



USING THE SUN LIGHT IN DEGRADATION OF TERACOTTON , CIBANONN DYES BY ADVANCED OXIDATION PROCESSES (AOP's).

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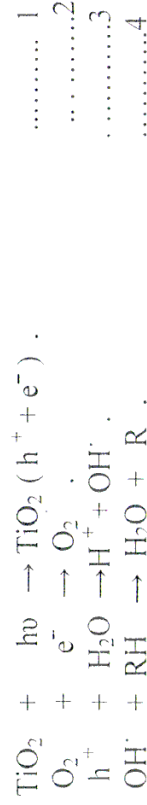
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Abstract

Advanced Oxidative Processes (AOP,s) and direct sun light were applied as a pretreatment process to degrade non-biodegradable organic matter (industrial dyes)such as TERACOTTON , CIBANONN, in aqueous solution . The highest degradation rate was obtained by H₂O₂ /Fe(II) .The oxidation process with efficiency more than 70% for Teracotton and 66% for Cibanonn ,after exposing the dyes solution (50 mg/L) to 36 hours of continuous irradiation by sun light . The dyes concentration was detected by using UV-Visible Spectroscopy at the λmax of dyes (λ=575nm for Teracton , and λmax = 526nm for Cibanonn) . The experiments included studying the effect of irradiation time of exposing and concentration of catalysts .

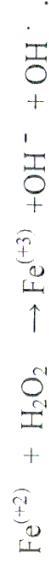
Introduction

Advanced oxidative processes (AOP,s) are very promising for effluent treatment mainly due to their high efficiency and simplicity of operation . Interest in this photocatalytic process stems mainly from the low cost of the catalyst (TiO₂ , ZnO) and the fact that it can be powered by sun light .The reduce significantly the electric power requirements so their operating costs are low . The present paper evaluates the efficiency of applying photocatalysis to degrade (TERACOTTON , CIBANONN) in suspensions of (TiO₂ , ZnO) and aqueous solution of(H₂O₂ , H₂O₂ /Fe(II)) ⁽¹⁻⁵⁾ under direct solar irradiation .it is well known now that when an aqueous TiO₂ suspension is irradiated with light energy greater than the band gap energy of the semiconductor (hv> Eg=3.2 ev) conduction band electrons (e⁻) and valence band holes (h⁺) are formed .The photo generated electrons react with the adsorbed molecule O₂⁻ , reducing it to super oxide radical anion O₂⁻ and the photo generated holes can oxidize either the organic molecules directly or the OH⁻ ions and the H₂O molecules adsorbed at the TiO₂ surfaces to OH⁺ radicals ⁽⁶⁾ . These will act as strong oxidizing agents and can easily attack the adsorbed organic molecules or these located close to the surface of the catalyst , thus leading finally to their complete mineralization (eq. 1-5) ⁽⁷⁾ .

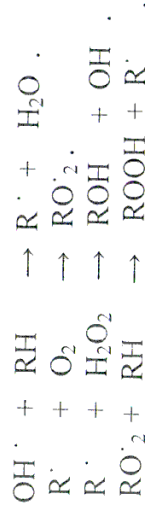




The Fenton process was reported in literatures ^(8,9), the rate constant of the reaction of ferrous ion with hydrogen peroxide is high and Fe(II) oxides to Fe(III) from few second to minutes in the presence of excess amounts of hydrogen.



The hydroxyl radicals generated by the above processes attack the organic compounds . The degradation of these compounds follows way ⁽¹⁰⁾ .



The direct photolysis of hydrogen peroxide leads to the formation of OH radicals
 $H_2O_2 \rightarrow 2OH^{\cdot}$

Oxidation processes in heterogeneous and homogeneous media are used to the degradation of Remazol Black B dye and its simulated dye bath ⁽¹¹⁾ , hv and h ν /H₂O₂ treatment is used for pharmaceuticals degradation ^(11,12) . TiO₂ photo catalytic oxidation of monchloroacetic acid and pyridine influence of ozone .

Experimental .

A. Materials and Methods .

A commercial sample of TERACOTTON , CIBANONN dyes was supplied by cotton textile factory at Diwaniya city and used in this study without further purification .The photo catalyst employed was (Titanium dioxide (TiO₂) Degussa - P25 mainly anatase 70 % with surface area of 55 m²/g and mean size of 22-35 nm) ⁽¹³⁾ .Zinc oxide (Riedel De Hean) 99.99 % . 50 %H₂O₂ (Merck) Ferrous chloride (BDH) . UV-VIS. Spectra was recorded on a Citra 5 Spectrophotometer .

B- Photo catalytic studies .

Experiments were performed in aqueous solution of the dyes were performed , a solution of 50 mg of dye in water (1L) . The photo catalysts (TiO₂,ZnO) concentration in the range (0.1- 1) g/L was added separately to the aqueous solution of dye .Hydrogen peroxide in the rang (10-20) mg /L was added to the aqueous solutions of dyes (50mg/L) . Fenton and photo-Fenton homogenous solution were prepared by mixing H₂O₂/ferrous in molar ratio rang (10-28) at 50 mg/L dyes solution at pH 2.8 due to Fenton's reagent which has a maximum activity at this pH .

Prior to irradiation , the dye solution after addition of the photocatalyst was magnetically stirred in the dark for 30 minutes to equilibrate no adsorption was observed (no change in the solution absorbance) to occur during this period . The irradiation was then commenced when the suspension exposed to direct sun light for 36 hrs in summer (July , 2004) suspensions were magnetically stirred during exposing to sunlight. Aliquots were removed at intervals and, after centrifugation and or filtration through 0.20 μm syringe filter, the absorbance spectrum was determined on a Citra 5

spectrophotometer . Blank experiments were also conducted (without photo catalytic) under direct sunlight, and no decolouration was observed after 36 hrs of irradiation.

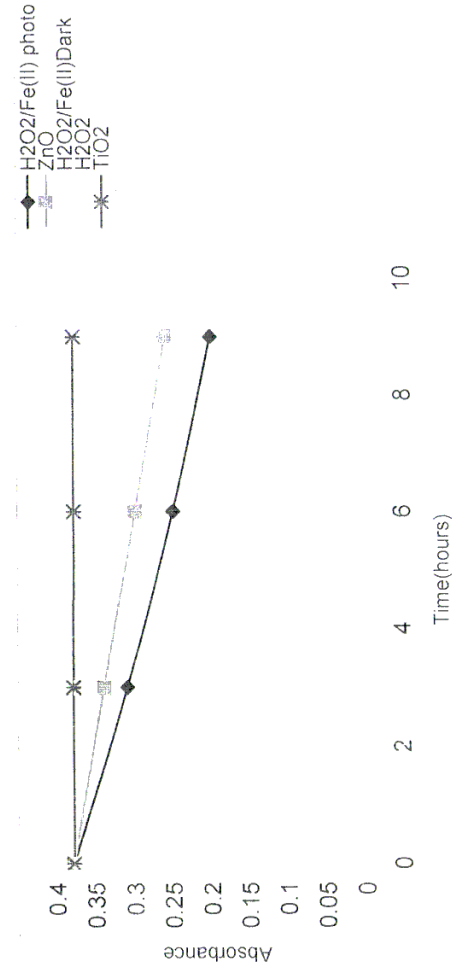
Results and Discussion:

In an attempt to relate our present study to actual situations involving the decolouration of industrial wastewater containing Teracotton , Cibanonn dyes, by advanced oxidative processes (AOP'S), after exposing to direct sunlight for 36 hours in sunny days in August, 2004. Figure (1), shows the absorption spectra for dyes.

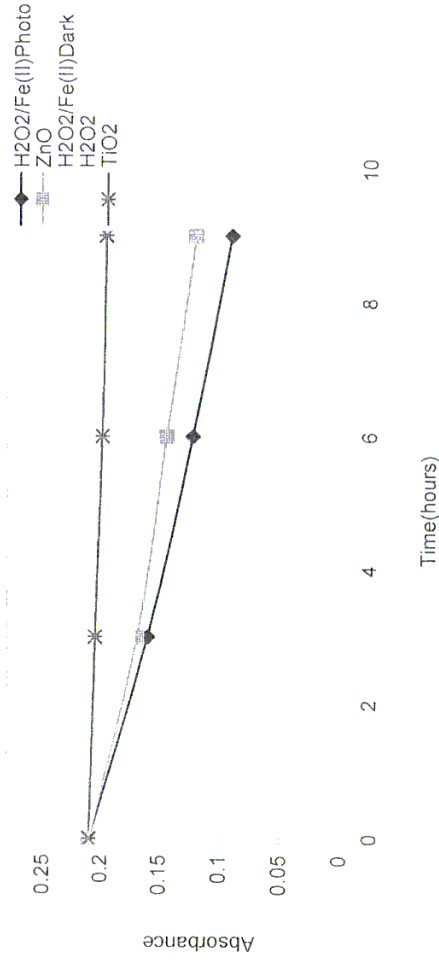


Figure (1): Visible spectrum of reactive dyes.

Plot of decolouration with the time is shown in figure (2,3). The degradation was slower in the first hours and it increases later with the increasing of the radiation period.



Figure(2):Effect of Irradiation time on the degradation of Cibanonn dye .



Figure(3): Effect of Irradiation time on the degradation of Teracotton dye.

Figure 4 ,5,6,7 ,8 , shows the plot of decolorization efficiency of dyes versus catalyst (TiO_2 , ZnO , H_2O_2 , $\text{H}_2\text{O}_2 / \text{Fe(II)}$) concentration after exposing to direct sun light for 36 hrs .As shown in these figure the degradation process increase as the photo catalyst concentration is increase .

The best result were reached 77.7% (Teracotton dye) , 66.8 % (Cibanon dye)Color removal with $\text{H}_2\text{O}_2 / \text{Fe(II)}$ under sun light for 36 hours . The literatures indicate that Fenton s reagent ($\text{H}_2\text{O}_2 / \text{Fe(II)}$)is able to destroy different industrial dyes ^(14,15,16) , this is agree with result of the reachers .Thus , the Fenton process is very effective for hydroxyl radicals generation ^(17,18) ; however , it involves consumption of one molecule of Fe(II) for each hydroxyl radical produced ,demanding a high concentration of Fe(II) .

The use of $\text{H}_2\text{O}_2 / \text{Fe(II)}$ as an oxidant for waste water treatment is attractive ^(19,20) , due to the facts that : 1- Iron is highly abundant and non-toxic element and 2- hydrogen peroxide is easy to handle and environmentally benign .

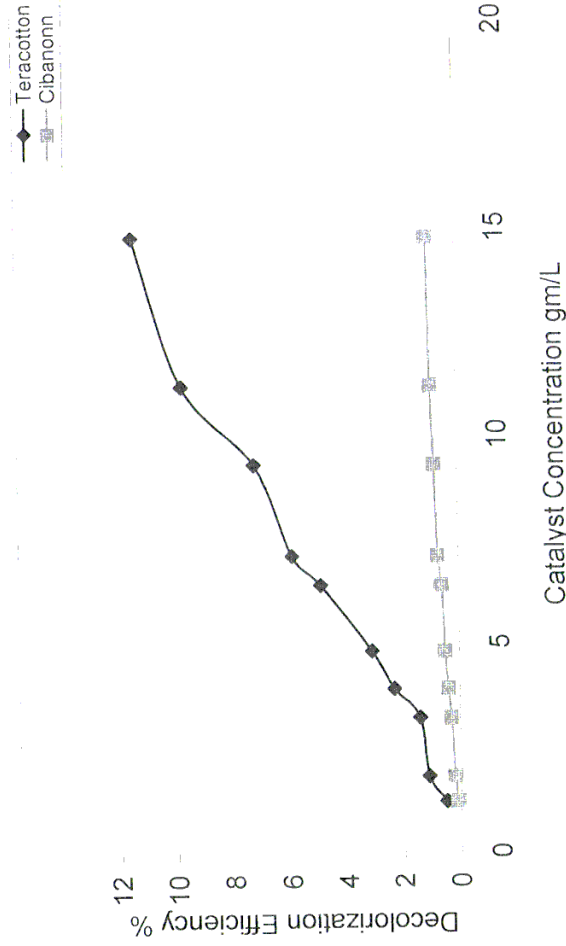


Figure (4) Influence of TiO₂ concentration .

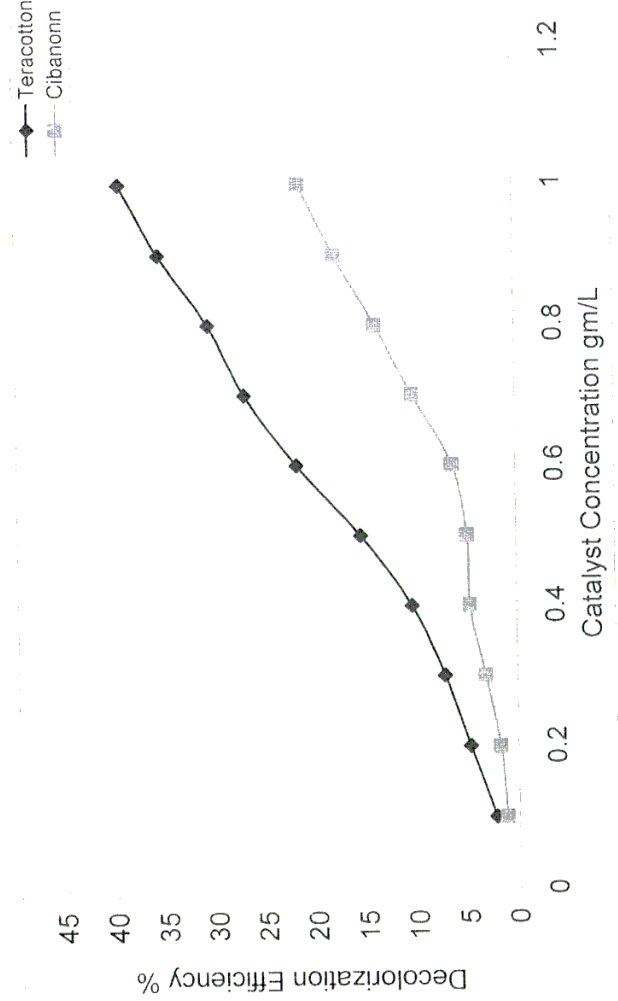


Figure (5) Influence of ZnO concentration .

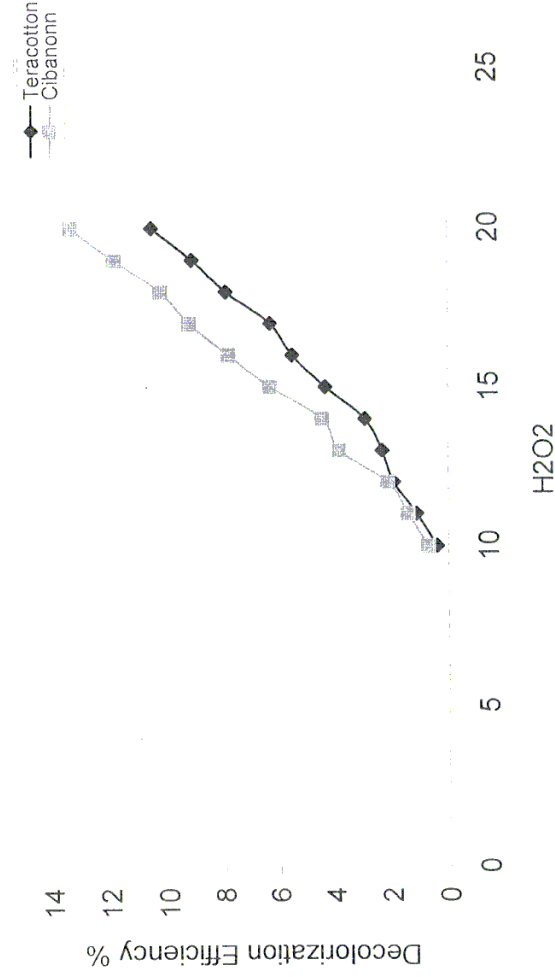


Figure (6) Influence of H₂O₂ concentration .

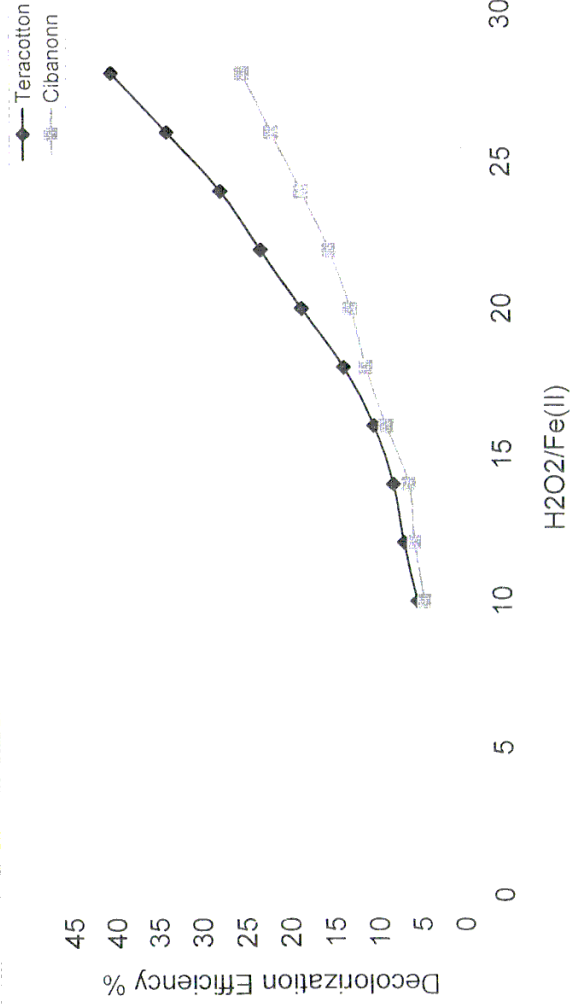


Figure (7) Influence of H₂O₂/Fe(II) ratio in dark .

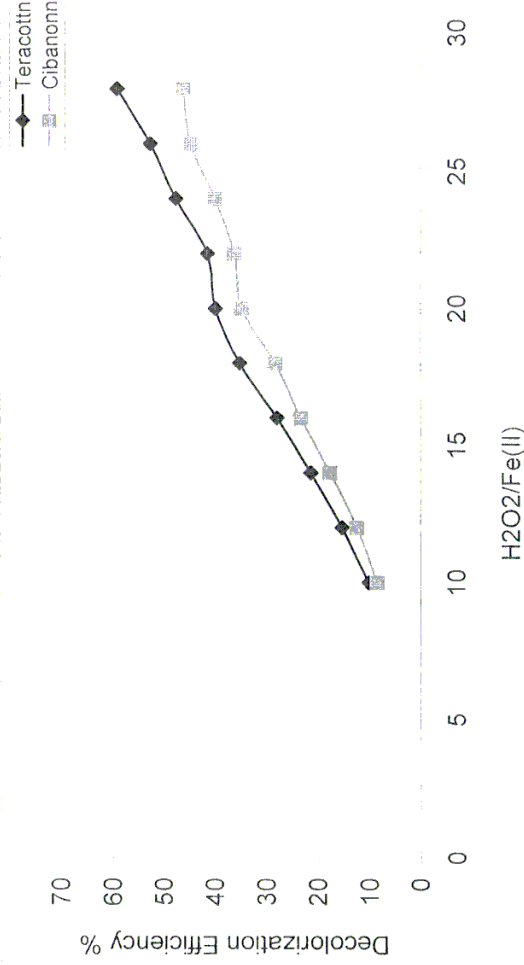


Figure (8) Influence of H₂O₂/Fe(II) ratio under sun light .

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