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# CATALYTIC WET AIR OXIDATION - AN ON-LINE TREATMENT AND/OR AN END-OF-PIPE ALTERNATIVE PRE-TREATMENT METHOD FOR POLLUTION ABATEMENT

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## Abstract

Material production always is the main pollution resource, particularly pulping (PI) and textile industries (TI). Among all pollution abatement technologies wet air oxidation (WAO) is a promising alternative. In the one hand it can be applied as an in-plant measure to mineralize organics in wastewater (WW), therefore remained inorganic chemicals can be recovered and/or reused, on the other hand it can also be used as a WW pretreatment before popular biological treatment to get discharge demands. The best, and may be the most economical way to widen application of conventional WAO process is application of catalysts. Conventional oxidation catalysts contain precious metals, they also require stable to hydrothermal conditions supporting materials that bring additional high cost. The utilization of solid wastes (SW) from some industries for catalysts production can get multi-purpose goal: in one side reduction of SW in some industries, in the other side their use in CWO can reduce pollution in the other industries. Besides, due to low pressure and temperature required it can make application of WAO much easier and widened. With pretreatment prior to biological treatment purpose it can partially degrade persistent and toxic compounds that make following biological treatment more efficient. First application trials of CWO were made with black liquor from PI and dyeing WW from TI showed possibility of such idea.

**Keywords:** Wet air oxidation (WAO), Catalytic wet air oxidation (CWO), liquid-phase oxidation, wastewater treatment, chemical recovery and/or color removal

## Introduction

A large portion of waste generated by different industries is in the form of WW. In some case, for example, in PI it still contains a lot of chemicals, which must be recovered for either reuse to minimize production cost and to reduce pollution. Along with chemicals recovery a large amount of organics must be eliminated. In the other hand, many organic compounds are either toxic or poorly biodegradable, so that direct common biological treatments are not feasible (Cao The Ha, 2002a). The last is well known in the case of TI too, which discharges into WW about 10-15% of dyestuffs used (Vaidya, 1982). In this context, the first idea coming to the mind of engineers is to use conventional incineration following by chemical recovery (in the case of conventional Kraft pulping process), or chemical oxidation and/or coagulation to remove color (in the case of TI). A possible less expensive alternative is partial oxidation of organics to intermediates, which are less toxic and much more amenable to biological treatment.

In the last years WAO has been demonstrated to be an effective technology for treatment of different kinds of WW (Copa, 1989; Luck, 1999), and even chemical war stockpiles (Nat. Acad. Press, 1993). The main disadvantage of WAO process is severe conditions to achieve sufficient oxygen activation, typically being in the range of 180-315 °C and 20-150 bar (Luck, 1999). Under such extreme conditions, reactor material selection and safety requirements become very critical as corrosion rate are high, and most materials are susceptible to stress corrosion cracking in the present of chloride ions. In addition, high pressure required huge thickness of the reactor wall. All these together are blocking attempts to spread WAO in practice. Therefore, application of catalysts, especially heterogeneous ones, which thank to easy post-reaction separation have clear "technological" advantage over homogeneous ones, to make WAO effective in much milder conditions is a natural option.

The aim of this paper is to briefly review recent achievements in WAO, particularly in CWO, and first results gained at Hanoi University of Science.

## Liquid-phase or wet air oxidation catalysts

In comparison with biological treatment WAO requires much lesser reaction volume (figure 1). Usually, liquid detention time may range from 15 minutes to 2 hours, and the chemical oxygen demand (COD) removal may typically be about 75-90%. In such conditions organics, even insoluble ones, are converted into simpler soluble compounds, which are in turn oxidized and eventually converted to  $\text{CO}_2$  and water without emissions of  $\text{NO}_x$ ,  $\text{SO}_x$ ,  $\text{HCl}$ , dioxins, furans, fly ash etc. which are abundant in the flue gas of incinerators. In conventional WAO some low molecular weight organic oxygenated compounds (eg. acetic and propionic acids, me-, ethanols, and acetaldehyde) can not be significantly mineralized at temperature lower 300 °C and/or without a suitable catalyst.

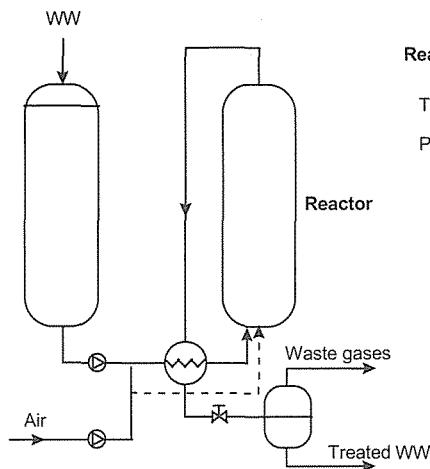


Figure 1- Scheme of WAO

### Reaction conditions:

$T=185-315\text{ }^{\circ}\text{C}$

$P=20-150\text{ bar}$

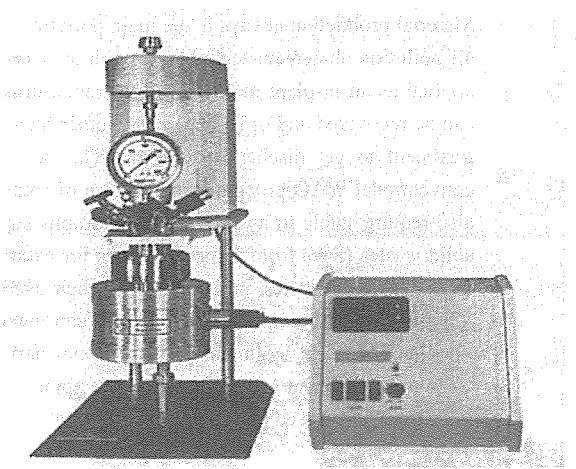


Figure 2- Parr Autoclave for CWO

Sweden R.W. Strehlenert (1911, 1915) is known as a pioneer in attempts of using compressed air for oxidation of a sulphite liquor from pulp production. May be, due to described disadvantages of WAO process that lead to high machinery and even operation cost, this invention has fallen into oblivion, and could not find any application for nearly half a century. That was before study of Zimmerman on testing WAO to treat spent pulp mill liquor (Zimmerman, 1958), then the Zimpro company built in the early 1960s several large WAO plants for the treatment of municipal sludge, either to improve sludge dewatering characteristics, or to achieve complete oxidation of sludge (Seiler, 1987). Nowadays, more than 130 Zimpro units, the first commercial WAO process, were installed in the US and Europe mostly for the oxidation of sewage sludge, some of them were used for spent activated carbon regeneration in PACT® process (Luck, 1999). Naturally, to extend the application of WAO it is necessary to develop CWO. Since the eighties other Zimpro units were built in chemical, petrochemical and pharmaceutical plants (Chowdury, 1986). In the 1990s, 25 units were built for oxidation of ethylene plant spent caustic (Zimpro®, 1999).

In CWO process the key issue is finding a suitable catalyst. The main demand of this material is: as high as possible oxidation activity and durability in hydrothermal conditions and cost must be reasonable. Due to economic reason, especially in the case of WW treatment, the last is getting serious attention.

The earliest studies well-known from catalytic chemistry oxidation catalysts such as Pt, Pd, and Rh were applied (Muller, 1930; Heyns, 1957; Kolotusha, 1975). In 1959 Rieche et al. (1959) reported about activity of powder coal and ash in WAO of phenol in WW. Later, in 1969 Hamilton et al. (1969) patented an oxidation process in aqueous phase at 100°C of pollutants in WW using  $\text{MnO}_2$  catalyst. Intensive researches in this field may be directed to seventies. Thus, Sadana, Katzer (1974a, 1974b) and Ohta (1980) found  $\text{CuO}$  supported on high surface and hydrothermal stable  $\gamma\text{-Al}_2\text{O}_3$  is an efficient catalyst for WAO of phenol in the temperature range of 96-246°C while unsupported  $\text{CuO}$  was not active. Njiribeako et al. (1978a, 1978b) found that in conditions of CWO, solid  $\text{CuO}$  can be dissolved to form ion  $\text{Cu}^{2+}$ , which can act as a

homogenous oxidation catalyst, and cupric ions contributed from 20%, in the case of more stable  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, to 40%, in the case of less stable silica used as supporting materials, to the total oxidation rate. In 1974 Box patented (1974) using a mixture of Cu, Mn and La oxides on Zn aluminate spinel as an oxidation catalyst. Levec et al. (1976a, 1976b) used this catalyst in oxidation of acetic acid solutions and found that no early deactivation was detected and its activity was one order as high as compared with the iron oxide catalyst. Besides, they proved that Pd(0.1%)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and CuO.ZnO, typical oxidation catalysts in gas phase, were not active in oxidation of acetic acid solutions. Meanwhile, CuO.ZnO was active in oxidation of formic acid solutions (Baldi, 1974). In 1975, Chowdhury and Ross (1975) tried various metals, metallic oxides and salts and found that Pt showed highest activity among solid materials. In 1974 Takahashi et al. (1974) also patented MnO<sub>2</sub> as an active catalyst for oxidation of organics in WW at 60°C. At 100°C mixtures of oxides of Cu, Co, Ni, and Fe and Pt, Pd, Rh, Ru and Ir was active in WAO (Komabashiri, 1974, 1975). At higher temperature Komabashiri (1974, 1975) also found that CuO in combination with two of the following oxides of Co, Ce, Sn, Ni, Zn and Fe was active in WAO too. From the eighties works of Japanese chemists on using precious metals were emerged. Group of Imamura (1982, 1986 and 1988) effectively applied catalytic systems such as Ru/Ce, Mn/Ce, and Co/Bi, while Ito (1989) proposed Co<sub>2</sub>O<sub>3</sub>.

### **Situation in Pulp and Paper Industry (PPI)**

The main problems in PPI are COD, AOX and color (Hodgson, 1998). Besides, half of COD in WW from PPI is not biodegradable (Baruna, 1998).

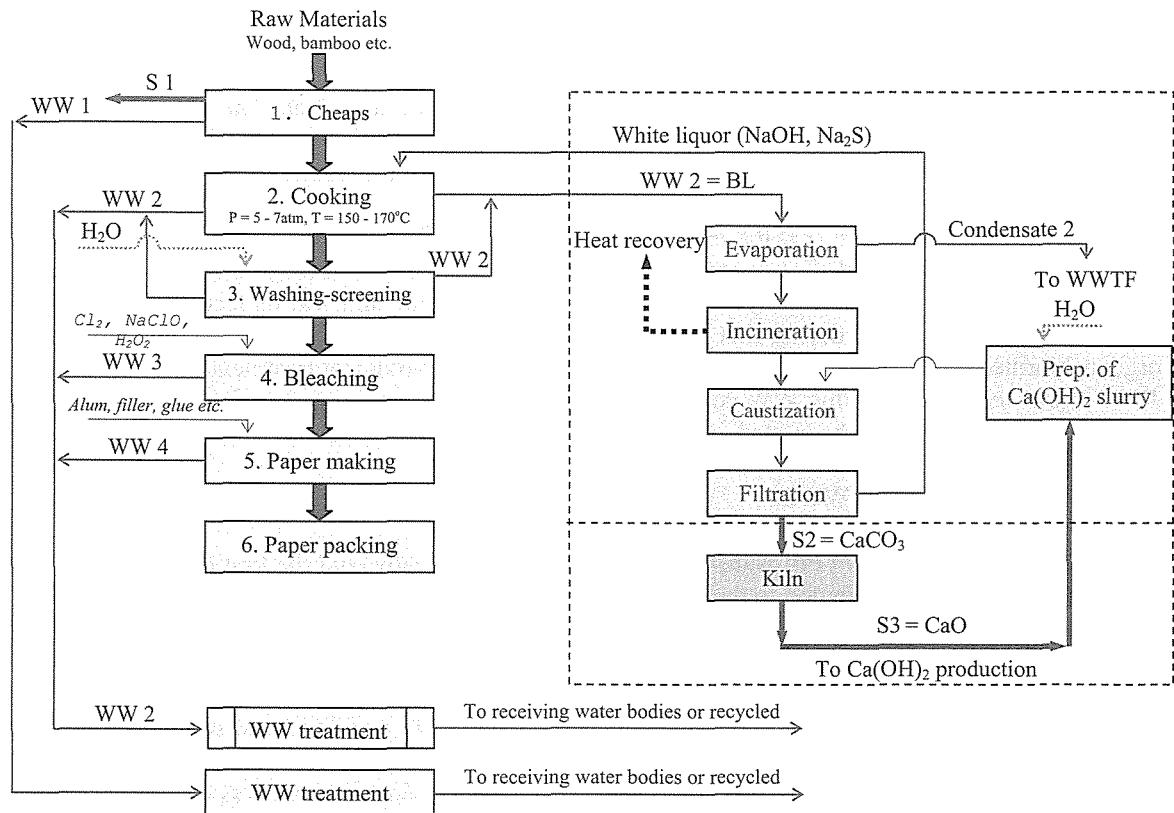


Figure 3 - Scheme of pulp and paper production using Kraft pulping and waste streams

Vietnam is a tropical country with very high biomass production, therefore PPI has a good potential for growth. That is why there is an US\$ 3.6 Bil. Government Master Plan to develop Vietnamese PPI in coming period of 2000-2010. The target production capacity of the plan is 1 Mil. Ton papers/year by the year 2010 (Ministry of Industry, 1997). Besides its undoubted benefits, PPI is the most environmental pollution producer, particularly in regard to water environment (Reeve, 1994).

The sketch of materials flows and waste streams of PPI is given in figure 3.

Thus, in PPI there are the following types of wastewaters:

1. *WW1 from raw material washing*: This kind of WW contains mainly solid dregs, mud, bamboo or wood husks and chips, ect. They can be easily removed by settling techniques with or without coagulation. Due to simplicity of treatment technology this is not a subject of our research.

2. *WW2-Black liquor*: Black liquor (BL) is the effluent from cooking vessel after fiber recovery, herein washing water is commonly included. Although this kind of WW contributes only a small amount of total WW volume, but it contains 80-90% organic load of entire paper mill. In BL organics are lignins, pentosa, resin and others aliphatic acids etc. Besides, BL contains a large number of chemicals used in cooking stage, for instance, in most popular Kraft pulping they are NaOH, Na<sub>2</sub>S. Aesthetically, BL is bad due to its color, smell, and foaming characteristic. In model Kraft pulping mills, to decrease manufacturing expense and also to treat BL, chemical recovery stage is well established including 1- vacuum evaporation system, 2- incinerator or steam recovery boiler for organics combustion and heat utilization, 3- caustization to recover NaOH and Na<sub>2</sub>S from the ash coming from incinerator to return to cooking vessel. This unit is called recovery one and is described in dotted rectangles in the right of figure 3. Therefore, organic contaminants are combusted; 93-95% inorganic chemicals (caustic, sulfide) are being recovered and reused in cooking, only solid CaCO<sub>3</sub> is produced (from caustization) and a small amount of overflow water. There are only two factories in Vietnam, Bapaco and Cogido, have this technique, the others have not, thus, black liquor is discharged without adequate treatment.

3. *Condensate*: Condensate derives from two stages, cooking and BL evaporation. The main composition of cooking condensate is methanol, volatile organic compounds, and a significant quantity of S compounds, which are main odor resource. Usually it is being discharged with the other kinds of WW in factories.

4. *WW3-Bleaching wastewater (BWW)*: Bleaching technology in Vietnam mainly is of 70s, that means CEHH one (Chlorination-alkali Extraction-Hypochlorite-Hypochlorite). Recently, the largest Vietnamese paper mill-Bapaco has implemented hydrogen peroxide in E-bleaching and will replace partly C with O in the future bleaching sequence during first phase of expanding plan (2001). BWW is the principal resource of organochlorines (OXs), therefore, it is persistent to conventional biological treatments.

5. *WW4-Paper making WW*: this WW comes from paper making machines, therefore it contains mostly suspended solids and easily to be treated.

The target of our study is BL (WW2).

As mentioned above, WW from PPI is difficult to be treated biologically, and the first attempt to use WAO for the treatment of BL is attributed to the early years of the 20th Century. Since the nineties possibility of using CWO for oxidation of BL attracts attention of many researchers (Kolaczkowski, 1999; Mishra, 1995; Tukac, 1998; Fortuny, 1998; Fortuny, 1999; Alejandre, 1998; Miro, 1999; Beziat, 1999; Fortuny, 1995).

Thus, Canadian researchers (An, 2001; Zhang, 1998a; 1999a; 1998b); 1999b; 1999c) found that Pd and Pd-Pt/alumina showed very high activity and stability in reduction (70%) of TOC and color from bleaching WW by CWO at 175 °C, and pressure of 18.5 Mpa, contact time is just 5 minutes. The same way of using precious metal catalysts or activated carbon followed by French and Spain researchers using Rh catalyst on different kind of supporting materials (Pintar, 2001a; 2001b; Gallezot, 1997; Fortuny, 1998).

A shortage of reviewed works is the cost of precious metals applied following by complicated regeneration, and the target WW is only "dilute" bleaching WW, no work is done with the most strong BL, which has COD of 25,000-100,000 mg/L.

In this paper we present our first results on CWO using very cheap catalyst from industrial waste solids for COD and color removal from BL. If this succeed, then conventional caustization may be employed to recover NaOH, and then expensive catalysts and complicated and very expensive evaporation-incineration may be avoided.

## Situation in Textile Industry

When the main problems in PPI are persistent COD, AOX and color, problems in TI, may be in less extend but nearly the same: persistency to biological treatments, toxicity and especially offensive color.

The difficulty of optimization of the treatment technology for dye-containing WW is its extremely complex nature by the thousands of dyestuffs commercially available. Only in Vietnam, a dyestuff importer, there are more than 12 groups, and used amount constantly increases (table 1) (Dong N.T., 2002).

Table 1- Situation in usage of dyestuff in Vietnam textile industry

No	Group of dyestuff	Amount of usage, kg/year		
		1996	2000	2010
1	Disperse	451,800	1,545,100	3,033,300
2	Reactive	258,500	887,500	1,816,500
3	Direct	13,400	45,800	89,900
4	Azo	11,700	40,000	58,500
5	Pigment	80,300	274,600	539,100
6	Other	251,620	801,890	1,425,780
<b>Total</b>		<b>1,055,620</b>	<b>3,594,890</b>	<b>6,963,080</b>

Concerning treatment technologies of WW, analysis, regulation in TI there is very comprehensive book (Reife, 1996). It listed all kinds of treatment technologies, including carbon adsorption, coagulation-flocculation using different kinds of coagulants and polymers, chemical oxidation and reduction, electrochemical treatment, biological treatment, that includes enhanced conventional activated sludge PACT®, sequence of anaerobic-aerobic treatment, membrane filtration etc.

Among all kinds of treatment technologies only the two, which are WAO/CWO and membrane technologies, showed their universal capability, that means they can be applied to any kind off dyestuff as pre-treatment tool to remove color and toxicity, and even to recover dye (in the case of membrane technique).

## Materials and Methods

BL was taken from Hoang Van Thu Pulp Mill, Dyeing WW was from 8/3 Textile Co. Characteristics of WWs were given in table 2.

Table 2- WW characteristics

Type of WW	pH	ABS <sub>390</sub>	COD, mg/L	NaOH, g/L	Na <sub>2</sub> CO <sub>3</sub> , g/L
BL from pulp mill	11.76	72.9	44,433	2.44	2.99
Dyeing WW	3.55	84.0	3,200		

Catalyst precursors were the solid waste from: 1- Superphosphate Lam Thao-Super (it was a solid waste-SW from SO<sub>2</sub> production by incineration of pyrite-FeS<sub>2</sub>); 2- Tan Binh Chem. Co.-TB (it was a SW in alumina production from boxite); 3- Gia Lam Water Plant-GL (sludge from ground water processing), and 4- Vietnam Ford Co.-Ford (SW from WW treatment facility by FeCl<sub>3</sub> + lime coagulation for WW from metal processing shop). The common future of these SW is they are rich in Fe<sub>2</sub>O<sub>3</sub>. Catalysts preparation is simple: drying, grinding, and seiving to take particles under 0.5 mm, then calcining at 400 °C. All precursors and catalysts were checked by XRD, phase composition of precursors was given in table 3.

Table 3- Catalysts precursors XRD characteristics

No	Catalyst precursor	Main phase composition
1	Super	Hematite ( $Fe_2O_3$ ), chlorite-vermiculite - montmorillonite,
2	TB	Hematite ( $Fe_2O_3$ ), $[Na_6(CO_3)_2SO_4]$ , quartz ( $SiO_2$ )
3	GL	Quartz ( $SiO_2$ ), $Fe_2O_3$ ??
4	Ford	Calcite ( $CaCO_3$ ), Magnetite ( $Fe_2O_3$ )

Preparation of catalysts was carried out by modification of base precursors by addition into as prepare precursor of desired amount of solutions of  $Cu(NO_3)_2$ ,  $Mn(NO_3)_2$  and  $NaOH$ . In the case of  $MgO$  it was used in the powder form. All chemicals were technical grade. Detail procedure was described elsewhere (Cao The Ha, 2002b). Catalysts of the following compositions were prepared (table 4).

CWO was conducted in an autoclave (Parr, USA) equipped with a sampling valve. Mixing speed was set at 700 rpm (fig. 2). Oxygen was technical grade from Yen Vien Gas Co. Oxygen pressure applied was 15 atm. Reactions were conducted in batch mode. Oxidation efficiency was evaluated through COD, color removal E. E was calculated as following:

*COD removal efficiency (%)*:

$$E_{COD} = \frac{COD_0 - COD_t}{COD_0} \times 100\%$$

*Color removal efficiency (%)*:

$$E_{Color} = \frac{ABS_0 - ABS_t}{ABS_0} \times 100\%$$

$COD_0$ ,  $COD_t$  is chemical oxygen demand of WW and treated WW respectively. Samples were taken at interval  $t$  from beginning of reaction, filtered and analysed by dichromate method (APHA, 1995). Colour was measured as absorption value (ABS) at 390nm using a cuvet with the thickness of 1 cm, and UV-VIS 1201 Schimadzu (Japan).

Table 4- Composition of catalyst applied and abbreviation

No	Base material-precursor	$CuO$ % w	$MnO_2$ % w	$MgO$ % w	Abbreviation
0	Ford				Ford
1	Ford +	12			FordCu12
2	Ford +			12	FordMg12
3	Ford +		12		FordMn12
4	Ford +	4	4	4	FordCu4Mn4Mgb4
5	Ford +	6		6	FordCu6Mg6
6	Ford +		6	6	FordMn6Mg6
7	Ford +	6	6		FordCu6Mn6

Likewise, other catalysts on other base material precursors were abbreviated, eg. SuperCu6Mn6.

## Results and Discussion

### Comparative determination of catalytic activity

#### Reaction conditions:

Reaction temperature:  $150^\circ C$ , for TI WW:  $90^\circ C$ ;

Rate of temperature elevation:  $3.5^\circ C/min$ ;

Reaction time: 60 minutes;

Catalyst concentration: 2% w.

Comparative activity of catalysts can be evaluated via conversion of COD under the same reaction conditions. Results of comparative study were given in table 5 and figure 4. Obviously, CWO is much better conventional WAO. Non-catalytic WAO could remove only 13% COD of BL, meanwhile all CWO experiments got more than 30%, as much as 2,3 time. Note that  $150^\circ C$  and 15 bar were very mild conditions for WAO. In the case of dyeing WW result was even better: COD removal was close to 70% at very mild temperature ( $90^\circ C$ ), less then dyeing temperature ( $125^\circ C$ ). These values of temperature were employed because they are close to the actual discharge conditions. The surprising result is excellent efficiency of color removal from TI WW (99%).

Table 5 - Results of catalysts trials in CWO

No	Catalysts	$COD_o, mg/L$	$COD_b, mg/L$	$E_{COD} \%$	$ABS_o$	$ABS_t$	$E_{ABS} \%$
0	Non-catalytic (WAO)	44433	38657	13	72.9	53.2	27
1	Super	44433	31550	29	72.9	34.1	53
1.1	SuperCu12	44433	28883	35	72.9	44.0	40
1.2	SuperMg12	44433	28716	35.4	72.9	36.3	50
1.3	SuperMn12	44433	30716	31	72.9	40.5	44
1.4	SuperCu4Mn4Mg4	44433	28216	36.5	72.9	36.8	49.5
1.5	SuperCu6Mg6	44433	27716	37.6	72.9	44.0	40
1.6	SuperMn6Mg6	44433	28216	36.5	72.9	36.8	49.5
1.7	SuperCu6Mn6	44433	28550	35.7	72.9	44.4	39
2	Ford	44433	29383	34	72.9	36.2	50
2.1	FordCu12	44433	30216	32	72.9	40.05	45
2.2	FordMg12	44433	30050	32.4	72.9	38.7	47
2.3	FordMn12	44433	31883	28	72.9	41.6	43
2.4	FordCu4Mn4Mg4	44433	30383	31.6	72.9	36.8	49.5
2.5	FordCu6Mg6	44433	29150	34.4	72.9	37.2	49
2.6	FordMn6Mg6	44433	29550	33.4	72.9	39.1	46
2.7	FordCu6Mn6	44433	30500	31.4	72.9	38.2	48
3	TB	44433	30216	32	72.9	40.5	44
4	GL	44433	29383	34	72.9	37.9	48
5	Ford + Dyeing WW	3200	1100	66	84.0	0.5	99

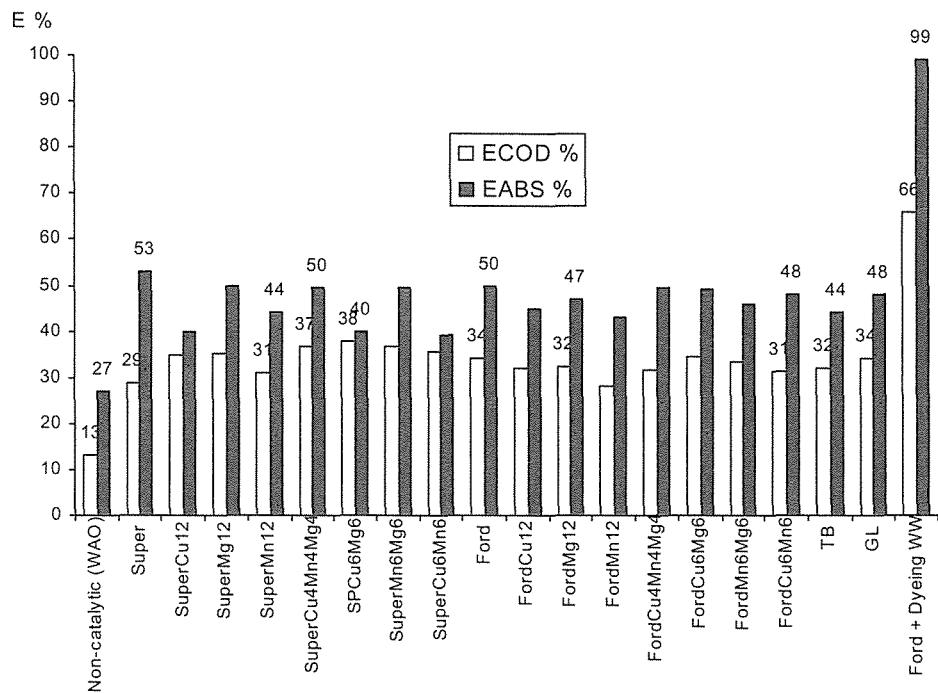


Figure 4- Comparative activity of different catalysts in CWO of BL

In one component system (only basal material) the best were Ford and GL, which showed COD removal efficiency 34% in BL treatment at mild temperature of 150°C. To make it more active, some well-known active components, e.g. CuO and MnO<sub>2</sub> were added. Particularly, in the case of BL, some amount of MgO-

non-catalytic component was added to check the evidence of Robert (Tutorski, 1998), that Mg salt is active oxygen delignification.

Among two component systems, we have the order of activity Mg>Cu>Mn. That means, MgO was more active than two well-known catalysts. In these components systems, it was found that in both cases with Super and Ford base material, composition of base material+Cu6+Mg6 was the best. In four component systems Super had advantage over Ford.

Comparison of COD removal with color removal showed that in all cases color was easier to be removed. This suggests using this process as a universal color removal tool for TI WW, because in this case it needs only destructive oxidation but not completing oxidation, which requires much severe reaction conditions. Thereafter, nearly complete oxidation may be accomplished by most economic biological treatment (Marco, 1997).

To get higher activity and to determine core kinetic data of BL oxidation, series of experiments at different temperature were conducted.

### ***Dependence of catalytic activity on reaction temperature***

In these experiments samples were taken along reaction time, samples were filtered before analysis.

#### *Reaction conditions:*

To evaluate basal precursors and catalysts the following conditions were applied:

Catalyst: FordCu6Mn6

Temperature: 150-180°C

Reactant: Washing WW

Other conditions were unchanged. Results were given in table 6 and figures 5-7.

Table 6- COD conversion versus temperature

Reaction time min.	Reaction temperature, °C							
	180		170		160		150	
	COD	ABS	COD	ABS	COD	ABS	COD	ABS
0	23467	51	23476	51	23476	51	23467	51
15	17803	47.9	20216	43.5	20550	48.45	21216	45.25
30	16383	43.7	19050	40.75	20000	-	20516	41.5
45	14883	38.8	17383	38.5	19383	45.15	19216	40.4
60	13716	34.25	16383	32.95	18716	41.65	19000	30.5
75	12716	30.25	15883	31.2	17500	-	18050	33.1
90	12000	27.35	14883	27.05	16883	36.5	17416	32.1
120	11550	23.4	14716	26.75	16716	32.3	17383	30.5
150	10500	-	14050	24.75	16383	28.55	16716	26.1
180	9883	13.85	13383	17.7	15716	25.7	15216	21.25
E, %	58	73	43	65	33	50	35	58

From these data one can calculate important kinetic data like the reaction order  $n$  toward COD, rate constants  $k$  and activation energy  $E^\#$  using Arrhenius plot (figures 6, 7).

### ***Determination of reaction order and rate constant at 180 °C***

To determine reaction order it needs from data of kinetic curves  $C$  vs  $t$  (figure 5) to build a plot of  $\lg(C_0/C_t)$  versus reaction time  $t$  (figure 6).  $C_0$  and  $C_t$  are concentrations of organics at reaction time  $t = 0$  and  $t = t$  respectively, in this case  $C$  = COD value. The linearity of the graph (figure 6) means that the order  $n = 1$  (table 7 and figure 6). Therefore, from figure 6 one can calculate kinetic rate constant  $k_{180} = 2.303 \times 0.0025 = 5.76 \cdot 10^{-3} \text{ min.}^{-1} = 0.345 \text{ h}^{-1} = 9.59 \cdot 10^{-5} \text{ s}^{-1}$ . Likewise, rate constants at other temperatures were determined and given in table 8.

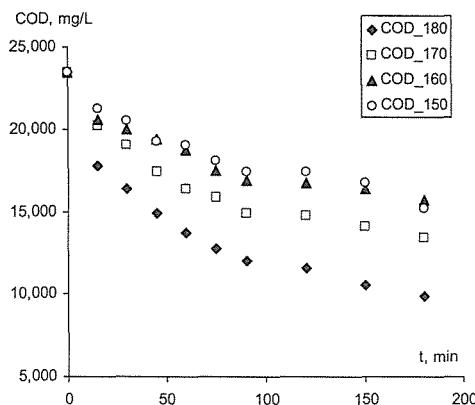


Figure 5- Kinetic curves C-t at different temperature

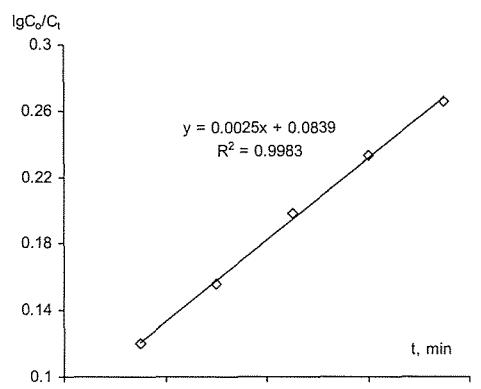


Figure 6- Dependence  $\lg(C_o/C_t)$ -t and determination of reaction order n and rate constant k

Table 7- Calculations for n and k determination

Time, min.	$C_o/C_t$	$\lg C_o/C_t$
15	1.318	0.120
30	1.432	0.156
45	1.568	0.198
60	1.711	0.233
75	1.845	0.266

Results of k calculation were given in table 8.

Results showed that value of k nearly doubled when temperature increased 10 K. In the case of BL, our catalysts showed good activity at temperature more than 443 K.

#### Determination of energy activation

To determine energy activation  $E^\#$  one have to use Arhenius equation ( $k = k_0 e^{-E^\#/RT}$ ), then it needs to build a plot of  $\lg k_T$  versus  $1/T$ , and the slope gave  $E^\#$ .

At first k at different reaction temoeratures must be calculated. The results were given in table 8.

Table 8- Calculation for  $E^\#$  determination

Temperature, K	$10^3 k, s^{-1}$	$1/T$	$\ln k$
453	9.59	0.002208	-9.25
443	6.03	0.002257	-9.72
433	3.10	0.002309	-10.38
423	1.70	0.002364	-10.98

Secondly, from data of table 8 build a plot of  $\lg k_T$  versus  $1/T$  (figure 7), the graph had exellent accuracy ( $R^2 = 0.9988$ ) and gave the slope = -11,578, then activation energy  $E^\#$  can be calculated as follow:

$$E^\# = - \text{slope} \times R = -(-11,578) \times 1.985 = 22,980 \text{ cal/mol} \cong 23 \text{ kcal/mol} \cong 96 \text{ kJ/mol}$$

This value was close to reported literature data in the range of 90-100 kJ/mol for Pt/alumina and Rh/activated carbon catalysts in oxidation of acetic acid (Klinghoffer, 1998 and Gallezot, 1997). This may serve as an evidence of similar mechanisms of oxidation processes.

## Influence of catalyst's mass: reactant (BL) volume ratio

Experiments on the influence of catalyst's mass: reactant volume ratio were conducted at 150°C, reactant was black liquor, catalyst was FordCu6Mg6. Reaction duration was 1 hour. Results were given in table 9 and figure 8. It was showed that either conversion of COD, or color removal (ABS reduction) followed linear dependence. That means, that both COD and color reduced with increasing of the mass:volume ratio and in all cases color removal was better than COD removal. Regarding to application purpose the found simple dependence is very important in the future designing of this process.

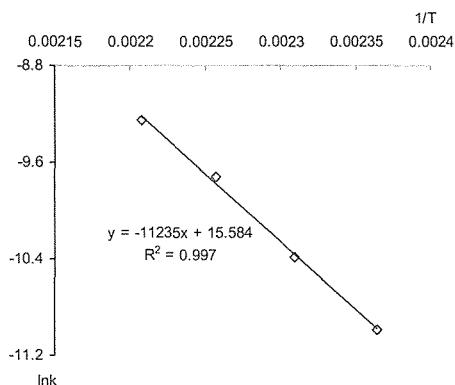


Figure 7- Determination of activation energy  $E^\#$

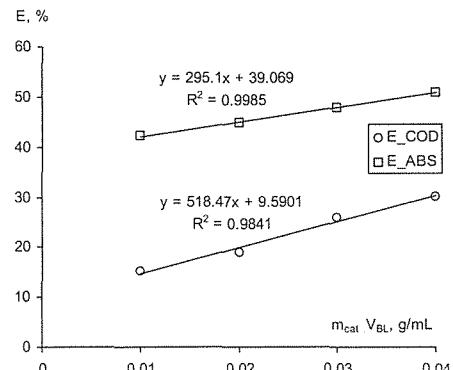


Figure 8- Influence of catalyst's mass: BL volume ratios

Table 9- Influence of catalyst's mass: BL volume ratios

Ratio $m_{cat} \cdot V_{BL}, \text{g/mL}$	$COD_o$	$COD_t$	$ABS_o$	$ABS_t$	$E_{COD}, \%$	$E_{ABS}, \%$
0.01	23,467	19,883	51.0	29.5	15.27	42.16
0.02	23,467	19,050	51.0	28.2	18.82	44.80
0.03	23,467	17,383	51.0	26.6	25.93	47.84
0.04	23,467	16,383	51.0	25.0	30.19	50.98

Generally speaking, activity of our catalysts may not as high as Pd, Pt and Rh catalysts. But their undoubtedly advantage is the cost. To increase COD removal, besides elevation of reaction temperature, because the low cost one can apply higher mass:reactant ratio. The other advantage of our catalysts is no need in complicated regeneration procedure, after about ten batches it may be wasted.

Concerning BL treatment and alkali recovery, it requires further study on possible alkali recycling by conventional caustization process. Herein, a lot of questions remained. The first is about the way to enhance catalytic oxidative activity of catalysts. The second is about actual reactor design. The third is on possibility of reusing treated BL, does it influence on fiber-product properties. Economic benefit is another serious problem. Just consider that the investment cost of chemical recovery unit (evaporation-incineration-caustization) contributes about 25-30% of total pulp and paper mill construction and machinery cost.

## Conclusion

1. It is the first time industrial solid wastes containing  $\text{Fe}_2\text{O}_3$  are proven to be active in CWO for black liquor from pulping process and dyeing wastewater from textile industry treatment. Also,  $\text{MgO}$  is a new active component too.
2. Activity of the catalysts can be enhanced by addition of well-known catalytic component such as  $\text{CuO}$ . Other oxides can be considered too.
3. Activity of the catalyst regarding to color removal from dyeing WW is very high. This makes CWO a potential universal pre-treatment tool before conventional biological treatments for all kind of dyestuffs.

4. For practical application, further research on reduction of WW toxicity, biodegradability improvement as well as detail catalyst's composition and nature, and reactor engineering aspects as well as economic aspects should be conducted.

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