

Advanced oxidation of photographic processing effluents on novel heterogeneous fibrous catalyst

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Abstract

A novel heterogeneous catalyst, based on Fenton's chemistry, was evaluated for the treatment of KODAK Silver Bearing (SB) photographic processing effluents with high Chemical Oxygen Demand (COD) value. The effect of temperature, the nature and concentration of the oxidant (air and/or hydrogen peroxide), the duration of catalytic treatment and the dilution factor of the effluent on the reduction in COD were investigated. The catalyst and bubbled air (with no hydrogen peroxide present) resulted in a significant COD reduction of the effluent of 56 % after 18 hours of treatment at room temperature. It was found that most of the COD reduction occurred within the first four hours of treatment. Using air on its own, as oxidant was found to be sufficient, with only a slight improvement on the addition of hydrogen peroxide. Ambient temperature was preferred for the catalytic treatment of the effluent, as an increase in temperature up to 60°C led to less COD reduction which may arise from a change in the redox potential of the active transition metal (Fe^{3+}) complex or to the formation of recalcitrant products.

Keywords: Advanced oxidation, photographic processing effluents, heterogeneous catalyst, Fenton's chemistry.

1 Introduction

The treatment of wastewater is one of the most important subjects in the area of pollution control. In the monitoring and control of wastewaters, including trade complex effluents, such as photographic processing effluents (PPE), chemical oxygen demand (COD) is used as a measure of the extent of pollution as it is the



oxygen required to oxidise organic compounds to CO_2 and H_2O by a strong chemical oxidant. A number of organic and inorganic pollutants found in PPE, such as ammonium salts, ferrocyanide, thiocyanate, organic acids, aminophenols and phenylenediamines, are of special interest in waste treatment. Photographic processing effluents as water pollutants were of concern in the early 1970s, and ever since then, numerous studies have been undertaken in the treatment of PPE [1, 2]. A number of methods have been investigated in order to treat PPE, such as reduction in COD by oxidation [2-5], UV radiation [6, 7], biological treatment [8, 9], incineration [10] and a combination of oxidation and UV radiation [11], with most of the published work in the patent literature. Since photographic processing effluents have very high oxygen demand (COD value 90,000–150,000 mg O_2/L), the use of chemical oxidation to reduce this is very attractive, particularly, the use of hydrogen peroxide as it is an ecologically friendly and pure product. Fenton's reagent ($\text{H}_2\text{O}_2\text{-Fe}^{2+}$) is extensively used in oxidation of photographic processing effluent [2, 3, 12] though other oxidative treatments, involving H_2O_2 alone [13], H_2O_2 and Fe powder (which is based on the homogeneous Fenton's reagent by dissolution of iron) [14], ClO^- [15], and O_3 [11] are also used.

In the present study we evaluated the activity of a novel heterogeneous fibrous catalyst [16], based on Fenton's chemistry towards oxidation of silver-bearing (SB) photographic processing effluents from KODAK. The ability of the catalyst to decompose the effluent was measured as the reduction in COD value with respect to that of the initial feed. The effect of temperature, nature and concentration of the oxidant and the duration of catalytic treatment on the reduction in COD value were investigated.

2 Experimental section

2.1 Reagents

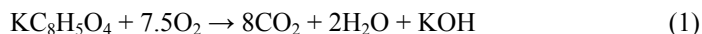
The following reagents were used in present study: Mercury Sulphate (Aldrich), Sulphuric Acid (98%, Aldrich), Potassium Dichromate (Aldrich), Hydrogen Peroxide (27.5%, Aldrich), Potassium Hydrogen Phthalate (KHP). All chemicals were of analytical grade.

SB_1 and SB_2 effluents used in this study have an initial COD value around 80,000 and 40,000 mg/L, respectively. SB_1 and SB_2 effluents were from different batches of photo-processing effluent collected at different times and delivered to our laboratory by KODAK Ltd. These effluents mainly contained triethanolamine (up to 20%), acetic acid (up to 43%), ammonium bromide (up to 77%), ammonium ferric ethylenediaminetetraacetic (up to 25%), ammonium thiocyanate (up to 25%), ammonium thiosulphate (up to 60%), ammonium nitrate (up to 10%), ammonium sulphite (up to 10%), ferric ammonium propylenediaminetetraacetic (up to 20%), hexamethylenetetramine (up to 30%), organic silicone (15%), sodium bisulphite (up to 30%), sodium bisulphite (up to 10%) and silver thiosulfate complex (up to 5 mg/L).



2.2 Analysis

COD determination is based on the theoretical amount of oxygen required to oxidize organic compounds to CO_2 and H_2O . The most commonly used standard chemical is potassium hydrogen phthalate (KHP) [17]. The theoretical oxygen demand of KHP is expressed by Equation (1)



According to the equation, the theoretical oxygen demand for KHP is 1.175 mg O_2 per mg KHP.

In the present study a stock standard solution of 1202 mg/L KHP which was equivalent to 2000 mg/L COD was prepared. The KHP concentration series equivalent to 2000, 1000, 750, 300 and 150 mg/L COD for calibration curve construction were prepared from the stock KHP standard solution. For each COD test 0.05g of mercury sulphate was put in a test tube, followed by the addition of 2.50 ml concentrated sulphuric acid, and 0.5 ml 1N (0.167M) potassium dichromate. 2ml KHP standard solution of each concentration was then added to the test tubes with COD reagent. The blank was prepared the same way except that 2ml sample was replaced by 2ml double distilled water. After thoroughly shaking to mix the solutions, the test tubes were put in the COD reactor (HACH, Camlab) that was preheated up to 150 °C in advance of test tube insertion. The test tubes were left in the reactor for 2 hours. Absorbance of the standard was determined at 620 nm using UV/VIS Spectrophotometer (UNICAM UV2-100) after the samples had cooled to room temperature. Calibration graph was plotted of absorbance against COD value for the standard series. All standards were performed in triplicate and results averaged.

The COD determination process for the samples was the same as for the standard curve construction except that 2ml KHP was replaced by 2 ml sample.

2.3 Catalytic oxidation of SB effluent under static conditions

The experimental set up for catalytic oxidation of KODAK SB photographic processing effluent under static conditions consisted of a 100 ml three-necked round flask (reactor) operated in batch mode, condenser, thermometer, magnetic stirrer, compressor and rotameter for air supply and control. Initial feed from KODAK SB₁ effluent was diluted 100 times before catalysis followed by filtration of the diluted solution to remove suspended solids. For KODAK SB₂ effluent, the dilution factors were either 15 or 50.

Fibrous catalyst was placed into the reactor containing 50 ml of the filtered solution. Preparation procedure of the catalyst, containing Fe^{3+} cations is described in our previous papers [16, 18]. Hydrogen peroxide of a known concentration was added into this solution before catalysis. Air was delivered to the solution from compressor through the rotameter at a rate of 0.154 m³/h. The magnetic stirrer was used only when H_2O_2 (without bubbled air) was the oxidant for catalysis. Experiments were carried out at temperatures of 25 °C, 40 °C and 60 °C. The amount of hydrogen peroxide was varied from 10 up to 200 mg/L.



Experiments investigating the effect of duration of catalysis, which was 0.5, 1, 2, 3, 4 and 18 hours, were individually set up. Samples of reaction medium of 2ml were withdrawn for COD analysis after completing the catalysis. Feed without catalyst but in the presence of oxidants (air and/or hydrogen peroxide) and under the same experimental conditions was used as a reference sample in each experiment. The procedures were repeated twice per each sample. Concentration of Fe^{3+} on the catalyst was determined through inductive coupled plasma (ICP) technique and expressed as amount of Fe^{3+} (mmol) per gram of fibre [16].

3 Results and discussion

3.1 Effect of duration of catalysis

As can be seen from Figure 1, the maximum rate of COD reduction in the presence of catalyst and bubbled air occurred within the first 30 minutes of catalysis followed by a further slow decrease in COD value up to 18 hours of treatment. 44 % and 56 % COD reduction was achieved after 4 and 18 hours of catalytic oxidation, respectively. Photographic processing effluents contain oxidisable inorganic substances, such as SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$, NH_3 , which may contribute to the COD reduction. Inorganic sulphur-oxo compounds can easily be oxidised using air or hydrogen peroxide to SO_4^{2-} . However, there was no significant decrease in the COD value of the original feed after oxidation with bubbled air with no catalyst present (control sample) suggesting that the feed contained little easily oxidisable sulphur compounds. COD reduction values were calculated with respect to those of the control sample of the feed.

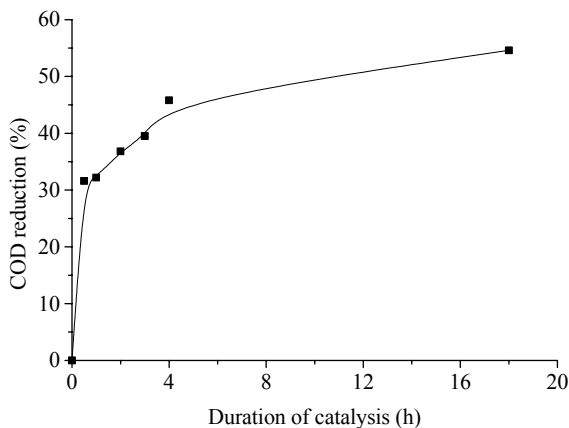


Figure 1: COD reduction of KODAK SB₁ effluent as a function of time in the catalytic oxidation using Fe^{3+} fibrous catalyst and bubbled air at room temperature.

3.2 Effect of temperature

As shown in Table 1, increase in temperature from 25^oC to 40^oC does not result in significant COD reduction, with 34.6% and 36.5% COD reduction, respectively, after 4 hours of catalytic oxidation. However, increasing the temperature up to 60^oC resulted in just 10.8% of COD reduction. This phenomenon could be explained by the formation of more complex substances during the high-temperature catalytic oxidation (dimeric compounds, for example), which is an object of our future research. However, we do not exclude, that the temperature effect may arise from a change in the redox potential of the active transition metal (Fe³⁺) complex on the catalyst, as the structure and nature of the complex and hence the resultant redox state of the active metal site could be temperature dependent. All these effects would influence the ability of the catalyst to switch between Fe³⁺/Fe²⁺ redox states and hence affect its catalytic activity [19, 20]. It is unlikely to arise from Fe³⁺ leaching into solution from the catalyst, as has been described in detail in our earlier publications [16, 18]. The COD of the initial feed after oxidation with bubbled air but with no catalyst was found to be little different from that of the original feed. Based on the results, room temperature is the optimal temperature for catalytic treatment and all the following work was therefore conducted at room temperature.

Table 1: COD reduction on oxidation of KODAK SB₁ effluent using Fe³⁺ fibrous catalyst and bubbled air as a function of temperature.

Sample	Temperature (°C)	Duration of catalysis (hour)	COD _{ref} (mg/L)	COD _{cat} /COD _{ref}	COD reduction (%)
Initial feed	25	0	840.0	1	
1	25	4	839.8	0.654	34.6
2	40	4	839.4	0.635	36.5
3	60	4	839.8	0.892	10.8

Experimental conditions: solution volume 50 ml, feed 100 times diluted, amount of catalyst 2.5 g, air supply 0.154 m³/h, [Fe³⁺] on the fibre 0.078 mmol/g, COD_{ref} – COD value after oxidation of feed with bubbled air but no catalyst (reference sample), COD_{cat} - COD value after oxidation of feed with bubbled air and catalyst.

3.3 Effect of concentration of H₂O₂

From the results shown in Figure 2, maximum reduction of COD of 25-26% after 30 minutes catalytic treatment was achieved for concentrations of hydrogen peroxide of 10 and 50 mg/l, respectively. Higher concentrations of H₂O₂ of 100 and 200 mg/L are shown to result in less reduction of just 10-6 % (Fig. 2), which indicates an excess of residual H₂O₂. According to Talinli and Anderson [21],



COD measured in the sample taken after catalysis must be calculated according to equation (2) to yield a corrected value. For the ranges of residual H_2O_2 from 20 to 1000 mg/L, the percent of COD removal (η) is then determined through equation (3).

$$S_E = \text{COD}_t - R_p \times 0.25 \quad (2)$$

where S_E is the corrected value of COD after the reaction, COD_t is the 'reading' value of COD after the reaction, R_p is the residual amount of H_2O_2 left in solution after the reaction.

$$\eta = [(S_0 - S_E)/S_0] \times 100 \quad (3)$$

where S_0 is the initial value of COD of the feed.

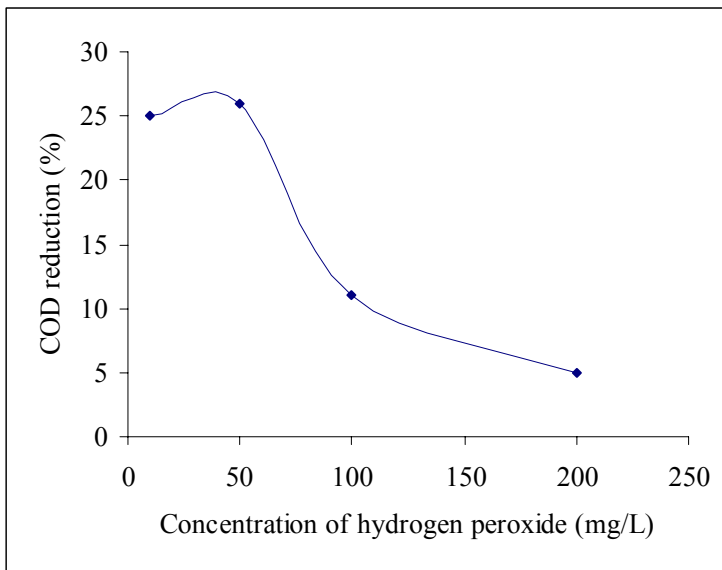


Figure 2: COD reduction of KODAK SB₁ effluent as a function of H_2O_2 concentration in the catalytic oxidation using Fe^{3+} fibrous catalyst at room temperature.

Using 50 mg/L of H_2O_2 for the catalysis and assuming that none of the hydrogen peroxide was consumed during the reaction, the difference between observed COD reduction (26 %) and COD reduction corrected for hydrogen peroxide in accord with formulas 2 and 3 (27.5 %) gives 1.5% maximum relative error, which is very minor. With 200 mg/L of hydrogen peroxide and again assuming that none of the H_2O_2 was consumed during the reaction the maximum relative error would now be 11.95 %, which is more significant. The degree of COD reduction may also depend on the type and concentration of pollutants in

wastewater with the most advantageous results of reduction in COD at lower hydrogen peroxide concentration [22]. Thus, the effective amount of hydrogen peroxide of 50 mg/l for SB₁ effluent was selected for further research studies as the optimum amount in terms of COD reduction. Additionally, one of the main targets of this study was to test whether air rather than hydrogen peroxide could be used for the catalytic oxidation. This would reduce cost and allow the use of less than a stoichiometric amount of H₂O₂.

3.4 Effect of the nature of oxidant

According to Figure 3 there is little difference in COD reduction between the three oxidant systems air, H₂O₂ and air+H₂O₂ after 4 hours of treatment. Catalytic oxidation of the feed in the presence of both air and hydrogen peroxide seems to be slightly more promising. It can be concluded that using air on its own as oxidant (0.154 m³/h) is sufficient, but presence of H₂O₂ gives slight improvement in COD reduction. Any reduction in COD values due to volatile organic pollutants being stripped from the feed by the bubbling air was accounted for by the use of a blank containing no catalyst. COD reductions due to catalysis were reported throughout this work relative to the COD reductions experienced by the blank.

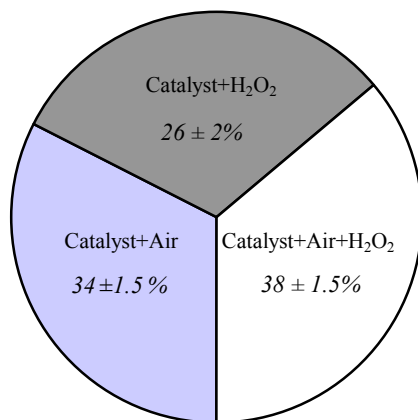


Figure 3: COD reduction of KODAK SB₁ effluent by catalytic oxidation using Fe³⁺ fibrous catalyst in the presence of air and/or hydrogen peroxide at room temperature.

3.5 Effect of dilution factor of SB effluent

KODAK SB₂ feed was treated for 1 hour using catalyst, air and hydrogen peroxide. Table 2 shows that for 50 times diluted SB₂ effluent (COD around 800 mg/L), using 2.5g of catalyst and 50 mg/L hydrogen peroxide gives a better COD reduction than using 75mg/L H₂O₂, this is in agreement with the results for

SB₁ effluent. Table 2 also shows that for 15 times diluted SB₂ effluent (COD around 2760 mg/L), 21% COD reduction can be achieved when 5g catalyst mesh and 75 mg/L hydrogen peroxide were used. Therefore the amount of catalyst as well as the concentration of hydrogen peroxide plays a role in COD reduction of KODAK SB effluent, which needs to be studied more extensively.

Table 2: Effect of reaction conditions on the COD reduction of KODAK SB₂ effluent at room temperature.

Dilution factor	H ₂ O ₂ (mg/L)	Amount of catalyst (g)	COD (mg/L)	COD _{ref} (mg/L)	COD _{cat} /COD _{ref} (%)	COD reduction (%)
50	75	2.5	642	813	79	21
50	50	2.5	479	761	63	37
15	75	5	1570	2546	62	38

Experimental conditions: solution volume 50 ml, duration of catalysis of 1 hour, [Fe³⁺] on the fibre 0.078 mmol/g, COD_{ref} – COD value after oxidation of feed with bubbled air but no catalyst (reference sample), COD_{cat} - COD value after oxidation of feed with bubbled air and catalyst.

4 Conclusions

The use of a Novel heterogeneous fibrous catalyst and bubbled air (with no hydrogen peroxide present) resulted in significant COD reduction of silver-bearing photo-processing effluent with a maximum value of COD reduction of 56% at room temperature after 18 hours of treatment. Most of the COD reduction occurred within the first four hours of treatment. Ambient temperature is preferred for the catalytic treatment of the effluent, as an increase in temperature up to 60°C leads to less COD reduction which may arise from a change in the redox potential of the active transition metal (Fe³⁺) complex. Range between 10 and 50 mg/L of H₂O₂ was the optimum range in concentration of hydrogen peroxide (when used without air) for the oxidation of SB₁ effluent in terms of COD reduction. In this work using hydrogen peroxide as the catalytic oxidant together with air shows little evidence of an improvement in COD reduction over using air alone.

Acknowledgments

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