

Photocatalytical degradation of methyl orange (MO) using ZnO nanoparticles from alkaline wasted batteries. The effect of the MO, catalyst, and organic loads

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The photocatalytic degradation of methyl orange (MO) using ZnO nanoparticles is reported. NPs in the range of 40-60 nm were obtained from wasted alkaline batteries anodes. The effect of the MO concentration and the catalyst load were analyzed finding that NPs exhibited similar photocatalytic activities than those reported for ZnO-NPs obtained from pure sources when similar conditions are used. The effect of the organic loads (COD from 60 to 900 ppm) in the catalyst efficiency was studied detecting that COD:60 ppm does not affect the ZnO photocatalytical properties. However, high COD loads (600-900 ppm) make the degradation efficiency almost null.

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1. Introduction

Water quality is one of the main problems in the world. Some of the main aquatic contaminants has found to be industrial dyes, surfactants, insecticides, pesticides and heavy metals [1, 2]. According to the National Water Commission, the Mexican industry generates 218.1 m³ / sec of wastewater and only 83.7 m³/s are treated [3]. This wastewater contains diverse contaminants, being of great importance the dyes that present high toxicity and can be carcinogenic and mutagenic [4]; and because of their high resistance to degradation and discoloration they are difficult to eliminate in conventional treatment plants. Therefore, there is a constant search for new methods that allow the remediation of water with these pollutants at reasonable costs [5].

Among these methods, is the advanced oxidation process (AOP) an important alternative for the decontamination of wastewater. The process involves the production of hydroxyl radicals (OH) which are highly reactive due to their high oxidation potential that allows the oxidation of contaminants in CO₂ and H₂O [4]. These advanced oxidation processes have followed two development pathways, photochemical and non-photochemical processes depending on the use of light radiation [6]. The advanced oxidation processes have advantages over conventional processes for the decontamination of industrial wastewater, these advantages are: a) Pollutants are destroyed, do not concentrate or change phase. b) The total mineralization of organic pollutants can be achieved. c) Do not generate sludge or sludge that requires treatment and / or elimination. d) Reagents used as oxidants are substances that decompose in harmless products during the process. e) They are tools to eliminate contaminants that resist other treatment methods. f) Improves the biodegradability of wastewater. g) It serves to treat pollutants at very low concentration [7,8].

The efficiency of these techniques is mainly due to the participation of the hydroxyl radical, since it provides higher oxidation rates, as well as thermodynamically more favorable processes, this radical is capable of reacting (106 - 1012) times faster than alternative oxidants like ozone [9], with an oxidation potential of 2.80 V. Heterogeneous photocatalysis is an advanced oxidation process that uses the ability of UV light (natural or artificial) to excite a semiconductor material and thus generate oxidation-reduction reactions through the generation of electron-hole

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pairs [10]. In quantitative and qualitative terms, the variables that affect the photocatalysis process are the following: a) Initial concentration of the contaminant. b) Type of catalyst and its concentration. c) Amount of oxygen. d) Quality of the water to be treated. e) Temperature. f) Hydrogen potential (pH). g) Wavelength and intensity of light [7,9].

Some of the semiconductors that has been used for photocatalysis are: TiO_2 , ZnO , ZnS , ZrO_2 , MoS_2 , WO_3 , SnO_2 and CdS [10-14]. Among these semiconductor materials, capable of oxidizing industrial dyes such as methyl orange, is the zinc oxide (ZnO), which is a material with a band gap of 3.37 eV and with binding energy of an exciton of 60 meV [4]. The difference in electronegativity that exists between Zn and Oxygen generates a strong ionic bond. The Zinc Oxide can be found in various forms, the Wurzite phase being the most thermodynamically stable since it has a hexagonal crystalline structure in which the atoms are located far enough away to compensate for the electronic repulsions between the oxygen and zinc atom [15]. When Zinc Oxide is irradiated with light, whose energy is greater than or equal to the band gap corresponding to ZnO , an electron in the valence band is excited to the conduction band. The electron-hole pair can recombine or the gap in the valence band can react with the water molecules to form hydroxyl radicals and later these radicals will be in charge of oxidizing the dye molecule [4]. In the last decades, several authors have probed the ZnO efficiency to degrade carcinogenic dyes such as the methyl orange and despite this material is considered as first generation photocatalytic material, it is still considered as a feasible option (doped or undoped) for its good efficiency, non-toxicity, low cost and simple synthesis methodologies [10].

One of the main challenges regarding photocatalysts for degradation of industrial dyes in industrial effluents is that there is no clear way to show how the photocatalytic reactions proceed in an actual reactor. Chemical reactions, mechanisms of degradation, by-products formation, are not well understood when water not only contains a carcinogenic dye but also contains grease, oils or other contaminant [16]. Many of the research work has studied the photocatalytic efficiency of a nanostructure with water and different concentrations of azoic dyes but the effect on the efficiency of common contaminants in water such as grease and oils is not well understood [17].

The chemical demand of oxygen (COD) is frequently used as a measurement of wastewater's pollutants. The toxic materials do not interfere with this measurement and generally can be complete in 2 or 3 h. Despite it is an artificial test, it is considered to provide accurate and reproducible values of the COD in wastewaters [18].

In this work, the photocatalytic efficiency of ZnO for methyl orange degradation is determined and compared with the efficiency obtained when real wastewater is used. The ZnO NPs are obtained from wasted alkaline batteries to contribute to a sustainable product culture. The process to obtain these NPs has been previously reported by our research group [19].

2. Material and Methods

2.1. Synthesis of ZnO nanoparticles

The ZnO NPs were synthesized by a sol gel methodology using starch as a gelling and reducing agent [19]. In this procedure, anodes from alkaline type D batteries were used as the source of Zinc (Zn). The first step is to cut and dismantle the batteries and separate the anode from the rest of the materials to be weighed. Subsequently, the Zn powders from the anode are grinded and washed with water. Once the washed powders are obtained, the sol gel preparation method is continued. To prepare the zinc nitrate, 5 grams of the Zn powder from the anodes were mixed with approximately 25 grams of concentrated nitric acid HNO_3 , (9621-02 JTBaker) in a ratio of approximately 1: 3 and with hydrogen peroxide (H_2O_2 , Jaloma S.A.) in 2% relative to the weight of the nitric acid. The mixture is stirred for 30 minutes at 30 ° C. Then, 10 grams of starch (S7260, Sigma-Aldrich) are mixed in 150 ml of distilled water and stirred for 30 minutes at 75° C. Subsequently, the mixture with Zn is poured over the stirring solution containing the starch and the stirring continues during 10 h at 80 ° C. After 10 h, the mixture is dried for 24 hours at 100 ° C. The resulting material is pulverized in a mortar, placed for calcination at 650d° C during 8 hours and finally is characterized by Transmission Electron Microscopy (Jeol JEM-2200FS), Energy

Dispersive X-Ray spectroscopy (EDAX) and X-Ray Diffraction (XRD, X'Pert Pro PANalytical, $\lambda=0.1542$ nm).

2.2. Photocatalytic experiment

Photocatalytic experiments were conducted using a solution volume of 100 ml with methyl orange at the nominal concentrations. These samples were prepared using DI water. The samples were placed at dark for reaching the adsorption equilibrium. The pH was controlled using NaOH or HNO₃ diluted solutions. The radiation of UV light was achieved by placing the UV lamp (300 Watts) directly above the photocatalytic solution. The catalyst concentration were in the range of 50 to 200 mg/L. The progress of the reaction was followed and monitored each 20 minutes. 5 ml aliquots, taken for every sampling time, were centrifuged (bench-top centrifuge Marathon 22K from Fisher Scientific) in the dark during 5 minutes @ 3000 rpm. The supernatant liquid was analyzed in a UV-Vis Spectrometer (Varian Cary 50) using a calibration curve at 464 nm. Previously, the calibration curves were prepared in a range from 0 to 50 mg/L.

To check how much contaminant is absorbed by the ZnO nanoparticles, a control experiment were carryout showing no significant contamination absorption occurred on the ZnO/MO system. Also an experiment with no catalyst was performed using a solution of 20 ppm of methyl orange where no changes were detected after 120 minutes irradiation with UV light (300 watts). The percentage of degradation was calculated as follow:

$$\text{Degradation\%} = (\text{Co}-\text{Ct})/\text{Co} \times 100$$

where Co is the initial contaminant concentration and Ct is the concentration after a period of light exposure.

2.3. Effect of a typical organic load from an actual water discharge (measured as COD) in the removal of MO

To evaluate the photocatalytic activity of the ZnO NPs in conditions closer to reality, a local company cafeteria discharge water was used to prepare the solutions of methyl orange. The Chemical Oxygen Demand (COD) was determined in accordance with the official Mexican standard NMX-AA-030/2-SCFI-2011 "Determination of Chemical Oxygen Demand". Samples with concentrations of 60, 110, 300, 600 and 900 ppm of COD were prepared by dilution using DI water.

The COD digester was preheated at 150 ° C for 30 minutes. 1.5 ml of a digestion solution consisting of potassium dichromate, sulfuric acid and mercury sulfate were placed in the reaction tubes. Then, 2.5ml of the samples to be analyzed, previously homogenized, were taken and carefully deposited in the reaction tubes. After that, 3.5 ml of a solution of silver sulfate in sulfuric acid were added using a burette. Gently, the tubes were inverted several times, uncapping after each inversion to relieve pressure. The reaction tubes were placed in the digester in closed reflux for 2 hours. After completing the digestion time, the reaction tubes were removed and cooled to room temperature. The absorbance at 600 nm was measured on the UV-Vis spectrophotometer (Varian Cary 50) using the appropriate calibration curve.

3. Results and discussion

The ZnO NPs were obtained from the anode of waste alkaline batteries type D. The Zinc weight agrees with that reported by Hines and our previous work, which is approximately the 15% wt. of the complete battery [19, 20].

The results of the X-ray Energy Dispersion Spectrometry (EDS) and Transmission Electron Microscopy (SEM) are shown in Figure 1a and 1b. The NPs are made of oxygen and zinc with a particles size in the range of 40-60 nm. No impurities were found in the ZnO NPs by EDS. This is also in agreement with our previous report. Figure 1 c shows the results of the X-ray diffraction analysis where the main diffraction peaks are found at 2θ angles of 31.91 °, 34.58 °,

36.39 ° and 47.52 ° that can be indexed as the planes [100], [002], [101], [102] of the ZnO Wurtzite hexagonal phase (PDF # 01-075-0576).

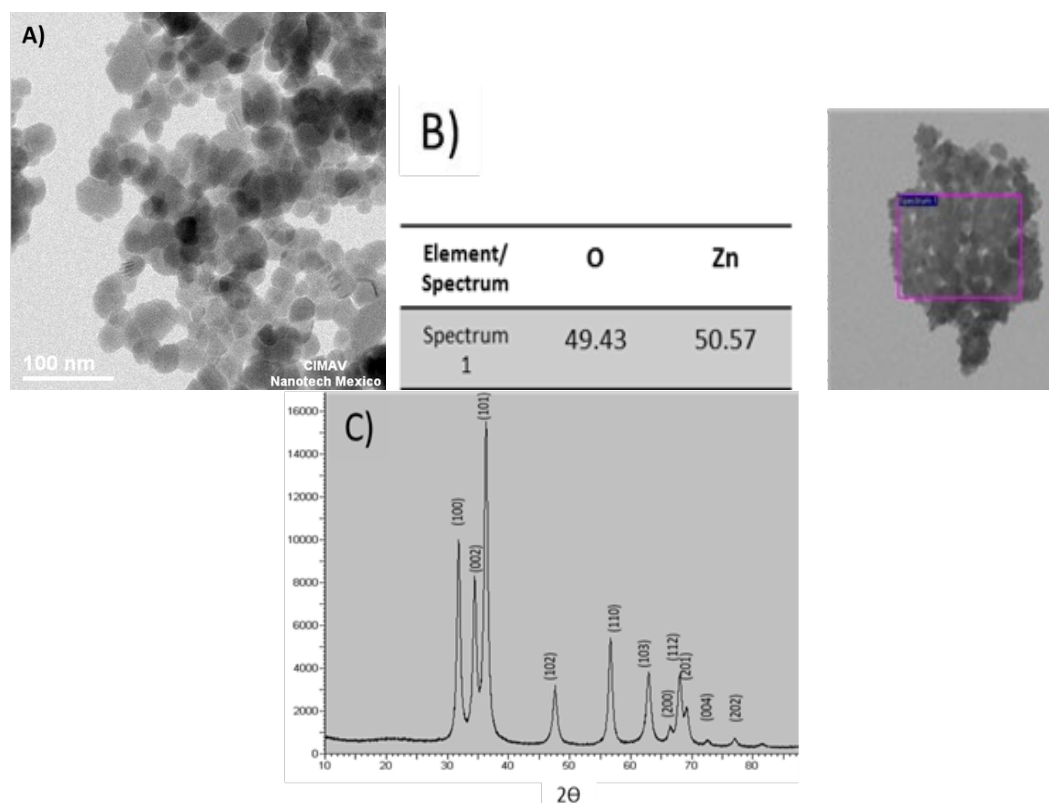


Fig. 1. TEM image (A), EDS analysis (B) and XRD (C) of the synthesized ZnO NPs.

The effect of the initial Methyl Orange (MO) concentration was determined using concentrations of this reagent in the range from 10 to 40 mg/L with a neutral pH (6.7). The ZnO catalyst load was 200 ppm. Figure 2 shows the progress in the MO degradation. As can be observed the contaminant removal goes from 50.5 to 87 % when 20 and 40 mg/L of catalyst are used, respectively. This represent a decrease in the removal level of 42 % when the MO initial concentration is increased by 100 % (from 20 to 40 mg/L).

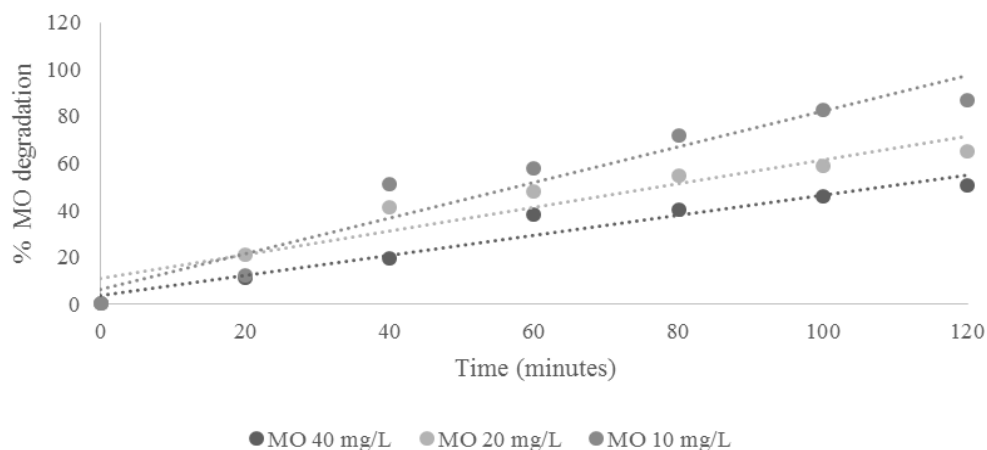


Fig. 2. Effect of MO concentration in its degradation. (Catalyst load: 200 mg/L of ZnO NPs).

The kinetic of degradation of MO can be represented like a first order equation $\ln(C_0/C_t) = K_{app} t$ [4, 21] where the K_{app} is the first order kinetics (min^{-1}), C_0 is the initial concentration, C_t is the MO concentration of the methyl orange in the time t (min). Figure 3 shows linear graphs of the $\ln(C_0/C_t)$ vs. different MO concentration with a catalyst load of 200 mg/L. R^2 values are larger than 0.9.

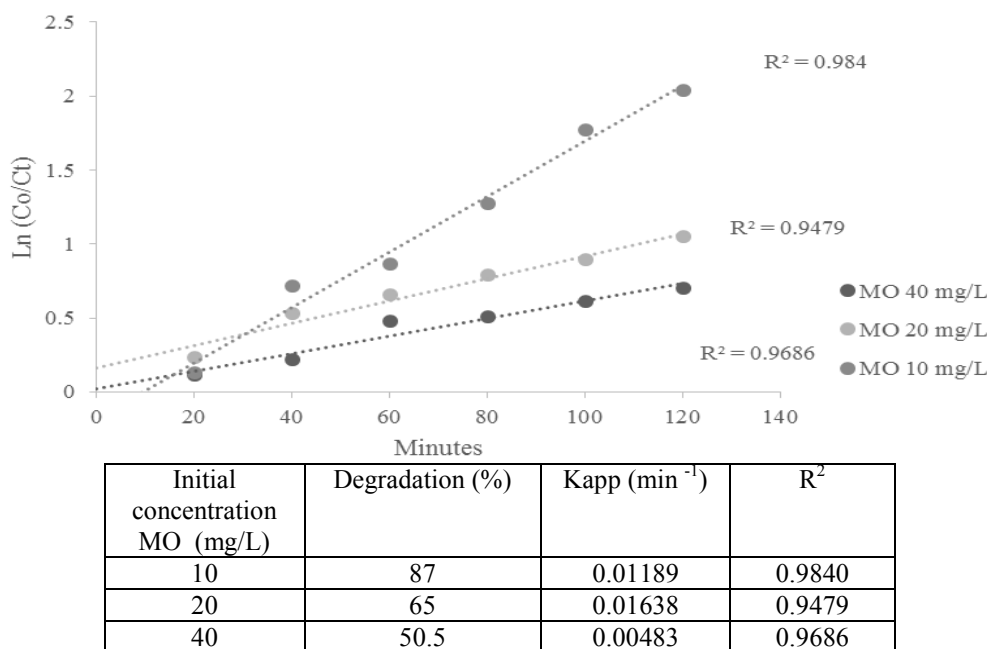
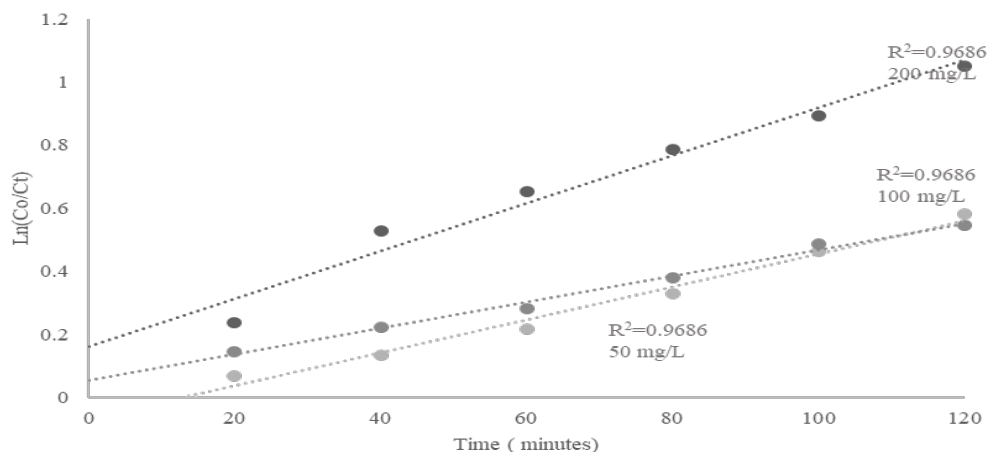


Fig. 3. $\ln(C_0/C_t)$ vs. different M.O concentration with a catalyst load of 200 mg/L and UV radiation.

The degradation rate is related to the catalyst surface availability of the generation of electron-hole pairs and hydroxyl radical. In this case, the load of catalyst was constant, and consequently, the number of hydroxyl group generated remains the same, meanwhile the contaminant concentration increase, generating an increment of the degradation time.

In order to study the effect of the catalyst load in the degradation of M.O., an experiment was performed using 20 mg/L of MO and a pH of 6.7. The catalyst range was varied from 50 to 200 mg/L. It can be observed that the degradation percentage increase from 44 to 65 % in 120 minutes when the catalyst load was increased from 50 to 200 mg/L (See Figure 5).

The rate constant increase as the catalyst load increase obtaining the highest degradation at 200 ppm. This rate constant increment can be explained by the fact of having more catalyst (more surface active sites), and in consequence, more generation of hydroxyl radicals that can degrade more contaminants. Despite the nanoparticles used in this work were obtained from wasted alkaline batteries, their photocatalytic performance was not affected. Their efficiency is similar to the reported values from several authors as shown in table 1. This can be explained by the fact that the characterization analysis did not reveal contaminants in the synthesized particles.

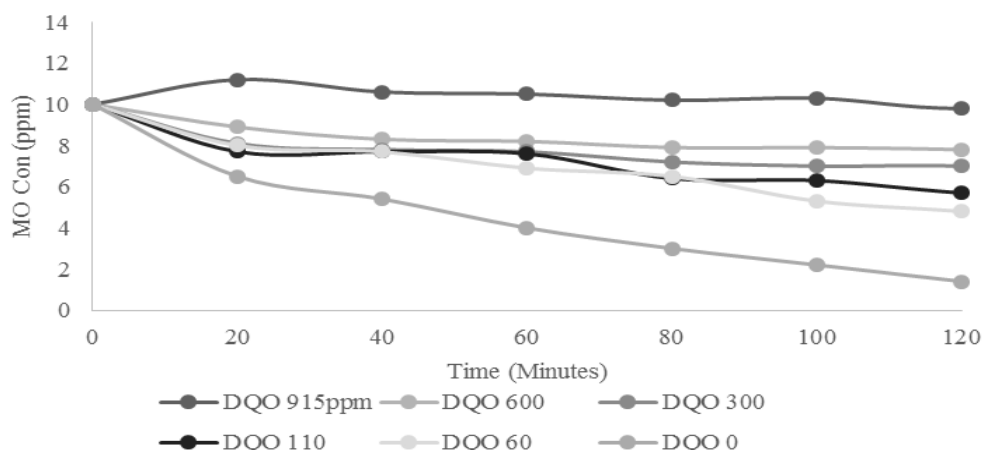


Catalyst concentration (mg/L)	Degradation (%)	Kapp (min ⁻¹)	R ²
50	42	0.01189	0.9921
100	44	0.01638	0.9857
200	65	0.00483	0.9686

Fig. 5. Effect of the catalyst concentration in the Methyl orange degradation. (MO concentration: 20 mg/L, UV radiation).

Table 1. Comparison of MO removal efficiency of ZnO nanoparticles according several authors.

ZnO particle size (nm)	Catalyst load (ppm)	Volume (ml)	MO concentration (mg/L)	UV source	Time and % of maximum MO removal	Reference
50 nm	200 ppm	100 ml	10	UV 125 Watts	210 min-92%	22
20 nm	250 ppm	100 ml	10	UV 300 Watts	120 min-100%	23
20 nm	150 ppm	100 ml	20	UV	300 min-100%	24
27 nm	1000ppm	100 ml	10	UV	80 min-100%	4
34-43 nm	20 ppm	100 ml	10	UV 9 Watts mercury lamp	60 min-98%	25
25-40 nm	1500 ppm	50 ml	20	UV 25 Watts	180 min-92%	26
40-60 nm	200 ppm	100 ml	10	UV 300 Watts	120 min-87%	This work
40-60 nm	200 ppm	100 ml	20	UV 300 Watts	120 min-65%	This work
40-60 nm	200 ppm	100 ml	40	UV 300 Watts	120 min-55%	This work
40-60 nm	50 ppm	100 ml	20	UV 300 Watts	120 min-42%	This work
40-60 nm	100 ppm	100 ml	20	UV 300 Watts	120 min-44%	This work



COD measured values at 0 and 180 min				
Time (min)	COD 915 ppm	COD 600 ppm	COD 300 ppm	COD 60 ppm
0	935	600	300	62
180	944	497	97	23
Removal %	0	17.16	67.6	61.90

Fig. 6. Effect of the COD in the M.O. degradation. (MO 10 ppm; ZnO 200 mg/L, UV radiation).

4. Conclusions

ZnO nanoparticles were synthesized from waste alkaline batteries by a sol gel methodology using starch as precursor. The nanoparticles are ZnO (Wurtzite phase) with sizes in the range from 40 to 60 nm. These NPs show similar MO degradation efficiency than NPs obtained from pure sources when similar conditions are used. The degradation of methyl orange by these NPs follows a first-order kinetics.

In real wastewater, the photocatalytic capacity of the ZnO NPs for the M.O. degradation decreases. The additional contamination into the methyl orange solution interfere with the catalyst efficiency capacity. At COD values of 600 ppm and 900 ppm, the degradation efficiency is almost null. When the COD levels are lower (60 ppm), the methyl orange degradation is around 83%, which is a closer value to that obtained for the same load of methyl orange, but without COD.

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