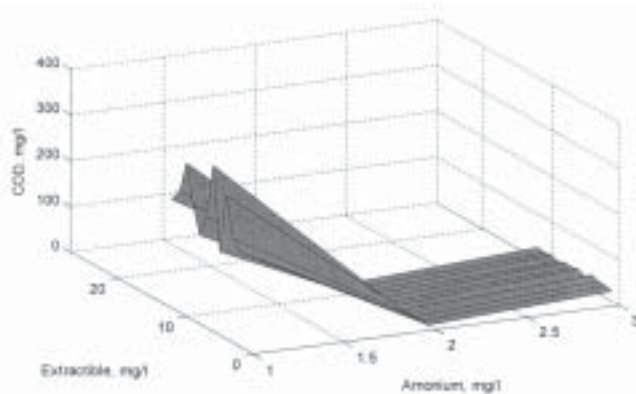
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